

# On the expected order of kinetics in a series of thermoluminescence (TL) and thermally stimulated conductivity (TSC) peaks



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## ABSTRACT

As reported in the literature, both in experimental results and in simulated glow curves, in a series of TL peaks associated with a series of trapping states and a single recombination center, the peaks tend to be of first order. In the present work we show theoretically and demonstrate by examples of numerical simulations that the last peak in a series obtained by a model of a single recombination center and multiple traps may be of second order whereas the lower-temperature peaks are usually of first order. This is the case even when retrapping is significantly faster than recombination. In some cases, the last peak has a long tail, longer than that of second-order peaks, which has to do with a different mechanism that has been discussed in a recent paper. Similar simulations of a more complex and more realistic situation of a model with multiple trapping states and multiple recombination centers have been performed. The prevalence of first-order appearance of both the curves of free electrons, associated with thermally stimulated conductivity (TSC) and of TL, evaluated for randomly chosen sets of trapping parameters, is shown by histograms. The occurrence of a small number of very high values of the symmetry factor is also discussed.

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## 1. Introduction

The basic theory of a single thermoluminescence (TL) peak has been initiated by Randall and Wilkins [1]. They suggested that such a single peak results from the occurrence of an electron trapping state in the forbidden gap of the solid at hand and a hole center. During the heating, following irradiation, electrons are thermally raised from the trap into the conduction band and can then perform recombination with a trapped hole in center, thus yielding a TL photon. Randall and Wilkins [1] assumed that once an electron is in the conduction band, it would immediately recombine with a hole and wrote the governing equation

$$I(T) = -\frac{dn}{dt} = s \cdot n \cdot \exp(-E/kT), \quad (1)$$

where  $n$  ( $\text{cm}^{-3}$ ) is the concentration of trapped electrons,  $E$  (eV), the activation energy,  $s$  ( $\text{s}^{-1}$ ) is the frequency factor,  $k$  (eV/K) Boltzmann's constant,  $t$  (s) the time during heating and  $T$  (K) the temperature. The temperature and time are connected by the heating function and very often linear heating function is utilized,  $T = T_0 + \beta t$  where  $T_0$  is the initial temperature and  $\beta$  ( $\text{Ks}^{-1}$ ) is the heating rate. The solution of this differential equation is,

$$I(T) = s \cdot n_0 \cdot \exp(-E/kT) \exp \left[ -(s/\beta) \int_{T_0}^T \exp(-E/k\theta) d\theta \right], \quad (2)$$

where  $n_0$  is the initial concentration of trapped electrons at the beginning of the heating. This represents a peak-shaped curve with the following properties. The peak is asymmetric, which is defined by the shape factor,

$$\mu_g = \delta/\omega, \quad (3)$$

where  $\delta = T_2 - T_1$  and  $\omega = T_2 - T_1$  and where  $T_m$  is the temperature at the maximum and  $T_1$  and  $T_2$  are the lower and higher temperatures at half maximum intensity, respectively. The shape factor of a typical first-order peak is  $\sim 0.42$  (Chen [2]).

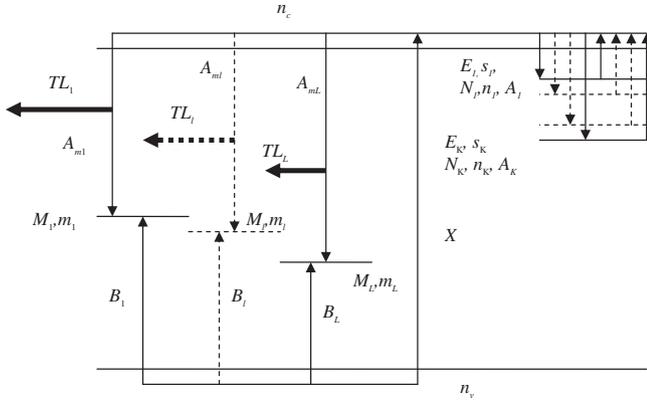
Garlick and Gibson [3] extended this work and considered the situation where an excited electron can either recombine with a hole in center or retrap into one of the empty electron traps. Assuming that retrapping is relatively strong, they received the governing equation

$$I(T) = s' \cdot n^2 \exp(-E/kT), \quad (4)$$

where  $s'$  ( $\text{cm}^3 \text{s}^{-1}$ ) is a pre-exponential constant factor. The solution of this equation for linear heating function is

$$I(T) = \frac{n_0^2 s' \exp(-E/kT)}{[1 + (s'n_0/\beta) \int_{T_0}^T \exp(-E/k\theta) d\theta]^2}. \quad (5)$$

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**Fig. 1.** Schematic energy-level diagram with  $K$  trapping state ( $N_i$ ) and  $L$  kinds of recombination center ( $M_i$ ). Transitions occurring both during excitation and during heating are shown. The dashed lines mean that these levels and transitions may represent multiple levels/transitions of the same kind. The thick arrows denote the different TL emissions.

This second-order curve is nearly symmetric, typically with a shape factor of  $\sim 0.52$ .

In the present work, we deal with a complex but more realistic model of a crystal with multiple trapping states and multiple recombination centers as shown in Fig. 1. As a first step, we consider the model by Halperin and Braner [4] who have given a more general treatment of the situation governing the kinetics of the process with one trapping state and one recombination center. The model and its consequences will be discussed below. The set of simultaneous differential equations governing the process is

$$\frac{dn}{dt} = A_n(N - n)n_c - s \cdot n \cdot \exp(-E/kT), \quad (6)$$

$$I(T) = -\frac{dm}{dt} = A_m m n_c, \quad (7)$$

$$\frac{dn_c}{dt} = s \cdot n \cdot \exp(-E/kT) - A_n(N - n)n_c - A_m m n_c, \quad (8)$$

where  $N$  ( $\text{cm}^{-3}$ ) is the concentration of traps and  $n$  ( $\text{cm}^{-3}$ ) its instantaneous occupancy,  $m$  ( $\text{cm}^{-3}$ ) is the instantaneous concentration of trapped holes,  $A_m$  ( $\text{cm}^3 \text{s}^{-1}$ ) is the recombination probability coefficient and  $A_n$  ( $\text{cm}^3 \text{s}^{-1}$ ) the retrapping probability coefficient.  $E$  (eV) is the activation energy,  $s$  ( $\text{s}^{-1}$ ) the frequency factor,  $k$  ( $\text{eV} \cdot \text{K}^{-1}$ ) is the Boltzmann constant,  $T$  (K) the absolute temperature and  $t$  (s) the time.  $n_c$  ( $\text{cm}^{-3}$ ) is the instantaneous concentration of electrons in the conduction band. It deserves mention that the curve  $n_c(T)$  is closely associated with the measurable thermally stimulated conductivity (TSC) through the relation

$$\sigma(T) = e\mu n_c(T), \quad (9)$$

where  $\sigma(T)$  is the conductivity,  $e$  the electronic charge and  $\mu$  the mobility which can usually be considered to be nearly temperature independent. This point will be discussed further in the broader context where multiple traps and multiple centers are considered.

