



LUMINESCENCE MODELS

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Abstract—This paper reviews the main models which have been proposed to describe thermally and optically stimulated luminescence phenomena for materials of interest in dating applications. The review starts from the fundamental models established for the descriptions of the kinetics of thermoluminescence (TL) production and develops these as necessary to account for a variety of experimental phenomena. Among the experimental features discussed are anomalous fading, non-linear growth of thermoluminescence as a function of dose, sensitivity and sensitization, bleaching of TL glow curves with light, photo-transferred TL (PTTL) and optically stimulated luminescence (OSL). The relevance of the models to some dating applications is highlighted and it is concluded that efforts to unify the disparate models for luminescence from these materials are now required. © 1998 Elsevier Science Ltd. All rights reserved

1. MODELING

The history of technique and procedure development in luminescence dating demonstrates a heavy reliance upon the establishment of models to explain the processes being used. The field is replete with explanations, suggestions, theories and ideas – many of which are labeled (rather loosely in some cases) “models” – in efforts to provide a theoretical basis from which to explain the observed effects and the gathered data. This, in fact, is an example of the scientific method at its best. Continually, models have been suggested, tested, modified and improved and, in doing so, the practical techniques and protocols used in luminescence dating have become established, and more acceptable to the user. Note that we speak here only about *acceptability*; *reliability* is another matter, and is dealt with much more satisfactorily in the accompanying papers in this issue. A procedure appears acceptable, or at least credible, to the community if the proposer can justify it on the basis of what is known, or what is thought to be known, about the physical processes that produce the observed effect. Only actual use of the procedure, and testing of the ultimate product, i.e. the age, against known age standards, will establish its reliability.

An important purpose of models, therefore, is to impose a feeling of security. By establishing models we can answer questions such as: “Under what circumstances can I expect an exponential optically stimulated luminescence (OSL) decay curve?”, or “When might I expect a linear growth of thermoluminescence (TL) as a function of dose?”, or “Can the correction procedure I propose really correct for the effect I observe?”. These and a myriad other such questions may appear esoteric at times, but at others they are absolutely fundamental to the val-

idity of the procedures and protocols adopted during dating.

A difficulty in understanding models for OSL and TL is that these are inherently complex, interactive, non-linear processes. Predicting the behavior of even the simplest model to explain these phenomena is not straightforward and can be full of frustrations. However, in recent years the arrival (at our desk-top computer keyboards) of the ability to perform complex numerical calculations to follow the behavior of the non-linear, coupled, differential equations which describe OSL and TL has opened a window to an understanding, at a fundamental level, of how such systems behave. This has presented us with the opportunity to test the behavior of our suggested models, in ways not so easily done in earlier years, to see if they can indeed produce the effect we observe in our experiments. The purpose of this paper is to review some of the progress that has been made in this area. We do not – and indeed cannot, within the confines of one article – propose to be all-embracing in this review. Undoubtedly some readers may be disappointed that we did not cover an effect of particular interest to them. Nevertheless, we believe that we do cover some of the topical subjects of current interest and importance to the luminescence dating community. A more detailed description of models and theories for TL, OSL and related phenomena is given, in depth, by Chen and McKeever (1997).

2. THERMOLUMINESCENCE

We begin the discussion with a presentation of the established models for TL. Inevitably, this is something of a historical account since the earliest of these models were introduced five decades ago.

However, this early work serves as a benchmark for the development of later models for both TL and OSL. As such, an understanding of these fundamental models is essential for an understanding of the behavior of the more complex scenarios introduced in later years.

2.1. Background

The traditional description of TL normally proceeds by invoking the absorption of energy from an ionizing source by an insulating or semiconducting material. The absorption causes the excitation of free electrons and free holes and the subsequent trapping of these electronic species at defects (trapping states) within the material. After removal of the excitation the sample is heated such that thermal energy causes the liberation of charge carriers of one sign (say, electrons) which are then able to recombine with charge carriers of the opposite sign. If the recombination is radiative, luminescence (TL) is emitted. This description of TL can be formalized in the following statements – statements which in fact describe most thermally stimulated relaxation phenomena: *TL requires the perturbation of the system from a state of thermodynamic equilibrium, via the absorption of external energy, into a metastable state. This is then followed by the thermally stimulated relaxation of the system back to its equilibrium condition.* As a description of a thermally stimulated process (TSP), this statement is quite general. In the specific case of TL, the perturbation is usually the absorption of energy from ionizing radiation, and the thermally stimulated relaxation back to equilibrium is followed by monitoring the emission of luminescence from the system during the transitions of the freed charges back to the ground state. As will become clear in the following sections, the intensity of the emitted luminescence is related to the *rate* at which the system returns to equilibrium.

The result is a characteristic “glow curve” consisting of a luminescence peak (or peaks) in a plot of luminescence against sample temperature, as illustrated in the many examples shown elsewhere in this issue. In other TSPs the form of the perturbation may differ along with the property being monitored during heating. For example, in thermally stimulated conductivity (TSC), ionizing radiation may still be used as the excitation source, but one detects the thermal relaxation back to equilibrium by monitoring the freed charges during their passage through the delocalized excited state (i.e. conduction band for electrons, or valence band for holes). For thermally stimulated exoelectron emission (TSEE) one monitors the exoemission of electrons, usually from surface traps, during the relaxation process. Alternatively, for either deep level transient spectroscopy (DLTS) or thermally stimulated capacitance (TSCap), the excitation can either be ionizing radiation or electrical energy, and one monitors the change in capacitance across a pn semiconductor junction, or a metal–semiconductor junction, during the thermally stimulated transition of the trapped charge from the traps into the delocalized bands.

Each of the above processes, and all related processes, can be described in terms of the free energy of the system and the perturbation of the equilibrium Fermi level in the material under study. At 0 K and in thermodynamic equilibrium one can expect from Fermi–Dirac statistics that all states above the Fermi level E_F are empty while all states below E_F are filled. The situation is illustrated in Fig. 1 in which we see a flat-band energy band diagram representing the bottom of the conduction band E_c , the top of the valence band E_v and a distribution of energy states (traps) in the forbidden gap between these two energy levels. We use “filling diagrams”, as described by Bräunlich (1979), to represent the extent to which the energy states are filled

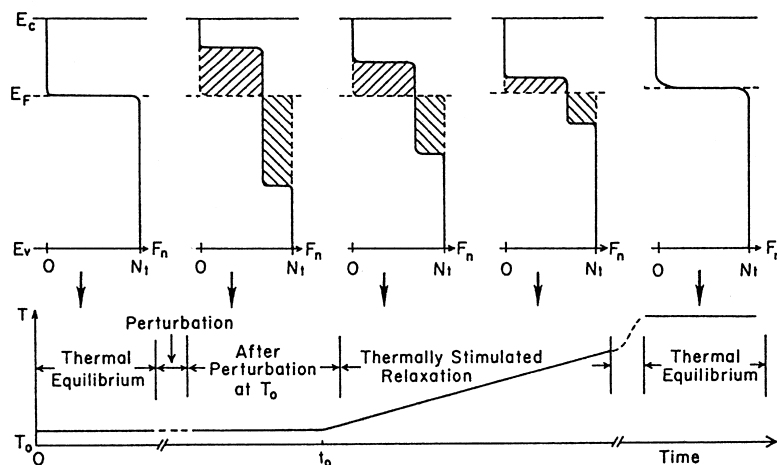


Fig. 1. Filling functions for a uniform trap distribution before and after perturbation by an external stimulus, and during thermally stimulated relaxation. (After Bräunlich (1979).)

$F_n(E)$ for a uniform trap distribution during a thermally stimulated relaxation experiment. Beginning with the left-hand figure, we see the Fermi–Dirac filling function at 0 K. After perturbation by ionizing radiation we find a new filling function showing a distribution of electrons trapped at localized states within the band gap above E_F and an equal concentration of holes trapped below E_F . One can define two quasi-Fermi levels, one each for electrons E_{Fn} and for holes E_{Fp} . These are useful devices for describing the non-equilibrium state which follows the perturbation in terms of equilibrium statistics by making the assumption that the trapped electron and hole populations are in thermal equilibrium over their available energy levels. During thermally stimulated relaxation, i.e. during heating, the filling function $F_n(E)$ gradually returns to its pre-perturbation state, albeit now at a higher temperature. During this process the quasi-Fermi levels gradually move back toward the equilibrium Fermi level as the trapped charge concentrations decay back to their equilibrium values. In Fig. 1 the heating is performed according to the function $T(t) = T_0 + \beta t$, where T_0 is the initial temperature, i.e. 0 K in the above example, and β is the (constant) rate of heating. In principle, however, any other heating function could be used.

To develop this picture into a simple description of TL we note several additional definitions and assumptions:

(a) All transitions into or out of the localized states involve passage of the charge (electrons or holes) through the delocalized bands, i.e. for the present we do not include direct transitions between localized states.

(b) We adopt the usual definition of “trapping” states to be those at which the probability of thermal excitation from the level into the respective delocalized band is greater than the probability of recombination of the trapped charge with a free charge carrier of opposite sign. Conversely, a “recombination center” is defined as one in which the probability of recombination with an opposite sign charge carrier is greater than that of thermal excitation of the trapped carrier. Therefore, one can define a *demarcation level* to be that energy level at which these two probabilities are equal. Thus, we have a demarcation level for electrons E_{Dn} , and one for holes E_{Dp} .

(c) Transitions of electrons from the conduction band ($E \geq E_c$) into electron traps of energy E , for which $E_c > E > E_{Dn}$, are non-radiative, emitting phonons. Similarly, hole transitions from $E \leq E_v$ to hole traps at $E_{Dp} > E > E_v$ are also non-radiative.

(d) Transitions of free electrons from $E \geq E_c$ to trapped hole recombination sites at $E_F > E > E_{Dp}$, or free holes from $E \leq E_v$ to trapped electron

recombination centers at $E_{Dn} > E > E_F$ are radiative, emitting photons.

(e) Once a trap is emptied, the freed carrier can no longer distinguish between it and all other traps of the same type.

In Fig. 1 the filling diagrams are illustrated for a uniform trap distribution. For any arbitrary density of states function $N(E)$, however, we may generalize the equations of Adirovitch (1956), Haering and Adams (1960), and Halperin and Braner (1960) and write a series of rate equations describing the flow of charge into and out of the delocalized bands during thermal stimulation *en route* to equilibrium, thus:

$$\begin{aligned} dn_c/dt = & \int_{E_{Dn}}^{E_c} p_n(E)N(E)f(E)dE \\ & - n_c v_n \int_{E_{Dn}}^{E_c} \sigma_n(E)N(E)(1-f(E))dE \\ & - n_c v_n \int_{E_{Dp}}^{E_F} \sigma_{mn}(E)N(E)(1-f(E))dE \quad (1) \end{aligned}$$

and

$$\begin{aligned} dn_v/dt = & \int_{E_v}^{E_{Dp}} p_p(E)N(E)(1-f(E))dE \\ & - n_v v_p \int_{E_v}^{E_{Dp}} \sigma_p(E)N(E)f(E)dE \\ & - n_v v_p \int_{E_F}^{E_{Dn}} \sigma_{np}(E)N(E)f(E)dE \quad (2) \end{aligned}$$

where $p_n(E)$ and $p_p(E)$ are the probabilities for thermal excitation from the traps, given in general by

$$p = s \exp\{-E/kT\} \quad (3)$$

where k is Boltzmann’s constant and T is temperature. The pre-exponential factor s is known as the “attempt-to-escape” frequency and is interpreted as the number of times per second ν that an electron interacts with the lattice, multiplied by a transition probability κ , multiplied by a term which accounts for the change in entropy ΔS associated with the transition from the trap to the delocalized band (Glasstone *et al.*, 1941; Curie, 1960). Thus, s may be written

$$s = \nu \kappa \exp\left\{\frac{\Delta S}{k}\right\} \quad (4)$$

One can expect, therefore, that s will take on a value similar to the lattice vibrational frequency, i.e. 10^{12} – 10^{14} s^{-1} . From detailed balance arguments, the frequency factor can also be equated to the capture cross-section σ of the metastable state (Bube, 1960), thus:

$$s = N_s \nu \sigma \quad (5)$$

where N_s is the effective density of states in the delocalized band, and v is the free carrier thermal velocity. Note that since N_s , v and σ all have a temperature dependence, so s also usually exhibits a temperature dependence.

In [1] and [2], $N(E)$ is the density of states function; $f(E)$ is the occupation, or filling function; n_c is the concentration of free electrons in the conduction band, and n_v is the concentration of free holes in the valence band; v_n and v_p are free electron and free hole thermal velocities; $\sigma_n(E)$ and $\sigma_p(E)$ are the capture cross-sections for the retrapping of free carriers; and $\sigma_{mn}(E)$ and $\sigma_{np}(E)$ are the recombination cross-sections for the free carriers.

2.2. Simplest model

Several authors (e.g. Adirovitch, 1956; Halperin and Braner, 1960) simplified the above equations by assuming only two types of localized state – namely a discrete electron trap at an energy E_t , where $E_c > E_t > E_{Dn}$, and a discrete recombination (trapped hole) center at an energy, E , where $E_{Dp} > E > E_v$.

With the above conditions the concentration of trapped electrons simplifies thus:

$$\int_{E_{Dn}}^{E_c} N(E)f(E)dE \longrightarrow n, \quad (6)$$

the concentration of empty traps becomes

$$\int_{E_{Dn}}^{E_c} N(E)(1-f(E))dE \longrightarrow N-n \quad (7)$$

and the concentration of available hole states (for recombination) becomes

$$\int_{E_{Dp}}^{E_F} N(E)(1-f(E))dE \longrightarrow m \quad (8)$$

Furthermore, since the trap energy and the recombination center energy are both single-valued, then σ_n and σ_{mn} are also single-valued. Finally, we assume that only trapped electrons are thermally freed during thermal stimulation (i.e. $p_p=0$); this in turn means that $n_v=0$. (Note that in the treatment which follows we will always assume that the TL signal is stimulated by the release of trapped electrons. Alternatively, one could just as easily assume that the holes were the thermally unstable charge carrier type. However, in this case the form of the equations would be identical to those which follow, and only the definitions of the terms would need to be modified.) Using [3], along with these simplifications, [1] and [2] become

$$\frac{dn_c}{dt} = ns \exp\left\{-\frac{E_t}{kT}\right\} - n_c(N-n)A_n - n_c mA_{mn} \quad (9)$$

and

$$\frac{dn_v}{dt} = 0 \quad (10)$$

where $A_n = v_n \sigma_n$ is the retrapping probability and $A_{mn} = v_n \sigma_{mn}$ is the recombination probability (both expressed in units of volume per unit time). With the same notation we may also write

$$\frac{dn}{dt} = n_c(N-n)A_n - ns \exp\left\{-\frac{E_t}{kT}\right\} \quad (11)$$

and

$$\frac{dm}{dt} = -n_c mA_{mn} \quad (12)$$

from which we see that $dn_c/dt = dm/dt - dn/dt$. Furthermore, charge neutrality dictates that

$$n_c + n = m \quad (13)$$

Finally we note that the intensity of TL emitted during the return of the system to equilibrium is given by

$$I_{TL} = -\eta \frac{dm}{dt} \quad (14)$$

where η is the radiative efficiency. If all recombination events produce photons and all photons are detected then $\eta = 1$. Unless specifically stated we shall assume $\eta = 1$ in the discussions to follow. [9]–[14] represent the system of rate equations describing the traffic of electrons during heating (at rate β) of a system initially perturbed from equilibrium. They are coupled, first-order, non-linear, differential equations and, in general, are analytically insoluble. Note that the concentrations n_c , n and m are all time and temperature dependent, with the t and T dependencies linked through the heating rate function $T = T(t)$. (In fact, n_c , n and m should each be considered as functionals $n_c\{T(t)\}$, $n\{T(t)\}$, etc., since they depend on the history of the system. They are solutions of the differential equations and as such they depend upon t , T and the initial values n_{c0} , n_0 and m_0 .) In writing the above equations we have placed severe restrictions on the transitions which are allowed during the return of the system to equilibrium and upon the energy levels which are available within the system. This simple scheme – known as the one-trap/one-center model – is depicted in Fig. 2 and forms the basis of many, if not most, analyses of TL phenomena. Despite these obvious limitations the challenge now is to use these equations to develop an analytical expression which gives explicitly the relationship between the TL intensity and the temperature, i.e. to determine the form of $I_{TL}(T)$. To do so, several simplifying assumptions concerning the relative sizes of the various transition rates must be introduced into the equations.

2.3. Approximations

2.3.1. *Quasiequilibrium.* Perhaps the most important of all the assumptions introduced into the model is that of quasiequilibrium (QE). The QE

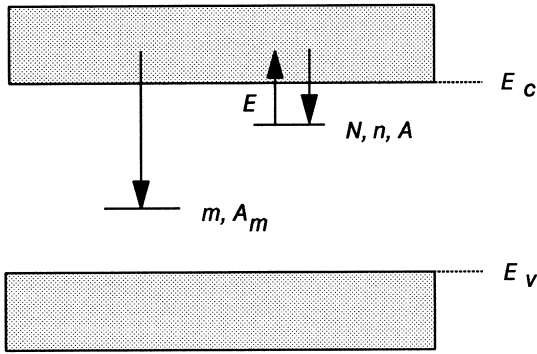


Fig. 2. The allowed transitions (thermal excitation, re-trapping and recombination) for the simple one-trap/one-center model for TL.

assumption is

$$\left| \frac{dn_c}{dt} \right| \ll \left| \frac{dn}{dt} \right|, \left| \frac{dm}{dt} \right| \quad (15)$$

This assumption is of profound importance and, stated simply, it requires that the free electron concentration in the conduction band is quasistationary. It is this inequality which allows a simplification of the rate equations ([9]–[12]). If combined with the additional dictate that the initial free carrier concentration is small (i.e. $n_{c0} \approx 0$), it means that free charge never accumulates in the conduction band during thermal stimulation. Applying the above inequalities leads to

$$-\frac{dn}{dt} \approx -\frac{dm}{dt} = I_{TL} \quad (16)$$

and thus:

$$I_{TL} = \frac{ns \exp\{-E_t/kT\} m \sigma_{mn}}{[(N-n)\sigma_n + m\sigma_{mn}]} \quad (17)$$

or

$$I_{TL} = ns \exp\left\{-\frac{E_t}{kT}\right\} \left[1 - \frac{(N-n)\sigma_n}{(N-n)\sigma_n + m\sigma_{mn}} \right] \quad (18)$$

[17] and [18] have been termed the “General One-Trap” (GOT) expression for TL emission (Levy, 1985, 1991). In [18] the term in square brackets is the probability that the thermally released electrons will *not* be re-trapped, and the ratio $(N-n)\sigma_n/m\sigma_{mn}$ is the ratio of the re-trapping probability to the recombination probability. Further approximations are normally introduced at this stage concerning the relative sizes of these terms.

2.3.2. First-order kinetics. Randall and Wilkins (1945a,b) assumed negligible re-trapping during the thermal excitation period, i.e. they assumed that $m\sigma_{mn} \gg (N-n)\sigma_n$. Note that this is a condition between functions $n(t)$ and $m(t)$ and thus while it may be true at the beginning of a peak, the possi-

bility exists that it may become progressively untrue at a later stage. Under these “slow-retrapping” conditions the GOT equation becomes

$$I_{TL} = ns \exp\left\{-\frac{E_t}{kT}\right\} \quad (19)$$

We note also from [16] that $-dn/dt \propto n$, and thus we have a first-order reaction. Integrating from $t = 0$ to t , using a constant heating rate, $\beta = dT/dt$, yields the well-known Randall–Wilkins first-order expression for the function $I_{TL}(T)$, namely

$$I_{TL} = n_0 s \exp\left\{-\frac{E_t}{kT}\right\} \exp\left\{-\left(\frac{s}{\beta}\right) \int_{T_0}^T \exp\left\{-\frac{E_t}{k\theta}\right\} d\theta\right\} \quad (20)$$

where n_0 is the initial value of n at $t = 0$, T_0 is the initial temperature and θ is a dummy variable representing temperature. The transitions allowed in the Randall–Wilkins model are the same as those illustrated in Fig. 2 – with the recombination transition more probable than the re-trapping transition. A typical first-order peak is shown in curve I of Fig. 3, whereas curve II corresponds to a second-order kinetics peak discussed below.

