Chapter 1

Recent Advances in the Theory of Thermoluminescence and Optically Stimulated Luminescence; Delocalized Transitions

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Several theories explain different facets of the phenomena of thermoluminescence (TL) and optically stimulated luminescence (OSL). In the present chapter we concentrate on models dealing with processes occurring when charge carriers are moving between traps and centers through the conduction and valence bands. The processes involved include transitions occurring during excitation and during read-out: optical stimulation in OSL and heating in TL. Older theories explaining the basic properties of first-and second-order kinetics as well as the effects of non-linear dose dependence of TL and OSL are briefly mentioned. More recent models, developed in the last decade are described in more detail. The effects of competition between traps and between centers both during excitation and read-out are discussed in some detail, yielding the interpretation of superlinear dose dependence, non-monotonic dose dependence as well as dose-rate dependence. The theories can also explain the experimentally observed concentration quenching and the prevalence of first-order peaks in various materials. A model for explaining an anomalous heating-rate effect and thermal quenching is discussed. The occurrence of anomalously high or low activation energies and frequency factors, sometimes evaluated by standard peak-shape methods is also briefly discussed. Finally, the recently studied subject of two-electron traps or two-hole centers and their effects on TL and OSL phenomena are discussed.

1.1. Introduction

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The phenomena of thermally stimulated luminescence, usually termed thermoluminescence (TL) and optically stimulated luminescence (OSL) consist of the emission of energy previously absorbed in a solid material in the form of light during thermal or optical stimulation. A prerequisite is that the energy be absorbed, usually by irradiating the sample in hand by ionizing or sometimes nonionizing radiation. The captured energy may be released in the form of emitted light either by heating the sample, in TL measurements or by illuminating it by some light source. In the latter case, the emitted stimulated light is usually of different wavelength than the stimulating light.

The basic theory of TL and OSL is based on the existence of imperfections, impurities and defects in the otherwise ordered crystals which give rise to allowed discrete energy levels in the forbidden gap of the crystal which may capture electrons or holes. During excitation, electron and hole pairs are produced by the radiation throughout the sample and certain fraction reach the conduction and valence bands, respectively. These carriers may be trapped in electron and hole traps located in the forbidden gap. It is rather conventional to talk about electron traps, located quite close to the conduction band and about hole centers located far from the valence band. Under these conditions, during TL read-out by heating, the trapped electrons may be raised into the conduction band, and following their motion in the conduction band, recombine with a hole in a luminescence center and recombine with it yielding an emitted photon. A schematic energy level diagram with one electron trap and one-hole recombination center is shown in Fig. 1. It should be noted that a mirror-image model is just as likely to occur. If the hole trap is located close to the valence band and the electron trap, now referred to as a center, is far from the conduction band, the process taking place during heating includes the thermal release of a trapped hole into the valence band and its recombination with an electron in a center, thus yielding a TL photon. The situation in OSL is the same as far as the excitation is concerned. As for read-out, photons, e.g. infra-red light, raise



Fig. 1. Schematic energy-level diagram showing an electron trap and a hole center.

electrons from the trap to the conduction band which then find counterpart holes in the center and recombine to yield OSL photons, usually with different wavelength than the stimulating IR light. Like in TL, the inverse picture of hole traps and electron centers can be considered as being relevant also to OSL. It should be mentioned that the models discussed in this chapter assume a homogeneous excitation of the sample which is a good assertion of the situation taking place with UV, X-ray and γ excitation and to a lesser extent, for β exposure.

The parameters shown in Fig. 1 are as follows: E (eV) is the activation energy for releasing a trapped electron, s (s⁻¹) is the frequency factor, A_m (cm³s⁻¹) and A_n (cm³s⁻¹) are the recombination and retrapping probability coefficients, B (cm³s⁻¹) is the trapping probability coefficient of free holes into centers, M (cm⁻³) is the concentration of hole centers and m (cm⁻³) its instantaneous occupancy, N (cm⁻³) is the concentration of electron traps and n (cm⁻³) its instantaneous occupancy. n_c (cm⁻³) and n_v (cm⁻³) are, respectively, the instantaneous concentrations of free electrons and holes. X (cm⁻³s⁻¹) is the rate of production of electron-hole pairs, proportional to the dose rate.

The set of simultaneous differential equations governing the process during excitation is (see e.g. Chen and Pagonis, [1])

$$\frac{dn}{dt} = A_n(N-n)n_c - sn\exp(-E/kT),\tag{1}$$

$$\frac{dm}{dt} = B(M-m)n_v - A_m m n_c, \qquad (2)$$

$$\frac{dn_c}{dt} = X - A_n(N-n)n_c - A_m m n_c, \tag{3}$$

$$\frac{dn_v}{dt} = \frac{dn}{dt} + \frac{dn_c}{dt} - \frac{dm}{dt}.$$
(4)

At the end of excitation one ends up with a finite concentration of free electrons, n_c , and free holes, n_v . If one wishes to mimic the experimental procedure of TL or OSL, one has to consider a relaxation time between the end of excitation and the beginning of heating or exposure to stimulating light. This is done by setting X to zero and solving Eqs. (1-4) for a further period of time so that at the end, both n_c and n_v are negligibly small. Obviously, the final values of n, m, n_c and n_v at the end of excitation are used as initial values for the relaxation stage. Finally, for the readout stage, we take the final concentrations in the relaxation stage as initial values for the next stage and simulate either the heating in TL or the optical stimulation in OSL. It is worth mentioning that in this, relatively simple case of one trapping state and one kind of recombination center, the final concentrations of traps and centers, which are the initial concentrations n_0 and m_0 for the readout stage must be the same. However, when several traps and/or centers are involved, the solutions of the excitation and relaxation stages prior to the read-out stage are crucial in order to get realistic results.

Before moving to the discussion of the heating stage in TL in the one-trap-one recombination center (OTOR) case shown in Fig. 1, let us mention briefly the preceding models given in the earlier literature. Randall and Wilkins [2] developed the first theory for a single TL peak. These authors assumed that once an electron is thermally raised into the conduction band it immediately performs

recombination with a trapped hole in center, and wrote the equation

$$I(T) = -dn/dt = sn \exp(-E/kT).$$
(5)

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I(T) is the intensity of emitted TL and k (eV/K) is the Boltzmann constant. Note that as is, the units of I(T) are cm⁻³s⁻¹ and in order to have it in light-intensity units a constant should be added which is arbitrarily set to unity. Equation (5) is a first-order equation and its solution for a linear heating function is an asymmetric glow peak with a fall-off half-intensity width smaller than the half-intensity in the increasing part. In a later work, Garlick and Gibson [3] took into consideration the possibility of having freed electrons retrap into their initial trapped state and reached a second-order TL peak with nearly symmetrical shape. Halperin and Braner [4] considered the traffic of carriers during the heating of the sample following excitation, taking into account thermal excitation, recombination and retrapping. The set of coupled differential equations governing the process during heating is

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

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

$$\frac{dm}{dt} = \frac{dn}{dt} + \frac{dn_c}{dt}.$$
(8)

Note that both here and in the simpler first-order case of Fig. 1, in order to simulate a conventional TL curve, one has to use some heating function which in most cases is chosen to be linear with time, i.e., a constant heating rate is used,

$$T = T_0 + \beta t, \tag{9}$$

where T_0 (K) and T (K) are the initial and running temperature and β (K/s) is the constant heating rate.

This set of coupled differential equations cannot be solved analytically and therefore two different approaches can be applied. In the earlier stages of TL study, simplifying assumptions were made in order to reach possible conclusions. The alternative which has been utilized broadly in more recent studies has been to assume

a plausible set of trapping parameters and solve the equations numerically. Both these approaches will be described here. The same two approaches can be pursued and the results of the two compared also in more complex situations where more trapping levels and/or more recombination centers are involved. Another approach recently developed by Kitis and Vlachos [5] is briefly mentioned. These authors dealt with TL, OSL and linearly modulated OSL (LM-OSL), and found general semi-analytical expressions, using the Lambert W-function.