Halperin and Braner [4] studied the heating stage and made the simplifying assertion, later termed the “quasi-equilibrium” assumption

$$\frac{dn_c}{dt} \approx 0. \quad (10)$$

With this assumption, they reached the equation

$$I(T) = -\frac{dm}{dt} = s \cdot n \cdot \exp(-E/kT) \frac{A_m m}{A_m m + A_n(N - n)}. \quad (11)$$

Obviously, this equation in two unknown functions,  $n$  and  $m$  cannot be solved without making further assumptions. Along with the strong recombination assumption made by Randall and Wilkins [1], one can assert that  $A_m m \gg A_n(N - n)$  and Eq. (11) reduces to Eq. (1). On the other hand, one can assume dominating retrapping, namely  $A_m m \ll A_n(N - n)$  which, along with the assumption that the trap is far from saturation,  $n \ll N$  and assuming  $m = n$  (which is approximately correct in the case where only one trapping state and one kind of recombination center take part in the process). The result is Eq. (4) with  $s' = sA_m/NA_n$ . It deserves mention that, as long as a single one-trap-one-recombination-center (OTOR) TL peak is concerned, it is difficult to say a priori whether retrapping or recombination dominate.

It is quite obvious that different kinds of intermediate cases neither of first, nor of second-order can be considered. May and Partridge [5] suggested the use of the kinetic equation

$$I(T) = -\frac{dn}{dt} = s'n^b \exp(-E/kT), \quad (12)$$

where  $b$  is the effective kinetics order and  $s'$  ( $\text{cm}^{3(b-1)} \text{s}^{-1}$ ) the appropriate pre-exponential factor. Rasheedy [6] suggested that in analogy with the second-order case, one can use here  $s' = s/N^{b-1}$ . Chen [7] has further studied the properties of this “general-order kinetics” and presented the relation between the kinetic order and the shape factor  $\mu_g$ . One should remember that Eq. (12) is merely an empirical approximation to the more complex Eq. (11) and the two may coincide only for the cases of first or second order. Thus, although one can get with Eq. (12) all the intermediate values of  $\mu_g$ , it may not include all the features of the more realistic Eq. (11).

One should note that whereas the first, second and general orders are defined respectively by Eqs. 1, 4, and 12, one may wish to use the value of the shape factor for defining the effective order of kinetics of experimentally measured peaks even in more complex situations. Thus,  $\mu_g \approx 0.42$  would mean that the peak is of first order,  $\mu_g \approx 0.52$  is associated with second order and intermediate values of  $\mu_g$  would define an appropriate intermediate value of the effective order  $b$ .

From the discussion so far, dealing with a single TL peak, it seems plausible that first-order kinetics is not expected to occur in most cases. Dominating retrapping appears to be just as likely to occur as dominating recombination. Note that cases with no retrapping cannot take place at all because during the excitation stage, trapping into the same states must occur which means that the trapping coefficient is not nil, and this is the same coefficient that is considered as the retrapping coefficient during the heating stage. Obviously, intermediate situations with intermediate values of  $\mu_g$  and therefore, of the effective order  $b$  are rather likely to take place. Also, situations where a peak starts having dominating recombination and ends with dominating retrapping can be envisaged.

In the literature, there is, however, vast evidence that first-order kinetics is quite prevalent in natural materials. Lewandowski and McKeever [8] state that first-order processes dominate in nature. Sunta et al. [9–11] suggest that the apparent dominance of first-order kinetics in nature is usually due to slow retrapping, but in multiple-trap-system models, it may occur under fast-retrapping conditions as well. Further statements concerning the dominance of first-order kinetics have been made by Bos [12] and Abd El-Hafez et al. [13]. Some authors described the prevalence of first-order shaped peaks in both TL and TSC peaks and mentioned the competition with deep trap as the reason. These include Haering and Adams [14], Dussel and Bube [15], Böhm and Scharmann [16], Simmons and Taylor [17], Agersap Larsen et al. [18] and Opanowicz [19]. The same reason of competition with deep trap has been mentioned by Smith and Rhodes [20] and by Bailey et al. [21] for the first-order behavior of OSL decay in quartz.

Pagonis and Kitis [22] have recently reported on the prevalence of first-order kinetics of TL based on multiple competition processes. They simulate TL peaks using two models. One is the one-trap-one-center (OTOR) model, which is the same as Eqs. (6)–(8) above. Here, they solve numerically the set of equations for different values of  $A_i/A_m$ , and show the gradual transition of the effective kinetic order  $b$  from 1 to 2 as well as the dependence of the maximum temperature  $T_m$  on this ratio. In the more comprehensive interactive multitrap system (IMTS) model, they choose sets of parameters at random within the reasonable ranges, solve the equations to get glow curves and study the effective order of kinetics of the peaks. Running 1000 random variants of the model, they get a distribution of effective kinetic orders weighted strongly toward first order. The distribution has a mean value of  $b = 1.08$  and a standard deviation of  $\sigma = 0.16$ . The authors ascribe the first-order or nearly first-order property found to the competition between the traps.

In the present paper, we follow up the work by Pagonis and Kitis [22]. We show analytically under what circumstances the peaks in a series can be expected to be of first order. In particular, we distinguish between the lower temperature peaks in a series and the high temperature ones. We start with a model with multiple trapping states and one recombination center and continue with a more general model of multiple traps and multiple centers. We give some specific numerical examples and try to follow the effect of certain combinations of trapping parameters on the results. We also consider the unique role of the highest temperature peak in a series, a peak occurring at a temperature range where the quasi-equilibrium condition may not hold.

## 2. Theoretical considerations

### 2.1. A series of peaks resulting from a series of traps and a single recombination center

Let us consider a series of peaks resulting from a series of  $K$  traps with different  $E$  and  $s$  values and different retrapping probability coefficients, and as a first step, a single recombination center. Experimentally, this would mean that the emission spectrum of the different peaks be the same. Let us also assume that the parameters are such that the peaks are quite well separated (see discussion below). The set of equations (6)–(8) will now be changed to

$$\frac{dn_i}{dt} = A_i(N_i - n_i)n_c - s_i \cdot n_i \cdot \exp(-E_i/kT), \quad \text{for } i = 1 \dots K \quad (13)$$

$$I(T) = -\frac{dm}{dt} = A_m m n_c, \quad (14)$$

$$\frac{dn_c}{dt} = \sum_{i=1}^K s_i n_i \exp(-E_i/kT) - \sum_{i=1}^K A_i(N_i - n_i)n_c - A_m m n_c. \quad (15)$$

Making the quasi-equilibrium assumption,  $dn_c/dt \approx 0$ , we get from Eq. (15)

$$n_c = \frac{\sum_{i=1}^K s_i n_i \exp(-E_i/kT)}{A_m m + \sum_{i=1}^K A_i(N_i - n_i)}. \quad (16)$$