2.3.3. Second-order kinetics. Garlick and Gibson (1948) considered the alternative possibility that re-trapping dominates, i.e. $m\sigma_{mn} \ll (N-n)\sigma_n$. Applying this inequality to the GOT expression, along with $N \gg n$ and $n = m$, yields

$$I_{TL} = -\frac{dn}{dt} = s \left(\frac{\sigma_n}{N\sigma_{mn}} \right) n^2 \exp\left\{-\frac{E_t}{kT}\right\} \quad (21)$$

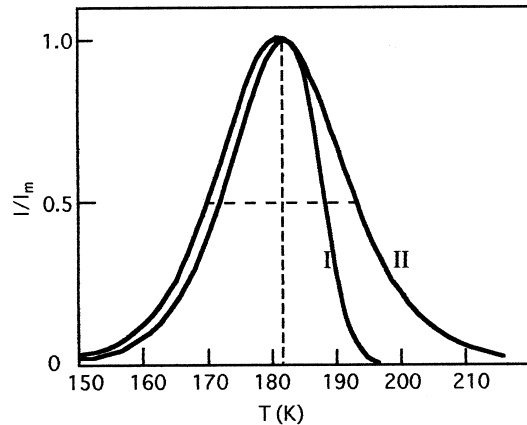


Fig. 3. A typical first-order peak calculated by the Randall–Wilkins equation (curve I) and a typical second-order peak (curve II). Both curves are numerically simulated with $E = 0.4$ eV. In curve I, the frequency factor is $s = 10^{10} \text{ s}^{-1}$. In curve II, the pre-exponential factor is $s' = 10^{-11} \text{ m}^3 \text{ s}^{-1}$. Both curves are normalized to a maximum intensity of unity.

In contrast to the first-order case, the inequality $m\sigma_{mn} \ll (N-n)\sigma_n$ will remain true throughout the TL peak, if it is true at the beginning. Note now that $dn/dt \propto n^2$ and, thus, this represents a second-order reaction. Integration of [21] gives

$$I_{TL} = \left(\frac{n_0^2 \sigma_n}{N \sigma_{mn}} \right) s \exp \left\{ -\frac{E_t}{kT} \right\} \left[1 + \left(\frac{n_0 s \sigma_n}{\beta N \sigma_{mn}} \right) \int_{T_0}^T \exp \left\{ -\frac{E_t}{k\theta} \right\} d\theta \right]^{-2} \quad (22)$$

where all the terms retain their previous meanings. This equation is the Garlick–Gibson TL equation for second-order kinetics. Note that one can also arrive at a similar equation directly from [17], without the assumption of dominating retrapping, using *only* the assumption $\sigma_n = \sigma_{mn}$, as long as $n = m$. Here, the ratio σ_n/σ_{mn} is unity and, therefore, it can be omitted from [22].

Equation [22] may be recast in both cases as

$$I_{TL} = n_0^2 s' \exp \left\{ -\frac{E_t}{kT} \right\} \left[1 + \left(\frac{n_0 s'}{\beta} \right) \int_{T_0}^T \exp \left\{ -\frac{E_t}{k\theta} \right\} d\theta \right]^{-2} \quad (23)$$

in which we have defined $s' = s/N$ (or $s' = s\sigma_n/N\sigma_{mn}$, if $\sigma_n \neq \sigma_{mn}$), as an “effective” pre-exponential factor (in units of $s^{-1}m^3$). [23] can also be written with s'' replacing $n_0 s'$, in which s'' (in units of s^{-1}) is equivalent (in units) to s in the first-order case. The allowed transitions for the Garlick–Gibson model are illustrated in Fig. 2. A characteristic second-order peak is shown in curve II of Fig. 3.

2.3.4. General-order kinetics. The Randall–Wilkins and Garlick–Gibson forms of the TL equation have been derived with the use of specific assumptions concerning the relative sizes of the retrapping and recombination probabilities. Considering the form of the expressions produced from these assumptions, specifically [19] and [21], May and Partridge (1964) wrote an empirical expression for general-order TL kinetics:

$$I_{TL} = n^b s' \exp \left\{ -\frac{E_t}{kT} \right\} \quad (24)$$

where s' has the dimensions of $m^{3(b-1)}s^{-1}$ and b is defined as the general-order parameter and is not necessarily 1 or 2. Integration of [24] for $b \neq 1$ produces

$$I_{TL} = s'' n_0 \exp \left\{ -\frac{E_t}{kT} \right\} \left[1 + \left((b-1) \frac{s''}{\beta} \right) \int_{T_0}^T \exp \left\{ -\frac{E_t}{k\theta} \right\} d\theta \right]^{-\frac{b}{b-1}} \quad (25)$$

where now $s'' = s' n_0^{(b-1)}$. May and Partridge (1964)

developed this expression in order to apply it to those cases where the inequalities used above do not apply. Indeed, one can easily envisage many combinations of values for N , n , m , σ_{mn} and σ_n for which the first- or second-order assumptions may be invalid, especially when it is remembered that each of these parameters is temperature dependent and in order for the Randall–Wilkins or Garlick–Gibson expressions to be valid one needs the restrictions concerning the relative sizes of these terms to apply across the whole temperature range of interest.

The question of interpreting the meaning of s' and the kinetic-order parameter b in the May and Partridge equation was dealt with by Christodoulides (1990) who considered the case of a single activation energy, *first-order* kinetics, and a distribution in the frequency factor s (i.e. $n(s)$). If one assumes a Γ -distribution function in s (actually in $\ln(s)$) and applies this to the case of first-order kinetics, one can obtain the “general-order” equation, i.e. [24]. With this interpretation s' and b are characteristic parameters of the distribution function for s .

2.4. More complex models

2.4.1. Mixed-order kinetics. The treatment presented so far relies on the simple one-trap/one-center model of Fig. 2. Over the years this has proved to be an extraordinarily effective teaching tool to describe the main features of TL production. However, despite the utility of this model and its subsequent treatment, the fact remains that there are no actual materials for which one can accurately claim that there is only one trap and only one recombination site. An important consequence of the model discussed so far is that $n = m$, i.e. the number of trapped electrons equals the number of trapped holes. This is a consequence of the charge neutrality condition ([13]) with the added assumptions of quasiequilibrium and $n_{c0} \simeq 0$ (which together lead to $n_c \simeq 0$). In most real materials, however, there inevitably exist additional trapping sites for which the thermal stability of the trapped charge is greater than that for the TL signal being monitored. In other words, at most temperatures, there are likely to exist deep traps which retain their trapped electron population during emptying of the shallower traps and readout of the TL signal. The result of this is that $n \neq m$. Indeed, retaining the condition $n_{c0} \simeq 0$, the charge neutrality expression now becomes

$$n + h = m \quad (26)$$

where h is the concentration of electrons trapped in these deeper traps. The deep traps are referred to as being “thermally disconnected”. Several authors have preferred to include these in the analysis of

TL processes (Dussel and Bube, 1967; Kelly and Bräunlich, 1970). The rate equations now include an additional term

$$\frac{dh}{dt} = (H - h)v\sigma_n \quad (27)$$

and, as a result,

$$\frac{dn_c}{dt} = \frac{dm}{dt} - \frac{dn}{dt} - \frac{dh}{dt} \quad (28)$$

where H is the total number of available, deep, thermally disconnected traps and σ_n is the capture cross-section of the deep traps. The expressions for dn/dt and dm/dt remain as in [11] and [12], respectively. Writing the equations in this way takes account of the fact that the deep, thermally disconnected traps may capture electrons released from the shallow trap at energy E_t . In this way the traps are said to be “interactive”, with the deep trap competing with the recombination sites for the capture of electrons freed from the shallow trap. Under the special circumstances that $h \simeq H$, then $dh/dt \simeq 0$ and we may write, following Kelly and Bräunlich (1970), the equivalent of the “General One-Trap” equation for this “two trap” case, thus:

$$I_{TL} = \frac{ns \exp\{-E_t/kT\}(n+h)\sigma_{mn}}{[(N-n)\sigma_n + (n+h)\sigma_{mn}]} \quad (29)$$

With this restriction, using the slow-retrapping assumption ($(N-n)\sigma_n \ll (n+h)\sigma_{mn}$) in [29] leads straightforwardly to the Randall–Wilkins, first-order TL equation (i.e. [20]; Böhm and Scharmann, 1971). Alternatively, the fast-retrapping case (i.e. $(N-n)\sigma_n \gg (n+h)\sigma_{mn}$) along with $n \ll N$, leads to

$$I_{TL} = \frac{ns \exp\{-E_t/kT\}(n+h)\sigma_{mn}}{N\sigma_n} \quad (30)$$

Or, for $\sigma_n = \sigma_{mn}$, we see that [29] becomes

$$I_{TL} = \frac{ns \exp\{-E_t/kT\}(n+h)}{(N+h)} \quad (31)$$

[30] and [31] can both be presented in the form

$$I_{TL} = s'n(n+h) \exp\left\{-\frac{E_t}{kT}\right\} \quad (32)$$

with $s' = s\sigma_{mn}/N\sigma_n$, or $s' = s/(N+h)$, respectively (Chen *et al.*, 1981). Expanding [32] produces

$$I_{TL} = s'nh \exp\left\{-\frac{E_t}{kT}\right\} + s'n^2 \exp\left\{-\frac{E_t}{kT}\right\} \quad (33)$$

and, as pointed out by Chen *et al.* (1981), this looks like a mixture of first- and second-order kinetics. Specifically, if $h \ll n$, the equation reduces to the second-order form, while for $h \gg n$ the equation reduces to the first-order form. For this reason this

was termed “mixed-order” kinetics by Chen *et al.* (1981). The solution of [33] is

$$I_{TL} = \frac{s'h^2\alpha \exp\{(hs'/\beta)\} \int_{T_0}^T \exp\{-E_t/k\theta\} d\theta \exp\{-E_t/kT\}}{\left[\exp\{(hs'/\beta)\} \int_{T_0}^T \exp\{-E_t/k\theta\} d\theta - \alpha \right]^2} \quad (34)$$

where $\alpha = n_0/(n_0+h)$.

From the foregoing treatments it is clear that the size, shape, position (in temperature) and behavior (as a function of trapped charge concentration and heating rate) can be encapsulated in one of several basic equations, depending upon the initial model used. In each case, the TL peak is described by just four basic parameters, i.e. n_0 , E , s and b (or α), and the complex rate equations have been reduced to either first-order, second-order or mixed-order kinetics by the application of several assumptions. Perhaps the two most fundamental of these assumptions are $dn_c/dt \simeq 0$ (i.e. quasiequilibrium (QE)) and $h \simeq H$ (i.e. non-interactive kinetics). The validity of the QE assumption will be dealt with in a later section, but the non-interactive kinetics assumption requires more discussion at this point.

2.4.2. *Interactive kinetics.* The most general way of writing the rate equations to describe the flow of electrons into and out of the conduction band for a system of multiple traps and multiple recombination centers was given in [1]. For the case of a set of discrete electron traps of index $i = 1$ to u and a set of hole traps (recombination centers) of index $j = 1$ to v we may rewrite the complete set of rate equations as follows.

For $i = 1$ to u

$$\frac{dn_i}{dt} = -n_i s_i \exp\left\{-\frac{E_{ti}}{kT}\right\} + n_c(N_i - n_i)A_{ni} \quad (35)$$

For $j = 1$ to v

$$\frac{dm_j}{dt} = -n_c m_j A_{mnj} \quad (36)$$

where $A_{ni} = v_n \sigma_{ni}$ and $A_{mnj} = v_n \sigma_{mnj}$.

The time rate of change of the free electron concentrations may be written

$$\frac{dn_c}{dt} = \sum_{i=1}^u n_i s_i \exp\left\{-\frac{E_{ti}}{kT}\right\} - n_c \left(\sum_{j=1}^v m_j A_{mnj} + \sum_{i=1}^u (N_i - n_i) A_{ni} \right) \quad (37)$$

and since only the thermal release of trapped electrons is considered we still have $dn_v/dt = 0$.

To analyze this model one can proceed in several ways. Levy (1985, 1991) retains the quasiequilibrium approximation and develops the equivalent of the ‘‘General One-Trap’’ equation for this more complex case, i.e.

$$I_{\text{TL}} = \sum_{j=1}^v E \frac{m_j A_{\text{mn}j}}{R + U} \quad (38)$$

where

$$E = \sum_{i=1}^u n_i s_i \exp\left\{-\frac{E_{\text{ti}}}{kT}\right\} \quad (39)$$

$$R = \sum_{j=1}^v m_j A_{\text{mn}j} \quad (40)$$

and

$$U = \sum_{i=1}^u (N_i - n_i) A_{\text{ni}} \quad (41)$$

In writing [38] we have assumed that all electron–hole recombination processes are radiative and contribute to the TL signal. If this is not so, then only a subset of the recombination terms would be used. Furthermore, the equation also assumes that all emitted photons are detected.

Bull *et al.* (1986) numerically solved the rate equations for a series of electron traps and recombination centers, using $u = 3$ and $v = 1$. They showed that when recombination dominates, the ‘‘interactive’’ glow curve can be well represented as the sum of first-order curves. This is to be expected since, if retrapping is slow, little interaction (i.e. trapping into other traps) will occur compared to recombination. For the case where recombination and retrapping are equally strong, however, the ‘‘interactive’’ glow curve is significantly different from that obtained from a sum of second-order components.

The discussions of the foregoing sections have assumed that the trap depths associated with the localized states are single-valued in energy. While this may be expected to be true for high quality single crystal materials, one can expect that in highly defective or, especially, amorphous or vitreous materials, the trap depths associated with particular defects will be spread over a range of values rather than being uniquely defined. In these latter materials the structure of the lattice surrounding the defect giving rise to the TL signal may exhibit random variations in the nearest neighbor bond angles and bond lengths. The result is that the activation energies (trap depths) tend to be distributed, rather than discrete. For amorphous materials it is no longer possible to talk about the forbidden energy gap that one normally associates with crystalline materials. Instead one refers to the ‘‘mobility gap’’ within which there can exist a finite density of states localized near the Fermi level (Mott and

Davies, 1979). Given the variety of lattice fluctuations that one might expect in highly defective or amorphous materials, several kinds of energy distribution can be used to describe these localized states.

2.4.3. *The Schön–Klasens model.* The entire discussion so far has been based on the consideration of charge release from electron traps only. In this context we wrote in [10] that $dn_v/dt = 0$, and since that point we have ignored hole transitions, stating only that the equations developed for the release of trapped electrons – if the trapped holes are stable – are identical to those for the release of trapped holes – if the trapped electrons are stable. However, what we have not considered is that *both* electrons and holes may be released from their traps at the same time, in the same temperature interval. Even this is not necessarily a difficulty; we can still treat the TL signals caused by hole and electron traps in the same way as we would treat multiple electron traps, or multiple hole traps. The difficulty presents itself when (say) the holes are being thermally released from the same centers as are acting as recombination sites for the thermally released electrons, and *vice versa*. These situations are summarized in Fig. 4. The situations depicted in Fig. 4(a)–(c) can each be treated using the same concepts that have been discussed so far. In (d), however, we see that the release of trapped holes removes recombination centers for electrons, and *vice versa*. This situation was first discussed by Schön (1942) and is the same model later used by Klasens (1946) to explain thermal quenching of luminescence in sulfide phosphors. The important point about this situation is that [16], i.e.

$$I_{\text{TL}} = -\frac{dm}{dt}$$

is no longer valid, since holes are being removed from the recombination site by pathways other than recombination (Fillard *et al.*, 1978). Furthermore, since the luminescence intensity is governed by the rate of recombination, which in turn is dependent upon the concentration m , then any process which results in a decrease in m will lead to a quenching of the luminescence. Hence, the thermal release of trapped holes from the recombination site will lead to thermal quenching of the luminescence signal. Although a process of the Schön–Klasens type is not the only possible cause of a breakdown of [16], or of thermal quenching, the common observation of both phenomena in TL materials makes it important to examine this process in some detail.

Referring to Fig. 4(d) we may write a set of rate equations describing the charge carrier transitions between the energy levels during thermal excitation. Simplifying the diagram to just one electron trap and one hole trap, and *adding* retrapping transitions of the freed carriers back into their respective traps,

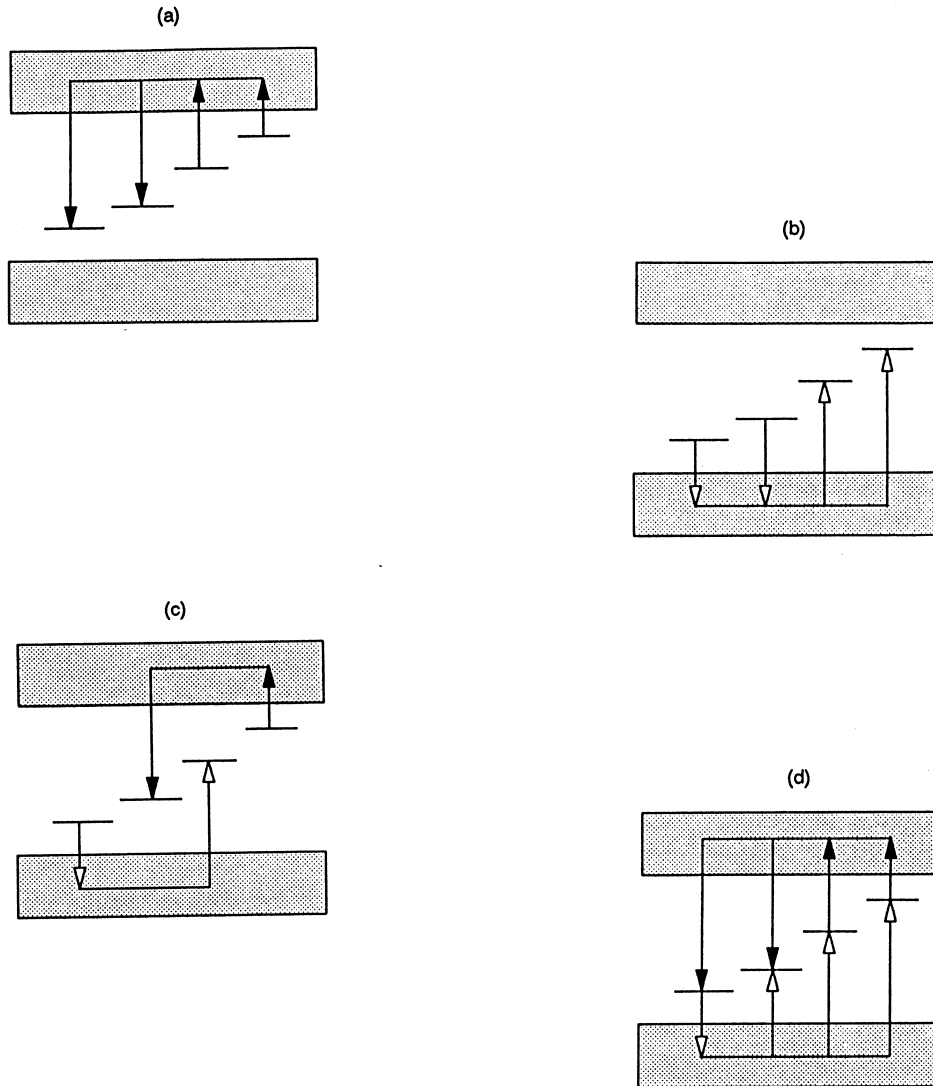


Fig. 4. (a) Multiple electron traps. (b) Multiple hole traps. (c) Multiple electron and hole traps. (d) Schön-Klasens kinetics.

allows us to write the following complete set of equations in which we retain the earlier definitions:

$$\frac{dn_c}{dt} = np_n - n_c(N - n)A_n - n_c mA_{mn} \quad (42)$$

$$\frac{dn_v}{dt} = mp_p - n_v(M - m)A_p - n_v n A_{np} \quad (43)$$

$$\frac{dn}{dt} = n_c(N - n)A_n - n_v n A_{np} - np_n \quad (44)$$

and

$$\frac{dm}{dt} = n_v(M - m)A_p - n_c mA_{mn} - mp_p \quad (45)$$

where $A_p = v_p \sigma_p$ and $A_{np} = v_p \sigma_{np}$. Here, v_p is the free hole thermal velocity, and σ_p and σ_{np} are the hole

trapping cross-section and the hole-electron recombination cross-section, respectively. M is the total concentration of available hole traps.