Halperin and Braner [4] have suggested an approximate expression for the dependence of the emitted light on the relevant occupancies of traps and centers, which also gave a better insight into the question of the effective order of kinetics. They made the simplifying assumptions later termed "quasi-equilibrium" or "quasisteady" assumptions

$$\left|\frac{dn_c}{dt}\right| \ll \left|\frac{dn}{dt}\right|, \quad \left|\frac{dm}{dt}\right|; \quad n_c \ll n, m,$$
 (10)

which state that the rate of change of free carriers is significantly smaller than that of the trapped carriers, and that the concentration of free carriers is significantly smaller than that of trapped carriers. It should be mentioned that Chen and Pagonis [6] suggested a somewhat different way of expressing the conditions leading to the simplified expression given by Halperin and Braner [4], namely

$$\left|\frac{dn_c}{dt}\right| \ll sn \exp(-E/kT), \quad n_c[A_n(N-n) + A_mm], \qquad (11)$$

which simply means that the net rate of change of free electrons is significantly smaller than the rates of thermal elevation of electrons into the conduction band and the depletion of free electrons into the trap and center together.

Using either of these sets of simplifying assumptions, one gets

$$I(T) = -\frac{dm}{dt} = sn \exp(-E/kT) \frac{A_m m}{A_m m + A_n (N-n)}.$$
 (12)

Obviously, this one equation in two unknown functions, n and m, cannot be solved without further assumptions. As long as only one

trap and one center are involved, and along with the original quasiequilibrium assumption, we can assume that $m \approx n$, and one gets an equation in one function, n, only (see Kanunnikov [7])

$$I(T) = -\frac{dn}{dt} = sn \exp(-E/kT) \frac{A_m n}{A_m n + A_n (N-n)}.$$
 (13)

Further simplifying assumptions would lead to the firstand second-order kinetics equations. If recombination dominates, $A_m m \gg A_n (N - n)$, one gets directly the Randall-Wilkins firstorder, Eq. (5). The second-order kinetics suggested by Garlick and Gibson [3] can also be reached from Eq. (13) by making different simplifying assumptions. If we assume that retrapping dominates, $A_n (N - n) \gg A_m m$ and that the trap is far from saturation, $N \gg n$, Eq. (13) reduces to

$$I(T) = -\frac{dn}{dt} = \frac{sA_m}{A_nN}n^2 \exp(-E/kT).$$
(14)

Another less likely possibility is that the retrapping and recombination probability coefficients are equal, $A_m = A_n$. Equation (13) reduces now to

$$I(T) = -\frac{dn}{dt} = \frac{s}{N}n^2 \exp(-E/kT).$$
(15)

Both these last expressions are second-order equations with somewhat different meaning of the effective pre-exponential coefficient.

It is quite obvious that cases intermediate between the first-order case (Eq. 5) and the second order (Eqs. 14, 15) are possible. A very popular approach is using the heuristic "general order" equation (see e.g. Chen [8])

$$I(T) = -\frac{dn}{dt} = s'n^b \exp(-E/kT), \qquad (16)$$

where b is different from 1 or 2. The disadvantage of this approach is that it has no real physical basis where $b \neq 1, 2$ and also that s' has the "strange" units of cm^{3(b-1)}s⁻¹. The advantage is that the solution of Eq. (16) may yield any symmetry between those of the first- and second-order kinetics.

Another possible way of presenting intermediate cases is that of the mixed-order kinetics (see e.g., Chen *et al.* [9])

$$I(T) = -\frac{dn}{dt} = s'n(n+c)\exp(-E/kT),$$
(17)

where here, s', the pre-exponential factor has the same units as in the second-order case, namely, cm³s⁻¹.

In the present chapter we elaborate on a number of aspects of TL and OSL that can be explained by models dealing with delocalized transitions taking place during the excitation and read-out stages.

1.2. Dose dependence

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One of the most important aspects of TL and OSL is the dependence of the signal on the excitation dose. This kind of measurement is of great interest from the pure scientific viewpoint, but also has importance in the applications in dosimetry and in geological and archaeological dating elaborated upon in this volume. It is obvious that for the applications, ideal dose dependence is a linear behavior in the broadest dose range possible. In real life, this is usually not the case and different kinds of non-linear dose dependence are observed. The most common one is that at relatively high doses, saturation effects take place, namely, the dose dependence is sublinear from a certain dose on. More interesting are situations where superlinearity occurs. Nonlinear growth of TL as a function of absorbed β or γ dose, mainly in the important dosimetry material LiF (TLD-100) has been discussed in some detail by Cameron et al. [10]. The characteristic behavior here was a rather broad linear dose dependence followed by more than linear range after which, an approach to saturation was observed. Another kind of superlinearity was discovered in the midsixties by Tite [11] in ancient ceramics. Here, the dose dependence curve is linear in a broad range, except for the lowest doses where the TL starts increasing at a small rate with the dose and the rate increases gradually until it reaches a steady value which prevails over a broad dose range. Another sort of superlinearity was reported by Halperin and Chen [12] who studied the dose dependence of UV-irradiated semiconducting diamonds. UV light in the range of

300–400 nm (4–3 eV) excited a TL peak at \sim 250 K and the initial dose dependence of the emitted light could be presented as

$$I_{\max} = \alpha D^k, \tag{18}$$

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where I_{max} is the maximum intensity, D the applied dose and k is a factor between 2 and 3 in the mentioned range of 300–400 nm. The superlinearity is expressed by having a k value larger than unity. Two other cases of such very strong superlinearity ($k \sim 3$) of TL have been reported. Chen *et al.* [13] described the effect in β -excited quartz and reported nearly cubic dose dependence and Otaki *et al.* [14] communicated on slightly more than cubic dose dependence of TL in CaF₂:Tb₄O₇.

1.2.1. Theory of superlinear dose dependence

The basic understanding of the superlinear dose dependence of TL and OSL usually includes different kinds of competition. The two main sorts of competition are competition that takes place during excitation and that which occurs during readout (heating in TL and optical stimulation in OSL) or both. The first model explaining superlinearity has been given by Cameron *et al.* [10] (see pp. 168–174). This model proposes the creation of additional traps by radiation and hypothesizes a maximum possible trap density. Another model was given by Suntharalingam and Cameron [15] and further elaborated upon by Bowman and Chen [16]. These authors assumed that the total concentration of traps is not changed by the irradiation and the superlinearity is associated with the competition of electrons being trapped into the active trap and into a competing, usually deeper trap. Intuitively speaking, let us assume a system with concentrations N_1 (cm⁻³) active traps and N_2 (cm⁻³) competing traps. Let us assume that the trapping probability coefficient A_2 is larger than that of the active trap, A_1 . At low doses, the excitation fills both traps linearly. However, at a certain dose the competing trap saturates and therefore more electrons are made available to the trap of interest N_1 . This causes faster though linear filling of the trap. However, the transition region from one linear range to the other would appear to be superlinear since this transition

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occurs continuously. Bowman and Chen [16] wrote the proper set of differential equations, made the relevant simplifying assumptions and reached an expression that with the appropriate choice of sets of trapping parameters yielded a dose-dependence curve which starts linearly, continues superlinearly and then tends to saturation.

Rodine and Land [17] reported on the dose dependence of some TL peaks in β -irradiated ThO₂ which were found to be quadratic with the dose starting at the lowest doses, and explained the effect qualitatively as being the result of competition during heating. Kristianpoller et al. [18] explained the effect in terms of competition during heating (see a more elaborate explanation in Chen and Pagonis [1], pp. 198–205). Without competition, one may expect the area S under a glow peak to be proportional to min (n_0, m_0) where n_0 and m_0 are, respectively, the concentrations of electrons in traps and holes in centers following excitation and relaxation and prior to readout. The maximum TL intensity is usually more or less proportional to the area under the curve. Thus, if n_0 and m_0 are linearly dependent on the dose of excitation, the measured TL intensity is also linear with the dose. Kristian poller et al. [18] showed that in the presence of a strong competing trap, the dependence of the area under the curve is, due to competition during heating

$$S \propto n_0 m_0, \tag{19}$$

and if $n_0 \propto D$ and $m_0 \propto D$, then $S \propto D^2$. In a later work, Chen *et al.* [19] have combined the two approaches and showed, using numerical simulation that with a model with two competing traps and one recombination center, more than quadratic dose dependence may be reached, the main effect being related to competition during heating. On the other hand, in a model with two competing centers and one kind of trap, a much weaker superlinearity can be explained, mainly associated with competition during excitation.