If we would like to consider the  $j$ -th peak in a series, the traps responsible for lower-temperature peaks can be considered to be empty (Mady et al. [23]). Thus, the sum can be taken only from  $i = j$ , namely, the sum in the denominator will be  $\sum_{i=j}^K A_i(N_i - n_i)$ . By inserting Eq. (16) into Eq. (14), we get the expression for TL,

$$I(T) = -\frac{dm}{dt} = \frac{A_m m \sum_{i=1}^K s_i n_i \exp(-E_i/kT)}{A_m m + \sum_{i=j}^K A_i(N_i - n_i)}. \quad (17)$$

Let us consider a peak which is followed by one or more subsequent peaks. This means that the trap has a number of competitors, which are probably deeper. It is obvious that in the range of temperatures of this peak, if the concentration of free electrons is relatively small,

$$m = \sum_{i=j}^K n_i. \quad (18)$$

This is so since in the excitation, the total number of trapped electrons is equal to the number of holes in the center, and since during the heating up to a certain peak the same number of electrons and holes perform recombination, the equality in Eq. (18) still holds at higher temperatures as long as electrons do not accumulate in the conduction band. Furthermore, as long as the peaks are fairly well separate, since the activation energies are different, the exponents in Eq. (17) are very different from one another, and at the temperature range of a certain peak, the contribution of the subsequent peaks is negligible. Therefore, Eq. (17) reduces to

$$I(T) = -\frac{dm}{dt} = \frac{A_m m s_j n_j \exp(-E_j/kT)}{A_m m + \sum_{i=j}^K A_i(N_i - n_i)}. \quad (19)$$

If in the range of the  $j$ -th peak there are still many electrons trapped at traps deeper than the  $j$ -th, the sum in Eq. (18) changes along the  $j$ -th peak only slightly, and therefore,  $m$  does not change a lot and can be considered constant. The amount of change of  $m$  can be considered to be small if the area under the  $j$ -th peak is rather small as compared to the accumulated area of the higher temperature peaks. If, in addition, the relevant traps with  $i > j$  are not too close to saturation, the denominator of Eq. (19) is rather close to be constant. The observation that glow peaks tend to be of first order at low trap occupancies has been made by Sunda et al. [10]. Note that if the peaks are relatively separate, and if the traps are saturated, within the range of the  $j$ -th peak,  $\frac{dm}{dt} \approx \frac{dn_j}{dt}$ . If, however, the traps from the  $j$ -th and deeper are not full, they may compete with the center over electrons so that the portion of electrons performing recombination is

$$\frac{A_m m}{A_m m + \sum_{i=j}^K A_i(N_i - n_i)}. \quad (20)$$

This would mean that in this range,

$$\frac{dm}{dt} = \frac{dn_j}{dt} \frac{A_m m}{A_m m + \sum_{i=j}^K A_i(N_i - n_i)}. \quad (21)$$

Comparing the right-hand side of Eqs. (19) and (21) results in

$$-\frac{dn_j}{dt} = s_j n_j \exp(-E_j/kT). \quad (22)$$

The solution of this equation is a simple first-order peak-shaped curve, with the original activation energy and frequency factor of the  $j$ -th peak. The solution for the rate of change of  $n_j$  is, obviously,

$$-\frac{dn_j}{dt} = n_{j0} s_j \exp(-E_j/kT) \exp\left[-(s_j/\beta) \int_{T_i}^{T_f} \exp(-E_j/k\theta) d\theta\right], \quad (23)$$

similar to Eq. (2). This, however, is not the TL intensity. Using Eq. (21), we get the TL intensity

$$I(T) = -\frac{dm}{dt} = n_{j0} s_j \exp(-E_j/kT) \times \exp\left[-(s_j/\beta) \int_{T_i}^{T_f} \exp(-E_j/k\theta) d\theta\right] \frac{A_m m}{A_m m + \sum_{i=j}^K A_i(N_i - n_i)}. \quad (24)$$

As long as the last term in Eq. (24) is approximately constant along the  $j$ -th peak, the function looks like a first-order peak and the analysis should yield the inserted  $E$  and  $s$  values. The approximate constancy of this term can be expected as long as  $m$  is not varying significantly along the  $j$ -th peak; this is usually the case for the lower temperature peaks in a series and ceases to be so for the last peak. Examples of such results are given below. If we combine Eq. (24) with Eq. (7), we can get an expression for  $n_c(T)$ , the temperature dependence of the conduction band electrons,

$$n_c(T) = n_{j0} s_j \exp(-E_j/kT) \times \exp \left[ -(s_j/\beta) \int_{T_i}^{T_f} \exp(-E_j/k\theta) d\theta \right] \frac{1}{A_m m + \sum_{i=j}^K A_i (N_i - n_i)}. \quad (25)$$

Here too, if the denominator in Eq. (25) is very slowly changing along the relevant  $n_c(T)$  peak, this peak can be expected to look approximately like a first-order peak. As pointed out above, the  $n_c(T)$  curve is very closely connected to the thermally stimulated conductivity (TSC) results. The numerical examples in the next section show that in most cases, the peaks have a symmetry characteristic of first order when a broad range of the parameters is used. It should be noted that the expected approximate constancy of  $m$  does not depend on the number of peaks following the  $j$ -th one, but rather on the total number of electrons still trapped in the deeper traps, which is equal to the number of remaining holes in centers.

Let us consider the expected shape of the last peak in such a series. In this temperature range, and provided that the quasi-equilibrium assumption still holds, the governing equation as derived from Eq. (19) would be

$$I_K(T) = -\frac{dm}{dt} = \frac{s_K A_m n_K m \exp(-E_K/kT)}{A_m m + A_K (N_K - n_K)}. \quad (26)$$

However, since this the last peak in the series, Eq. (18) reduces to  $m = n_K$ , and therefore,

$$I_K(T) = -\frac{dm}{dt} = \frac{s_K A_m m^2 \exp(-E_K/kT)}{A_m m + A_K (N_K - m)}. \quad (27)$$

If  $m$  is much smaller than  $N_K$  and  $A_m$  is not significantly larger than  $A_K$ , the denominator does not change a lot through the temperature range of the last peak and second-order or nearly second-order features can be expected.

It should be noted that if the highest-temperature peak occurs at very high temperature, the quasi-equilibrium condition may not hold anymore. As shown in a recent paper (Chen and Pagonis [24]), at high temperatures,  $n_c$  may be nearly as large as  $m$  (meaning that  $n$  is significantly smaller), which may affect the shape of the peak.