[42]–[45] are the rate equations describing the traffic of charge between the two energy levels. In order to define the TL intensity we must stipulate which of the two recombination transitions is radiative. In the most general case, we may consider both to be radiative, and, with the assumption that all the photons are detected with equal efficiency, the total TL intensity is then given by

$$I_{TL} = I_{TLn} + I_{TLp} = n_c mA_{mn} + n_v n A_{np} \quad (46)$$

Of course, it is possible that only one of these transitions may be radiative, or, if both are radiative, the emission wavelengths may be different such that only one is detected. The important point, however, is that, from [44] and [45], the recombina-

tion center concentrations (m and/or n) are changing by mechanisms other than the process of recombination.

Bräunlich and Scharmann (1966) considered these equations and introduced several simplifying assumptions in order to solve them. They defined the parameters

$$R = A_n/A_{mn} \quad (47)$$

and

$$R^* = A_p/A_{np} \quad (48)$$

each of which expresses the ratio of the probabilities of retrapping, compared to recombination. Four cases can thus be defined: (i) $R \ll 1$ and $R^* \ll 1$; (ii) $R \gg 1$ and $R^* \ll 1$; (iii) $R \ll 1$ and $R^* \gg 1$, and (iv) $R \gg 1$ and $R^* \gg 1$. For each of these cases the assumptions of $n \ll N$ and $m \ll M$ are also made, while the neutrality condition

$$n_c + n = n_v + m \quad (49)$$

holds throughout. Finally, the QE assumption is made for both electrons and holes (i.e. $dn_c/dt, dn_v/dt \ll 1$). Using these assumptions and conditions, for case (i) we may write $np_n \approx n_c mA_{mn}$ and $n_v \approx p_p/A_{np}$. Thus

$$\frac{dn}{dt} \approx -np_n - n_v n A_{np} \approx -(p_n + p_p)n \quad (50)$$

Writing

$$p_n = s_n \exp\left\{-\frac{E_{tn}}{kT}\right\} \quad (51)$$

and

$$p_p = s_p \exp\left\{-\frac{E_{tp}}{kT}\right\} \quad (52)$$

we have

$$n \approx n_0 \exp\left[-\frac{1}{\beta} \int_{T_0}^T \left(s_n \exp\left\{-\frac{E_{tn}}{k\theta}\right\} + s_p \exp\left\{-\frac{E_{tp}}{k\theta}\right\} \right) d\theta \right] \quad (53)$$

Thus we have, from [46]

$$I_{TL} \approx n_0 (s_n \exp\{-E_{tn}/kT\} + s_p \exp\{-E_{tp}/kT\}) \times \exp\left[-\frac{1}{\beta} \int_{T_0}^T (s_n \exp\{-E_{tn}/k\theta\} + s_p \exp\{-E_{tp}/k\theta\}) d\theta \right] \quad (54)$$

which is similar to the Randall–Wilkins equation for slow-retrapping, and becomes identical to this equation if we ignore either the transitions to the conduction band (i.e. $p_n \approx 0$) or to the valence band (i.e. $p_p \approx 0$). Furthermore, if we allow only the free electron \rightarrow trapped hole transition to be radiative, we should ignore the second term in the first bracket. Conversely, if we allow only the free

hole \rightarrow trapped electron transition to be radiative, we should ignore the first term in the first bracket.

For case (ii) we may write $n_c \approx np_n/A_n N$ and $n_v \approx p_p/A_{np}$. Thus

$$n \approx m \approx n_0 \exp\left[-\frac{1}{\beta} \int_{T_0}^T s_p \exp\left\{-\frac{E_{tp}}{k\theta}\right\} d\theta \right] \quad (55)$$

The TL intensity is thus

$$I_{TL} = (n_0^2 R/N) s_n \exp\{-E_{tn}/kT\} \exp\left[-\frac{1}{\beta} \int_{T_0}^T s_p \exp\{-E_{tp}/k\theta\} d\theta \right] + n_0 s_p \exp\{-E_{tp}/kT\} \exp\left[-\frac{1}{\beta} \int_{T_0}^T s_p \exp\{-E_{tp}/k\theta\} d\theta \right] \quad (56)$$

which is reminiscent of the Randall–Wilkins form. It becomes this equation exactly if we only consider free hole \rightarrow trapped electron transitions, or if we ignore the thermal release of trapped electrons (i.e. $p_n = 0$).

Case (iii) is symmetrical with case (ii), and yields the equivalent equation

$$I_{TL} = m_0 s_n \exp\{-E_{tn}/kT\} \exp\left[-\frac{1}{\beta} \int_{T_0}^T s_n \exp\{-E_{tn}/k\theta\} d\theta \right] + (m_0^2 R^*/M) s_p \exp\{-E_{tp}/kT\} \exp\left[-\frac{1}{\beta} \int_{T_0}^T s_n \exp\{-E_{tn}/k\theta\} d\theta \right] \quad (57)$$

which also reduces exactly to the Randall–Wilkins equation if we consider only free electron \rightarrow trapped hole transitions to be radiative, or if we ignore the thermal release of holes (i.e. $p_p = 0$).

For the remaining case (case (iv)) we have $n_c \approx np_n/A_n N$ and

$$\frac{dn}{dt} \approx -\frac{p_n R n^2}{N} - \frac{p_p R^* m^2}{M} \quad (58)$$

which gives

$$I_{TL} = \frac{(R/N) s_n \exp\{-E_{tn}/kT\} + (R^*/M) s_p \exp\left\{-\frac{E_{tn}}{k\theta}\right\} + \left(\frac{R^*}{M}\right) s_p \exp\left\{-\frac{E_{tp}}{k\theta}\right\}}{\left[\left(\frac{1}{n_0}\right) + \left(\frac{1}{\beta}\right) \int_{T_0}^T \left(\left(\frac{R}{N}\right) s_n \exp\left\{-\frac{E_{tn}}{k\theta}\right\} + \left(\frac{R^*}{M}\right) s_p \exp\left\{-\frac{E_{tp}}{k\theta}\right\}\right) d\theta\right]^2} \quad (59)$$

This is similar to the Garlick–Gibson second-order equation and becomes identical to it if we neglect all transitions to the valence band (i.e. $p_p=0$). Note, however, that the Garlick–Gibson equation was obtained with $R = 1$.

Later analyses of the Schön–Klasens model (McKeever *et al.*, 1985) solved [42]–[45] numerically without any of the assumptions of Bräunlich and Scharmann (1966) and reached the same conclusions – namely that the TL glow curve for this more complicated kinetic model retains the simple Randall–Wilkins or Garlick–Gibson shape, depending upon the chosen values of the parameters. The difficulty arises in the interpretation of the E_t and s values used in the Randall–Wilkins or Garlick–Gibson equations in order to obtain the fit. McKeever *et al.* (1985) concluded that the E_t value used in the simple equations is equal to the smaller of E_{tn} and E_{tp} when both electron–hole (e–h) and hole–electron (h–e) recombination transitions are radiative. If e–h transitions only are radiative, then $E_t \approx E_{tn}$, if $E_{tn} < E_{tp}$, or is somewhere between E_{tn} and E_{tp} , if $E_{tn} > E_{tp}$. The opposite situation is true for h–e radiative transitions.

2.5. An examination of the quasiequilibrium approximation

All of the preceding model analyses have been centered on the use of the very important quasiequilibrium (QE) approximation, namely that the free carrier density remains quasistationary during the process of TL production. This assumption allows the decoupling of the rate equations and the development of all of the analytical solutions described above. Maxia (1978, 1981) examined the concept of QE by considering the TL emission to be the result of two non-equilibrium phase transformations – namely, the release of an electron into the conduction band, and the recombination of the freed electron with a trapped hole. By assuming a linear relationship between the rate of entropy production and the transformation velocities for each of these reactions, Maxia applied Gibbs’ principle of minimum entropy production to arrive at the conclusion that the free carrier concentrations do indeed remain approximately steady throughout the TL process. However, the treatment is unsatisfactory in the sense that the minimum entropy production principle is in fact just another way of imposing the limitation of quasi-steady-state on the free carrier concentrations and begs the question of whether the principle is in fact valid during TL processes. Furthermore, the assumption of a linear relationship between the entropy production rate and the transformation velocities is also questionable, and is in fact invalid at the start of the reaction, only becoming reliable towards the end of the process

(i.e. when the concentrations have been restored to their equilibrium values anyway).

Other efforts to test the validity of the quasiequilibrium approximation have centered on the use of numerical solutions to the rate equations for the various models. Shenker and Chen (1972) conclude that the simplified expressions for TL arrived at using the QE approximation are valid solutions only if $|dn_c/dt| < 10^{-3}|dn/dt|$. They further show that, for the parameter sets examined by them, the ratio of $|dn_c/dt|$ to $|dn/dt|$ varies from 5×10^{-5} to 1.0, with the higher values of the ratio appearing toward the end of the peak – in opposition to the conclusions of the minimum entropy production principle. An extensive study by Kelly *et al.* (1971) supports the conclusions of Shenker and Chen, and concludes that the QE approximation is valid for only a part of the range of physically plausible parameters. Exact solutions to the rate equations lead to a wider variety of peak shapes, intensities and positions than can be predicted from use of the approximate solutions. Thus, application of the simplified solutions is potentially undermined by uncertainty surrounding the QE approximation. Similar pessimism also surrounds the application of the kinetic-order assumptions, since these too rely upon the assumption of inequalities between the various rate processes. Furthermore, a degree of “degeneracy” was found, in that different sets of parameters inserted into the model were found to yield similar TL curves. In fact Kelly *et al.* (1971) arrived at the altogether pessimistic conclusion that application of simplified phenomenological solutions to real systems is of limited value and is almost valueless at quantifying the trapping parameters (E_t , s , etc.; see also Bräunlich (1979)).

An entirely different approach was adopted by Lewandowski and colleagues (Lewandowski and McKeever, 1991; Lewandowski *et al.*, 1994). Here any assumptions regarding QE and kinetic order (KO) are abandoned and they are replaced by two physically meaningful functions – the Q - and P -functions, respectively. Instead of the QE assumption ([15]), we have the equality

$$-\frac{dn_c}{dt} = q \frac{dm}{dt} \quad (60)$$

or

$$Q \frac{dm}{dt} = \frac{dn}{dt} \quad (61)$$

where $Q = q + 1$. Both Q and q are functionals. As such they depend on the history of the system and are defined so that [60] and [61] are exactly true at all temperatures. The value of Q is a measure of the degree to which QE is maintained, as a function of T . QE means that $q \approx 0$, or $Q \approx 1$.

The distinction between first- and second-order kinetics was determined by the ratio $(N - n)\sigma_n/$

$m\sigma_{nm}$ as described above. Thus, a KO function $P(T)$ is defined by the ratio $(N-n)\sigma_n/m\sigma_{mn}$:

$$P(T) = \frac{(N-n)\sigma_n}{m\sigma_{mn}} \quad (62)$$

where we also emphasize the fact that the value of this ratio is a function of temperature. Slow-retrapping (first-order kinetics) is then given by $P \ll 1$, while fast-retrapping is given by $P \gg 1$. The main advantage of defining the Q - and P -functions is to separate the concepts of QE and KO and to allow the degree of adherence to these restrictions to vary with temperature. All analyses so far assume QE before introducing approximations regarding the KO. Furthermore, they require that the approximations be fixed for all temperatures.

If we define

$$\begin{aligned} R_{\text{recom}} &= \text{rate of recombination} \\ &= -\frac{dm}{dt} = n_c v_n \sigma_{mn} m \end{aligned} \quad (63)$$

R_{ex} = rate of (thermal) excitation

$$= n_s n \exp\left\{-\frac{E_t}{kT}\right\} \quad (64)$$

and

$$\begin{aligned} R_{\text{recap}} &= \text{rate of recapture} \\ &= n_c(N-n)v_n\sigma_n \end{aligned} \quad (65)$$

then we may write Q and P in terms of these reaction rates:

$$Q = \frac{1}{R_{\text{recom}}}(R_{\text{ex}} - R_{\text{recap}}) \quad (66)$$

and

$$P = \frac{R_{\text{recap}}}{R_{\text{recom}}} \quad (67)$$

We also note that

$$Q + P = \frac{R_{\text{ex}}}{R_{\text{recom}}} \quad (68)$$

and

$$\frac{Q}{P} = \frac{R_{\text{ex}}}{R_{\text{recap}}} - 1 \quad (69)$$

The Q - and P -functions are illustrated graphically in Fig. 5. Note that Q varies from $\gg 1$ at low T to ~ 0 at high T . Note also that $Q \approx 1$ at the peak maximum. (In fact, $Q = 1$ exactly at the maximum of the thermally stimulated conductivity, TSC peak;

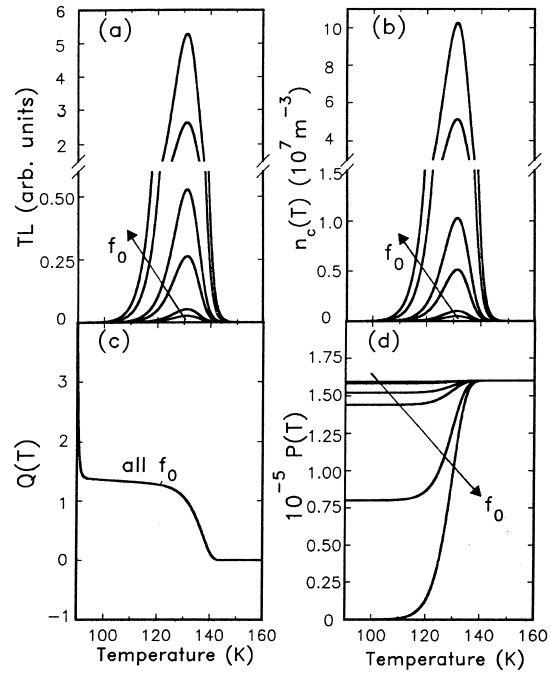


Fig. 5. Curve shapes for (a) TL, (b) TSC (actually, n_c), (c) Q and (d) P . In the figure, f_0 is the degree of trap filling, and values for f_0 range from 0.005 to 1.0. The curves have been obtained from numerical solution of the rate equations, with parameters chosen such that $P \ll 1$. Note that even though P varies dramatically with both T and f_0 , the absolute value of P is always $\ll 1$. (After Lewandowski and McKeever (1991).)

note that TSC and TL maxima do not always coincide.) Finally we note that Q is independent of the level of trap filling, but depends only upon temperature. P , on the other hand, increases as we progress through the peak, owing to the increased probability of retrapping as the trap empties. For the parameters chosen, however, $P \ll 1$ at all T .

Using these functions it is now possible to make some general statements regarding the various assumptions which are used when arriving at simplified solutions, each of which assume $Q \approx 1$.

(a) *Slow-retrapping*: This requires that $Q \approx 1$ and $P \ll 1$. This in turn requires that $R_{\text{recom}} \gg R_{\text{recap}}$ and $R_{\text{ex}} \gg R_{\text{recap}}$. This constitutes a legitimate, self-consistent set of inequalities. Such relationships may exist over wide temperature ranges. It is not obvious from this consideration alone if the pessimism of Kelly *et al.* (1971) is valid for this set of assumptions.

(b) *Fast-retrapping*: This requires that $Q \approx 1$ and $P \gg 1$. In other words, we require $R_{\text{ex}} \approx R_{\text{recap}}$ over all T . If this were strictly true (i.e. $R_{\text{ex}} = R_{\text{recap}}$) then the trap would not empty. Furthermore, from [66], in order to have $Q \approx 1$, we must have a very small value for R_{recom} , suggesting a poor likelihood of observing a TL signal in the first place, and the TSC signal which accompanies the TL peak would not be in the form of a peak at all, but would form a

step with a long, slowly decaying tail (Lewandowski *et al.*, 1994). Thus, in order to observe both TL and TSC *peaks* it appears unlikely that one would have simultaneously *both* QE and fast-retrapping.

Similar conclusions can be reached if $P = 1$ regarding the potential inconsistency of this restriction and QE (Lewandowski *et al.*, 1994).

This somewhat radical conclusion is supported by the analysis of Kelly *et al.* (1971). Examination of the curves produced by these authors from numerical solutions of the rate equations describing the simple model for TL, and comparison with those curves produced using the simplified first-order or second-order equations, show that in almost all cases where first-order kinetics do not apply there are gross discrepancies between the precise numerical solutions and the approximate analytical solutions. However, much improved agreement is observed when slow-retrapping conditions prevail.

A question arises concerning the generality of the above results, however. Numerical solutions can only be obtained after selection of particular parameter sets (i.e. specific values for E_t , s , σ_n , σ_{mn} , N , n_0 , m_0 , etc.) and since there is an infinite number of such sets to choose from, one inevitably questions the practice of arriving at general statements from a limited number of calculations. Lewandowski and colleagues (McKeever *et al.*, 1993; Lewandowski *et al.*, 1994) attempted to generalize the discussion by solving the rate equations *without* any assumption regarding QE and KO. They started with a model of one trap, one recombination center and one deep, thermally disconnected trap. From the rate equations ([9]–[12]), with the addition of [27], one arrives at

$$n = n_0 \exp \left[-\frac{1}{\beta} \int_{T_0}^T \left(\frac{Q}{Q+P} \right) s \exp \left\{ -\frac{E_t}{k\theta} \right\} d\theta \right] \quad (70)$$

which gives for the TL intensity

$$I_{TL} = n_0 \left(\frac{s}{Q+P} \right) \exp \left\{ -\frac{E_t}{kT} \right\} \exp \left[-\frac{1}{\beta} \int_{T_0}^T \left(\frac{Q}{Q+P} \right) s \exp \left\{ -\frac{E_t}{k\theta} \right\} d\theta \right] \quad (71)$$

This is the *perfectly general* equation for TL – within the confines of the chosen model – since it assumes neither QE nor a particular KO. It is easy to see how it reverts to the Randall–Wilkins equation when we impose $Q \approx 1$ and $P \ll 1$. However, it is not obvious how the Garlick–Gibson form may be obtained if $Q \approx 1$ and $P \gg 1$. Despite its generality, however, [71] is of little practical use since analytical expressions for Q and P , in terms of macroscopic, measurable parameters, do not

exist. These functions are defined only in terms of microscopic parameters, the values and temperature dependencies of which are unknown. What is required is a truly analytical solution to the rate equations in which values for Q and P are not predetermined, and which can be expressed purely in terms of measurable parameters. Unfortunately, at this time, this has not been achieved for the perfectly general case – but it has been performed for the special case of slow-retrapping, i.e. $P \ll 1$ (McKeever *et al.*, 1993; Lewandowski *et al.*, 1994). To see how this is done, we first of all set $P \ll 1$ in [71]. Since for most temperatures $Q \gg P$, we may rewrite [71] as

$$I_{TL} = \frac{n_0 s}{Q} \exp \left\{ -\frac{E_t}{kT} \right\} \exp \left[-\frac{s}{\beta} \int_{T_0}^T \exp \left\{ -\frac{E_t}{k\theta} \right\} d\theta \right] \quad (72)$$

If we represent the usual Randall–Wilkins equation, [20], as I_{TL}^{QE} , then we see that

$$I_{TL}^{QE} = Q I_{TL} \quad (73)$$

With the definition of the free carrier recombination lifetime τ_n as the lifetime of a free electron before it undergoes recombination, given by

$$\tau_n^{-1} = mA_{mn} = (n+h)A_{mn} \quad (74)$$

Lewandowski *et al.* (1994) were able to show that

$$I_{TL} = (n_0/\beta\tau_n) \exp\{- (T/\beta\tau_n)\} \int_{T_0}^T \exp\{(\theta/\beta\tau_n)s \exp\{-E_t/k\theta\}\} \times \exp \left[- (1/\beta) \int_{T_0}^{\theta} s \exp \left\{ -\frac{E_t}{k\Omega} \right\} d\Omega \right] d\theta \quad (75)$$

The approximations used in the development of this equation are (i) the model (one trap, one center, one deep trap), (ii) $P \ll Q$ and (iii) $\tau_n = \text{constant}$ (i.e. $h \gg n$). The last restriction can be removed by placing all the τ_n terms inside the integrals, but the form of the temperature function would need to be known. $P \ll Q$ is an entirely reasonable assumption for slow-retrapping, and the model will always be an approximation, no matter which model is adopted.