In recent years, it has been shown that under the appropriate circumstances, superlinearity of TL and OSL can take place even without competition, which was termed "intrinsic" superlinearity. Chen *et al.* [20] used the simple OTOR energy level diagram, Fig. 1 and considered the situation where relatively high dose rates

are being used. As stated by these authors, the second derivative d^2n/dD^2 being positive indicates superlinear dose dependence. Referring to the parameters shown in Fig. 1, the filling of traps with dose can be given as

$$n = aD + bD^2 + O(D^3), (20)$$

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where

$$a = \frac{A_n N}{A_n N + A_m m_0},\tag{21}$$

$$b = \frac{1}{2} \frac{A_m m_0 A_n N}{(A_n N + A_m m_0)^3} (A_m - A_n).$$
(22)

The coefficient *b* governs whether the initial response is superlinear, linear or sublinear. According to Eq. (22), the behavior is superlinear (b > 0) if $m_0 > 0$ and $A_m > A_n$. The initial dose dependence is expected to be linear if $m_0 = 0$ or, if $m_0 > 0$ but $A_m = A_n$. Chen *et al.* [20] gave also results of numerical simulations that at the lowdose range coincide with those given by Eq. (20). At higher doses, the D^3 and higher terms become important and on the other hand, saturation effects may set in, so that the semi-analytical result and the outcome of the numerical simulation tend to diverge. Another situation that may lead to superlinear dose dependence is associated with two-electron traps and two-hole centers which are explained in subsection 1.2.3.

1.2.2. Non-monotonic dose dependence

The TL intensity in different materials is usually a monotonically increasing function of the dose, which quite often reaches a saturation value. In several materials, however, non-monotonic dose dependence has been observed. The TL intensity reached a maximum at a certain dose and decreased at higher ones. For some examples, Cameron *et al.* [10] described the non-monotonic dose dependence in LiF:Mg, Ti as a function of ⁶⁰Co γ -ray excitation dose. Jain *et al.* [21] describe a significant decrease of the TL output of peak V in LiF, by a factor of ~2.5 from the maximum, and ascribe it to radiation damage. Yukihara *et al.* [22] described a somewhat superlinear dependence

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up to $\sim 10 \text{ Gy}$ of β irradiation of the 450 K peak in Al₂O₃:C. The peak reached a maximum value and declined at higher doses.

Chen et al. [23] suggested a rather general model which does not assume a radiation damage of destruction of trapping states and/or recombination centers. The authors assume the existence of two trapping states and two kinds of recombination centers. The competition over charge carriers during excitation and heating was examined using both numerical simulations and intuitive considerations. The authors chose a physically significant set of trapping parameters and performed the simulation of the three stages of the relevant experiment, namely, excitation, relaxation and heating. An example of the results is shown in Fig. 2. The results show an increase of the TL maximum (solid line) with the dose up to a maximum at a 'dose' of $\sim 7 \times 10^{20} \,\mathrm{m}^{-3}$, followed by a decrease of $\sim 35\%$ after which the maximum TL intensity tends to level off at higher doses. This behavior is very similar to experimental results reported in some materials, e.g., see Jain *et al.* [21]. A similar behavior is seen in the plot of m_2 at the end of the relaxation period (dashed line).



Fig. 2. Simulated dose dependence of the maximum TL (solid line) and radiative-center concentration at the end of irradiation, m_2 (dashed line), when competition during irradiation dominates. (After Chen *et al.* [23]).

Pagonis *et al.* [24] used a similar model to account for the nonmonotonic dose dependence of OSL. Such results had been observed by Yukihara *et al.* [22], [25].

A later work by Chen *et al.* [26] discussed the time and dose-rate dependence of TL and OSL due to competition between excitation and fading. The authors presented a model of two trapping states and one kind of a recombination center and using simulations, studied the dependence on the time of excitation of the filling of the active trap, to which the TL or OSL signal is proportional. The solution of the relevant set of coupled differential equations has revealed a time dependence of an increase up to a maximum value and then a decrease toward an equilibrium value where the rates of production and decay are equal. This model is more concise since it includes only one kind of recombination center, however, here, the non-monotonic effect occurred only when the dose changed by varying the time of excitation. Here, when the dose rate was varied with constant time of excitation, the curve increased monotonically until it reached the saturation value.

1.2.3. Double-charge traps and centers

In a recent work, Chen et al. [27], [28] have studied the effects of two-electron traps and two-hole centers on the behavior of TL glow curves. The concept of double-electron traps had been established before with regard to different solid state phenomena and also mentioned in connection with TL. Also have been mentioned in the literature two-hole centers and their effect on the TL properties. Mayhugh [29] and Townsend et al. [30] explained results of TL in LiF by the existence of V_3 centers containing two trapped holes. Böhm and Scharmann [31] mentioned the occurrence of two-electron F' centers in alkali-halides with relation to the general subject of TL dosimetry. Yazici et al. [32] who studied TL of LiF:Mg,Ti between 100 and 300 K suggested that their results are related to the V_3 two-hole centers. The same V_3 centers have been considered as being associated with TL by Horowitz [33] and by Eliyahu et al. [34]. Woda and Wagner [35] while explaining non-monotonic dose dependence of Ge- and Ti-centers in quartz, discuss a model of double-electron

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capture which can be expressed in both EPR and TL measurements. Chen et al. [28] wrote the relevant sets of equations for the excitation, relaxation and heating stages of TL relevant to the two-electron trap model. The model given in Fig. 2 represents the present situation except that the trap can capture either one or two electrons. Let us denote now by n_1 (cm⁻³) the traps with one electron and by n_2 (cm^{-3}) the traps with two electrons. Obviously, the instantaneous concentration of empty traps is $N - n_1 - n_2$. The activation energy of a single electron in a trap will be denoted by E_1 (eV) and the energy for releasing an electron from a double-occupied trap by E_2 (eV). One may assume that $E_1 > E_2$ since with two electrons in a trap there may be Coulombic repulsion whereas with one electron, there may be some Coulombic attraction of the electron to the impurity ion forming the trap. As for the trapping probability coefficients, A_1 (cm^3s^{-1}) is the probability coefficient into an empty trap and A_2 (cm^3s^{-1}) is the trapping probability coefficient into a trap with one electron. In most cases, one would predict that $A_1 > A_2$ since the probability of capturing a free electron is expected to be larger in the empty trap than in a trap holding an electron.

The results of the simulations and the approximate analytical analysis show that the lower-temperature peak has first-order features and is strongly superlinear with the excitation dose. As shown in Fig. 3, the dose dependence is slightly more than cubic with the excitation dose, which may explain the experimentally found strongly superlinear dose dependence mentioned above.

A rather similar situation has been studied by Chen *et al.* [28], namely the case where a recombination center may capture one or two holes. The authors have shown the expected TL behavior using in parallel numerical simulation and approximate analytical treatment. The outcome is two TL peaks and the two-hole center behaves in a sense like two centers with different recombination probabilities. The lower temperature peak has first-order features and is more than quadratically superlinear with the dose. The second peak has a second-order shape and both peaks shift to lower temperature with the dose which is explained by a change in the effective frequency factor with excitation dose.



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Fig. 3. Dependence of the area under the two simulated TL peaks on dose of excitation plotted on a log-log scale. (a) The lower temperature peak; the dashed line shows the analytical results and the triangles represent the numerical results. (b) The higher temperature peak; the solid line shows the analytical results and the diamonds are the numerical results. (After Chen *et al.* [27]).