## 2.2. Series of TSC and TL peaks resulting from multiple trapping states and multiple recombination centers

In real materials, one may expect more than a single recombination center. In the present subsection, we discuss the more realistic situation of multiple trapping states and multiple recombination centers. We still confine the discussion to transitions of electrons through the conduction band and exclude localized transitions. We also disregard at this stage the possibility of thermally stimulated conductivity associated with the thermal release of holes from hole traps and their recombination with electrons in electron recombination centers and of TL associated with such transitions. Like in the previous case, we assume that the parameters are such that the curve associated with a certain recombination center can be spectrally separated, by using appropriate optical filters or

monochromator, from the curves associated with the other centers. It should be noted, however, that this assumption does not mean that the glow curves due to the different recombination centers are independent of each other. In fact, since the electrons are all released into the conduction band, even when only one emission band associated with one recombination center is measured, the results are an intricate outcome influenced by all the parameters of all traps and centers. Eqs. (13)–(15) should now be replaced by the set

$$\frac{dn_i}{dt} = A_i (N_i - n_i) n_c - s_i \cdot n_i \cdot \exp(-E_i/kT), \quad \text{for } i = 1, \dots, K \quad (28)$$

$$I_l(T) = -\frac{dm_l}{dt} = A_{ml} m_l n_c, \quad \text{for } l = 1, \dots, L \quad (29)$$

$$\frac{dn_c}{dt} = \sum_{i=1}^K s_i n_i \exp(-E_i/kT) - \sum_{i=1}^K A_i (N_i - n_i) n_c - \sum_{l=1}^L A_{ml} m_l n_c, \quad (30)$$

where, in addition to the previously defined magnitudes, we deal here with  $L$  recombination centers (instead of one),  $m_1 \dots m_L$  with recombination probability coefficients of  $A_{m1} \dots A_{mL}$ . Using approximations similar to those discussed with regards to Eqs. (13)–(15), we can easily reach the extension to Eq. (16)

$$n_c = \frac{\sum_{i=1}^K s_i n_i \exp(-E_i/kT)}{\sum_{l=1}^L A_{ml} m_l + \sum_{i=1}^K A_i (N_i - n_i)}. \quad (31)$$

The extension to Eq. (17) will now be

$$I_l(T) = -\frac{dm_l}{dt} = \frac{A_{ml} m_l \sum_{i=1}^K s_i n_i \exp(-E_i/kT)}{\sum_{l=1}^L A_{ml} m_l + \sum_{i=1}^K A_i (N_i - n_i)}, \quad (32)$$

and the extension to Eq. (18) will be

$$\sum_{l=1}^L m_l = \sum_{i=1}^K n_i. \quad (33)$$

Under these circumstances, Eq. (24) will be replaced, for the emission of the  $l$ 'th center, by

$$I_l(T) = n_{j0} s_j \exp(-E_j/kT) \times \exp \left[ -(s_j/\beta) \int_{T_i}^{T_f} \exp(-E_j/k\theta) d\theta \right] \frac{A_{ml} m_l}{\sum_{l=1}^L A_{ml} m_l + \sum_{i=1}^K A_i (N_i - n_i)}, \quad (34)$$

and Eq. (24) by

$$n_c(T) = n_{j0} s_j \exp(-E_j/kT) \times \exp \left[ -(s_j/\beta) \int_{T_i}^{T_f} \exp(-E_j/k\theta) d\theta \right] \frac{1}{\sum_{l=1}^L A_{ml} m_l + \sum_{i=1}^K A_i (N_i - n_i)} \quad (35)$$

Here too, as long as the terms to the right of the square brackets are approximately constant, the individual  $n_c(T)$  and TL peaks can be expected to have symmetry factors typical of first-order kinetics. The prevalent occurrence of this situation in most cases as well as exceptional situations will be discussed below.

An important question concerns the initial values of  $n_i$ ,  $i = 1, \dots, K$  and  $m_l$ ,  $l = 1, \dots, L$ , the initial concentrations of the traps and recombination centers at the beginning of heating. Whereas in the OTOR case, one can assume that  $n_0 \approx m_0$  and choose any arbitrary value  $n_0 \leq N$ , this is not the situation here. The concentrations of the traps occupancies  $n_{i0}$  and centers  $m_{l0}$  depend on the excitation intensity and length as well as on the retrapping probability coefficients  $A_i$  and  $A_{ml}$  and the capacities of the traps  $N_i$  and centers  $M_l$ . In order to simulate the situation in a consistent manner, one has to solve the equations governing the excitation stage prior to the simulation of the heating stage, and use the final concentrations

of the former as initial values for the latter stage. The equations governing the excitation stage are

$$\frac{dn_i}{dt} = A_i(N_i - n_i)n_c - sn_i \exp(-E_i/kT), \quad i = 1, \dots, K, \quad (36)$$

$$\frac{dm_l}{dt} = B_l(M_l - m_l)n_v - A_{ml}m_l n_c, \quad \text{for } l = 1, \dots, L \quad (37)$$

$$\frac{dn_c}{dt} = X - \sum_{l=1}^L A_{ml}m_l n_c - \sum_{i=1}^K A_i(N_i - n_i)n_c, \quad (38)$$

$$\frac{dn_v}{dt} = \sum_{i=1}^K \frac{dn_i}{dt} + \frac{dn_c}{dt} - \sum_{l=1}^L \frac{dm_l}{dt}, \quad (39)$$

where, in addition to the magnitudes defined above, we have here  $n_v$  ( $\text{cm}^{-3}$ ), the concentration of free holes in the valence band,  $X$  ( $\text{cm}^{-3} \text{s}^{-1}$ ) the rate of production of electrons and holes by the irradiation, which is proportional to the dose rate. Thus, the total concentration of produced pairs of electrons and holes, proportional to the dose of excitation is  $D = X \cdot t_D$  where  $t_D$  (s) is the time of excitation,  $M_l$  ( $\text{cm}^{-3}$ ) are the total concentrations of centers and  $B_l$  ( $\text{cm}^3 \text{s}^{-1}$ ) are the capture coefficients of free holes in centers.

### 3. Numerical results

#### 3.1. Results of the model with five traps and one center

In the first part of this section, we show some representative glow curves consisting of five peaks, resulting from a model of five traps and only one center. Fig. 2 depicts a series of 5 peaks simulated by using Eqs. (13)–(15). The relevant energy-level diagram is Fig. 1 with a single recombination state and five traps. These have concentrations of  $N_i$  for  $i = 1, \dots, 5$ , with instantaneous occupancies of  $n_i$ , activation energies of  $E_i$  and frequency factors of  $s_i$ . In order to simulate the experimental procedure of excitation

properly, following the time of excitation  $t_D$ , we added a relaxation period, a time in which the set of equations (36)–(39) (with  $L = 1$  in this case) is solved following excitation, but with  $X = 0$ . Only following this period, which allows the capture of free electrons and holes in traps and centers, respectively, we start solving the heating stage as given in Eqs. (13)–(15).

The parameters chosen for Fig. 2 are given in the caption. The symmetry factor was evaluated for the five peaks and the results are  $\mu_{g1} = \mu_{g2} = \mu_{g3} = 0.42$ ,  $\mu_{g4} = 0.43$  and  $\mu_{g5} = 0.52$ . Although the recombination probability is equal in the five retrapping probabilities, the first four peaks have the symmetry factor of a first-order peak whereas the fifth peak has the symmetry of a second-order peak.