Although the above equation is complex, it represents the true shape of a slow-retrapping TL peak more accurately than does the simple Randall–Wilkins form. Lewandowski *et al.* (1994) tested the validity of [75] by comparing TL curve shapes produced using it, with those produced using the Randall–Wilkins equation, and with those produced

using exact numerical solutions of the rate equations. For certain parameter sets, all three solutions were found to agree, while for other sets some slight discrepancies exist between the exact solutions and the Randall–Wilkins solutions. In all cases, however, [75] gives the same solution as the numerical analysis. However, it is interesting to note that fitting the RW equation to the numerical data always results in an excellent fit (Lewandowski *et al.*, 1994), with associated errors in E_t only of the order of 1–2% in most cases. Thus, the reservations of Kelly *et al.* (1971) for the case of slow-retrapping do not appear to be serious.

The above analysis is for slow-retrapping processes only (i.e. $P \ll Q$). Equivalent expressions to [75] for other situations (e.g. $P \approx Q$ or $P \gg Q$) have not been developed, which is unfortunate since it is here that one suspects the arguments expressed by Kelly *et al.* may have greater validity. Furthermore, generalization of the Q -function to the case of multiple traps and centers, with interactive kinetics and multiple, overlapping TL peaks has not yet been forthcoming.

2.6. Tunneling

In the models discussed so far, the recombination of electrons from traps with holes in centers has occurred via the conduction band. In this way substantial diffusion of the electron through the crystal can occur with the recombination occurring between distant trap–center pairs. However, if the trap and the recombination center are spatially close to each other, one must be aware of the possibility that the trapped charge wavefunctions may overlap such that tunneling can occur between the centers. In this way we can have recombination without any involvement of the delocalized bands. Mechanisms of this type have been suggested for several TL and phosphorescence processes in a variety of materials (Delbecq *et al.*, 1974; Visocekas *et al.*, 1976; Visocekas, 1979, 1985, 1988).

To describe tunneling phenomena we make use of Fig. 6. Here we see the potential of the electron in the trap as a function of distance from the positive charge center. At distance r_1 the electron is at the bottom of a potential well of depth E_1 . Charge recombination occurs via tunneling through the potential barrier and usually occurs between shallow centers, since the shallower the trap the more delocalized is the wavefunction.

For a trap and recombination center separated by a distance r , the probability per unit time for a transition of the electron from the trap to the center (i.e. the tunneling rate) is given by

$$P(r) = P_0 \exp\{-r/a\} = P_0 \exp\{-\alpha r\} \quad (76)$$

where P_0 is the frequency factor, a is a constant (roughly one-half of the Bohr radius of the electron

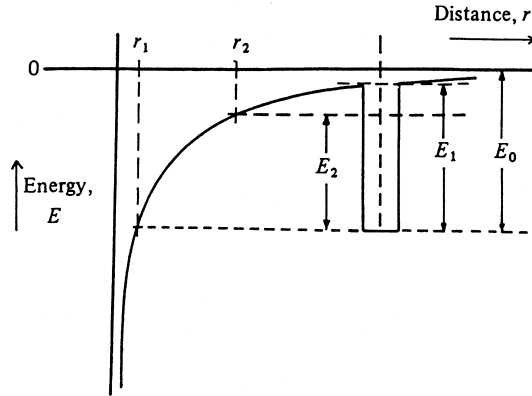


Fig. 6. Schematic diagram of the potential barrier used for the description of tunneling.

trap). The parameter α is given by

$$\alpha = \frac{2\sqrt{(2m^* E_1)}}{\hbar} \quad (77)$$

Here m^* is the electron effective mass, $\hbar = h/2\pi$ where h is Planck's constant.

For randomly distributed traps and recombination sites (Thomas *et al.*, 1965) the probability that the separation between them is equal to r is

$$S(r) = 4\pi n_0 r^2 \exp\{-4\pi n_0 r^3/3\} \quad (78)$$

where $n_0 = m_0$ is the number of electrons in traps or holes in recombination centers at time $t = 0$. If $n_0 r^3 \ll 1$, we can ignore separations that are not nearest neighbor and write that the concentration of nearest-neighbor pairs having a separation between r and $r + \Delta r$ is

$$dn(r) = n_0^2 4\pi r^2 dr \quad (79)$$

Thus, this concentration of trap–center pairs will decay with rate $P(r)$ given in [76]. From this we have the number of pairs surviving after time t

$$dn(r,t) = n_0^2 \exp\{-P(r)t\} 4\pi r^2 dr \quad (80)$$

This describes a fairly sharp step after long times at a distance r_c , defined by $P(r_c) = 1$.

Among the consequences of tunneling between traps and centers is that the number of trapped electrons diminishes with time after the irradiation (perturbation) of the samples has ceased. This gives rise to a “fading” of the subsequent TL signal, i.e. the longer the time interval between irradiation and heating to record the TL, the weaker the remaining TL signal. One should note that this type of fading is athermal, i.e. it is independent of temperature. It depends primarily upon the concentrations of trapped electrons and holes (n_0 and m_0) which in turn depends upon the amount of radiation absorbed by the sample. However, thermally-

assisted tunneling can also occur if there exists a state within the potential well at an energy E_2 (Fig. 6). Here the barrier width is reduced to r_2 and so the probability of tunneling recombination is enhanced.

As discussed by Templer (1986a), a distribution of r values with the same E_1 values will give rise to a distribution of $E_0 = E_t$ values (Fig. 6). Fading of the TL signal will now occur from the *highest* E_t ($= E_0$) first, since these correspond to the lowest values of r .

2.7. Localized transitions

Another process by which recombination can take place without a transition of the electron into the conduction band is depicted in Fig. 7. Here the electron is thermally stimulated into an excited state from which a transition into the recombination center is allowed. Halperin and Braner (1960) gave the following rate equations to describe this process:

$$I_{\text{TL}} = -\frac{dm}{dt} = n_e m A_{me} \quad (81)$$

$$\frac{dn}{dt} = sn_e - s \exp\left\{-\frac{E_c}{kT}\right\} \quad (82)$$

and

$$\frac{dn_e}{dt} = sn \exp\left\{-\frac{E_c}{kT}\right\} - n_e(mA_{me} - s) \quad (83)$$

Here, n_e is the concentration of electrons in the excited state, A_{me} is the transition probability for the recombination of an electron from the excited state into the recombination center, and E_c is the energy difference between the trap and the excited state.

In the above equations sn_e appears rather than the usual term of the form $n_e(N-n)A_e$ which might have been expected (where here we define A_e to be the probability of retrapping from the excited state

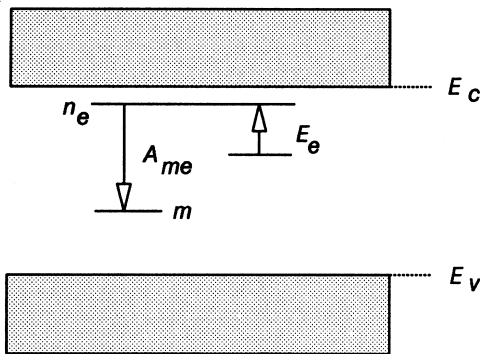


Fig. 7. Localized transition scheme for recombination, involving n trapped electrons (per unit volume), m trapped holes and n_e electrons in an excited state.

into the ground state). However, since the excited state is not delocalized, and the excited state electrons do not move through the lattice, the total number of available empty ground states, $(N-n)$, is irrelevant since retrapping can only occur into the ground state from which the electron was excited. Detailed balance arguments (Halperin and Braner, 1960) reveal that the rate of recapture is, in fact, given by s .

By similar argument we see that, since the excited state is localized, a transition into the recombination site can only occur if the trap and recombination center are spatially localized as a nearest-neighbor pair – analogous to the above discussion regarding tunneling. To account for this Chen (1976) replaced the term mA_{me} in the above equations with a *constant* probability v (in units of s^{-1}). With the additional assumption that the population of the excited states is always considerably less than that of the ground state (i.e. $m = n + n_e \approx n$) we have

$$I_{\text{TL}} = -\frac{dn}{dt} = -\frac{dm}{dt} = n_e v \quad (84)$$

where quasiequilibrium ($dn_e/dt \approx 0$) is implied. The above set of equations produces

$$I_{\text{TL}} = \left[\frac{vs}{v+s} \right] m \exp\left\{-\frac{E_c}{kT}\right\} = \bar{s} m \exp\left\{-\frac{E_c}{kT}\right\} \quad (85)$$

Upon integration, with the assumption that $v \gg s$, [85] produces an expression of the same form as the Randall–Wilkins first-order TL equation with a frequency factor $\bar{s} \approx s$. However, if the recombination rate is very low ($v \ll s$) then we have

$$I_{\text{TL}} \approx mv \exp\left\{-\frac{E_c}{kT}\right\} \quad (86)$$

and integration of this equation produces an expression which is also of the same form as the Randall–Wilkins equation, but with v replacing s . Thus we arrive at the conclusion that localized transitions of the type described should always be governed by first-order kinetics. Note that the value of v can be small, such that the typical TL peak seen in this case is very broad. Analysis of the peak using any of the traditional methods will produce a small value for the frequency factor (perhaps as low as (say) $10^5 s^{-1}$, compared to the more usual 10^{12} – $10^{14} s^{-1}$).

It should be recognized that the assumption of only nearest-neighbor transitions during recombination is itself an approximation which may not be entirely correct. Overlap of wavefunctions between, for example, next-nearest-neighbors, may also be possible, with a correspondingly reduced probability, v . A curious prediction arising from this consideration is that under such circumstances we

may expect to have a second (and possibly third, etc.) TL peak at higher temperatures.

We should also not forget that the above description uses quasiequilibrium ($dn_e/dt \approx 0$) and thus the questions regarding the compatibility of this approximation with the assumption of fast-retrapping ($\nu \ll s$ in this case) must be raised again.

During heating in a TL experiment, for the fast-retrapping case, the combination of a small frequency factor and a value of $E_c < E_t$ (Fig. 7) means that the lifetime of the electrons in the trap can be much reduced over that expected from a trap with a depth below the conduction band of E_t . For example, consider a trap with $E_t = 1.0$ eV and $s = 10^{12} \text{ s}^{-1}$, but with $E_c = 0.5$ eV and $\nu = 10^5 \text{ s}^{-1}$. Using the standard TL equations and assuming recombination via the conduction band, i.e. using the above values for E_t and s , one can predict that a TL peak should appear at approximately 120°C (for a heating rate of 1.0°C s^{-1}). However, if one considers recombination via the excited state, i.e. using E_c and ν , one would predict a TL peak at $\sim 160^\circ\text{C}$. Thus, recombination via the conduction band will occur first when the sample is heated at this rate. However, the lifetime of the electrons in the trap at room temperature, using $\tau = p^{-1} = s^{-1} \exp\{E/kT\}$ is approximately 17 h if we use $E = E_t = 1.0$ eV and $s = 10^{12} \text{ s}^{-1}$, but only ~ 0.5 h if we use $E = E_c = 0.5$ eV and $s = 10^5 \text{ s}^{-1}$. Thus the electrons leak away from the trap via the excited state and, as a result, the TL peak at 120°C will be smaller the longer one waits between irradiation and TL readout. The key issue here is the heating rate. The fact that recombination via the excited state can be more likely than via the conduction band if the sample is held at a constant temperature, but less likely if heated at a few degrees per second is related to the extreme dependence of the excited state recombination route on heating rate. This in turn is a result of the very low value for the frequency factor under conditions of fast-retrapping. Templer (1986a,b) used this to discuss the ‘‘anomalous fading’’ characteristics of several materials.

2.8. Growth of TL versus dose

An essential ingredient in any dating procedure is the production of a curve of TL (or OSL) versus dose (the ‘‘growth curve’’). From such data calibration parameters can be established which enable the measured natural luminescence signal to be converted into an equivalent dose and, from this, into a date. The ideal signal-versus-dose curve would, of course, be linear over the whole dose range of interest. Furthermore, one would hope for a curve that was single-valued such that the same luminescence signal was measured for the same absorbed dose, independent of the history of the sample and of the

number of measurements made. Regrettably, such an ideal situation is rarely the case in practice. The norm is to have a non-linear growth curve with, quite often, a faster than linear dependence being observed (i.e. superlinear, or supralinear, growth) and alterations in the sensitivity of the sample occurring as a result of radiation exposure and/or thermal or optical readout. An example of TL from pottery quartz is depicted in Fig. 8. It is seen that the dose dependence is more than linear up to ~ 250 rad and linear at higher doses. One of the major challenges of TL and OSL dating is to both account for and correct for these effects. In this context, an understanding of the causes of the effects aids greatly in our confidence of the adopted experimental procedures. To this end, a discussion of the models proposed to explain non-linearity and sensitization is necessary.

Both TL and OSL are two-stage processes, in that they involve an ‘‘excitation stage’’ and a ‘‘read-out stage’’. Models have been proposed to explain non-linear growth of luminescence which involve mechanisms occurring in each of these stages separately, or both together. In the following sections we briefly describe the effects in each stage, and then unify them to describe the overall process. We focus our attention in this review on competition models since, in recent years, competition has emerged to be the dominant process believed to contribute to most of the observed non-linear and sensitization effects.

2.8.1. *Competition during excitation.* The model usually adopted to explain growth curve superlinearity is shown in Fig. 9. We will confine our discussion to TL, although, in principle, the comments apply just as well to OSL. The model consists of an active trap (level 1) responsible for the TL signal (concentration N_1 , occupancy n_1), a deep, competing trap (concentration N_2 , occupancy n_2), and a radiative recombination center (concentration M , occupancy m). The allowed transitions during excitation (i.e. irradiation of the sample) are shown in

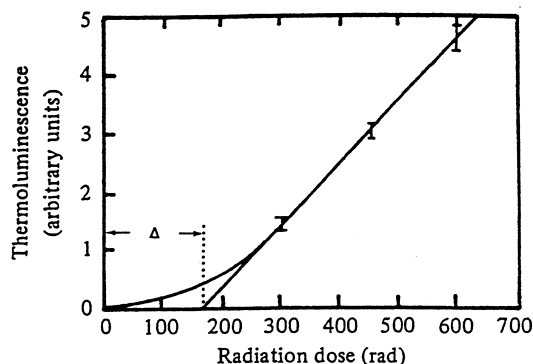


Fig. 8. Dose dependence of the TL from pottery quartz. The dose dependence is seen to be more than linear at low doses, and becomes linear at higher doses. (After Aitken (1974).)

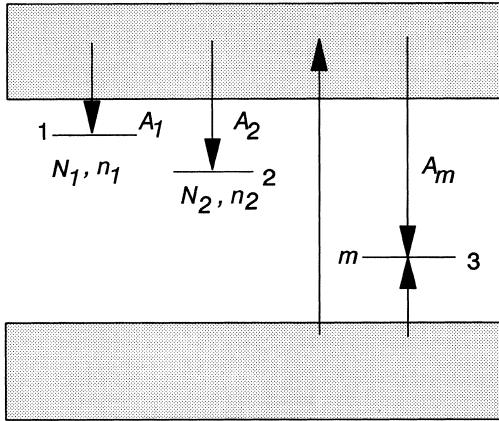


Fig. 9. Energy levels involved in the competition during excitation. The various parameters are defined in the text.

the figure. This model was initially proposed by Suntharalingham and Cameron (1967), with later modifications by Aitken *et al.* (1968) and by Chen and Bowman (1978). To begin with, we shall give an intuitive explanation for the superlinear filling of the active trap under these circumstances. Suppose that the concentration N_2 of the competitor is lower than that of the active trap N_1 , but the trapping probability A_2 of the competitor is larger than that of the active trap A_1 . Qualitatively, at low doses, the excitation fills both traps linearly. At a certain dose, however, the competing trap N_2 saturates, hence more electrons are made available to the trap of interest N_1 . This causes a faster, though linear, filling of this trap. The transition region from one linear range to the other would, however, appear to be superlinear since this transition obviously occurs continuously. As long as the measured TL is expected to depend mainly on the occupancy n_1 , the TL dose dependence is expected to be superlinear.

We shall consider the case of electrons being raised by the irradiation from the valence into the conduction band, and being trapped in levels 1 and 2. As a first step we neglect the possibility of band-to-band or band-to-center recombination during excitation (i.e. assume that they are less probable than trapping; note that this is not a necessary condition and computations show that the results extend to ranges where band-to-center recombination is more important). The equations governing the electron transitions are:

$$dn_1/dt = A_1(N_1 - n_1)n_c \quad (87)$$

$$dn_2/dt = A_2(N_2 - n_2)n_c \quad (88)$$

$$dn_c/dt = X - dn_1/dt - dn_2/dt \quad (89)$$

where n_c is the concentration of electrons in the conduction band, A_1 and A_2 are the transition probabilities (m^3s^{-1}) into levels 1 and 2 respectively,

and X is the rate of creation of electron-hole pairs by the irradiation. It is implicitly assumed here that the excitation of the whole sample is homogeneous, as is the case with irradiation by X-rays, γ -rays, etc. Also, the above assumptions lead to the conclusion that all the created holes are accumulated in the recombination center m . Defining the dose $D = \int_0^{t_d} X dt = X t_d$, where t_d is the duration of the irradiation, and using the usual quasiequilibrium assumption, it is possible to determine the conditions under which the active trap population n_1 will grow superlinearly with dose. This occurs when $d^2D/dn_1^2 > 0$, which is achieved when $A_2 > A_1$. Explicitly, this condition means that the trapping probability in the competitor is larger than the trapping probability in the active trap. Under these same conditions $d^2D/dn_2^2 < 0$, meaning that level 2 grows sublinearly, i.e. towards saturation. If the trapping probabilities are equal then both n_1 and n_2 grow linearly with D . An example of a superlinear dose dependence of n_1 as numerically calculated by Chen and Bowman (1978) is shown in curves (a) and (b) of Fig. 10.

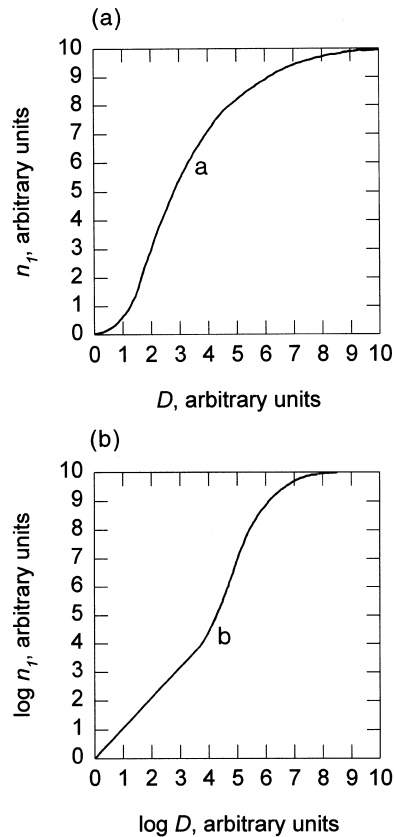


Fig. 10. The linear-superlinear-saturation dose dependence as numerically calculated from the competition during excitation model, on a linear scale (a) and on a log-log scale (b). The parameters used were $N_1 = N_2 = 10^{23} \text{ m}^{-3}$, $A_1 = A_2 = 10^{-22} \text{ m}^3\text{s}^{-1}$ and $A_2 = 3 \times 10^{-21} \text{ m}^3\text{s}^{-1}$. (After Chen and Bowman (1978).)

An important point to note in these considerations is that the dose dependence being discussed is that of the trapped charge concentration n_1 . It is not the thermoluminescence intensity I_{TL} , which is the main focus of our discussion. In order to determine how the TL intensity would behave, it is necessary to consider what happens to the trapped charge concentrations during the readout phase of the TL process – a stage in which the same competition processes are still active.

