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Review
Models in thermoluminescence

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The aim of this paper is to give a review of the main models of thermoluminescence, from the most simple postulated by Randal and Wilkins in 1945. After that, a computer simulation emphasizes some problems relative to the use of the models to describe the behaviour of the thermoluminescent glow curve. Some suggestions are also given for obtaining a correct interpretation from the experimental data. © *2004 Kluwer Academic Publishers*

1. Luminescence phenomena

Luminescence is defined as the emission of light above that expected for black body, from some solids commonly called phosphors. This emission is the release of energy stored within the solid through some type of prior excitation of the solid electronic system, i.e., by visible, infrared (IR) or ultra violet (UV) light and ionizing radiation. The light emitted has a longer wave length of the one of the incident radiation (Stoke's law). Furthermore, the wavelength of the emitted light is a characteristic of the luminescent material. The ability to store the radiation energy is important in luminescence dosimetry and is generally associated with the presence of activators (i.e., impurity atoms and structural defects) which act as trapping levels for the free electrons generated by excitation.

Luminescence occurring during excitation is called fluorescence. If a delay of more than 10 nanoseconds exists between excitation and emission of light, luminescence is called phosphorescence.

The luminescence effects can be used in solid state dosimetry for measurement of ionizing radiation dose; the main luminescence dosimetric techniques are:

(a) radio-thermoluminescence (RTL) or better thermoluminescence (TL) only: it consists in a transient emission of light from an irradiated solid when heated;
(b) radio-lyoluminescence (RLL): it consists in a transient emission of light from an irradiated solid upon dissolving it in water or some other solvent;
(c) radio-photoluminescence (RPL): it consists in an emission of light from an irradiated solid by excitation with U.V. light.

Techniques (a) and (b) are linked by three facts:

– they all show transient effects, superimposed on an intrinsic background,
– they offer a memory but not a permanent record of irradiation dose,
– the basic memory mechanism for all techniques is similar for a given inorganic material; only the readout of the radiation induced signal is different for the two different techniques.

Materials of interest in thermoluminescent dosimetry (TLD) are principally insulators in which conduction electrons are entirely due to absorbed radiation energy. Examples of such insulators are the cubic structured alkali halides, such LiF and NaCl. An extensive review of the thermoluminescent materials, including preparation and characteristics of the more recent production is given in [1].

Thermoluminescence is observed under condition of steadily increasing temperature. In the usual thermoluminescence experiments, the TL system is irradiated at room temperature (RT) and later heated through a temperature range where the luminescence is bright, until a temperature level at which all the charges have been thermally excited out of their metastable levels and the luminescence completely disappears.

If the light intensity is plotted as a function of temperature (or time) the resulting graphs is called glow-curve (Fig. 1). The glow-curves have one or more maxima called glow-peaks and are function of various energy level traps.

Efficient thermoluminescent phosphors have an high concentration of electron and hole traps, provided by structured defects and impurities.

2. Mathematical treatment

The aim of a mathematical analysis concerning the thermoluminescent emission of light is to achieve a satisfactory knowledge of the phenomena related to it. From a theoretical point of view, TL is directly connected to the band structure of solids and particularly to the effects of impurities and lattice irregularities. These can