1.2.4. Dose-rate dependence

In the previous sub-section, we discussed the dose dependence of TL and OSL, assuming that it does not matter whether the dose applied on the sample in hand is varied by changing the time of excitation or by changing the dose rate. In fact, dose rate and time of excitation are independent variables and in some cases, the resulting luminescence may depend on the dose rate even when the total dose applied is the same. It should be noted that when

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archaeological and geological dating is concerned, the natural dose rate may be as low as 10^{-3} Gy \cdot yr⁻¹ (3 × 10⁻¹¹ Gy \cdot s⁻¹), whereas the laboratory dose rate applied for calibration may be as high as several $Gy \cdot s^{-1}$. One has to distinguish between a dose-rate effect such as that reported by Facey [36], which has to do with the thermal decay during excitation, and "real" dose-rate effect where the TL or OSL signal is stable such that no thermal decay is expected at ambient temperature. Groom et al. [37] reported such a significant effect in quartz where no thermal decay takes place. Here, a decrease by up to a factor of ~ 5 was observed with increasing dose rate (and constant total dose) in powdered samples of Brazilian crystalline quartz when irradiated by ⁶⁰Co γ -rays at dose rates ranging from 1.4×10^{-3} to $3.3 \,\mathrm{Gy} \cdot \mathrm{s}^{-1}$. Also reported on the dose-rate effect in quartz Chawla et al. [38]. A smaller effect of the same sort in $CaSO_4$: Dy has been reported by Hsu and Weng [39]. Shlukov et al. [40] suggested that in archaeological and geological dating based on TL in quartz, the fact that there is a difference of 8-9 orders of magnitude in the dose rate between natural and calibration irradiations may cause a serious error in the age evaluation. A very interesting dose-rate effect has been reported by Valladas and Ferreira [41]. They distinguish between three components in the emission of TL from quartz, namely UV, blue and green. Applying the same total dose of excitation at two dose rates which are three orders of magnitude apart, they found different behaviors for the three components. The UV component was nearly twice as large with the high dose rate as with the low one. As for the green component, the low dose rate yielded about 10% less than in the high one. However, with the blue component, the low dose rate yielded about 50% more TL than the high one.

Chen and Leung [42] have explained by the use of simulations the occurrence of the dose-rate effect. The model they used included one trapping state and two kinds of recombination center and it simulates the mentioned situation reported by Valladas and Ferreira [41], namely that two spectral components in quartz behave in opposite ways, one increases and one decreases with the dose rate. Chen and Leung used the relevant sets of coupled differential equations for the three stages of excitation, relaxation and read-out (heating), and

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Fig. 4. The dose-rate dependence of the TL maximum intensities of $I_1(T)$ (crosses) and $I_2(T)$ (circles) from the simulations. (After Chen and Leung [42]).

recorded the two emissions, $I_1 = -dm_1/dt$ and $I_2 = -dm_2/dt$, where m_1 and m_2 are the concentrations of the two recombination centers, respectively.

The dose-rate dependence results of a simulation are given in Fig. 4.

1.3. A model for concentration quenching of TL and OSL

All luminescence effects in solids including TL and OSL are directly related to the occurrence of impurities and defects in the host crystal. One would normally expect that when a certain imperfection is responsible for the appearance of TL or OSL, higher imperfections level would mean more emitted luminescence for a given excitation. However, several experiments have shown that a non-monotonic dependence on the impurity concentration may take place. The response to a given irradiation may increase with the

impurity concentration up to a maximum, and then decline for higher concentrations. This effect has been termed concentration quenching (CQ). The first non-monotonic concentration dependence of TL on the relevant impurity concentration has been reported by Medlin [43]. He described the dependence of a TL peak on Mn⁺⁺ impurity in calcite at 350 K and showed that for a given irradiation, a maximum intensity was reached for a certain impurity concentration. Rossiter et al. [44] reported on the concentration dependence of peak #5 at 210°C, in LiF:Ti. They found a peak-shaped dependence on the Ti concentration with a maximum efficiency at $\sim 8 \text{ ppm}$. Nambi *et al.* [45] described the concentration quenching effect of CaSO₄, with Dy or Tm impurities. In both cases, the maximum efficiency occurred at ~ 0.1 weight percent of the dopant. Lai *et al.* [47] investigated the TL of ZrO₂ doped with Yb₂O₃ and found concentration quenching with a maximum at 5 mol[%], followed by a decrease at higher concentrations. Chen et al. [46] proposed a model based on the transitions of electrons and holes between trapping states, the conduction band and the valence band. The model is meant to demonstrate the possibility of explaining the CQ effect for two TL peaks, where the maximum intensity occurs at two different concentrations, similarly to the results by Medlin [43] in Pb⁺⁺ doped calcite. Note that in Medlin's work, the maxima for four peaks in Mn^{++} doped dolomite occurred at different concentrations and one might expect that assuming more trapping states may yield the CQ effect for more than two peaks.

The proposed energy level model includes three electron trapping states, each with N_i (cm⁻³) concentration, E_i (eV) activation energy, s_i (s⁻¹) frequency factor and A_i (cm³s⁻¹) retrapping-probability coefficient, for i = 1, ..., 3 and a recombination center with concentration M and instantaneous hole concentration of m. Chen *et al.* [46] wrote the set of equations governing the excitation stage and relaxation stage (with X = 0), analogous to Eqs. (1–4) but with two more equations for the additional two trapping states, and the set analogous to Eqs. (6–8) with the two additional traps. The results of the solution of the equations solved sequentially for excitation, relaxation and heating, in the same way as explained above for

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Fig. 5. Simulated results of the concentration dependence of the areas under two TL peaks (After Chen *et al.* [46]).

the simpler OTOR case and for a set of chosen plausible values of the trapping parameters is shown in Fig. 5. The authors state that if one starts the excitation stage with empty centers, the nonmonotonic concentration quenching effect is not seen. Instead, if one assumes that the initial occupancy of the centers is a given fraction of the total concentration of the centers, the effect takes place. For the simulation of Fig. 5, the authors chose a fraction $\alpha = 0.1$ of the centers being initially full, which yielded the results shown. The authors emphasize that the underlying reason for the non-monotonic dependence of the TL sensitivity on the concentration is the competition in trapping, both during excitation and read-out between the three traps.

1.4. Heating-rate effects in TL and thermal quenching

In practically all known cases, the TL glow peak shifts to higher temperature with increasing heating rate (see e.g. Hoogenstraaten [48]). This can be easily shown for the simple case of first-order kinetics. The solution of Eq. (5) is

$$I(T) = sn_0 \exp(-E/kT) \exp\left[-(s/\beta) \int_{T_0}^T \exp(-E/k\tau) d\tau\right].$$
 (23)

The well-known condition for the maximum, found by setting the derivative of Eq. (23) to zero, can be written as

$$\beta = (sk/E)T_m^2 \exp(-E/kT_m), \qquad (24)$$

where T_m (K) is the temperature at the maximum and β (Ks⁻¹) the heating rate. When β increases, the right-hand side must increase by the same amount. Furthermore, since $T_m^2 \exp(-E/kT_m)$ is an increasing function of T_m , the rise in its value implies that T_m must increase. It has been shown (e.g. Chen and Winer [49]) that although in more complex cases Eq. (24) does not hold precisely, it can serve in many instances as a good approximation. Anyway, the shift of a TL peak to higher temperatures with increasing heating rates is a general property.

Chen et al. [50] have pointed out that a distinction should be made between two alternative presentations of TL. As an example, one may consider the simple first-order case given by Eqs. (5) and (23). As mentioned above, a dimensional proportionality factor is missing between I(t) and -dn/dt in Eq. (5) which is arbitrarily set to unity. The units of I(t) are cm⁻³s⁻¹ whereas the real intensity is given in photons per second or energy per second. As shown before (e.g. Kumar *et al.* [51]), when increasing the heating rate, the maximum intensity increases nearly proportionally. The area under the curve must remain the same for all heating rates and the simple explanation for the increased intensity is that when heating is faster, the peak gets narrower on the time scale. An alternative, quite common presentation is reached by normalizing the intensity as defined in Eq. (5) by dividing it by the heating rate β . Unfortunately, this is also usually termed in the literature "intensity". This magnitude is usually plotted as a function of temperature rather than time. Thus, the area under the curve remains constant with different heating rates, and this normalized intensity, which is I(T) = -dn/dT $(cm^{-3}K^{-1})$ has a slightly decreasing maximum value associated with a slight broadening of the peak with increasing heating rates. The decrease of the normalized intensity with the heating rate is not limited to the first-order case and is observed in many more complicated situations.

Wintle [52] reported on thermal quenching of TL in quartz which is the decrease in luminescence efficiency with the rise in temperature. As reported by several authors (e.g. Subedi *et al.* [53]; Kafadar [54]) the decrease of the maximum of normalized TL with the heating rate is significantly faster than the slight decrease described above. The common explanation has been that since the peak shifts to higher temperature with the heating rate, its intensity decreases due to the thermal quenching. Thus, the area under the normalized curve is not constant but rather, it decreases with increasing heating rates.