2.8.2. *Competition during readout.* We will start by giving an intuitive explanation to the superlinearity which can result from competition during readout (i.e. during heating). Let us assume a situation in which the trap and center directly involved in the creation of a TL peak are linearly dependent on the dose, at least at low doses. At a very superficial evaluation of the situation one may think that since two entities, the trapping state and the recombination center are involved, with initial fillings of n_0 and m_0 respectively following the excitation, then the emerging TL should be dependent on the product $n_0 m_0$. If we are dealing with a dose range in which both n_0 and m_0 are linearly dependent on the dose, one would expect a quadratic dependence on the dose. As is well known, however, a common dependence of TL on the dose is linear or nearly linear, which suggests that the above explanation is incorrect in many cases. In fact, under most circumstances, if S denotes the measured TL (be it the area under the peak or the maximum intensity), we expect to have $S \propto \min(n_0, m_0)$ rather than $S \propto m_0 n_0$. The explanation for this is that the total number of recombinations should be determined by an integration over the TL intensity $I_{TL}(T)$ which can be written also as $I_{TL}(t)$ for a certain heating function $T = T(t)$. As explained above, with the appropriate choice of units, we have $I_{TL}(t) = -dm/dt$. For the sake of the present discussion, let us assume the existence of only one TL peak. We can integrate over $I_{TL}(t)$ from an initial time t_0 (which we can set to zero) to infinity, and get

$$m_0 - m_\infty = \int_0^\infty (-dm/dt)dt = \int_0^\infty I_{TL}(t)dt = S \quad (90)$$

If $m_0 < n_0$, the peak terminates because the center (m) is exhausted, therefore $m_\infty = 0$ and thus

$$m_0 = \int_0^\infty I_{TL}(t)dt = S \quad (91)$$

and the right-hand side is, in the appropriate units, the area S under the glow peak. If, however, $m_0 > n_0$, the peak terminates because the trap (n) is exhausted, thus we remain with $m_\infty = m_0 - n_0$ holes in the centers and therefore

$$S = \int_0^\infty I_{TL}(t)dt = m_0 - m_\infty = n_0 \quad (92)$$

Equations [91] and [92] can be summed up as

$$S = \min(n_0, m_0) \quad (93)$$

Thus, if $n_0 \propto D$ and $m_0 \propto D$, we still have $S \propto D$, which agrees with the behavior usually seen in the experiments. As for the maximum intensity I_m , it is normally close to being proportional to the total area S , and therefore, usually $I_m \propto D$. This situation may change substantially in the presence of a competitor.

Let us consider again the energy level scheme of one kind of recombination center and two trapping states, this time concentrating on the transitions during heating, as shown in Fig. 11. Continuing the intuitive, qualitative argument, we can slightly change the statement that $S \propto \min(n_0, m_0)$ by saying that the area under the peak should be proportional to the quantity n_0 or m_0 which expires first. When these two levels are the only active ones in existence this should indeed be $\min(n_0, m_0)$, however, in the presence of a strong competitor this may not be the case anymore. We may very well have a situation in which we start with $n_0 > m_0$, but since during the heating some of the electrons are trapped in the competitor rather than recombining with holes in the centers, the peak may terminate when n_0 is exhausted, whereas some holes still remained in the center. Therefore, we have $S \propto n_0$, where n_0 is assumed to depend linearly on the dose. In addition, if we consider the electrons in the conduction band during the heating, they will distribute so that some recombine with trapped holes m and others go into the competitor. Roughly speaking, we can say that if the concentration of empty competitors $N_2 - n_2$ does not depend strongly on the initial dose (i.e. if N_2 is far from saturation, or $N_2 \gg n_2$), then the larger the value of m , the more recombinations into the center are expected. Therefore, if m_0 is proportional to the dose, this is an additional dependence on the dose of the TL

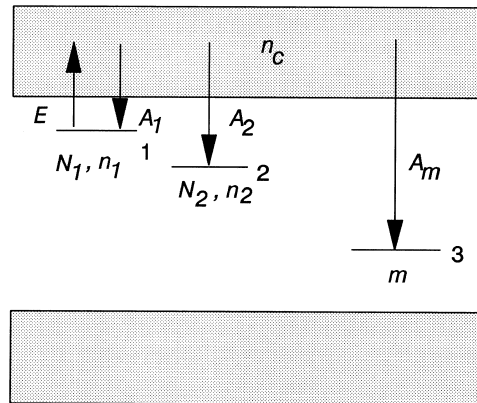


Fig. 11. Energy levels involved in the competition during heating (readout). The various parameters are defined in the text.

intensity, and therefore, under these circumstances, $S \propto n_0 m_0$ and thus, $S \propto D^2$. As will be shown below, if the competitor is in the range of an approach to saturation, the dependence of the TL intensity on the excitation dose may be even stronger than D^2 .

This hand-waving argument for explaining the superlinear dose dependence of TL under competition during heating has been given a more convincing mathematical formulation by Kristianpoller *et al.* (1974). With reference to Fig. 11, the equations governing the processes occurring during heating are

$$dn_1/dt = -\gamma n_1 + A_1 n_c (N_1 - n_1) \quad (94)$$

$$dn_2/dt = A_2 (N_2 - n_2) n_c \quad (95)$$

$$I_{TL} = -dm/dt = A_m m n_c \quad (96)$$

$$dm/dt = dn_1/dt + dn_2/dt + dn_c/dt \quad (97)$$

Kristianpoller *et al.* were able to demonstrate that under the assumptions of quasiequilibrium the dose dependence of the TL signal S can be written

$$S = m_0 - m_\infty \cong [A_m/A_2(N_2 - n_{20})]m_0 n_{10} \quad (98)$$

Furthermore, if level 2 is far from saturation, $N_2 \gg n_{20}$, we get

$$S \cong (A_m/A_2 N_2) m_0 n_{10} \quad (99)$$

which yields a quadratic dose dependence, *even if both m_0 and n_{10} are in their linear range*. As pointed out by Chen *et al.* (1988), if n_{20} in [98] is dose dependent, the overall dose dependence of S can be more than quadratic, which may be very significant in ranges where the competitor is coming close to saturation. (Note that [98] is not valid when $N_2 - n_{20}$ is close to zero, since one of the conditions leading to this expression is $n_{10} \gg N_2 - n_{20}$ (Kristianpoller *et al.*, 1974) which is clearly not possible when all the competitors are nearly full.)

We can thus distinguish between two elements of superlinear dependence of TL due to competition during heating. When the competitor N_2 is far from saturation, we can expect a quadratic dependence on the dose in agreement with [99] while still assuming linear dependencies on the dose of the filling of the recombination center and the active trap (level 1). In addition, in the range of approach to saturation of the competitor, an extra element of superlinearity, which may be quite strong, may occur. Kristianpoller *et al.* (1974) simulated this situation by assuming the approach to saturation of n_{20} as

$$n_{20} = N_2 [1 - \exp(-\alpha D)] \quad (100)$$

where α is a positive constant. In a numerically cal-

culated result, at low doses, S grows quadratically with the dose up to a point where the approach to saturation of the competitor becomes noticeable, at which point the dose dependence function becomes steeper. At still higher doses S grows linearly with D as the competitor is practically full and is therefore ineffective as a competitor. A more accurate treatment of the model should take into account the real dose dependence of n_{10} and m_0 . The idea of assuming an exponential approach to saturation of all three relevant trap and center occupancies has been further discussed by Sunta *et al.* (1994), who describe results concerning the expected superlinearity of the dose dependence. Of course, the disadvantage of this treatment is in assuming the simplest kind of approach to saturation rather than the real results of the same energy level model during the excitation stage.

A rather similar situation, which at first glance may appear to lead to a similar kind of superlinearity, is a model with one trapping state n and two kinds of centers, m_1 and m_2 , as shown in Fig. 12(a) and (b). As far as the filling of the center is concerned, the general considerations given in the previous section hold. This means that one of the centers, say m_2 , which we consider as being the radiationless competitor, starts linearly with the dose, and tends to saturation when it is about to be filled to capacity. The center m_1 , which is considered to be the *active* one (assuming that during the heating phase transition into it will result in TL emission), starts linearly with the dose, becomes superlinear at the range where m_2 is saturated, and finally goes itself to saturation as it is close to being filled to capacity. The situation is entirely different when the traffic of carriers during the heating phase is considered. Although our main concern here is the competition during heating, let us write first, for the sake of completion, the set of simultaneous differential equations governing the processes modelled in Fig. 12, since in the next section we will discuss the combined effects of competitions during excitation and heating. We have, again, a set of five simultaneous equations:

$$dm_h/dt = X - A_{h1} m_h (M_1 - m_1) - A_{h2} m_h (M_2 - m_2) \quad (101)$$

$$dm_1/dt = A_{h1} m_h (M_1 - m_1) - A_{m1} m_1 n_c \quad (102)$$

$$dm_2/dt = A_{h2} m_h (M_2 - m_2) - A_{m2} m_2 n_c \quad (103)$$

$$dn/dt = A_n (N - n) n_c \quad (104)$$

$$dm_1/dt + dm_2/dt + dm_h/dt = dn/dt + dn_c/dt \quad (105)$$

Here, M_1 and M_2 are the concentrations of the two centers and m_1 , m_2 are their occupancies. A_{h1}

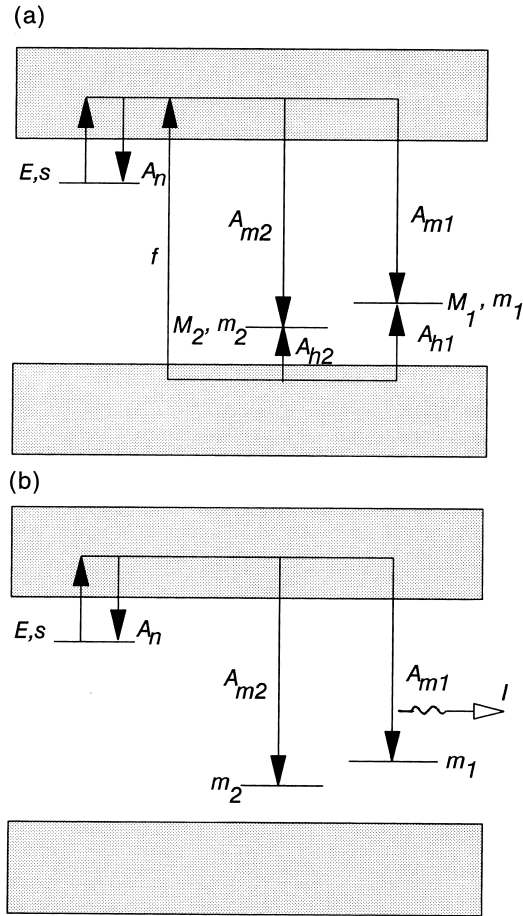


Fig. 12. (a) An energy level scheme for a model consisting of two competing recombination centers and one trap. The meanings of the different parameters are given in the text. The transitions shown are those occurring during the excitation period. (b) The transitions occurring in the model shown in (a) during heating. It is assumed that the measured emission is only from m_1 , and therefore, the TL intensity I is directly related to $-dm_1/dt$. (After Chen *et al.* (1996).)

and A_{h2} are the probabilities of capturing free holes from the valence band, and A_{m1} , A_{m2} are the recombination probabilities of free electrons. X is the rate of creation of free electrons and holes in the conduction and valence bands, respectively. n_c and m_h are the concentrations of these free electrons and holes. N is the concentration of traps and n its instantaneous occupancy. A_n is the trapping probability from the conduction band into the traps. The dose D is again given by $D = Xt_d$, assuming that the excitation intensity X is constant.

If we wish to follow, analytically or numerically, the whole procedure of excitation and heating in the model, we have to consider here a relaxation period which simulates the period of time between the end of excitation and the beginning of the heating stage. Mathematically, this would mean the sol-

ution of [101]–[105] with X set to zero, for a period of time such that n_c and m_h decay to negligible values.

The transitions in the next stage of heating are shown in Fig. 12(b). Here, E_t and s are the trap depth and the frequency factor of the trap, respectively. The governing set of equations is now

$$I_{TL} = -dm_1/dt = A_{m1}m_1n_c \quad (106)$$

$$-dm_2/dt = A_{m2}m_2n_c \quad (107)$$

$$-dn/dt = sn \exp(-E_t/kT) - A_n(N - n)n_c \quad (108)$$

$$dn/dt + dn_c/dt = dm_1/dt + dm_2/dt \quad (109)$$

The numerical solution of the simultaneous sets of equations ([101]–[105]) and subsequently [106]–[109] will be discussed in the next section. However, approximate considerations, similar to those made above in the case of competition between traps, show that competition between centers leads to an entirely different result. Making the analogous assumptions to those leading to [99], we get a very similar result with m_{20} replacing $(N_2 - n_{20})$, where m_{20} is the final filling of M_2 following the first stages of excitation and relaxation, i.e. the initial concentration for the heating stage. The result is

$$S \cong (A_{m1}/A_{m2}m_{20})m_{10}n_0 \quad (110)$$

Although this expression is analogous to [99], the consequences concerning the dose dependence are entirely different. If, for example, n_0 and m_{20} behave in a certain dose range in a similar manner, say, both grow linearly with the dose, the measured TL dependence on the dose will behave in the same way as m_{10} . If, due to competition during excitation, m_{20} is sublinear with the dose, the superlinearity of TL will be stronger in this range. As opposed to the case of competition between traps, however, this kind of trap and center filling may account for a behavior that starts linearly, becomes superlinear at higher doses and approaches saturation. This is opposite to the previous case, where the initial dose dependence was expected to be quadratic, and at higher doses became even more superlinear before starting its approach to saturation. The reason for the fundamentally different behavior between the competing trap and the competing center cases lies in the fact that the number of competing traps $(N_2 - n_2)$ decreases with dose, whereas the number of competing centers m_2 increases with dose.

Since these conclusions are based on simplifying assumptions, it would be advisable to support them by numerical calculations demonstrating the two kinds of possible behaviors. This has been done by Chen *et al.* (1996) who chose particular sets of par-

ameters for each of the two different models. Of course, the advantage is that no simplifying assumptions were required, and the calculated results were the direct outcome of the properties of the physical situation embodied by the relevant model. At the same time, it is obvious that results based on the choice of specific sets of parameters are just special cases that may demonstrate that certain behavior is possible, but do not prove a general attribute. In this sense, each of the two mathematical approaches, i.e. numerical solutions of specific cases versus quasi-general results based on approximations, are complementary methods that can be used to understand trends, including the dose dependence of the models, as discussed here.

2.8.3. Combined competition during excitation and readout. It is obvious that the complete separation of competition during excitation and competition during heating, as discussed so far, is rather artificial, and can point mainly to trends in the expected behavior rather than be used to explain details. As alluded to above, the obvious reason is that following a given irradiation of a sample, one measures the resulting TL without being able to observe directly the filling of the active trap. Also, the assumptions of linear dose dependence of m_0 and n_{10} as well as an exponential approach to saturation of n_{20} on the dose, do give an idea of the possible expected dose dependence of the measured TL, but in doing so, we are assuming externally given dose dependencies rather than solving the model equations from scratch. In fact, in principle one should start with the set of [87]–[89], along with the condition for charge neutrality, and solve them during the excitation period. In order to mimic the experimental results, one should then consider at this point a period of relaxation, during which time the free electrons and holes left in the conduction and valence bands, respectively, relax and become trapped, or recombine, prior to the heating. As noted earlier, the equations governing this process are the same with X set to zero. The contribution of this relaxation may or may not be significant, depending on the set of parameters being used. More often than not, the addition to the trapped carriers during this time is negligible.

Finally, one has to solve the set of [94]–[97] with a chosen heating function $T = T(t)$, be it linear or not. Of course, the same energy level scheme with exactly the same parameters is used in the heating stage as is utilized in the excitation and relaxation stages. The procedure explained so far appears to be rather difficult, and in most cases it is. As mentioned before, since the differential equations under consideration are not linear, we cannot expect to be able to get an analytical solution. In principle, we can choose one of two routes to tackle the problem. Unfortunately, each of them has its own serious pitfalls. One way is to use assumptions which may lead to analytical, albeit approximate, expressions.

Taking this route, it may happen that the combination of the assumptions made will lead the analytical results astray, and in this sense, the “general” result obtained is questionable. The alternative is to solve numerically the set of differential equations during the three stages. With modern numerical methods, this can be done very accurately. We believe that the combination of the two mentioned routes can bring about a better understanding of the possible dose dependencies.

Example numerical solutions of the relevant equations are presented by Chen and Fogel (1993) who consider the two-trap/one-center model, and by Chen *et al.* (1996), who consider the two-center/one-trap model. In the former case, competition during heating is shown to be the dominating effect, as shown in Fig. 13, whereas in the latter case competition during excitation is the governing process, as shown in Fig. 14.

2.8.4. Summary remarks. To conclude this section on the growth of TL with dose, the following points may be made.

1. It is inadequate to consider the two kinds of competition (i.e. during excitation or during heating) separately.
2. The superlinear effect due to competition during heating has two elements. One has to do with the final result being proportional to the concentrations of charge carriers in both traps and centers in the presence of a strong competitor. Thus, if each of them is proportional to the dose, the total dose dependence is quadratic. The other is that in the dose range where the competitor approaches saturation, the reduction in

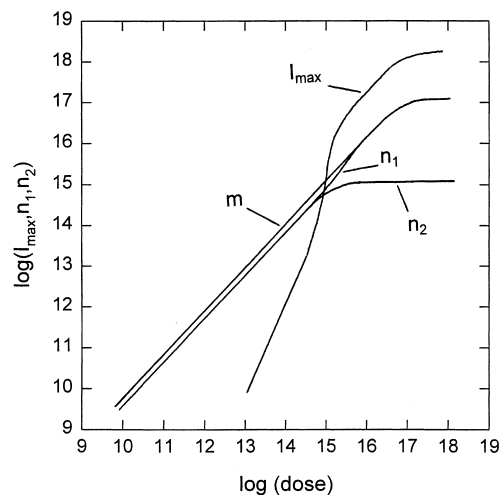


Fig. 13. Representative results of the numerical calculations related to a model with two traps and one center. n_1 , n_2 and m are the values attained for given doses of irradiation following the first two stages of excitation and relaxation. I_{\max} is the resulting maximum of TL, calculated from the heating stage. The parameters chosen were $N_1 = 10^{23} \text{ m}^{-3}$, $N_2 = 10^{-19} \text{ m}^3 \text{ s}^{-1}$. (Redrawn from Chen and Fogel (1993).)

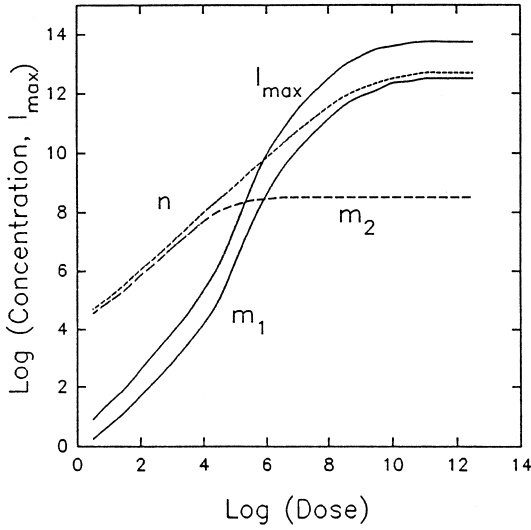


Fig. 14. A sample result of the model with two centers and one trap. The parameters chosen are $E_t = 1.0$ eV, $s = 10^{13} \text{ s}^{-1}$, $X = 10^{21} \text{ m}^{-3} \text{ s}^{-1}$, $A_{m1} = A_{m2} = 10^{-21} \text{ m}^3 \text{ s}^{-1}$, $A_n = 2 \times 10^{-21} \text{ m}^3 \text{ s}^{-1}$, $M_1 = 9 \times 10^{23} \text{ m}^{-3}$, $M_2 = 10^{23} \text{ m}^{-3}$, $A_{h1} = 10^{-21} \text{ m}^3 \text{ s}^{-1}$, $A_{h2} = 10^{-20} \text{ m}^3 \text{ s}^{-1}$ and $N = 10^{24} \text{ m}^{-3}$. (After Chen *et al.* (1996).)

competition causes some extra superlinearity (more than quadratic behavior).