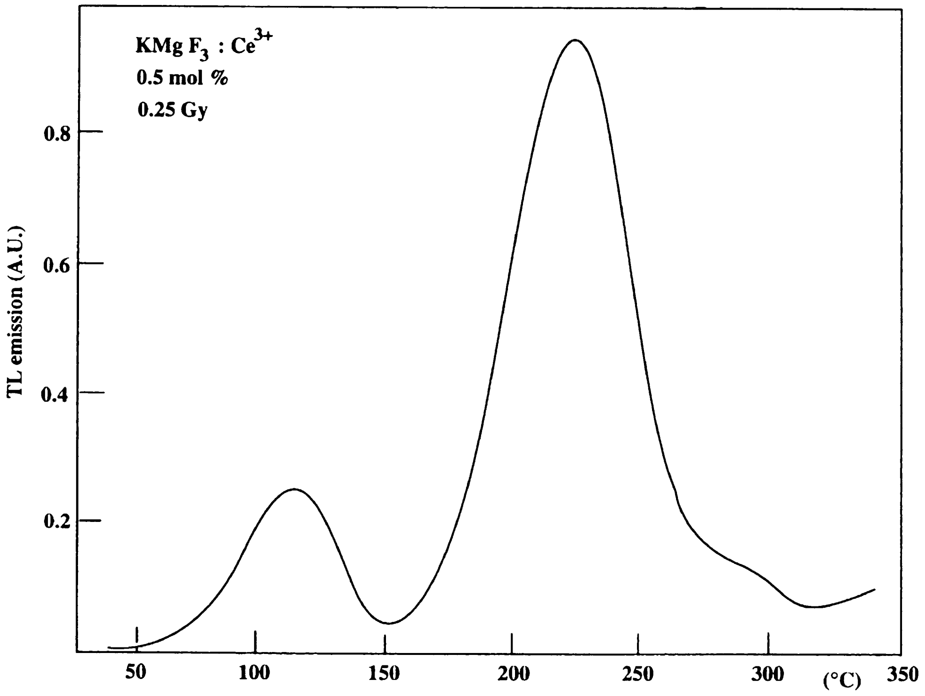

Figure 1 Glow curve.

be described as centers that may occur when ions of either signs move away from their original sites, thus leaving vacancy states, able to interact with free charge carriers and to trap them; alternatively, ions can diffuse in interstitial positions and break locally the ideal lattice geometry; finally, impurity ions can perturb the lattice order, because of their sizes and valences, generally different from their neighbor ones. Moreover, these extrinsic defects can interact with the intrinsic ones, and eventually either of them can aggregate in more complex configurations. From an atomic standpoint a defect can be described by means of the sign and number of charge carriers it may interact with, and the eventual existence of excited states; to such a description, a characteristic energy for each center corresponds: this may be defined as the amount of energy able, when supplied, to set the trapped charges free, thus destroying the center and restoring a situation of local order.

It is feasible therefore to describe the band structure in term of valence and conduction bands, parted from each other by a forbidden gap in which the defects are represented as sites localized at different depths, below the conduction band, where free charge carriers of either sign may be trapped. Therefore, the mapping of the forbidden gap reveals quite a complex configuration, and the experimental TL emission study can provide a satisfactory tool to get detailed information on its most meaningful parameters. These are, for each site, the characteristic energy (E), a frequency factor (s), connected to the transition frequency, and a kinetic order (b) synthesizing the quality of the involved phenomena. The kinetic order ranges between 1 and 2. The former value corresponds to a situation where a charge (electron) is supplied energy to raise in the conduction band and, consequently, to fall to a center where it undergoes recombination with hole; the latter one stands for a situation where this phenomenon has the same probability of retrapping. Intermediate cases are likely to occur as well as contributions from non radiative events ($b = 0$).

The mathematical models based upon these definitions are consisting of convenient differential equations systems, yielding for each case, the evolution of charged carriers populations, the analytical forms of which are to be checked by means of suitable experimental data. It is therefore evident how the involved parameters are to be conveniently adjusted until a fair agreement between theory and practice is attained. The most promising tool is the observation and the recording of TL emission, under several experimental conditions, as a function of temperature which the TL sample is heated to, or of heating up time. For a constant heating rate, these two observations are equivalent. The plot shape depends on the physical and chemical properties of the material and on the kind of the treatment it is submitted to. However it is always a single- or multi-peaks structure, as may be expected from the general equations, and a correspondence can be pointed out between a peak and an electron trap level. This is explained by considering how, at a certain temperature, the amount of thermal energy supplied reaches, for a given level, the threshold necessary to raise the relative trapped charges in the conduction band from where they can give rise to radiative recombination events. For this purpose, other centers, able to trap positive charge carriers, are involved, and they are likely to be connected to the quality of the emitted light.