In recent years, a number of reports on an inverse, anomalous heating rates effect have been published. Kitis *et al.* [55] have reported on a heating-rate effect in fluorapatite in which the maximum normalized TL intensity and the integral under the curve increased with the heating rate. Bos *et al.* [56] have described a similar effect in YPO₄:Ce³⁺,Sm³⁺. Delice *et al.* [57] have described the results of TL in GaS. Two peaks were reported for different heating rates. Whereas the lower-temperature normalized peak decreased with the heating rate β , the higher-temperature normalized peak increased with β . Mandowski and Bos [58] explained the effect in YPO₄:Ce³⁺,Sm³⁺ by a semi-localized transitions model. Pagonis *et al.* [59] used a simplified semi-localized-transition model to explain the anomalous heating-rate effect.

Chen and Pagonis [50] suggested another model for explaining the anomalous heating-rate effect. The model with one electron trap N, one recombination center M_1 and one reservoir M_2 is shown in Fig. 6. It is assumed that the electron trap is close enough to the conduction band so that electrons are thermally raised into the conduction band during the heating stage. One also assumes that M_1 , the recombination center is far enough from the valence band so that no holes are thermally released from it into the valence band during heating. Concerning M_2 , one assumes that it may capture holes from the valence band during excitation and that electrons from the conduction band may recombine with holes both during the excitation and the heating stages. In a sense, this is a Schön-Klasens model (see Schön [60]; Klasens [61]) with an additional reservoir center.





Fig. 6. Schematic energy level diagram describing the model explaining the anomalous heating-rate effect (After Chen and Pagonis [50]).

The instantaneous concentrations of free electrons and holes are n_c and n_v , respectively. The activation energy of electrons is E_1 and the frequency factor is s_1 . The activation energy of holes from m_2 is E_2 and the relevant frequency factor is s_2 . The trapping probability coefficient of electrons is A_n and of holes into M_1 and M_2 are B_1 and B_2 , respectively. The recombination probability coefficients into M_1 and M_2 are A_{m1} and A_{m2} , respectively. The rate of production of electron and hole pairs, proportional to the dose rate, is denoted by X.

The set of simultaneous differential equations governing the relevant processes is

$$\frac{dn}{dt} = A_n (N - n) n_c - s_1 n \exp(-E_1/kT),$$
(25)

$$\frac{dm_1}{dt} = B_1 n_v (M_1 - m_1) - A_{m1} m_1 n_c, \qquad (26)$$

$$\frac{dm_2}{dt} = B_2 n_v (M_2 - m_2) - A_{m2} m_2 n_c - s_2 m_2 \exp(-E_2/kT), \quad (27)$$

$$\frac{dn_c}{dt} = X - A_n(N-n)n_c - A_{m1}m_1n_c - A_{m2}m_2n_c.$$
 (28)

$$\frac{dn_v}{dt} = \frac{dn}{dt} + \frac{dn_c}{dt} - \frac{dm_1}{dt} - \frac{dm_2}{dt}.$$
(29)

Chen and Pagonis [50] have chosen a reasonable set of trapping parameters and solved numerically the equations in the above mentioned sequence of excitation, relaxation and heating using a linear heating function $T = T_0 + \beta t$ where β is the constant rate. One may assume that the emitted light is associated with the recombination of free holes into M_1 or into M_2 . In the former, if transition into M_1 is radiative and into M_2 is non radiative, the emitted light intensity is given by

$$I(t) = A_{m1}m_1n_c, (30)$$

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and the mentioned normalized intensity is

$$I(T) = A_{m1}m_1n_c/\beta. \tag{31}$$

The authors note that in more elementary TL models, where valence-band holes are not involved in the read-out process, the way to present the TL intensity is $I(t) = -dm_1/dt$, but since here m_1 varies by two channels, recombination with electrons from the conduction band and trapping of holes from the valence band, Eqs. (30) and (31) are the correct way to present the emission of light. By varying the heating rate in the simulation, the authors could show, by using a set of plausible parameters, the anomalous heating-rate effect, namely that with increasing heating rate, the normalized intensity of the TL signal increased. Chen and Pagonis [50] also showed that a strong decrease of the normalized TL intensity with increasing heating rate, similar to that usually explained as the result of thermal quenching, can be reached by nearly the same model. One uses the same set of equations and the same sequence of three stages and the only different assumption made is that now, the transition into M_2 is considered to be radiative whereas the transition into M_1 is assumed to be non-radiative and therefore, this center acts only as a competitor. The TL intensity is given by

$$I(t) = A_{m2}m_2n_c, (32)$$

and the normalized intensity is

$$I(T) = A_{m2}m_2n_c/\beta. \tag{33}$$

By using the same set of parameters and increasing the heating rate, Chen and Pagonis [50] found that the normalized intensity given by





Fig. 7. Simulated TL curves with both transitions into M_1 and M_2 being radiative. The heating rates vary by a factor of 2 between (a) 0.5 Ks^{-1} and (e) 8.0 Ks^{-1} (After Chen and Pagonis [50]).

Eq. (33) reduced significantly with an increase in the heating rate, similarly to the well recognized thermal-quenching effect of TL.

Finally, Chen and Pagonis consider the situation that both trasitions into M_1 and M_2 are radiative and therefore, the measured (or simulated) curve includes two peaks. With increasing the heating rate, the simulated lower-temperature peak decreases whereas the higher-temperature peak increases. The results of the simulations are shown in Fig. 7. These results are qualitatively similar to the mentioned results in GaS crystals, given by Delice *et al.* [57].

1.5. The expected order of kinetics in a series of TL peaks

As can be understood from the discussion in the introduction, single TL peaks may be of first order or second order and obviously, many intermediate possibilities may occur. At first sight, one may think that this should be the case also when peaks which are part of a

series of peaks from the same material are measured. However, in the literature, there is vast evidence that in glow curves consisting of a series of peaks, first-order kinetics is prevalent in natural materials. Lewandowski and McKeever [62] state that first-order processes dominate in nature. Sunta et al. [63] 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 [64] and Abd El-Hafez *et al.* [65]. Some authors described the prevalence of firstorder shaped peaks in both TL and TSC peaks and mentioned the competition with deep traps as the reason. These include Haering and Adams [66], Dussel and Bube [67], Böhm and Scharmann [68], Simmons and Taylor [69], Agersap Larsen et al. [70] and Opanowicz [71]. The same reason of competition with deep traps has been mentioned by Smith and Rhodes [72] and by Bailey et al. [73] for the first-order behavior of OSL decay in quartz. Pagonis and Kitis [74] have 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). These authors solve numerically the set of equations for different values of A_n/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 multi-trap system (IMTS) model, they choose sets of parameters at random within the reasonable ranges, solve the equations to get glow curves and determine 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 $\sigma = 0.16$. They ascribe the nearly first-order property to the competition between the traps.

Chen and Pagonis [75] discuss the circumstances under which most of the peaks in a series can be expected to be of first order. In particular, they distinguish between the lower temperature peaks in a series and the highest temperature one. They start with a model with





Fig. 8. Schematic energy-level diagram with K trapping states and L kinds of recombination center. Transitions occurring during excitation and during heating are shown. The thick arrows denote the different TL emissions. (After Chen and Pagonis [75]).

multiple trapping states and one recombination center and continue with a more general model with several trapping states and multiple kinds of recombination centers. In the former, simpler case, a series of K traps with different E_i and s_i values and different values of the retrapping probabilities A_i are assumed. For simplicity, the authors also assert that the parameters are such that the peaks are quite well separated. The energy-level diagram is shown in Fig. 8. The set of equations (6–8) now changes into

$$\frac{dn_i}{dt} = A_i (N_i - n_i) n_c - s_i n_i \exp(-E_i/kT), \quad \text{for } i = 1, \dots, K$$
(34)

$$I(T) = -\frac{dm}{dt} = A_m m n_c, \tag{35}$$

$$\frac{dn_c}{dt} = \sum_{i=1}^{K} s_i n_i \exp(-E_i/kT) - \sum_{i=1}^{K} A_i (N_i - n_i) n_c - A_m m n_c.$$
 (36)

Making the quasi-equilibrium assumption $dn_c/dt \approx 0$, one gets from Eq. (36)

$$n_c = \frac{\sum_{i=1}^{K} s_i n_i \exp(-E_i/kT)}{A_m m + \sum_{i=1}^{K} A_i (N_i - n_i)}.$$
(37)