3. The numerical solutions of the sets of simultaneous differential equations enable us to bypass the possible problems of artifacts due to the approximations made. Thus, if a certain behavior is observed, we can be sure that it is a net effect of the model under consideration and, therefore, can be compared with the relevant experimental results. On the other hand, the numerical results are associated with the chosen sets of parameters, and it is rather difficult to draw general conclusions. It is felt, however, that it is of prime importance to be able to demonstrate that the experimentally observed behaviors can, indeed, be associated with these models.
4. As opposed to what might have been thought, it is found, both from analytical considerations and numerical results, that there is a big difference between a situation with a competition of two trapping states and a competition between two centers. In the former, a typical behavior is an initially quadratic dose dependence followed by stronger superlinearity before saturation effects set in. In the latter, a typical dependence is an initial linear range, followed by moderate superlinearity, and in turn, going back to linearity and saturation. It appears that the main difference between a trap competitor and a center competitor is that, in the former case $N_2 - n_2$, which competes with m_{10} for released electrons, decreases with the dose. In the latter case m_{20} , which is the relevant competitor, increases with the dose.

2.9. Optical bleaching of TL

2.9.1. *Kinetics.* Removal of an electron from a trap by optical absorption reduces the subsequent TL signal. Assuming the simplest model of one trap and one recombination center, the rate of detrapping may be expressed by the usual rate equations:

$$\frac{dn}{dt} = -nf + n_c(N - n)A \quad (111)$$

with

$$\frac{dn_c}{dt} = nf - n_c(N - n)A - n_c mA_m \quad (112)$$

Here f is the optical excitation rate, given by

$$f(\lambda) = \phi(\lambda)\sigma_o(\lambda) \quad (113)$$

in which ϕ is the photon fluence (photons/m²/s), $\sigma_o(\lambda)$ is the optical cross-section, and all the other terms in [111]–[113] have already been defined. For the simplest case of no retrapping ($nf \gg n_c(N - n)A$) we arrive at

$$n = n_0 \exp\{-ft\} \quad (114)$$

where n_0 is the original trapped charge level at time $t = 0$, and $1/f = \tau_d$ is the decay constant. For a single trap the subsequent TL signal S decays in a similar first-order process as a function of illumination time

$$S = S_0 \exp\{-t/\tau_d\} \quad (115)$$

equivalent to the isothermal decay of phosphorescence. Eventually the TL signal due to this concentration of trapped charge must asymptotically decay to zero under constant illumination. This is true even if retrapping events become important at longer illumination times, although in this latter case the decay is no longer exponential. With retrapping, the second term in [111] cannot be ignored and to proceed, one has to eliminate n_c by adopting the same procedure as used in the case of thermal detrapping. Here the usual assumption of quasiequilibrium is made and, using the rate equations [111] and [112], the optical equivalent of the ‘‘General One-Trap’’ (GOT) equation is obtained, i.e.

$$\frac{dn}{dt} = -\frac{nf mA_m}{(N - n)A + mA_m} \quad (116)$$

With $N \gg n$, $R = A/A_m$, $n = m$, and fast-retrapping ($(N - n)A \gg mA_m$), [116] becomes

$$\frac{dn}{dt} = -\frac{n^2 f}{NR} \quad (117)$$

Rearranging yields

$$\frac{dn}{n^2} = -\frac{f}{NR} dt \quad (118)$$

or

$$\frac{n_0}{n} = 1 + n_0 \frac{ft}{NR} \quad (119)$$

As $t \rightarrow \infty$, $n \rightarrow 0$. Thus, a TL signal due to this charge concentration will approach zero for long optical bleaching times. An example of a TL peak which appears to behave in this straightforward fashion is the so-called 325°C peak in quartz, the detailed behavior of which is described by Spooner (1994).

Sometimes, however, it may be observed that a TL signal is reduced by prolonged illumination, but does not go to zero. Experimentally, there may be several causes for this – for example, an overlap of several TL peaks, some of which are emptied by the particular wavelength used, and some of which are not. However, notwithstanding experimental problems such as this, one may ask if it is intrinsically possible that a TL peak, due to a single trap level, may be reduced initially, but not to zero – no matter for how long the illumination is applied. An apparent example of this type of behavior was noted by McKeever (1994) who described the decay of a TL peak at 245°C from a sample of natural (Arkansas) hydrothermal quartz following ^{60}Co irradiation and illumination with 460 nm light at room temperature. The data obtained can be described by the summation of a first-order decay plus an unbleachable residual.

In order to explain these effects it is necessary to consider a model which is significantly more complex than the simple one-trap/one-center model described above. Chen *et al.* (1990) introduced a model in which they allowed for retrapping into the electron trap, but also included the optical excitation of electrons from the recombination level into the conduction band during illumination. A similar mechanism is discussed by Shlukov *et al.* (1993). The model of Chen *et al.* is illustrated in Fig. 15(a). The significance of this latter transition is that the recombination center lies below the Fermi level, and thus the concentration of holes at this center actually *increases* during the illumination phase. As a result, it is impossible for the subsequent TL signal to decay to zero as a result of the illumination. An important prediction is that the final residual level is independent of the original absorbed dose, or the intensity of illumination. In fact, from Fig. 16 we see that the residual level at long illumination times is the same whether the traps are initially empty or initially full. Thus, with this model, the illumination is seen to generate a TL signal in a previously unirradiated specimen. With respect to the results for quartz, insufficient data presently exist to determine if the residual level observed by McKeever is dose dependent or independent.

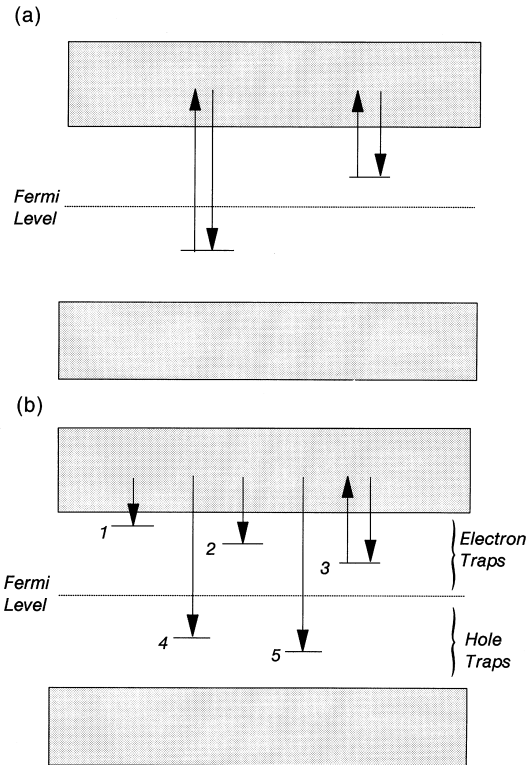


Fig. 15. The models of (a) Chen *et al.*, and (b) McKeever, to explain optical bleaching of TL in which a finite residual level is reached at long illumination times. (After Chen *et al.* (1990) and McKeever (1991).)

An alternative model for the explanation of a non-zero residual level after bleaching is illustrated in Fig. 15(b). Here the TL signal of interest is due to the release of electrons from level 2, but the illumination does not bleach this level; instead it empties charge from a deep level –

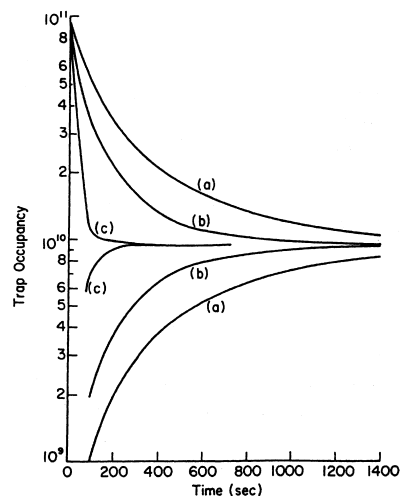


Fig. 16. Example bleaching and excitation curves from the model of Chen *et al.* (Fig. 15(a)). The curves (a), (b) and (c) refer to three different illumination intensities. (After Chen *et al.* (1990).)

level 3. Also included in the model is a shallow trap (level 1) and two recombination centers (4 and 5), only one of which (level 4) is radiative. The important features of the model are that the charge is *not* bleached from the level of interest (level 2) during illumination and thus this trapped charge concentration does not go to zero during illumination. In fact, because of phototransfer from level 3, it may actually increase during the illumination process. Some example data obtained from solutions to the rate equations describing this model are shown in Fig. 17. In this particular example, the TL from level 2 decreases from its initial level to an unbleachable, residual level. The cause of the reduction in the TL signal can be found in the fact that there are two recombination centers competing for the charge released from level 3 during bleaching. Furthermore,

during heating, the model of Fig. 15(b) represents a classic competition-during-heating situation, as described in the previous section. In general, several possible behaviors are possible, dependent upon the relative concentrations of the trapped charges in the various levels. The bleaching process stops when the charge from level 3 is depleted. At this stage, a residual ("hard-to-bleach") component remains, such that $n_{1\infty} + n_{2\infty} = m_{4\infty} + m_{5\infty}$, where $n_{1\infty}$, $n_{2\infty}$, $m_{4\infty}$ and $m_{5\infty}$ are the concentrations of electrons and holes in level 1, 2, 4 and 5 remaining when the concentration of electrons in level 3 has been depleted. If n_3 is large enough at the start of the bleaching procedure, $m_{4\infty}$ may be ~ 0 , and thus the final residual TL level will also be zero. However, if n_3 is such that $m_{4\infty} \neq 0$, a non-zero residual TL level will be reached.

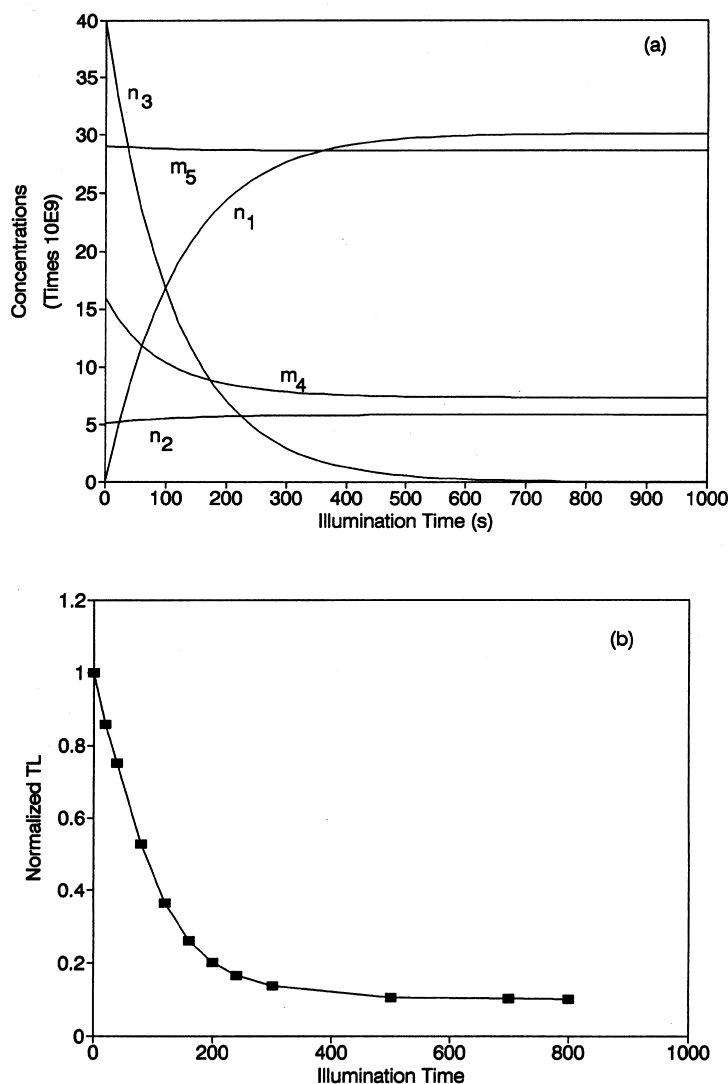


Fig. 17. (a) Trapped charge concentrations (refer to Fig. 15(b)) versus bleaching time for the model of McKeever. (b) Predicted TL versus bleaching time, illustrating the non-zero residual TL level at long bleaching times. (After McKeever (1994).).

2.9.2. *Thermal assistance.* It may be that transitions from a defect ground state to a delocalized band do not take place directly, but instead occur via a localized excited state. The most direct evidence for this in materials relevant to dating comes not from TL studies, but from OSL studies. Although we will be dealing with OSL in a later section in this paper, it is of interest to discuss these results at this point.

Illumination of LiF containing *F*-centers at a wavelength of 250 nm is able to transfer electrons from the *F*-centers to stable electron trapping states. The transfer is observed to be temperature dependent, with an activation energy of 0.12 eV (Sunta and Watanabe, 1976). The *F*-center in LiF is believed to have an excited state 0.16 eV below the conduction band and the measured activation energy for phototransfer is suggested to correspond to thermal activation from this excited state into the conduction band. Similar mechanisms have been suggested by Hütt and colleagues (Hütt *et al.*, 1988; Hütt and Jaek, 1993) who monitored the OSL which results from illumination of irradiated feldspar samples with infrared light (~825–950 nm). The production of OSL in this manner was observed to have an activation energy of ~0.10 eV. The TL traps emptied by this illumination are deep, however, and thus it was suggested by Hütt *et al.* that the infrared illumination excited the trapped electrons from a localized ground state to a localized excited state, from where thermal excitation into the conduction band (activation energy 0.10 eV) leads to bleaching of the TL traps and production of OSL.

Poolton *et al.* (1995a,b,c) examined this proposal further for a variety of feldspars. Using the Bohr model for the hydrogen atom, the energy E_n and radius R_n of the n th excited state can be calculated using

$$E_n = -E_h \frac{(m^*/m_e)}{(\epsilon_r n)^2} \quad (120)$$

and

$$R_n = \frac{R_h n \epsilon_r}{(m^*/m_e)} \quad (121)$$

where E_h and R_h are the ionization energy and Bohr radius of free hydrogen, respectively (13.6 eV and 0.53 Å), m^* is the electron effective mass, m_e is the free electron mass, and ϵ_r is the relative permittivity. Assuming a hydrogenic model for the defects responsible for IR-stimulated OSL, with $m^* = 0.757m_e$ for each feldspar type, the transition energies to the first excited state are calculated to be 1.441 eV, 1.422 eV and 1.225 eV for orthoclase, albite and anorthite, respectively. This compares very well with the measured IR absorption energies required for production of OSL in these materials,

i.e. 1.440 ± 0.003 eV, 1.422 ± 0.003 eV and 1.275 ± 0.004 eV, respectively. This gives broad support to the model proposed by Hütt and colleagues for thermal assistance of the OSL mechanism. However, Poolton *et al.* (1995b) demonstrate that the measured thermal activation energies for the three feldspar types are inconsistent with the Hütt *et al.* model. The thermal activation energies, measured using the IR energies noted above, are 0.105 eV (orthoclase), 0.065 eV (albite) and 0.03 eV (anorthite) – the opposite of what one might expect based on the measured (and calculated) excited state energies. These authors point out, however, that the radii of the first excited states, calculated using [121], increases as one goes from orthoclase to anorthite. Thus, Poolton *et al.* (1995b) propose that the measured thermal activation energy is the hopping energy from the excited state of the “donor” defect to an “acceptor” defect, which acts as a recombination center. This donor–acceptor recombination model predicts a zero value for the thermal activation energy if the overlap between the excited state wavefunction is high enough, and Poolton *et al.* suggest that this explains why the measured activation energy decreases as one goes from orthoclase to anorthite.

Spooner (1994) also observed that the OSL from quartz when illuminated with visible light is dependent upon temperature. In this material, the measured thermal activation energy for OSL production depends smoothly upon the wavelength of the light used. This is also inconsistent with a Hütt-type mechanism for which one would expect that either the thermal activation energy would be independent of the wavelength, or it would vary discretely as higher excited states are populated. Because of this Spooner suggests a model based on the thermal excitation of charge within an array of ground state levels, from where optical excitation into the conduction band then occurs.

2.10. Phototransferred thermoluminescence

2.10.1. *General.* Phototransferred thermoluminescence (PTTL) is the TL from shallow traps resulting from the transfer by light of charge from deeper traps. PTTL has been observed and studied for a wide variety of materials and has been suggested as a tool in radiation dosimetry and in dating of ceramic samples (Jain, 1984; Bailiff *et al.*, 1977; Bowman, 1979; Milanovich-Reichhalter and Vana, 1990, 1991). Examinations of the PTTL properties lead to useful information regarding the optical energies likely to be most efficient in transferring charge between centers and help to identify the mechanisms involved in the optically stimulated and TL processes.

2.10.2. *Models.* The simplest model to describe phototransfer is that of one shallow trap into which the charge is transferred, one deep trap from which the charge is excited, and one recombination center. If n and h are the concentrations of electrons in the shallow and deep traps, respectively, and m is the concentration of holes in the centers, an analysis of PTTL may start from the initial condition that $n_0=0$, and $h_0=m_0$ at some point after the irradiation and immediately before illumination. If the illumination excites electrons from the deep traps at rate f then we may write the following rate equations during the illumination period:

$$\frac{dh}{dt} = -hf + n_c(H-h)A_h \quad (122)$$

$$\frac{dn}{dt} = n_c(N-n)A_n \quad (123)$$

and

$$\frac{dm}{dt} = -n_c mA_m = \frac{m}{\tau} \quad (124)$$

where $\tau = (n_c A_m)^{-1}$ is a lifetime and all the other terms have their usual meanings. With the additional stipulations of quasiequilibrium and no retrapping into the source traps ($hf \gg n_c(H-h)A_h$) the solutions to the above equations are

$$h(t) = h_0 \exp\{-tf\} \quad (125)$$

$$n(t) = N[1 - \exp\{-Bt\}] \quad (126)$$

and

$$m(t) = m_0 \exp\{-t/\tau\} \quad (127)$$

where $B = n_c A_n$. Note that B and τ are considered approximately constant only if the quasiequilibrium approximation ($dn_c/dt \ll 0$) is true. Thus, at the end of the illumination period, i.e. at $t = t^*$, there will be a certain concentration of charges in each of the traps and centers, as defined by [125]–[127].

We now consider warming of the sample after the illumination has been switched off. This is a classic competition-during-heating situation and one which has already been fully analyzed in an earlier section. With the assumptions of quasiequilibrium and $n(t^*) \ll H - h(t^*)$, we arrive at

$$S(t^*) = \frac{Cm(t^*)n(t^*)}{(H - h(t^*))} \quad (128)$$

or

$$S(t^*) = \frac{C \exp\{-t^*/\tau\} N [1 - \exp\{-Bt^*\}]}{(H/h_0 - \exp\{-t^*f\})} \quad (129)$$

Under the restrictions described, [129] describes the variation in the PTTL peak due to the shallow trap as a function of the illumination time during

PTTL stimulation. Note that as $t^* \rightarrow \infty$, $h \rightarrow 0$, $m \rightarrow n$ and S will start from 0 at $t^* = 0$, and increase smoothly to a maximum, given by

$$S(\infty) = \frac{Cn_\infty^2}{H} \quad (130)$$

where $n_\infty = m_\infty$ = the final concentrations at $t^* = \infty$.

The analysis of PTTL based on this simplest energy level scheme results in a PTTL versus time curve which grows monotonically from zero to a maximum level. However, one often finds experimental PTTL versus time curves which show an initial increase up to a maximum, and are then followed by a decrease at longer illumination times. One obvious interpretation of this behavior is that the illumination, in addition to filling the traps in question, is also emptying the traps via optical bleaching. Such processes have already been described for the main TL peak from Al_2O_3 in which transfer of charge from deep traps can occur simultaneously with optical bleaching out of the trap, dependent upon wavelength (Walker *et al.*, 1997). This has also been suggested to be the explanation of the similar observation for the PTTL from the 110°C peak in quartz (Wintle and Murray, 1997). Sometimes, however, it is uncertain whether or not the illumination does in fact optically empty the trap in question. An example of this is the PTTL signal for some of the low temperature ($< RT$) peaks in crystalline quartz. It was noted above that McKeever and colleagues had discussed a model which explains how one can get partial bleaching of a TL signal down to a residual level, with no further bleaching of the signal being possible. A similar model can be used to explain how a PTTL peak can exhibit a growth, and then a decay, *without* invoking the requirement of optical excitation out of the trap. Referring to Fig. 18, the model allows for the transfer of charge into the trap in question (in this case, transfer from level 2 to level 1) but does not include the optical emptying of charge from level 1. Nevertheless, an increase in the PTTL signal from level 1, followed by a decrease at longer illumination times is observed (Alexander *et al.*, 1997).