As could be understood from Eq. (24), the condition for the penultimate peak to be of first order has to do with the capacity of the deepest trap. For Fig. 3, we reduced  $N_5$  to  $3 \times 10^8 \text{ cm}^{-3}$  and used a lower value of  $X = 10^8 \text{ cm}^{-3} \text{ s}^{-1}$ . We found here  $\mu_{g1} = 0.41$ ,  $\mu_{g2} = 0.42$ ,  $\mu_{g3} = 0.42$ ,  $\mu_{g4} = 0.50$  and  $\mu_{g5} = 0.52$ . Whereas the first three peaks look like first-order peaks, due to the small capacity of peak 5, both peaks 4 and 5 have second-order features.

In the OTOR case, second-order peaks usually result from a large value of the retrapping coefficient  $A_n$  as compared to the recombination coefficient  $A_m$ . In Fig. 4, we tried the situation where  $A_m$  is  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$  as compared to  $A_i = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . The symmetry factors here were found to be  $\mu_{g1} = \mu_{g2} = 0.42$ ,  $\mu_{g3} = \mu_{g4} = 0.41$  and  $\mu_{g5} = 0.49$ . Obviously, the first four peaks look like first-order peaks and the fifth one is rather close to be of second order. A possible explanation for the last peak not to be exactly of second order has been given in the paper by Chen and Pagonis [24]. In the high-temperature range beyond the maximum of the last peak, one may expect that  $m \sim n_c$ . As a result, one may get a peak, the apparent width of which may depend on the heating rate  $\beta$ , and therefore, different values of  $\mu_g$  may result.

Fig. 5 was simulated with a relatively small value of  $N_5$ , namely  $10^9 \text{ cm}^{-3}$  and relatively low value of the dose rate,  $X = 10^8 \text{ cm}^{-3} \text{ s}^{-1}$ , when the other parameters are the same as in Fig. 2. The values

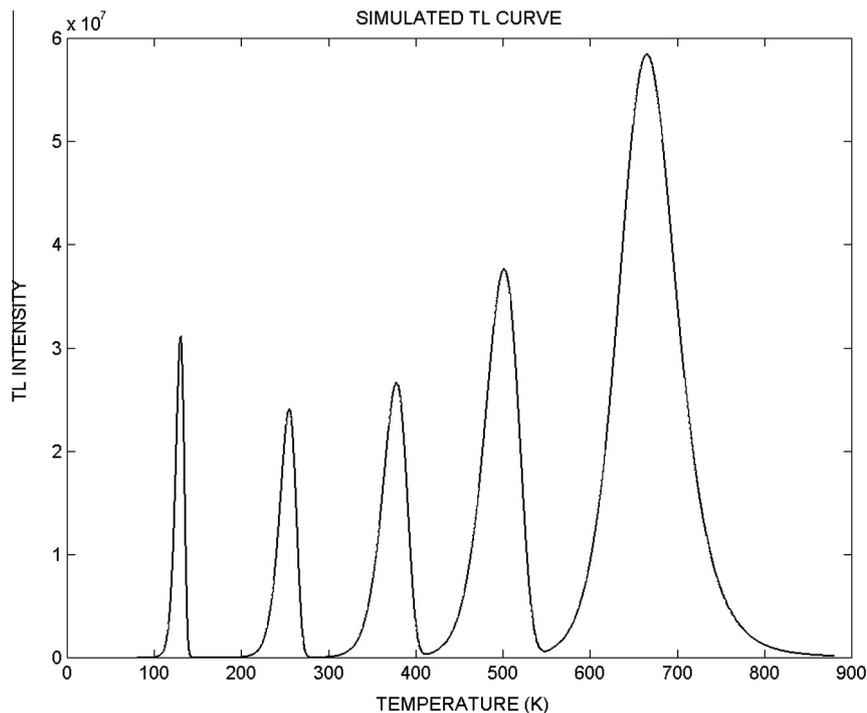


Fig. 2. A five-peak curve reached by solving Eqs. (36)–(39) for one center, followed by the solution of Eqs. (13)–(15). The parameters used were:  $M = 10^{12} \text{ cm}^{-3}$ ,  $B = 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ,  $N_i = 10^{10} \text{ cm}^{-3}$ ,  $A_i = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ,  $s_i = 10^{11} \text{ s}^{-1}$ , for  $i = 1, \dots, 5$  and  $E_i = (0.3, 0.6, 0.9, 1.2, 1.6) \text{ eV}$ ,  $A_m = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . The dose-rate was  $X = 10^9 \text{ cm}^{-3} \text{ s}^{-1}$  and the time of excitation was  $t_D = 10 \text{ s}$ .

of the symmetry factors are  $\mu_{g1} = \mu_{g2} = 0.42$ ,  $\mu_{g3} = 0.43$  for the first three peaks. Note that the first three peaks are relatively weak in this case, and in order to be able to observe them, their intensity has been multiplied by a factor of 50. For the higher temperature peaks  $\mu_{g4} = 0.54$  and  $\mu_{g5} = 0.59$ . In a sense, since the last trap has a relatively small capacity, the penultimate peak serves as the last peak with a symmetry factor characteristic of second order. As for the unusual shape of the last peak, its very long tail seems to be the result of a different mechanism which has been explained by Chen and Pagonis [24].

### 3.2. Results of the model with five traps and five recombination centers

In the second stage of the numerical simulations we have solved numerically Eqs. (36)–(39) for the excitation stage with  $K = 5$  and  $L = 5$ . This was followed by solving these equations for the relaxation period as explained above, and by solving Eqs. (28)–(30) with the same parameters, for the heating stage.  $I_i(T)$  was separately recorded for the different centers so that for each run, we have had five TL curves each consisting of five peaks. Also was recorded the curve of  $n_c(T)$  which, as explained, represents the TSC curve. Generally speaking, the curves looked quite similar to those found from the 1 center cases, Figs. 2–5. Whereas the activation energies were chosen always to be (0.25, 0.45, 0.8, 1.4, 2.5) eV, the other parameters, namely, the  $N_i$ 's,  $M_i$ 's,  $A_m$ 's,  $A_i$ 's,  $s_i$ 's and  $B_i$ 's were chosen in random within a range of four orders of magnitude. In some cases, the center of the  $A_m$ 's range was the same as that of the  $A_n$ 's and in other cases, the range of the  $A_m$ 's was significantly smaller than that of the  $A_n$ 's. Even in the former case, since the simulated irradiation was not long enough to saturate the traps and centers, the values of  $A_i(N_i - n_i)$  were in most cases larger than those of  $A_m m_i$ , and yet, the first-order appearance was prevalent in the first four peaks of the resulting  $n_c(T)$  and  $I_i(T)$  curves. The histogram of the symmetry factor of all the TL peaks from all the five centers is shown in Fig. 6. The number of points in the histogram is 400. A very distinct peak is seen at  $\mu_g = 0.42$  with a distribution between 0.4 and 0.5. These will be discussed below. As for the fifth peak in each glow curve, in some cases, it occurred at very high tempera-

ture beyond the range of the simulation, and therefore, the symmetry factor could not be evaluated. In the majority of the other cases, the value of  $\mu_g$  was very high, up to  $\sim 0.8$ , and in other cases, some second-order like peaks were observed as well as some first-order looking peaks. All these cases are discussed below. Note that although we are talking here about a much more complex situation than that discussed by Pagonis and Kitis [22], the distribution of symmetry factors is quite similar. We have here a mean value of 0.4260 and a standard deviation of 0.0167.