When one considers the *j*-th peak in a series, the traps responsible for lower-temperature peaks can be considered to be empty. Thus, the sum in the denominator of Eq. (37) can be taken only from i = j. By inserting Eq. (37) into (35), one gets the expression for TL,

$$I(T) = -\frac{dm}{dt} = \frac{A_m m \sum_{i=1}^K n_i s_i \exp(-E_i/kT)}{A_m m + \sum_{i=1}^K A_i (N_i - n_i)}.$$
 (38)

One may consider a peak followed by one or more subsequent peaks. This means that the relevant trap has a number of deeper competing traps. If the concentration of free electrons is small, as is usually the case, the instantaneous concentration of holes in centers must be

$$m = \sum_{i=j}^{K} n_i. \tag{39}$$

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As long as the peaks are fairly well separate, since the activation energies are different, the exponents in Eq. (38) are very different from one another, and at the temperature of a certain peak, the contribution of the subsequent peaks is negligible. Therefore, Eq. (39) reduces to

$$I(T) = -\frac{dm}{dt} = \frac{A_m m s_j n_j \exp(-E_j/kT)}{A_m m + \sum_{i=j}^K A_i (N_i - n_i)}.$$
 (40)

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. (40) changes along the *j*-th peak only slightly, and therefore, *m* can be considered constant. The amount of change of *m* can be considered to be relatively small as compared to the area under the higher temperature peaks. If, in addition, the relevant traps with i > j are not too close to saturation, the denominator of Eq. (40) is rather close to be constant. The observation that glow peaks tend to be of first order at low occupancies has been made by Sunta *et al.* [63]. It should be noted that if the peaks are rather separate, and if the traps are saturated, within the range of the *j*-th peak, $dm/dt \approx dn_j/dt$. 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

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recombination is

$$\frac{A_m m}{A_m m + \sum_{i=j}^K A_i (N_i - n_i)}.$$
(41)

This would mean that in this range,

$$\frac{dm}{dt} = \frac{dn_j}{dt} \frac{A_m m}{A_m m + \sum_{i=j}^K A_i (N_i - n_i)}.$$
(42)

Comparing the right-hand side of Eqs. (40) and (42) results in

$$-\frac{dn_j}{dt} = s_j n_j \exp(-E_j/kT).$$
(43)

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

$$-\frac{dn_j}{dt} = n_{j0}s_j \exp(-E_j/kT) \exp\left[-(s_j/\beta)\int_{T_i}^{T_f} \exp(-E_j/k\theta)d\theta\right].$$
(44)

This first-order expression is not the TL intensity, but using Eq. (43) we can get the TL expression

$$I(T) = -\frac{dm}{dt} = n_{j0}s_j \exp(-E_j/kT)n_{j0}s_j \exp(-E_j/kT)$$
$$\times \exp\left[-(s_j/\beta)\int_{T_i}^{T_f} \exp(-E_j/k\theta)d\theta\right]$$
$$\times \frac{A_m m}{A_m m + \sum_{i=j}^{K} A_i(N_i - n_i)}.$$
(45)

As long as the last term in Eq. (45) 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 in a series. Chen and Pagonis [75] show that under these circumstances, the last peak in such a series tends to be of second order.

Chen and Pagonis [75] have demonstrated the properties of a glow curve resulting from a model of five traps and one recombination

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Fig. 9. A simulated five-peak TL curve (After Chen and Pagonis [75]).

center by solving sequentially the set of equations which are the extension of Eqs. (1–4) for excitation and relaxation (X = 0), followed by Eqs. (34–36). The results are shown in Fig. 9 and, indeed, the symmetry of the first four peaks is characteristic of first order and the 5-th peak looks like a second-order peak. The authors also discuss cases where the last peak in a series has a long high-temperature tail, which is associated with the failure of the quasi-equilibrium assumption in this range. Finally, the authors show that even in the more general situation, where several traps and several recombination centers take part in the process, all TL peaks except for the last in a series tend to be of first order.

1.6. Anomalous evaluated trapping parameters from TL curves

Several methods have been developed for the evaluation of the activation energy and frequency factor from TL curves (see e.g. Chen [76]). As an example, a simple method for finding the activation

energy of a first-order peak is given by

$$E = 2.29kT_m^2/\omega, \qquad (46)$$

where T_m is the maximum intensity temperature and $\omega = T_2 - T_1$ and T_1 and T_2 are the low and high half-intensity temperatures. Equation (46) shows immediately the inverse relation between the width of the peak, ω , and the activation energy.

Once E is known, inserting T_m , E and the heating rate β into Eq. (24) yields the frequency factor s. One should note that the usually acceptable values of s are between 10^8 and 10^{13} s⁻¹ (e.g., Chen [76]). In the literature, there are reports on evaluated frequency factors many orders of magnitude larger or smaller than the mentioned range. For example, Taylor and Lilley [77] reported an activation energy of 2.06 eV and frequency factor of $2 \times 10^{20} \,\mathrm{s}^{-1}$ in LiF:Mg,Ti (TLD-100) and other authors reported even higher values. On the other hand, very low values of evaluated s have been reported such as by Haake [78] who determined for ZnS·ZnO-Cu,Cl and ZnS-Cu, Cl as low values as $1 \, \text{s}^{-1}$ to $2000 \, \text{s}^{-1}$. Chen and Hag-Yahya [79] presented a model with three recombination centers, one radiative and two non-radiative (or radiative in a different range of the spectrum). The model yields a very narrow glow peak which gives by using Eq. (46) a very high effective activation energy and, in turn, using Eq. (24), an effective frequency factor many orders of magnitude higher than usually acceptable. It is worth mentioning that Chen and Hag-Yahya [80] used a very similar model to explain anomalous fading of TL as being normal fading in disguise. As for the very low frequency factors reported in the literature, Chen et al. [81] have studied a model with two trapping states and one recombination center which yield two neighboring TL peaks that may appear as a very broad single peak. This yields in the analysis very low effective activation energy and a very low frequency factor. The authors use simulations by solving the relevant differential equations to demonstrate this possibility and suggest that it should be considered in particular when a complex glow curve with overlapping peaks is studied, e.g. by deconvolution, when the number of individual peaks is not always known.

1.7. Conclusion

In this chapter, some models of thermoluminescence (TL) and optically stimulated luminescence (OSL), associated with delocalized transitions during excitation and read-out have been discussed. The analytical results reached by making plausible approximation have been considered and compared to experimental results in different materials. These were accompanied by the results of numerical simulations consisting of the solution of the relevant set of simultaneous differential equations in the sequence of excitation, relaxation and read-out, namely heating in TL and optical stimulation in OSL. The effects covered included different kinds of dose dependence, linear, sublinear and superlinear as well as non-monotonic dose dependence. Also the possibility of dose-rate dependence sometimes mentioned in the literature has been considered. Other effects discussed have been the concentration-quenching effect, the predominance of the occurrence of first-order TL peaks and an anomalous heating-rate effect. The model for the latter may be associated with an alternative explanation to the well-known thermal quenching effect, as seen in TL measurements at various heating rates. Also are briefly discussed the reasons for anomalously high or low evaluated activation energies and frequency factors.

References

- [1] R. Chen and V. Pagonis, Thermally and Optically Stimulated Luminescence: A Simulation Approach, Chichester: John Wiley & Sons Ltd., 2011.
- [2] J.T. Randall and M.H.F. Wilkins, "The phosphorescence of various solids," Proc. Roy. Soc. London, vol. A184, pp. 347–365, 1945.
- [3] G.F.J. Garlick and A.F. Gibson, "The electron trap mechanism of luminescence in sulphide and silicate phosphors," *Proc. Phys. Soc.*, vol. 60, pp. 574– 590, 1948.
- [4] A. Halperin and A.A. Braner, "Evaluation of thermal activation energies from glow curves," *Phys. Rev.*, vol. 117, pp. 408–415, 1960.
- [5] G. Kitis and N.D. Vlachos, "General semi-analytical expressions for TL, OSL and other luminescence stimulation modes from OTOR model using Lambert W-function," *Radiat. Meas.*, vol. 48, pp. 47–54, 2013.
- [6] R. Chen and V. Pagonis, "On the quasi-equilibrium assumptions in the theory of thermoluminescence (TL)," J. Lumin., vol. 143, pp. 734–740, 2013.