The analytical form for a single peak, which the overall curve is a superposition of, can fully described by means of some geometrical parameters as the peak position, its left and right widths, the ratio between them, the overall width, the height. This last one is dependent on the heating rate and increases, for given experimental conditions, with the increasing of it. These geometrical parameters can be shown to correspond to the main physical ones: the mathematical expressions can be evaluated by a convenient analytical manipulation

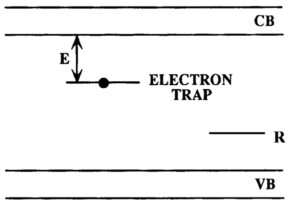

Figure 2 Randal Wilkins model.

of the involved equations. It is also to be remarked that the experimental uncertainties, obtained by means of the glow-curve plot, allow for an estimate of the physical errors related to them, and their evaluations can point out a well defined method as the fittest one.

3. Randall-Wilkins model

In 1945, Randall and Wilkins [2] extensively used a mathematical representation for each peak in a glow curve, starting from studies on phosphorescence. Their mathematical treatment was based on the energy band model and yelds the well-known first order expression.

The following figure, Fig. 2, shows the simple model used for the theoretical treatment. Between the delocalized bands, conduction band, CB, and valence band, VB, two localized levels (metastable states) are considered, one acting as a trap, T, and the other acting as a recombination center, R. The distance between the trap T and the bottom of the CB is called activation energy or trap depth: E. This energy is the energy required to liberate a charge, i.e., an electron, which is trapped in T. The probability p, per unit of time, that a trapped electron will escape from the trap, or the probability rate of escape per second, is given by the Arrhenius equation, having considered that the electrons in the trap have a Maxwellian distribution of thermal energies

$$p = s \cdot \exp\left(-\frac{E}{kT}\right) \tag{1}$$

where E is the trap depth (eV), k the Boltzmann's constant, T the absolute temperature (K), s the frequency factor (sec^{-1}), depending on the frequency of the number of hits of an electron in the trap, seen as a potential well.

The life time, τ, of the charge carrier in the metastable state at temperature T, is given by

$$\tau = p^{-1} \tag{2}$$

If n is the number of trapped electrons in T, and if the temperature is kept constant, then n decreases with time t according to the following expression:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -pn \tag{3}$$

Integrating this equation

$$\int_{n_0}^{\mathrm{n}} \frac{\mathrm{d}n}{n} = -\int_{t_0}^{t} p \cdot \mathrm{d}t \tag{4}$$

one obtains

$$n = n_0 \exp\left[-s \exp\left(-\frac{E}{kT}\right) \cdot t\right] \tag{5}$$

where n_0 is the number of trapped electrons at the initial time $t_0 = 0$.

Assuming now the following assumptions:

- irradiation of the thermoluminescent material at a low enough temperature so that no electrons are released from the trap,
- the life time of the electrons in the conduction band is short,
- all the released charges from trap recombine in luminescent center,
- the luminescence efficiency of the recombination centers is temperature independent,
- the concentrations of traps and recombination centers are temperature independent,
- no electrons released from the trap is retrapped

According to the previous assumptions, the TL intensity, I, at a costant temperature, is directly proportional to the detrapping rate, $\mathrm{d}n/\mathrm{d}t$:

$$I = -c\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right) = cpn \tag{6}$$

where c is a constant which can be set to unity. Equation 6 represents an exponential decay of phosphorescence.

Using Equation 5 in Equation 6 one obtains:

$$I(t) = n_0 s \exp\left(-\frac{E}{kT}\right) \exp\left[-st \exp\left(-\frac{E}{kT}\right)\right] \tag{7}$$

Introducing a constant heating rate, $\beta = \mathrm{d}T/\mathrm{d}t$, from Equation 4 we have:

$$\int_{n_0}^{n} \frac{\mathrm{d}n}{n} = -\left(\frac{s}{\beta}\right) \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) dT'$$

$$\ln(n) - \ln(n_0) = -\left(\frac{s}{\beta}\right) \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) \mathrm{d}T'$$

and again

$$n = n_0 \exp\left[-\frac{s}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) \mathrm{d}T'\right] \tag{8}$$