A distribution of the symmetry factors of the  $n_c(T)$  peaks is shown in Fig. 7. The number of points in this histogram is 80. The mean value of the symmetry factor here is 0.4233 and the standard deviation is 0.0126. This distribution is rather similar to that of the TL peaks, but is not exactly identical to it.

### 4. Evaluation of the effective $E$ and $s$ values

As discussed above in relation to Eq. (24), as long as the term in Eq. (20) is approximately constant along a certain peak, one may expect the original  $E$  and  $s$  values to result from any analytical method used. We have used the full-width method (Chen [2,7]) which, for the first-order case is

$$E = kT_m \left( 2.52 \frac{T_m}{\omega} - 2 \right). \quad (40)$$

Once  $E$  is found, the maximum condition may be used to evaluate the effective frequency factor,

$$s = \frac{\beta E}{kT_m^2} \exp(E/kT_m). \quad (41)$$

when the peak is of “general order”, the constant 2.52 in Eq. (3) should be replaced by  $C_\omega = 2.52 + 10.2(\mu_g - 0.42)$  where  $\mu_g$  is the shape factor described above.

An example of the analysis of the glow peaks is given in Table 1. We are reporting these results only for the case of one center although the outcome is quite similar for the more elaborate case with five centers. In the reported case, the parameters are chosen

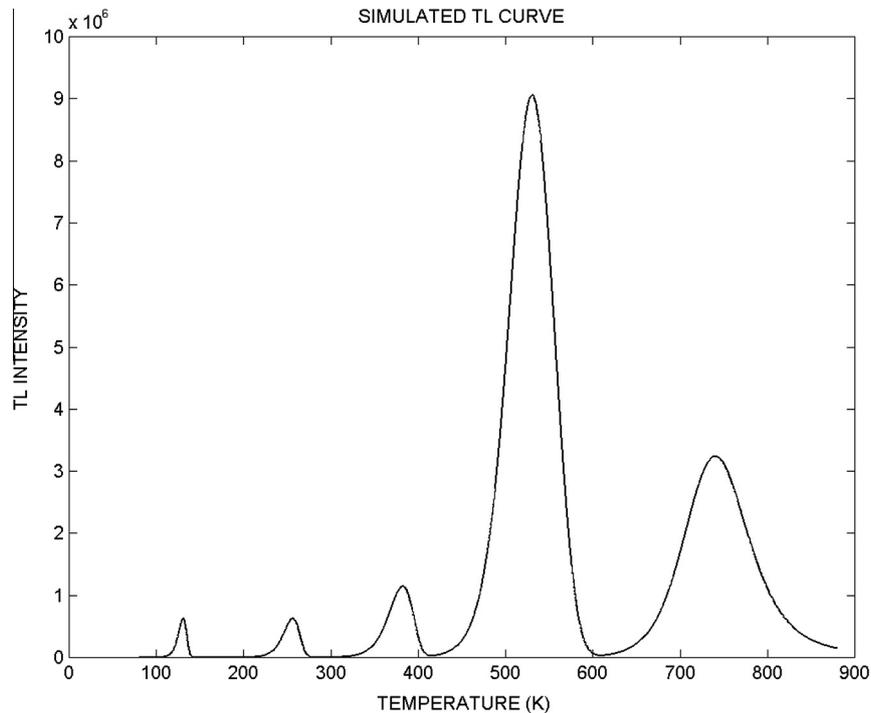
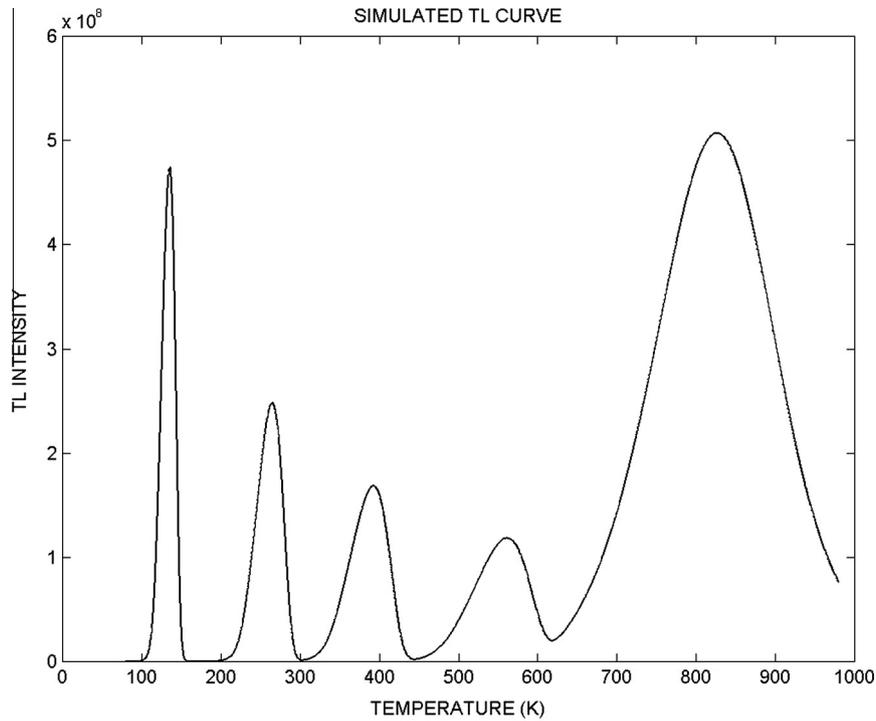
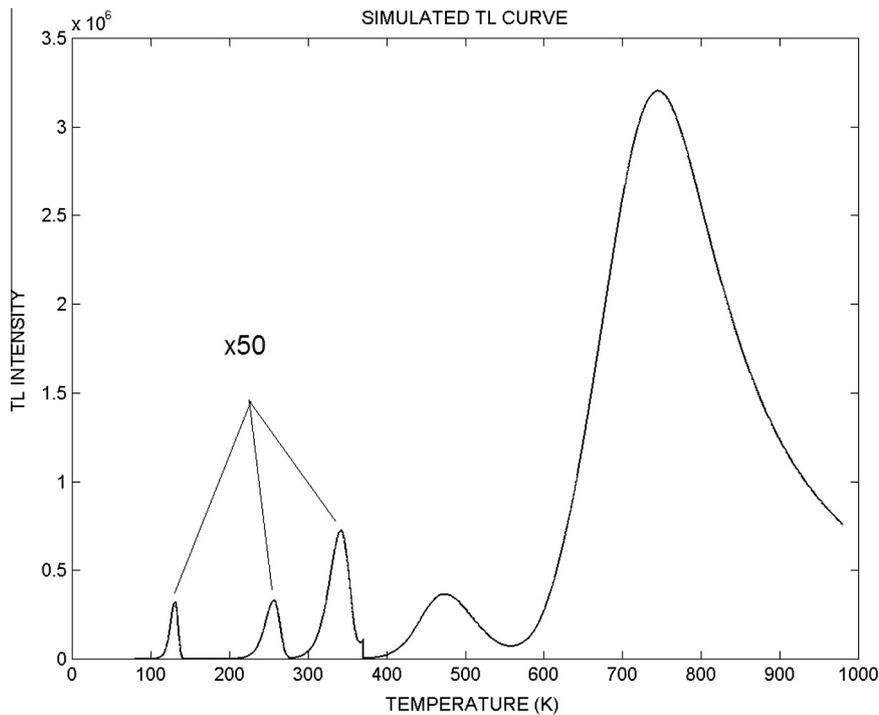