- [7] I.A. Kanunnikov, "Reaction order of thermally stimulated recombination," J. Appl. Spect., vol. 28, pp. 597–599, 1978.
- [8] R. Chen, "Glow curves with general-order kinetics," J. Electrochem. Soc., vol. 116, pp. 1254–1257, 1969.
- R. Chen, N. Kristianpoller, Z. Davidson and R. Visocekas, "Mixed first and second order kinetics in thermally stimulated processes," *J. Lumin.*, vol. 23, pp. 293–303, 1981.
- [10] J.R. Cameron, N. Suntharalingam and G.N. Kenney, Thermoluminescent Dosimetry, Madison, USA: The University of Wisconsin Press, 1968.
- M.S. Tite, "Thermoluminescent dating of ancient ceramics: A reassessment," *Archaeometry*, vol. 9, pp. 155–169, 1966.
- [12] A. Halperin and R. Chen, "Thermoluminescence in semiconducting diamonds," Phys. Rev., vol. 148, pp. 839–845, 1966.
- [13] R. Chen, X.H. Yang and S.W.S. McKeever, "The strongly superlinear dose dependence of thermoluminescence in synthetic quartz," J. Phys. D: Appl. Phys., vol. 21, pp. 1452–1457, 1988.
- [14] H. Otaki, H. Kido, A. Hiratsuka and N. Takeuchi, "Estimation of UV radiation dose using CaF₂:Tb₄O₇ as a thermoluminescence dosimeter," *J. Mater. Sci. Lett.*, vol. 13, pp. 1267–1269, 1994.
- [15] N. Suntharalingam and J.R. Cameron, "Thermoluminescence response of lithium fluoride to radiations with different LET," *Phys. Med. Biol.*, vol. 14, pp. 397–410, 1969.
- [16] S.G.E. Bowman and R. Chen, "Superlinear filling of traps in crystals due to competition during irradiation," J. Lumin., vol. 18, pp. 345–348, 1979.
- [17] E.T. Rodine and P.L. Land, "Electronic defect structure of single crystal ThO₂ by thermoluminescence," *Phys. Rev. B*, vol. 4, pp. 2701–2724, 1971.
- [18] N. Kristianpoller, R. Chen and M. Israeli, "Dose dependence of thermoluminescence peaks," J. Phys. D: Appl. Phys., vol. 7, pp. 1063–1074, 1974.
- [19] R. Chen, G. Fogel and C.K. Lee, "A new look at the models of the superlinear dose dependence of thermoluminescence," *Radiat. Prot. Dosim.*, vol. 65, pp. 63–68, 1996.
- [20] R. Chen, J.L. Lawless and V. Pagonis, "Intrinsic superlinear dose dependence of thermoluminescence and optically stimulated luminescence at high dose rates," *Radiat. Meas.*, vol. 71, pp. 220–225, 2014.
- [21] V.K. Jain, S.P. Kathuria and A.K. Ganguly, "Radiation damage in thermoluminescent LiF TLD-phosphor," J. Phys. C: Sol. St. Phys., vol. 8, pp. 2191– 2197, 1975.
- [22] E.G. Yukihara, V.H. Whitley, J.C. Polf, D.M. Klein, S.W.S. McKeever, A.E. Akselrod and M.S. Akselrod, "The effect of deep trap population on the thermoluminescence of Al₂O₃:C," *Radiat. Meas.*, vol. 37, pp. 627–638, 2003.
- [23] R. Chen, D. Lo and J.L. Lawless, "Non-monotonic dose dependence of thermoluminescence," *Radiat. Prot. Dosim.*, vol. 119, pp. 33–36, 2006.
- [24] V. Pagonis, R. Chen and J.L. Lawless, "Nonmonotonic dose dependence of OSL intensity due to competition during irradiation and readout," *Radiat. Meas.*, vol. 41, pp. 903–906, 2006.

- [25] E.G. Yukihara, V.H. Whitley, S.W.S. McKeever, A.E. Akselrod and M.S. Akselrod, "Effect of high-dose irradiation on the optically stimulated luminescence of Al₂O₃:C," *Radiat. Meas.*, vol. 38, pp. 317–333, 2003.
- [26] R. Chen, V. Pagonis and J.L. Lawless, "Time and dose-rate dependence of TL and OSL due to competition between excitation and fading," *Radiat. Meas.*, vol. 82, pp. 115–221, 2015.
- [27] R. Chen, J.L. Lawless and V. Pagonis, "Thermoluminescence associated with two-electron traps," *Radiat. Meas.*, vol. 99, pp. 10–17, 2017.
- [28] R. Chen, J.L. Lawless and V. Pagonis, "Thermoluminescence associated with two-hole recombination centers," *Radiat. Meas.*, vol. 115, pp 1–6, 2018.
- [29] M.R. Mayhugh, "Color centers and thermoluminescence mechanism in LiF," J. Appl. Phys., vol. 41, pp. 4776–4782, 1970.
- [30] P.D. Townsend, G.C. Taylor and M.C. Wintersgill, "An explanation of the anomalously high activation energies of TL in LiF (TLD 100)," *Radiat. Eff.*, vol. 41, pp. 11–16, 1979.
- [31] M. Böhm and A. Scharmann, "Theory," in Applied Thermoluminescence Dosimetry, M. Oberhofer and A. Scharmann, Eds., Bristol, Adam Hilger Ltd., 1981, pp. 11–38.
- [32] A.N. Yazici, T. Karali, P.D. Townsend and M. Ari, "Thermoluminescence studies of LiF:Mg,Ti between 100 and 300 K," J. Phys. D: Appl. Phys., vol. 37, pp. 3165–3173, 2004.
- [33] Y. Horowitz, "A unified comprehensive theory of the TL dose response of thermoluminescence systems applied to LiF:Mg,Ti," in *Macrodosimetric Response of Physical and Biological Systems applied to LiF:Mg,Ti Radiations*, Y. Horowitz, Ed., Amsterdam, Elsevier, 2006, pp. 75–202.
- [34] I. Eliyahu, S. Druzhyna, Y. Horowitz, G. Reshes and L. Oster, "Kinetic simulation of charge transfer following 5.08 eV (F band) optical excitation of irradiated LiF:Mg,Ti (TLD-100): Participation of holes released via V₃-V_k transformation," *Radiat. Meas.*, vol. 90, pp. 27–32, 2016.
- [35] C. Woda and G.A. Wagner, "Non-monotonic dose dependence of the Geand Ti- centers in quartz," *Radiat. Meas.*, vol. 42, pp. 1441–1452, 2007.
- [36] R.A. Facey, "Heating-rate effects in glow peak measurements for thermoluminescence dosimetry," *Health Phys.*, vol. 12, pp. 717–720, 1966.
- [37] P.J. Groom, S.A. Durrani, K.A. Khazal and S.W.S. McKeever, "The doserate dependence of thermoluminescence and sensitivity in quartz," *Europ. PACT J.*, vol. 2, pp. 200–210, 1978.
- [38] S. Chawla, T.K. Gundu Rao and A.K. Singhvi, "Quartz thermoluminescence: Dose and dose-rate effects and their implications," *Radiat. Meas.*, vol. 29, pp. 53–63, 1998.
- [39] P.C. Hsu and P.S. Weng, "Reaffirmation on the low exposure rate dependence of the CaSO₄:Dy thermoluminescence dosimeter," *Nucl. Instrum. Meth.*, vol. 174, pp. 73–76, 1980.
- [40] A.I. Shlukov, A.I. Shakhovets and M.G. Lyashenko, "A criticism of standard TL dating technology," *Nucl. Instrum. Meth. Phys. Res. Sect. B*, vol. 73, pp. 373–381, 1993.