Then, using Equation 6

$$I(T) = n_0 s \exp\left(-\frac{E}{kT}\right) \times \exp\left[-\frac{s}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) \mathrm{d}T'\right] \tag{9}$$

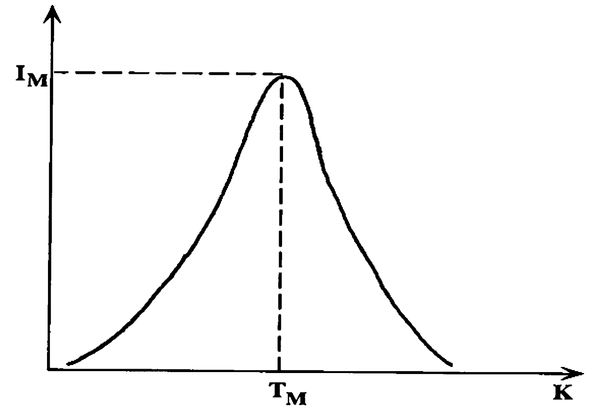

Figure 3 TM and glow curve.

This expression can be evaluated by mean of numerical integration, and it yields a bell-shaped curve, as in Fig. 3, with a maximum intensity at a characteristic temperature T_{M}.

Some observation can be done on Equation 9:

– $I(T)$ depends on three parameters E, s and b,

– E has values around $20kT$ in the range of occurance of TL peaks,

– $\exp(-\frac{E}{kT})$ is of the order of 10^{-7},

– when T is slightly greater than of T_0, the argument of the second exponential function is about equal to unity and decreases with increasing temperature. $I(T)$ is then dominated by the first exponential and increases very fast as the temperature increases. At a certain temperature, T_{M}, the behaviour of the two exponential functions cancel: at this temperature the maximum temperature occurs,

– above T_{M}, the decrease of the second exponential is much more rapid than the increase of the first exponential and $I(T)$ decreases until the traps are totally emptied.

An important relationship, the so called condition at the maximum, is obtained by Equation 9 by setting its first derivative equal to zero at $T = T_{\mathrm{M}}$, i.e.,

$$\frac{\mathrm{d}I}{\mathrm{d}T} = 0 \quad \text{at } T = T_{\mathrm{M}}$$

For practical purposes, the logarithm derivative is considered:

$$\frac{\mathrm{d}(\ln I)}{\mathrm{d}T} = \frac{1}{T}\frac{\mathrm{d}I}{\mathrm{d}T}$$

Then from Equation 9 we get

$$\left[\frac{\mathrm{d}(\ln I)}{\mathrm{d}T}\right]_{T=T_{\mathrm{m}}} = \frac{E}{kT_{\mathrm{M}}^2} - \frac{s}{\beta}\exp\left(-\frac{E}{kT_{\mathrm{M}}}\right) = 0$$

and the following expression is obtained

$$\frac{\beta E}{kT_{\mathrm{M}}^2} = s\exp\left(-\frac{E}{kT_{\mathrm{M}}}\right) \tag{10}$$

From Equation 10, the frequency factor is easily determined as

$$s = \frac{\beta \cdot E}{k \cdot T_{\mathrm{M}}^2}\exp\left(\frac{E}{kT_{\mathrm{M}}}\right) \quad [\sec^{-1}] \tag{11}$$

From Equation 10 we can obtain some interesting remarks:

– for a constant heating rate T_{M} shifts toward higher temperatures as E increases or s decreases;

– for a given trap (E and s are constant values) T_{M} shifts to higher temperatures as heating rate increases;

– T_{M} is independent of n_0.

4. Garlick-Gibson model

In 1948 Garlick and Gibson [3], in their studies on phosphorescence, considered the case when a free charge carrier has probability of either being trapped or recombining within a recombination center. The term second order kinetics is used to describe a situation in which retrapping is present.

They assumed that the escaping electron from the trap has equal probability of either being retrapped or of recombining with hole in a recombiantion centre.