To explain this result we consider the non-radiative recombination center in Fig. 18. This center provides a competing, non-radiative recombination pathway and the conditions for charge neutrality are

$$n_c + n_1 + n_2 + n_3 = m_4 + m_5 \quad (131)$$

Here n_1 , n_2 and n_3 are the concentrations of electrons in the three electrons traps, and m_4 and m_5 are the concentrations of holes in the radiative and non-radiative recombination centers, respectively. The description of PTTL using this model now follows the principle described earlier, in which the reduction in the PTTL as the illumination proceeds is

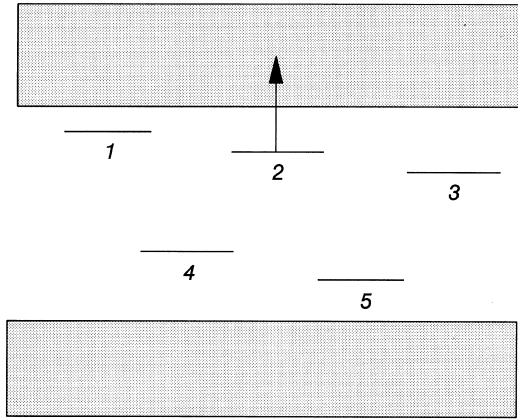


Fig. 18. Model for PTTL and OSL, including an optically active trap (level 2); a deep, competing trap (level 3); a shallow, competing trap (level 1); a radiative recombination center (level 4); and a non-radiative recombination center (level 5).

caused by the removal of holes from the radiative recombination sites during the illumination period. This removal occurs via recombination and is the source of the OSL signal observed during illumination. Although a similar removal also takes place with the simpler model described above, it is important to recognize that in that model n_1 is always less than (or equal to) m_1 , because of the charge neutrality condition. Thus, if n_1 is increasing during illumination, there are always enough holes available such that the resulting PTTL signal simply follows n_1 . However, in the more complex model of Fig. 18, n_1 may be less than, or greater than, m_4 , according to the new charge neutrality condition ([131]). This means that even though n_1 may be increasing, there may, for a given illumination time, no longer be enough holes in the radiative recombination site to accommodate this. Of course, the total number of available holes ($m_4 + m_5$) will always be greater than (or equal to) the number of electrons in the shallow traps. Thus, at the start of the illumination, the number of electrons in the shallow traps will be less than the number of holes in the radiative recombination center and the PTTL intensity will grow as n_1 grows. At longer times, however, n_1 may (depending upon the values of the various parameters) become greater than m_4 . The PTTL intensity will now follow m_4 and will decrease as m_4 decreases. This reasoning follows that given earlier in the section concerning the dose dependence and can be summarized in the present case as

$$S_{\text{PTTL}} = \min(n_1, m_4) \quad (132)$$

However, as already explained, this simple, hand-waving argument is too simplistic when there is competition and multiple recombination/retrapping pathways for the electrons. Under these circum-

stances the PTTL intensity will not always follow the minimum of n_1 or m_4 . In fact, the only way to be sure where the charge is going, and what the resultant PTTL intensity will be for a given set of conditions and parameter values, is to solve the appropriate rate equations numerically. Figure 19 shows the numerical solution to this more complex model for PTTL. The wavelength dependence was built into the model using the relationship between excitation intensity f , the intensity of the illuminating light ϕ , and the photoionization cross-section σ from deep traps and an expression for the wavelength dependence of σ assuming deep levels and parabolic bands, namely

$$\sigma_o = C\sqrt{E_o} \frac{(hv - E_o)^{3/2}}{hv(hv - \gamma E_o)^2} \quad (133)$$

Here, C is a constant and hv is the incident photon energy. $\gamma = 1 - m^*/m_e$ is a constant dependent upon the effective mass m^* of the electron and the free electron mass m_e . E_o is the threshold photon energy required for photoionization.

The solution shown in Fig. 19 is typified by an increase in the PTTL intensity at short illumination times, and a decrease at longer times. The exact form of the curve is seen to vary with the wavelength of the light used to stimulate the effect. At shorter wavelengths both the growth and decay are more rapid than at longer wavelengths. The point to observe about the result is that a decrease in the PTTL intensity is obtained even though there is no optical excitation out of the shallow traps. In the examples shown, the steady-state PTTL is not zero and is attained when there are no more electrons to be excited from the source traps (i.e. $n_2 \rightarrow 0$ as $t \rightarrow \infty$). Clearly, depending upon the relative initial values of n_2 and m_4 , one could have a final steady-state value of m_4 which is approximately zero, and thus the PTTL steady-state value must also be approximately zero, even without optical stimulation out of the traps. Alternatively, the final, steady-state level $m_{4\infty}$ may not be zero, and hence the corresponding steady-state PTTL level will also be non-zero.

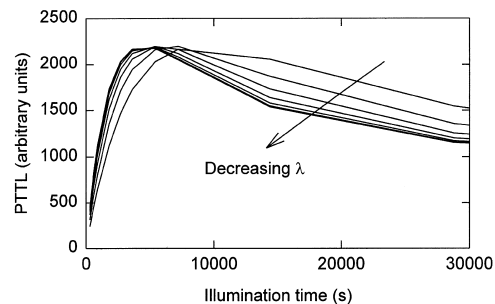


Fig. 19. Numerical simulations of the PTTL versus illumination time using the model described in the text. (After Alexander *et al.* (1997).)

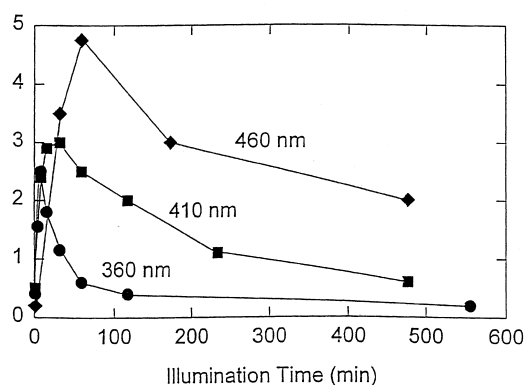


Fig. 20. Experimental data showing the illumination time dependence of the 358 K PTTL peak from quartz. (After Alexander *et al.* (1997).)

Experimental data showing the wavelength dependence of the PTTL response from quartz are shown in Fig. 20. It is clear that extracting the PTTL excitation spectrum from such data by simply taking the PTTL intensity at a fixed time can be equivocal, in that the result will depend upon the time chosen to extract the PTTL intensity. At short illumination times the PTTL after short wavelength illumination is greater than that after long wavelength illumination. However, at longer illumination times, the reverse is true. Nevertheless, published examples of PTTL excitation spectra extracted in this way are common (e.g. Jain, 1984; Milanovich-Reichhalter and Vana, 1990, 1991). Using the numerical solutions to the rate equations, as described above, Alexander *et al.* (1997) showed that the true excitation spectrum is obtained by taking the *initial slope* of the PTTL versus time curves.

3. OPTICALLY STIMULATED LUMINESCENCE

3.1. Background

OSL has become a popular method for determining equivalent doses for sedimentary deposits in dating applications and is growing in popularity in dosimetry applications. The method was first introduced for dating by Huntley *et al.* (1985), and since then the technique has been developed into an important dating procedure. In each of these studies the optical excitation is continuous wave (cw) and is either a high power arc lamp source, along with a monochromator or filter system to select the excitation wavelength, or a laser operating at or near the desired wavelength. The luminescence is monitored continuously while the excitation source is on, and narrow band and/or cut-off filters are used in order to discriminate between the excitation light and the emission light, and to prevent scattered excitation light from entering the detector. Usually, the OSL is monitored from the instant the exci-

tation light is switched on and is observed to take the form of a luminescence decay curve, following an exponential-like function, until all the traps are emptied and the luminescence ceases. The integrated emission signal (i.e. the area under the decay curve) is then recorded and used to determine the absorbed dose.

3.2. OSL models

3.2.1. General features. In general, the shape of an OSL decay curve does not lend itself to analysis using simple descriptions. The decay is often non-exponential, typically exhibiting a long tail at long illumination times. Under some circumstances, and for some samples, the OSL may even display an initial slow increase after the illumination is applied, followed by the more usual decrease at longer times. Overall, the decay shape is dependent upon the sample, the absorbed dose, the illumination intensity and the temperature. An earlier analysis of the infrared-stimulated OSL decay from a collection of feldspar samples by Bailiff and Poolton (1991) illustrated that, for microcline, sanidine and albite, the decay followed a $A(1 + Bt)^{-P}$ law, with $P = 1$ and where A and B are constants and t is time. Furthermore, the constant A was observed to be exponentially related to temperature, suggesting a thermally activated process, as previously proposed by Hütt and colleagues (Hütt *et al.*, 1988). In contrast, for labradorite, the OSL followed a $(1 + Bt)^{-P}$ law and was independent of temperature, with $P = 2$.

Later measurements on potassium feldspars by Bailiff and Barnett (1994) gave values of P varying between 1 and 2. Poolton *et al.* (1994) suggested that the infrared-stimulated OSL from feldspar is influenced by localized, donor-acceptor pair recombination. Evidence for this was obtained by observing the decay of the OSL signal after successively longer exposures of an irradiated sample to green light. For long green light exposures, the IR-stimulated OSL displayed a clear increase as a function of IR illumination time, up to a maximum, before a decay was observed. The longer the green light exposure, the longer the IR illumination time required for the IR-induced luminescence to reach a maximum. This was interpreted as being caused by an increase in the mean donor-acceptor distances for lower concentrations of donors and acceptors. It should be stressed that donor-acceptor recombination is not predicted for OSL stimulated by green light for which delocalized transport via the conduction band is believed to be the case.

Smith and Rhodes (1994) and Bailey *et al.* (1997) attempted to fit the decay of the green-light-stimulated OSL from quartz using a summation of three exponentials. One might expect a multi-component OSL decay curve if more than one trap is being

emptied at the illumination wavelength being used. Smith and Rhodes (1994) also note an increase in the OSL decay rate as the temperature increases. The thermal dependence of the OSL from quartz was studied further by Spooner (1994) who presented evidence for a thermally assisted process for OSL production.

A long tail is often observed in the OSL decay curve. This may be caused by either the influence of shallow traps – which localize charges released during illumination and slowly release them again at a rate determined by the trap depth and the sample temperature – or a contribution from traps which are emptying slowly at the excitation wavelength used in the experiment. The shallow traps yield an optically-stimulated phosphorescence component to the OSL decay, and they give rise to a temperature-dependent OSL component, since at higher temperatures the shallow traps become less effective at trapping charge.

3.2.2. *Simplest model: one trap/one center.* Most models for OSL assume transport of the optically excited charge through the delocalized bands in order to reach the recombination site. Thus, the simplest model by which OSL can be produced is shown in Fig. 21(a). Here light stimulates trapped electrons, concentration n , into the conduction band at rate f , followed by recombination with trapped holes, concentration m , to produce OSL of intensity I_{OSL} . With the usual definitions, the rate equation describing the charge flow is

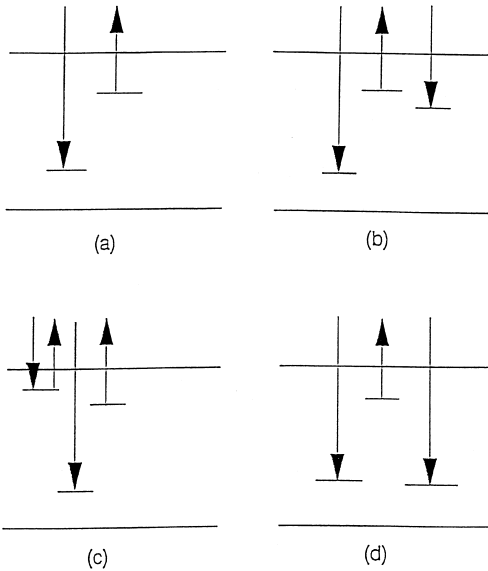


Fig. 21. (a) Simplest model for OSL, involving one electron trap, one hole trap (which acts as a radiative recombination center) and transport through the conduction band. (b) Model containing an additional, deep competing trap. (c) Model containing a shallow competing trap. (d) Model containing two recombination sites – one radiative and one non-radiative.

$$\frac{dn_c}{dt} = -\frac{dn}{dt} + \frac{dm}{dt} \quad (134)$$

which can be derived from the charge neutrality condition

$$n_c + n = m \quad (135)$$

With the assumptions of quasiequilibrium ($dn_c/dt \ll dn/dt$, dm/dt and $n_c \ll n$, m) and negligible retrapping we have

$$I_{OSL} = -\frac{dm}{dt} = -\frac{dn}{dt} = nf \quad (136)$$

the solution of which is

$$I_{OSL} = n_0 f \exp\{-tf\} = I_0 \exp\{-t/\tau\} \quad (137)$$

Here, n_0 is the initial concentration of trapped electrons at time $t = 0$, I_0 is the initial luminescence intensity at $t = 0$, and $\tau = 1/f$ is the decay constant. One can observe a straightforward relationship in which the initial intensity is directly proportional to the excitation rate and the decay of the OSL with time is a simple exponential. The excitation rate is given by the product of the excitation intensity ϕ and the photoionization cross-section ($f = \phi\sigma$).

3.2.3. *Competing, deep trap.* For two optically active traps (concentrations n_1 and n_2 and excitation rates f_1 and f_2) the same assumptions yield

$$\frac{dm}{dt} = -\frac{dn_1}{dt} - \frac{dn_2}{dt} \quad (138)$$

Along with the charge neutrality condition of $n_1 + n_2 = m$ we have

$$n_1 = n_{10} \exp\{-tf_1\} \quad (139)$$

and

$$n_2 = n_{20} \exp\{-tf_2\} \quad (140)$$

Thus

$$\begin{aligned} I_{OSL} &= n_{10} f_1 \exp\{-tf_1\} + n_{20} f_2 \exp\{-tf_2\} \\ &= I_{10} \exp\left\{-\frac{t}{\tau_1}\right\} + I_{20} \exp\left\{-\frac{t}{\tau_2}\right\} \end{aligned} \quad (141)$$

and the OSL decay curve is the sum of two exponentials.

Alternatively, if the additional trap is optically (and thermally) inactive, i.e. it acts as a deep, competing trap only (Fig. 21(b)), the OSL intensity may be written

$$I_{OSL} = n_{10} f \exp\{-tf\} - \frac{dn_2}{dt} \quad (142)$$

where

$$\frac{dn_2}{dt} = n_c(N_2 - n_2)A_2 \quad (143)$$

adopting the standard definitions. With an additional assumption of $N_2 \gg n_2$ then

$n_c N_2 A_2 \approx \text{constant}$, C . Therefore

$$I_{\text{OSL}} = n_{10} f \exp\{-tf\} - C \quad (144)$$

and the OSL is reduced in intensity by the extent of the retrapping into the deep traps. In the limit, as $t \rightarrow \infty$, $n_c \rightarrow 0$ and therefore $C \rightarrow 0$. Thus, C is in fact a very slowly varying function of time.

3.2.4. *Competing, shallow trap.* If the competing traps are shallow traps which are thermally metastable at the temperature of the OSL measurement (Fig. 21(c)), [143] becomes

$$\frac{dn_2}{dt} = n_c(N_2 - n_2)A_2 - n_2p \quad (145)$$

where p is the rate of thermal excitation out of the trap. Now we have

$$I_{\text{OSL}} = n_{10} f \exp\{-tf\} + n_2p - n_c(N_2 - n_2)A_2 \quad (146)$$

The last two terms in [146] combine to produce a long-lived, temperature-dependent tail to the OSL decay. The form of this component will be an initial increase, followed by a decrease at longer times. Depending upon the relative size of this component compared with the first term, the overall OSL decay curve may exhibit an initial increase, followed by a decrease. The relative size of the two components also depends upon the excitation rate f such that at low values of f , the temperature-dependent term may be significant.

3.2.5. *Competing recombination center.* For the case of two recombination centers (Fig. 21(d)), one of which (m_1) is radiative and the other (m_2) is non-radiative, we have $n = m_1 + m_2$, $n = n_0 \exp\{-tf\}$, and

$$I_{\text{OSL}} = n_0 f \exp\{-tf\} - \frac{dm_2}{dt} \quad (147)$$

As with the case of the deep traps, the OSL intensity is reduced by the existence of a non-radiative pathway. Since

$$\frac{dm_1}{dt} = -n_c m_1 A_{m1} \quad (148)$$

and

$$\frac{dm_2}{dt} = -n_c m_2 A_{m2} \quad (149)$$

then, with quasiequilibrium ($dn_c/dt \approx 0$) we have

$$m_1 \approx m_{10} \exp\{-n_c A_{m1} t\} \quad (150)$$

and

$$m_2 \approx m_{20} \exp\{-n_c A_{m2} t\} \quad (151)$$

from which we have

$$\frac{m_1}{m_2} \approx \frac{m_{10}}{m_{20}} \exp\{-n_c [A_{m1} - A_{m2}] t\} \quad (152)$$

from which we see that the ratio m_1/m_2 is a time-dependent function. However, if $A_{m1} = A_{m2}$, then $m_1/m_2 = a$ constant, k . In these circumstances the charge neutrality condition is written

$$m_1 + \frac{m_1}{k} = n \quad (153)$$

or

$$m_1 = \frac{n}{1 + 1/k} = \frac{n}{K} \quad (154)$$

where $K = 1 + 1/k$. From this

$$\frac{dm_1}{dt} = \frac{1}{K} \frac{dn}{dt} = -\frac{nf}{K} \quad (155)$$

and

$$I_{\text{OSL}} = \frac{1}{K} n_0 f \exp\{-tf\} = I'_0 \exp\{-t/\tau\} \quad (156)$$

In this way we see that the OSL decay curve may still be exponential in the case of two types of recombination centers, but only if the recombination cross-sections are the same. Comparing [137] with [156] we observe that, as expected, the latter case describes a weaker OSL signal (by a factor $1/K$).

An alternative approach is to assume that retrapping into the optically active trap is allowed. For the simple case of one trap and one center we may write

$$I_{\text{OSL}} = \frac{dm}{dt} = -\frac{dn}{dt} = nf - n_c(N - n)A \quad (157)$$

and again the decay is no longer exponential. For the case of $N \gg n$, $A/A_m = R$ and $R \gg n/(N - n)$, a bimolecular (second-order) function results:

$$I_{\text{OSL}} = \frac{n^2 f}{NR} = \frac{dm}{dt} = -\frac{dn}{dt} \quad (158)$$

Rewriting

$$\frac{dn}{n^2} = -\frac{f}{NR} dt \quad (159)$$

which yields, after integration,

$$I = I_0 \left(1 - \frac{n_0 f t}{NR}\right)^{-2} \quad (160)$$

where $I_0 = n_0^2 f / NR$. For the more general case, where $I = n^b f / NR$, the OSL decay curve is described by

$$\left(\frac{I}{I_0}\right)^{\frac{1-b}{b}} = \left(1 - \frac{n_0 f t}{NR}\right) \quad (161)$$

or

$$I = I_0 \left(1 - \frac{n_0 f t}{NR} \right)^{-\frac{b}{1-b}} \quad (162)$$

3.2.6. *A realistic model?* It must be stressed that a real material is likely to have several optically active traps, and a combination of deep competing traps, shallow competing traps, and both radiative and non-radiative centers. In consideration of this, it should be recognized that a simple exponential shape for the OSL decay curve will only occur in real materials under certain special circumstances and sets of experimental conditions. The curve shape will, in general, be temperature and excitation rate dependent.