Fig. 3. The same as Fig. 2 except that  $N_5 = 3 \times 10^8 \text{ cm}^{-3}$ ,  $E_i = (0.3, 0.6, 0.9, 1.2, 1.8) \text{ eV}$  and  $X = 10^8 \text{ cm}^{-3} \text{ s}^{-1}$ .



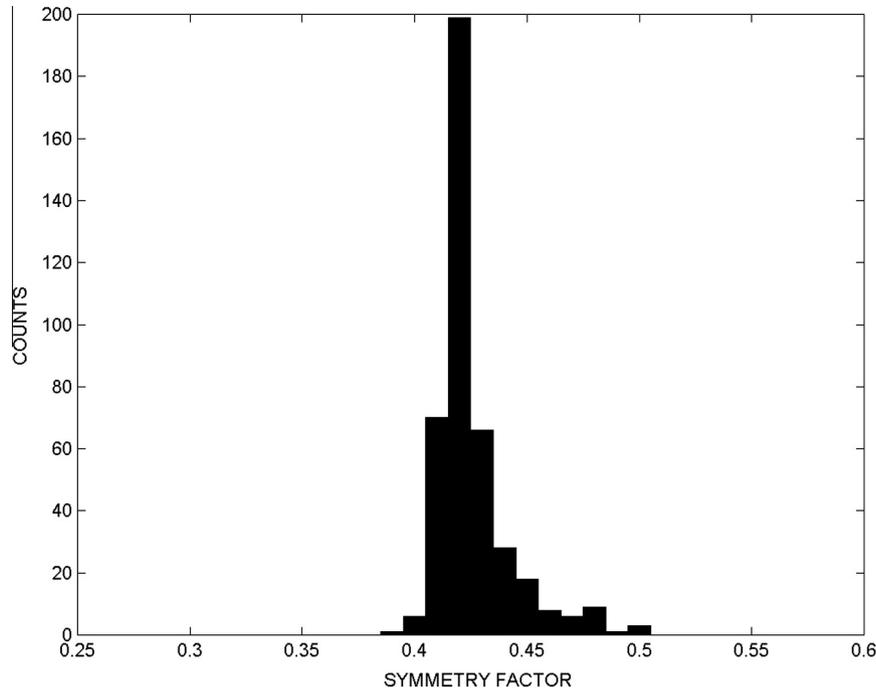
**Fig. 4.** The same as Fig. 2, but  $A_m = 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ,  $N_5 = 10^{11} \text{ cm}^{-3}$ ,  $E_i = (0.3, 0.6, 0.9, 1.3, 1.8) \text{ eV}$ , and  $X = 2 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$ .



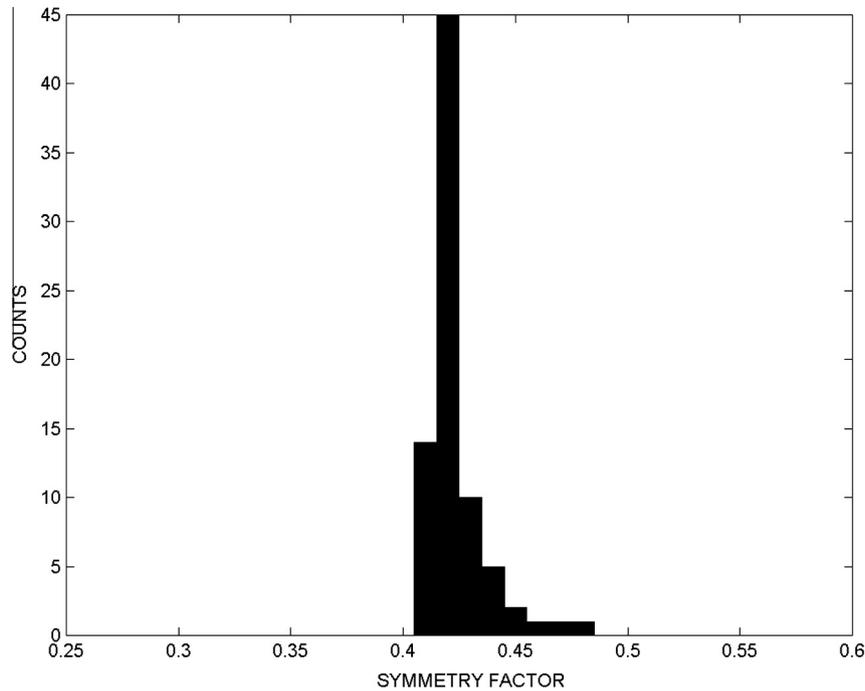
**Fig. 5.** The same as Fig. 2, but  $A_m = 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ,  $N_5 = 10^9 \text{ cm}^{-3}$ ,  $E_i = (0.3, 0.6, 0.8, 1.0, 1.6) \text{ eV}$  and  $X = 10^8 \text{ cm}^{-3} \text{ s}^{-1}$ .

in such a way that the traps are far from saturation. The inserted activation energies are (0.3, 0.6, 0.9, 1.2, 1.6) eV and the frequency factors are  $s_i = 10^{11} \text{ s}^{-1}$  for  $i = 1 \dots 5$ .  $A_i$  are all  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and all  $s_i$  are  $10^{11} \text{ s}^{-1}$ .  $N_1 = 10^{13} \text{ cm}^{-3}$  and  $N_i = 10^{14} \text{ cm}^{-3}$  for  $i = 2 \dots 5$ . Also,  $M = 10^{12} \text{ cm}^{-3}$  and  $A_m = 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . The dose-rate factor is  $X = 10^5 \text{ cm}^{-3} \text{ s}^{-1}$  and the length of excitation is  $t_D = 10 \text{ s}$ . It is readily seen that all four peaks have a shape factor characteristic of

first-order kinetics. The fifth peak occurs in this case at a much higher temperature and as elaborated in the paper by Chen and Pagonis [24], obeys a different kinetics. The evaluated activation energies of the four peaks are within <2% from the original values. The calculated frequency factors are within a factor of 2 from the inserted values. One should note that very small changes in the activation energy correspond to relatively large variations in



**Fig. 6.** Histogram of the symmetry factors of the first four TL peaks simulated using random sets of the trapping parameters. The fixed chosen parameters were  $E_i = (0.25, 0.45, 0.8, 1.4, 2.5)$  eV and  $X = 2 \times 10^8 \text{ cm}^{-3} \text{ s}^{-3}$ .