Let us indicate: N = concentration of traps, n = electrons in N, m = concentration of recombination centres, $n = m$ for charge neutrality condition.

The probability that an electron escapes from the trap and recombine in a recombination centre is

$$\frac{m}{(N-n)+m} = \frac{n}{N} \tag{12}$$

So, the intensity of phosphorescence, I, is given by the rate of decrease of the occupied trap density, resulting in the recombination of the released electrons with holes in the recombination centres:

$$\begin{aligned} I(t) &= -\frac{\mathrm{d}n}{\mathrm{d}t} = c\left(\frac{n}{N}\right)\cdot\left(\frac{n}{\tau}\right) \\ &= c\frac{n^2}{N}s\exp\left(-\frac{E}{kT}\right) \end{aligned} \tag{13}$$

where τ is the mean trap lifetime.

Equation 13 can be rewritten as

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -n^2 s'\exp\left(-\frac{E}{kT}\right) \tag{14}$$

The quantity $s' = s/N$ is called pre-exponential factor and it is a constant having dimensions of $\mathrm{cm}^3\ \sec^{-1}$. Equation 14 is different from that one obtained in the case of first order kinetics, where the recombination probability was equal to 1, since no retrapping is possible.

The integration of Equation 14, considering the temperature as a constant, gives the occupancy function $n(t)$

as

$$n = n_0\left[1 + s'n_0 t \exp\left(-\frac{E}{kT}\right)\right]^{-1} \tag{15}$$

and then, the TL intensity $I(t)$ is:

$$\begin{aligned} I(t) &= -\frac{\mathrm{d}n}{\mathrm{d}t} = n^2 s' \exp\left(-\frac{E}{kT}\right) \\ &= \frac{n_0^2 s' \exp\left(-\frac{E}{kT}\right)}{\left[1 + s' t n_0 \exp\left(-\frac{E}{kT}\right)\right]^2} \end{aligned} \tag{16}$$

which describes the hyperbolic decay of phosphorescence.

The luminescence intensity of an irradiated phosphor under rising temperature, i.e., thermoluminescence, is obtained from Equation 14 introducing a linear heating rate $\beta = \mathrm{d}T/\mathrm{d}t$:

$$\frac{\mathrm{d}n}{n^2} = -\frac{s'}{\beta} \exp\left(-\frac{E}{kT}\right) \mathrm{d}T$$

Therefore, by integration, the function $n(T)$ is obtained as:

$$n = n_0\left[1 + \left(\frac{s'n_0}{\beta}\right) \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) \mathrm{d}T'\right]^{-1} \tag{17}$$

and the intensity $I(T)$ is then given by

$$\begin{aligned} I(T) &= -\frac{\mathrm{d}n}{\mathrm{d}t} = n^2 s' \exp\left(-\frac{E}{kT}\right) \\ &= \frac{n_0^2 s' \exp\left(-\frac{E}{kT}\right)}{\left[1 + \frac{s'n_0}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) \mathrm{d}T'\right]^2} \end{aligned} \tag{18}$$

Equation 18 can be rewritten as

$$I(T) = \frac{n_0 s \exp\left(-\frac{E}{kT}\right)}{\left[1 + \frac{s}{\beta} \int_{\mathrm{T}_0}^{T} \exp\left(-\frac{E}{kT'}\right) \mathrm{d}T'\right]^2} \tag{19}$$

where $s = s'n_0$. In this case s has units of s^{-1} like the frequency factor in the first-order kinetics, but it depends on n_0.