Examples of OSL decay curves calculated by solving numerically the rate equations for the model of Fig. 18 (McKeever *et al.*, 1997) show that at low temperatures, the shallow traps, deep traps and non-radiative recombination centers conspire to produce a weak, non-exponential OSL decay curve, as illustrated in Fig. 22. As the temperature increases, so the shallow traps begin to play less of a role. The OSL intensity increases accordingly and a peak appears in the OSL curve at short times. At the highest temperatures the shallow traps play no part and the intensity is the highest. In general, the presence of the deep traps and non-radiative centers may still produce a non-exponential decay curve, however, Bailey *et al.* (1997) argue that if the relative probabilities for the various trapping and

recombination pathways do not change during the OSL emission, then exponential curves will still be obtained. Accordingly, they present experimental, *non-exponential* OSL decay data for quartz and interpret this to be due to the sum of three *exponential* decay curves. They propose that the three curves are caused by the emptying of three different traps.

The preceding analyses presume that the released charge is transported via the delocalized bands to the recombination site. As such, the analyses will be valid whether or not the optical transition is direct to the conduction band, or is thermally assisted via an excited state (Hütt *et al.*, 1988; Hütt and Jaek, 1993). The latter process merely imposes a temperature dependence on the excitation rate, thus

$$f = f_o \exp \left\{ \frac{W}{kT} \right\} \quad (163)$$

where W is the required thermal activation energy. Since the OSL decay constant $\tau = f^{-1}$, then the OSL decay rate will also be thermally activated according to

$$\tau = \tau_o \exp \left\{ -\frac{W}{kT} \right\} \quad (164)$$

This provides a means by which thermally assisted processes may be recognized experimentally.

However, Poolton *et al.* (1995a,b,c) suggest that IR-stimulated OSL from feldspars may not proceed via the conduction band, but instead may occur via a donor-acceptor recombination mechanism. These authors argue that once excited into the excited states of the donor, wavefunction overlap with the acceptor allows for recombination to occur via a hopping process. The phenomenon of donor-acceptor pair recombination has been well established in the luminescence properties of semiconductors for many years (Dean, 1973). The probability of recombination in this fashion depends upon the separation distance between the donor (d) and the acceptor (a). This can be estimated for a given concentration N of donors and acceptors using the donor-acceptor pair distribution function $G(r)$, where r is distance:

$$G(r) = 4\pi r^2 N \exp \left(-4\pi N \int_0^r r'^2 dr' \right) \quad (165)$$

where $G(r)$ is normalized such that $\int_0^\infty G(r) dr = 1$. The decay kinetics for d-a recombination luminescence are complex and depend critically upon concentration, with faster decays occurring for higher concentrations. For high concentrations, the decay proceeds as t^{-2} at long times, while it proceeds as t^{-1} for low concentrations. At short times the decay is much faster and cannot be expressed analytically (Dean, 1973).

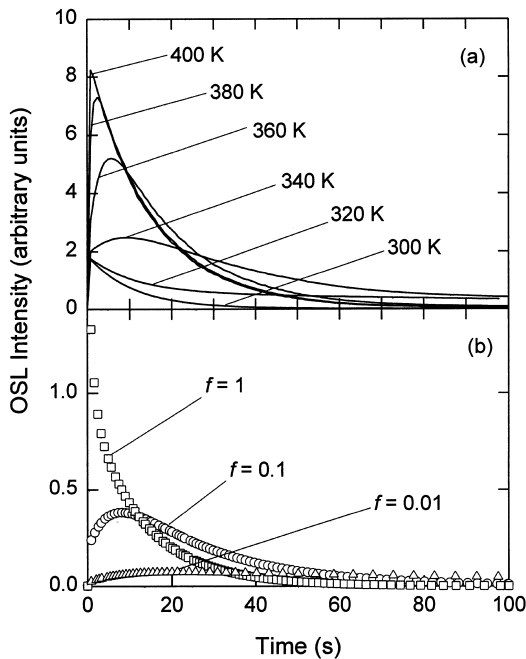


Fig. 22. Theoretical OSL curve shapes obtained from a solution to the rate equations for the model of Fig. 18. (a) Temperature dependence. (b) Excitation intensity dependence.

4. SOME IMPLICATIONS FOR DATING

4.1. Anomalous fading

Anomalous fading is the fading of a TL (or OSL) signal at a temperature which is far below the temperature at which the trap is known to empty during heating. That is, it is an abnormal fading at temperatures at which the trap may be expected to be thermally stable from a consideration of its trapping parameters (trap depth, etc.). It is a characteristic of anomalous fading that the initial fading rate is quite rapid, followed by a slower decay at longer times. The conclusions reached by Visocekas and Geoffroy (1977) from a study of the fading from calcite is that the intensity I of the afterglow observed during anomalous fading follows a hyperbolic law, namely $I \propto t^{-1}$, where t is time. A temperature-independent hyperbolic law is indicative of a tunneling mechanism in accordance with Mikhailov's model for tunneling (McKeever, 1985). Here, an electron in a trap of depth E_t is separated by a distance r from a positive charge, at which recombination would produce the emission of a photon. The rate of tunneling of the electron through the potential barrier separating the two centers was given in [76] as $P(r) = P_0 \exp\{-\alpha r\}$ where P_0 is a frequency factor and α was given in [77]. By approximating the electron trap to a square potential well, as shown in Fig. 6, and assuming the decrease in the number of trapped electrons n follows a first-order reaction, the luminescence (afterglow) intensity is given by

$$I = -\frac{dn}{dt} = \int_0^\infty n_0^2 \exp\{-P(r)t\} 4\pi r^2 dr \quad (166)$$

where n_0 is the initial trapped electron concentration. For large $r \approx r_c$, this becomes

$$I_{\text{tot}} \simeq -K/t \quad (167)$$

where K is approximately constant, and thus the observed t^{-1} law is obtained (Templer, 1986a).

[167] holds if $t \gg t_i$ where t_i is the irradiation time and t is measured from the end of the irradiation at $t = 0$. If an extended irradiation time is taken into account, then

$$I = \frac{K}{t_i} \int_{-t_i}^0 \frac{dt'}{(t-t')} = \frac{K}{t_i} \ln(1 + t/t_i) \quad (168)$$

Beyond $t = 10t_i$ the difference between [167] and [168] is negligible.

Alternatively, instead of monitoring the phosphorescence (afterglow) emitted during charge leakage from the trap, one could monitor the remnant TL, i.e. the TL remaining after the charge has escaped. If we define the parameter R to be the ratio of the TL at time t to the initial TL at time t_0 , then we may write

$$R = \frac{\text{TL}(t)}{\text{TL}(t_0)} = \frac{\ln(t/t_m)}{\ln(t_m/t_0)} \quad (169)$$

where t_m is the maximum time for which the tunneling mechanism holds. It should be noted that since tunneling is more likely for the deeper traps (Fig. 6, and [76] and [77]) then, as pointed out by Templer (1986a), the loss of the TL signal is expected to be more rapid from the *high temperature side* of the glow curve than from the low temperature side. This is the opposite that one would expect from thermal fading or, as we will see below, from fading due to a localized transition model, and thereby provides an experimental tool by which fading due to tunneling can be recognized.

Visocekas *et al.* (1976) also considered the possibility that the electron had to be thermally excited to an intermediate state (energy E_2 in Fig. 6) before tunneling could take place. The tunneling probability will now include a Boltzmann term and the probability of this "thermally assisted tunneling" will increase as the temperature increases. Such appears to be the case in calcite (Visocekas *et al.*, 1976). If n_2 is the population of the excited state and n_1 is the population of the ground state in Fig. 6, then

$$\frac{n_2}{n_1} = \exp\left\{-\frac{E_2}{kT}\right\} \quad (170)$$

where the total charge density is $n_0 = n_1 + n_2$. The total tunneling probability is now

$$P(r) = \frac{P_0(\exp\{-\alpha_1 r\} + \exp\{-\alpha_2 r\})}{1 + \exp\{-E_2/kT\}} \quad (171)$$

where

$$\alpha_1 = 2\sqrt{(2m^* E_1)/\hbar}$$

and

$$\alpha_2 = 2\sqrt{(2m^*(E_1 - E_2))/\hbar}$$

and a temperature dependence is expected.

As noted above, Templer (1986a,b) suggested an alternative to tunneling to describe anomalous fading. This was the localized transition model in which an alternative pathway to transport via the conduction band is available via an intermediate, localized state. The mathematics describing this case have been described above. Here we note that the phosphorescence (afterglow) intensity expected from this case is obtained from [85] and is

$$I = n_0 \left[\frac{vs}{v+s} \right] \exp\left\{-\frac{E_c}{kT}\right\} \exp\left\{-\left[\frac{vs}{v+s} \right] t \exp\left\{-\frac{E_c}{kT}\right\}\right\} \quad (172)$$

where all the terms have been previously defined. Templer (1986a) describes the shape of the phosphorescence decay expected from the localized tran-

sition model if the traps are distributed in energy. For a general distribution of traps the afterglow intensity is given by

$$I = \int_0^{\infty} n(E_c) \left[\frac{v(E_c)s}{v(E_c) + s} \right] \exp\left\{ -\frac{E_c}{kT} \right\} \exp\left\{ -\left[\frac{vs}{v+s} \right] t \exp\left\{ -\frac{E_c}{kT} \right\} \right\} dE_c \quad (173)$$

For a uniform distribution $n(E_c)dE_c = n_0 dE_c$ we get

$$I = \frac{n_0 kT}{t} \left[\exp\left\{ -\frac{t}{t_{\max}} \right\} - \exp\left\{ -\frac{t}{t_{\min}} \right\} \right] \quad (174)$$

where t_{\max} and t_{\min} are the trapped charge lifetimes corresponding to the upper and lower limits of the energy distribution.

Again, the $1/t$ component dominates except at short times when the exponential part causes a slower than $1/t$ decay. If the irradiation time t_i is to be accounted for we have

$$I = n_0 kT \int_{-t_i}^0 \left[\frac{\exp\{-(t-t')/t_{\max}\} - \exp\{-(t-t')/t_{\min}\}}{t-t'} \right] dt' \quad (175)$$

where t' is a dummy variable for time. Tyler and McKeever (1988) argue that the localized transition model fits the data better than the tunneling model in olivine feldspar, and that the misfit between the data and the former model probably arises from the assumption of a uniform trap distribution.

If the remnant TL is monitored, rather than the afterglow, one observes that the fading occurs from the *low temperature side* of the glow curve for the localized transition model, in contrast to that expected for tunneling (Templer, 1986a). In this case the remnant TL parameter R is described by

$$R = \frac{Ei[-t/t_{\min}] - Ei[-t/t_{\max}]}{Ei[-t_0/t_{\min}] - Ei[-t_0/t_{\max}]} \quad (176)$$

where $Ei[x]$ is the exponential integral function.

4.2. Bleaching of OSL and TL

At various points throughout the discussion of the various luminescence models we have referred to examples of TL and OSL behavior extracted from studies of materials of significance for dating, i.e. quartz and feldspars. The detailed experimental behavior is described more fully in the accompanying papers in this issue, and we do not intend to repeat this information here. We wish to emphasize, however, some additional general points which emerge from a consideration of the possible luminescence models described in the preceding sections.

With regard to the bleaching of TL, the central assertion is that exposure of the material to light (sunlight) will give rise to a reduction of the TL signal due to the emptying of the charge from the trap responsible for that signal. In this way, the "TL clock" is reset to zero. There are a number of practical issues which need to be accounted for in determining whether or not the TL is in fact "zeroed" (including the wavelength distribution of the light, the intensity and time of bleaching, the temperature at which the bleaching took place, whether the bleaching was in air or in water, etc.). Notwithstanding these serious practical considerations, however, one of the points considered in the foregoing discussions was the possibility that a certain TL signal may not be zeroed *in principle*. Two possible models were reviewed, each of which could lead to the situation where a TL peak may be reduced by light exposure, but for which it would be impossible for the light to completely zero the signal – even if the exposure were to take place for an infinite amount of time. These models were those of Chen *et al.* (1990), and McKeever (1991) (Fig. 15).

The point here is not that these models have been proved (or disproved) to be representative of the actual situation with any given material, but simply that it *is* possible that such an effect could occur. As a result, there emerges the necessity of thorough experimental investigations to verify in fact that the mechanism giving rise to the reduction of a given TL signal is indeed that of the release of charge from the responsible trap. Such appears to be the case for the so-called "325°C" TL peak in quartz, as described in the accompanying paper by Spooner. The situation regarding the so-called "370°C" peak, however, is far from clear. This "hard-to-bleach" signal may indeed be one that it is not possible to zero, as originally suggested by McKeever (1991). Franklin *et al.* (1995) go further to suggest that the "325°C traps" and the "370°C traps" are part of two different "families" of centers within quartz. The former group includes the traps responsible for the OSL signal (probably the same traps as those responsible for the 325°C TL peak) and those responsible for the 110°C TL peak.

4.3. Sensitivity changes

Throughout the history of TL studies there have been many models put forward to explain changes in the sensitivity of TL materials. Studies of such changes in TL dosimetry materials have demonstrated a link between the changes in sensitivity and the non-linear properties of the TL dose-response curve. As noted in this paper, such non-linear properties may be linked to competition effects between the various trapping and recombination levels that exist in the materials of interest. In recent studies it

has become clear that such competition effects may also be responsible for sensitivity changes in materials of interest to TL (and OSL) dating. Also relevant here is how and why sensitivity differences exist between similar materials of different origin. For example, large differences in OSL sensitivity exist between sedimentary quartz and quartz from heated archaeological samples (Aitken and Smith, 1988; Bøtter-Jensen and Duller, 1992). Sensitivity variations from sample to sample are especially problematic in the use of silicate materials as luminescence dosimeters in retrospective dosimetry in which a range of materials must necessarily be collected from a wide geographical area (Bøtter-Jensen *et al.*, 1995a). (For a detailed description of retrospective dosimetry the reader is referred to the paper by Bailiff in this issue.) It becomes relevant to ask, therefore, if all such sensitivity changes and variations can be explained on the basis of competition effects.

Bøtter-Jensen *et al.* (1995b) examined TL, PTTL and OSL sensitivity changes in quartz as a result of annealing using the same model as illustrated in Fig. 18 (namely an optically active trap, a shallow trap, a deep trap, a radiative center and a non-radiative center). Changes in sensitivity as a result of annealing are well known for quartz. Studies have highlighted the increase in the luminescence efficiency of TL and radioluminescence (RL) (McKeever *et al.*, 1983; Chen *et al.*, 1988), and of OSL (Bøtter-Jensen *et al.*, 1993), along with alterations in the TL emission spectra (Hashimoto *et al.*, 1994). Other observations included the inducement of a non-linearity into the TL or OSL growth curve after annealing (Bøtter-Jensen *et al.*, 1995b). Based on these observations Bøtter-Jensen *et al.* (1995b) used the model of Fig. 18 to propose that the annealing either removed non-radiative, competing recombination centers, or created radiative recombination centers. Numerical solutions to the rate equations describing the production of OSL using this model were shown to mimic the sensitivity changes found in practice, including the inducement of the non-linear growth curve. No distinction could be made, however, between the "center-removal" or the "center-creation" models.

4.4. Single-aliquot procedures

OSL single-aliquot dating is growing in popularity as a dating tool and detailed descriptions of it can be found in the paper on dating protocols by Wintle in this issue. Sensitivity changes associated with the re-use of the same aliquot are also problematic with these protocols, especially the regeneration single-aliquot method (Duller, 1991, 1994, 1995; Richardson, 1994). Speculations based on experimental data (Li and Wintle, 1992) and computer simulations (McKeever and Morris, 1994) have

indicated that here too the sensitivity changes may be the result of changes in the occupancies of the various traps altering the competition pathways available for charge during irradiation and readout. McKeever and colleagues therefore used the model of Fig. 18 once again to simulate sensitivity changes for both annealed (McKeever *et al.*, 1996) and unannealed quartz (McKeever *et al.*, 1997). The simulations showed that sensitivity changes will result from the accumulation of charge in deep, hard-to-bleach, competing traps and the results of the simulations compared very well with the experimental data obtained for both quartz and feldspar. Example data for a simulated regeneration single-aliquot procedure are shown in Fig. 23.

Using the model of Fig. 18 McKeever *et al.* (1997) predicted the dependence of the sensitivity changes upon various parameters, including natural dose, readout method and laboratory added dose. With respect to the latter they showed that the sensitivity changes are insensitive to the size of the added dose. This in fact is the central assumption in the single aliquot regeneration and added dose (SARA) method suggested by Mejdahl and Bøtter-Jensen (1994). In this technique one gives a different added dose ($0, \beta_1, \beta_2, \beta_3$) to each of four samples and performs a single-aliquot regeneration procedure on each of them, so determining the apparent equivalent doses, D_{E1}, D_{E2}, D_{E3} and D_{E4} in each case. A plot of D_E against added dose then reveals the true equivalent dose from the intercept on the added dose axis by extrapolation of the line to $D_E = 0$. The major assumption that the sensitivity changes are approximately the same for all added doses seems to be supported by the computer simulations.

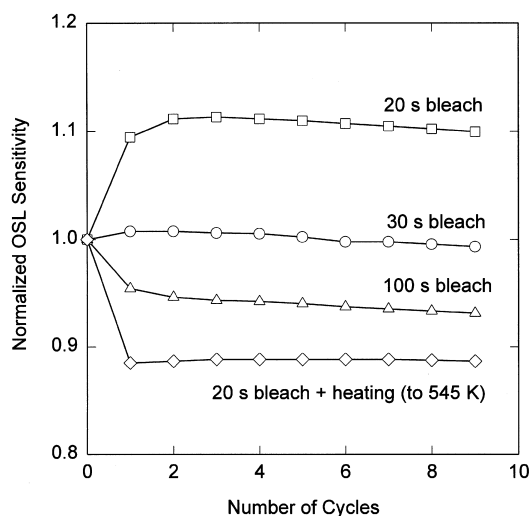


Fig. 23. Simulated OSL sensitivity changes, using the model of Fig. 18, for different bleaching times and conditions.

5. WHERE DOES MODELING GO FROM HERE?

Returning to the remarks made in the Introduction to this paper concerning the need for modeling studies, we believe that the detailed discussions which we have presented do indeed support the view that modeling is important for the purpose of determining if suggested mechanisms can indeed produce the effects observed in practice. We believe we have demonstrated that the detailed examinations of proposed models can point to the way to proceed in practical developments and can give confidence and support to the adopted protocols.

However, we perceive some problems with modeling and the way that such studies have developed over the years. The first is the fact that many authors propose this model or that model to explain their data without any attempt to test actual behavior of the model proposed. Hand-waving arguments are the norm. While acceptable as a starting point, leaving the model at that juncture is unsatisfactory. Even the simplest of models to explain TL and OSL involve sets of coupled, non-linear, first-order, differential equations. The detailed behaviors of such systems are notoriously difficult to predict. The systems described by these equations are almost chaotic in that the behavior is deterministic but unpredictable. Certain behaviors are sensitive to certain parameters, but not to others. Other behaviors are sensitive to different sets of parameters. What does emerge from a study and testing of particular models is an appreciation of what is possible with the model, and what is not possible.

A second disturbing feature of model development is that it has proceeded entirely *ad hoc*, i.e. models have been proposed to explain a certain observation – most often without regard to how well that model succeeds in explaining other behaviors in the same material. Indeed, often two or more models may be suggested to explain different behaviors of a material without regard as to whether or not the models are compatible with each other. One obvious example of this is the model suggested to explain the pre-dose effect in quartz, and the model suggested to explain other sensitivity changes in the TL, PTTL and OSL in the same material, as described in the previous section. The pre-dose effect (the model for which has not been described in this paper) was observed initially by Zimmerman (1971) and a model was proposed based on the transfer of holes between centers (so-called luminescence (L) and reservoir (R) centers). The effect may be reversed by illuminating the sample with light (UV-reversal). This effect, and the sensitization effects already discussed in this paper (e.g. during single-aliquot usage) each involve irradiation, heating and illumination phases, but each model has

been developed entirely separately from the other. So far, no attempt has been made to unify the models, i.e. to present a single model to explain both effects.

In our view unification of models is an essential step for the future. When developing models to explain our data we should be continuously mindful of existing suggestions to explain other data in the same material. Our aim should be to reduce the plethora of models which have emerged, and which only serves to confuse.

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