**Fig. 7.** Histogram of the symmetry factors of the  $n_c(T)$  peaks simulated using random sets of the trapping parameters with the same fixed parameters as in Fig. 6.

the frequency factor, so deviation by a factor of  $<2$  in the latter should be considered rather small.

## 5. Discussion and conclusion

When one deals with a TL curve, resulting from a single trapping state and a single kind of recombination center, one may not know whether recombination or retrapping dominate, leading to first-order or second-order peaks, and in most cases, intermedi-

ate situations of different forms are likely to occur. It has been shown before (see e.g., Sunta et al. [11]; Pagonis and Kitis [22]) that when one has a material with a single recombination center and more than one trapping state, it is likely that in most cases the peaks would be very close to having first-order features. In the present work we show, both analytically and by using simulations, that in the case of multiple trapping states and one recombination center, the lower temperature peaks tend to have first-order features and the last peak is either closer to be of second order or has a very broad tail. Furthermore, we have shown that in the more

**Table 1**

Inserted values of the parameters and  $T_m$  and  $\mu_g$  of the first four peaks. Also are shown the calculated  $E$  and  $s$  values found by using Eqs. (40) and (41).

	Peak 1	Peak 2	Peak3	Peak4	Peak5
Inserted $E$ (eV)	0.3	0.6	0.9	1.2	1.6
Inserted $s$ ( $s^{-1}$ )	$10^{11}$	$10^{11}$	$10^{11}$	$10^{11}$	$10^{11}$
$T_m$ (K)	129.6	255.3	379.2	505.6	>980
$\mu_g$	0.416	0.417	0.421	0.420	
Calculated $E$ (eV)	0.295	0.598	0.910	1.205	
Calculated $s$ ( $s^{-1}$ )	$6.1 \times 10^{10}$	$7.0 \times 10^{10}$	$9.1 \times 10^{10}$	$5.6 \times 10^{10}$	

realistic and complex situation where multiple trapping states and a number of recombination centers take part in the TL process, the prevalence of first-order peaks is still expected in spite of the very intricate processes involving simultaneously all the traps and centers. This is the case even when retrapping is significantly stronger than recombination. In the literature, in experimental results, first-order peaks are reported to be prevalent, which agrees with the above statement. It is possible that in real-life cases, very high-temperature peaks that are not measurable due to black-body radiation may contribute, as explained above, to the first-order appearance of the preceding peaks. These may possibly have second- or higher order features, but since they are not measurable, the impression that first-order peaks are so prevalent may be further strengthened. The simulated curves of  $n_c(T)$  which represent the TSC measurements have also been recorded and analyzed, and a similar occurrence of long-tail last peak and prevalent first-order lower temperature peaks have been found. In most cases but not always, the TSC and corresponding TL peaks have had rather similar shapes and therefore similar symmetry factors. This has been more so in the lower temperature peaks and more variance was found in the fourth peak. Comparing Eq. (24) and (25) one can understand that in this higher temperature peak, the value of  $m$  which is smaller toward the end of the curve varies percentage-wise more, which can explain the difference in shape between the curves described by these equations. The same is true with regard to Eqs. (34) and (35). A similar explanation can be given to the small number of cases in which high (up to  $\sim 0.5$ ) values of the shape factors are observed. If at a range where a peak occurs, the term in Eq. (20) or its equivalent in the multi-center case changes abruptly due to the exhaustion of a center, the TSC or TL peak may be distorted which may result in an unusual value of  $\mu_g$ . Another way to understand this unusual shape of peaks has to do with competition between centers. Chen and Hag-Yahya [25] discussed the possibility of getting unusually high effective activation energies and frequency factors from TL peaks, considering a model of one trap and three recombination centers, one radiative and two non-radiative. Due to the effect of competition with the non-radiative centers, one at the low-temperature side and one at the high-temperature side, a TL peak may look significantly narrower than “normal”, and as a result, one may get very high apparent activation energy (see Eq. (40)) and consequently, a very high apparent frequency factor (see Eq. (41)). In fact, similar competition may take place at one side of the radiative peak which may distort the shape so as to get unusual values of  $\mu_g$  up to  $\sim 0.5$  even for a peak which is not the highest-temperature one in a series. One might expect an anomaly of having low values of the symmetry factor, but with the cases chosen here in random, only one peak with  $\mu_g = 0.39$ , slightly smaller than the characteristic first-order factor (0.42) has been found. This explanation of getting high and low symmetry factors may apply both for TL and TSC peaks but, as seen in the statistics for multiple randomly chosen parameters, this seems to have occurred in a small number of cases.

It is obvious that the simulated curves given here are merely examples, and large variation of the properties of the curves can

be expected with the infinite number of possible sets of parameters (for more on TL simulations see Chen and Pagonis [26]). However, since the parameters have been chosen in random within a broad range, it seems reasonable, both from the theoretical considerations and the numerical examples that in most cases, in such a situation of many traps-many centers model one can expect the lower temperature peaks to look like first-order peaks whereas the last one or occasionally two peaks will tend to be of second order, although exceptions concerning the shape of the highest-temperature peak may occur, as explained in detail by Chen and Pagonis [24]. A number of last peaks in a series were found to have second-order features, and as mentioned, in a small number of cases, first-order appearance was seen in the last peak in a series. However, this has occurred in the last peak of a series associated with a certain recombination center only if another center which can act as a competitor is still active.

One should note that this study is limited to the cases where the peaks are, more or less, separate and no deconvolution is required for seeing the individual components. This however is an inherent limitation that is not caused by the treatment given here. The point is that when electron traffic is through the conduction band and recombination and retrapping occur simultaneously into multiple traps and centers, there are not really separate peaks that can be deconvoluted into individual peaks. Strictly speaking, deconvolution is useful when, for example, one deals with different peaks originating from different components in a mixture of materials or, when only one material is involved, if there is a single peak associated with transition through the conduction band, along with other possible peaks resulting from localized transitions.

Finally, the results of the activation energies found by a peak-shape method were found to match in most cases rather accurately the inserted values. As for the effective frequency factors, they were found to be within a factor of  $<2$  in the example given which can be considered as a good agreement. This point is very relevant since, if one wishes to consider the stability of a TL peak, say, at room temperature, the knowledge of the real activation energy and frequency factor is of great importance.

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