The condition at the maximum is obtained by differentiating Equation 18, setting

$$\frac{\mathrm{d}I}{\mathrm{d}T} = 0 \quad \text{at } T = T_{\mathrm{M}}$$

As usual, the logarithm derivative is considered:

$$\begin{aligned} &\left[\mathrm{d}\left(\frac{\ln I}{\mathrm{d}T}\right)\right]_{T=T_{\mathrm{M}}} \\ &= \frac{E}{kT_{\mathrm{M}}^2} - 2\frac{\frac{s'n_0}{\beta} \exp\left(-\frac{E}{kT_{\mathrm{M}}}\right)}{1 + \frac{s'n_0}{\beta} \int_{T_0}^{T_{\mathrm{M}}} \exp\left(-\frac{E}{kT'}\right) \mathrm{d}T'} = 0 \end{aligned}$$

Then

$$\frac{E}{kT_{\mathrm{M}}^2} = 2\frac{\frac{s'n_0}{\beta} \exp\left(-\frac{E}{kT_{\mathrm{M}}}\right)}{1 + \frac{s'n_0}{\beta} \int_{T_0}^{T_{\mathrm{M}}} \exp\left(-\frac{E}{kT'}\right) \mathrm{d}T'}$$

and rearranging

$$\begin{aligned} &\frac{\beta E}{2kT_{\mathrm{M}}^2}\left[1 + \frac{s'n_0}{\beta} \int_{T_0}^{T_{\mathrm{M}}} \exp\left(-\frac{E}{kT'}\right) \mathrm{d}T'\right] \\ &= s'n_0 \exp\left(-\frac{E}{kT_{\mathrm{M}}}\right) \end{aligned} \tag{20}$$

From this expression, the pre-exponential factor can be determined:

$$s' = \frac{1}{n_0}\left[\frac{2kT_{\mathrm{M}}^2 \exp\left(-\frac{E}{kT_{\mathrm{M}}}\right)}{\beta \cdot E} - \frac{\int_{T_0}^{T_{\mathrm{M}}} \exp\left(-\frac{E}{kT'}\right) \mathrm{d}T'}{\beta}\right]^{-1} \tag{21}$$

5. Effects of the kinetics order on the glow-curve shape

The practical effect of the order of kinetics on the glow-peak shape is illustrated in Fig. 4, in which two glow-curves from a single type of trap are compared.

In the case of second order kinetics T_{M} increases by the order of 1% respect to the temperature at the maximum of a first order peak. The main difference is that the light is produced at temperatures above T_{M} because the trapping delays the release of the electrons. Furthermore, for a fixed value of E, T_{M} increases as β increases or s' decreases; for a fixed value of β, T_{M} results to be directly proportional to E.

6. Adirovitch model

Adirovitch in 1956 [4] used a set of three differential equations to explain the decay of phosphorescence in the general case. The same model has been used by Haering-Adams (1960) [5] and Halperin-Braner (1960) [6] to describe the flow charge between localized energy levels and delocalized bands during trap emptying The energy level diagram is shown in the following Fig. 5.

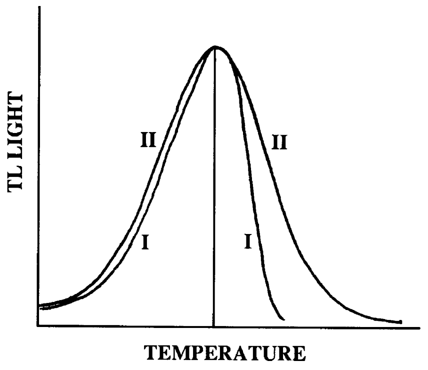

Figure 4 Effects on the glow-curve shape.

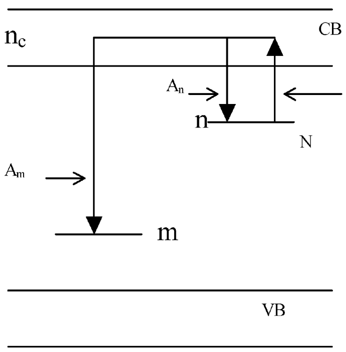

Figure 5 Adirovitch model.

With the assumption that retrapping of electrons occurs into trapping states of the same kind as those from which they had been released, the intensity of emission, I, is given by

$$I = -\frac{\mathrm{d}m}{\mathrm{d}t} = A_{\mathrm{m}} m n_{\mathrm{c}} \tag{22}$$

where m is the concentration of recombination centers (holes in centers), (cm^{-3}); n_{c} is the concentration of free electrons in the conduction band, (cm^{-3}); A_{m} is the recombination probability (cm^3 sec^{-1}).