- [41] G. Valladas and J. Ferreira, "On the dose-rate dependence of the thermoluminescence response of quartz," *Nucl. Instrum. Meth.*, vol. 175, pp. 216–218, 1980.
- [42] R. Chen and P.L. Leung, "A model for dose-rate dependence of thermoluminescence intensity," J. Phys. D: Appl. Phys., vol. 33, pp. 846–850, 2000.
- [43] W.L. Medlin, "Thermoluminescence properties of calcite," J. Chem. Phys., vol. 30, pp. 451–458, 1974.
- [44] M.J. Rossiter, D.B. Rees-Evans, S.C. Ellis and J.M. Griffiths, "Titanium as a luminescence centre in thermoluminescent lithium fluoride," J. Phys D: Appl. Phys., vol. 4, pp. 1245–1251, 1971.
- [45] K.S.V. Nambi, V.N. Bapat and A.K. Ganguly, "Thermoluminescence of CaSO₄ doped with rare earths," J. Phys. C: Sol. St. Phys., vol. 7, pp. 4403– 4415, 1974.
- [46] R. Chen, J.L. Lawless and V. Pagonis, "A model for explaining the concentration quenching of thermoluminescence," *Radiat. Meas.*, vol. 46, pp. 1380–1384, 2011.
- [47] L.J. Lai, H.S. Sheu, Y.K. Lin and T.C. Chu, "Thermoluminescence of ZrO₂ doped with Yb₂O₃ following excitation with X rays," *J. Appl. Phys.*, vol. 100, p. 103508 (5pp), 2006.
- [48] W. Hoogenstraaten, "Electron traps in ZnS phosphors," *Philips Res. Repts.*, vol. 13, pp. 515–693, 1958.
- [49] R. Chen and S.A.A. Winer, "Effects of various heating rates on glow curves," J. Appl. Phys., vol. 41, pp. 5227–5232, 1970.
- [50] R. Chen and V. Pagonis, "A model explaining the anomalous heating-rate effect in thermoluminescence as an inverse thermal quenching based on simultaneous thermal release of electrons and holes," *Radiat. Meas.*, vol. 106, pp. 20–25, 2017.
- [51] M. Kumar, G. Chourasiya, B.C. Bhatt and C.M. Sunta, "Dependence of peak height of glow curves on heating rate in thermoluminescence," J. Lumin., vol. 130, pp. 1216–1220, 2010.
- [52] A.K. Wintle, "Thermal quenching of thermoluminescence in quartz," Geophys. J.R. Soc., vol. 41, pp. 107–113, 1975.
- [53] B. Subedi, G. Kitis and V. Pagonis, "Simulation of the influence of thermal quenching on thermoluminescence glow peaks," *Phys. Stat. Sol. (a)*, vol. 207, pp. 1216–1226, 2010.
- [54] V.E. Kafadar, "Thermal quenching of thermoluminescence in TLD-200, TLD-300 and TLD-400 after beta irradiation," *Phys. B*, vol. 406, pp. 537– 540, 2011.
- [55] G. Kitis, G.S. Polymeris, V. Pagonis and N.C. Tsirliganis, "Thermoluminescence response and apparent anomalous fading under Durango fluorapatite as a function of the heating rate," *Phys. Stat. Sol. (a)*, vol. 203, pp. 3816– 3823, 2006.
- [56] A.J.J. Bos, N.R.J. Poolton, J. Bessière and P. Dorenbos, "Energy levels in YPO₄:Ce³⁺,Sm³⁺ studied by thermally and optically stimulated luminescence," *Radiat. Meas.*, vol. 45, pp. 343–346, 2010.

- [57] S. Delice, E. Bulur and N.M. Gasanly, "Thermoluminescence in gallium arsenide crystals: an unusual heating rate dependence," *Phil. Mag.*, vol. 95, pp. 998–1006, 2015.
- [58] A. Mandowski and A.J.J. Bos, "Explanation of the anomalous heating rate dependence of thermoluminescence in YPO₄:Ce³⁺,Sm³⁺ based on the semilocalized transition (SLT) model," *Radiat. Meas.*, pp. 1376–1379, 2011.
- [59] V. Pagonis, L. Blohm, M. Brengle, G. Mayonado and P. Woglam, "Anomalous heating rate effect in thermoluminescence intensity using simplified semi-localized transition (SLT) model," *Radiat. Meas.*, Vols. 51–52, pp. 40– 47, 2013.
- [60] M. Schön, "Zum Leuchtmechanismus der Kristallophore," Z. Phys., vol. 19, pp. 463–471, 1942.
- [61] H.A. Klasens, "Transfer of energy between centers in zinc sulphide phosphors," *Nature*, vol. 158, pp. 306–307, 1946.
- [62] A.C. Lewandowski and S.W.S. McKeever, "Generalized description of thermally stimulated processes without quasiequilibrium approximation," *Phys. Rev. B*, vol. 43, pp. 8163–8178, 1991.
- [63] C.M. Sunta, W.E.F. Ayta, J.F.D. Chubaci and S. Watanabe, "A critical look at the kinetic models of thermpluminescence: I. First-order kinetics," *J. Phys. D: Appl. Phys.*, vol. 34, pp. 2690–2698, 2001.
- [64] A.J.J. Bos, "On the energy conversion in thermoluminescence dosimetry materials," *Radiat. Meas.*, vol. 33, pp. 737–744, 2010.
- [65] A.I. Abd El-Hafez, M.N. Yasin and A.M. Sadek, "GCAFIT-A new tool for glow curve analysis in thermoluminescence nanodosimetry," *Nucl. Inst. Meth. Phys. Res. A*, vol. 637, pp. 158–163, 2011.
- [66] R.H. Haering and E.N. Adams, "Theory and applications of thermally stimulated centers in photoconductors," *Phys. Rev.*, vol. 117, pp. 451–454, 1960.
- [67] G.A. Dussel and R.H. Bube, "Theory of thermally stimulated conductivity in previously photoexcited crystal," *Phys. Rev.*, vol. 155, pp. 764–779, 1967.
- [68] M. Böhm and A. Scharmann, "First-order kinetics in thermoluminescence and thermally stimulated kinetics," *Phys. Stat. Sol. (a)*, vol. 4, pp. 99–104, 1971.
- [69] J.G. Simmons and G.W. Taylor, "High-field isothermal currents and thermally stimulated currents in insulators having discrete trapping levels," *Phys. Rev. B*, vol. 5, pp. 1619–1629, 1972.
- [70] N. Agersap Larsen, L. Bøtter-Jensen and S.W.S. McKeever, "Thermally stimulated conductivity and thermoluminescence from Al₂O₃," *Radiat. Prot. Dosim.*, vol. 84, pp. 87–90, 1999.
- [71] A. Opanowicz, "Analysis of thermally stimulated luminescence and conductivity without quasi-equilibrium approximation," J. Phys. D: Appl. Phys., vol. 40, pp. 4980–4990, 2007.
- [72] B.W. Smith and E.J. Rhodes, "Charge movements in quartz and their relevance to optical dating," *Radiat. Meas.*, vol. 23, pp. 329–333, 1994.

- [73] R.M. Bailey, B.W. Smith and E.J. Rhodes, "Partial bleaching and the decay from characteristics of quartz OSL," *Radiat. Meas.*, vol. 27, pp. 123–126, 1997.
- [74] V. Pagonis and G. Kitis, "Prevalence of first-order kinetics in TL materials: an explanation based on multiple competition processes," *Phys. Stat. Sol.* (a), vol. 249, pp. 1590–1601, 2012.
- [75] R. Chen and V. Pagonis, "On the expected order of kinetics in a series of thermoluminescence (TL) and thermally stimulated conductivity peaks," *Nucl. Inst. Meth. Phys. Res. B*, vol. 312, pp. 60–69, 2013.
- [76] R. Chen, "On the calculation of activation energies and frequency factors from glow curves," J. Appl. Phys., vol. 40, pp. 570–585, 1969.
- [77] G.C. Taylor and E. Lilley, "The analysis of thermoluminescence glow peaks in LiF (TLD-100)," J. Phys. D: Appl. Phys., vol. 11, pp. 567–581, 1978.
- [78] C.H. Haake, "Critical comment on a method for determining electron trap depths," J. Opt. Soc. Am., vol. 47, pp. 649–652, 1957.
- [79] R. Chen and A. Hag-Yahya, "Interpretation of very high activation energies and frequency factors in TL as being due to competition between centres," *Radiat. Prot. Dosim.*, vol. 65, pp. 17–20, 1996.
- [80] R. Chen and A. Hag-Yahya, "A new possible interpretation of the anomalous fading in thermoluminescent material as normal fading in disguise," *Radiat. Meas.*, vol. 27, pp. 205–210, 1997.
- [81] R. Chen, V. Pagonis and J.L. Lawless, "Evaluated thermoluminescence trapping parameters-What do they really mean?," *Radiat. Meas.*, vol. 91, pp. 21–27, 2016.