This equation states that the recombination rate is proportional to the number of free electrons, n_{c}, and the number of active recombination centers, m.

A second equation deals with the population variation of electrons in traps, n (cm^{-3}), and it takes into account of the excitation of electrons into the conduction band as well as the possible retrapping. Then we have:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -sn \exp\left(-\frac{E}{kT}\right) + n_{\mathrm{c}}(N-n)A_{\mathrm{n}} \tag{23}$$

where A_{n}(cm^3 s^{-1}) is the retrapping probability and N (cm^{-3}) is the total concentration of traps. A_{m} and A_{n} are assumed to be independent of temperature.

The third equation, relates to the charge neutrality, can be expressed as

$$\frac{\mathrm{d}n_{\mathrm{c}}}{\mathrm{d}t} = \frac{\mathrm{d}m}{\mathrm{d}t} - \frac{\mathrm{d}n}{\mathrm{d}t} \tag{24}$$

or better, using Equations 22 and 23, as

$$\frac{\mathrm{d}n_{\mathrm{c}}}{\mathrm{d}t} = sn \exp\left(-\frac{E}{kT}\right) - n_{\mathrm{c}} m A_{\mathrm{m}} - n_{\mathrm{c}}(N-n)A_{\mathrm{n}} \tag{25}$$

Equation 25 states that the rate of change of n_{c} is given by the rate of release of electrons from N, minus the rate of recombination in m and retrapping in N.

Two basic assumptions have been made for solving the previous set of equations:

$$n_{\mathrm{c}} \ll n \tag{26}$$

and

$$\left|\frac{\mathrm{d}n_{\mathrm{c}}}{\mathrm{d}t}\right| \ll \left|\frac{\mathrm{d}n}{\mathrm{d}t}\right| \tag{27}$$

The condition (27) means that the concentration of carriers in the conduction band does not change; that is to say

$$\mathrm{d}n_{\mathrm{c}} = 0 \tag{28}$$

In this case Equation 25 transforms in

$$n_{\mathrm{c}} = \frac{sn \exp\left(-\frac{E}{kT}\right)}{mA_{\mathrm{m}} + (N-n)A_{\mathrm{n}}} \tag{29}$$

The TL intensity is given by

$$I = -\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{sn \exp\left(-\frac{E}{kT}\right)}{mA_{\mathrm{m}} + (N-n)A_{\mathrm{n}}} \cdot mA_{\mathrm{m}} \tag{30}$$

Introducing the retrapping-recombination cross-section ratio

$$\sigma = \frac{A_{\mathrm{n}}}{A_{\mathrm{m}}} \tag{31}$$

Equation 30 becomes

$$I = -\frac{\mathrm{d}m}{\mathrm{d}t} = ns \exp\left(-\frac{E}{kT}\right)\left[1 - \frac{\sigma(N-n)}{\sigma(N-n)+m}\right] \tag{32}$$

Equation 32 gives the general one-trap equation (GOT) for the TL intensity. The term preceding the square brackets is the number of electrons thermally released to the conduction band per unit time. The term in square brackets is the fraction of conduction band electrons undergoing recombination. From this equation it is possible to obtain the first and second order kinetics equations.

Indeed, the first order kinetics is the case when recombination dominates and this means that

$$mA_{\mathrm{m}} \gg (N-n)A_{\mathrm{n}} \tag{33}$$

or

$$\sigma = 0 \tag{34}$$

The equation of intensity becomes then

$$I = -\frac{\mathrm{d}m}{\mathrm{d}t} = ns \exp\left(-\frac{E}{kT}\right) \tag{35}$$

The assumption (28) gives

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{\mathrm{d}n}{\mathrm{d}t} \quad \text{or} \quad m = n + \text{const}$$

and so Equation 35 becomes

$$I = -\frac{\mathrm{d}n}{\mathrm{d}t} = ns\exp\left(-\frac{E}{kT}\right) \tag{36}$$

that is the same equation of the first order kinetics.

The second order expression can be derived from Equation 32 using two assumptions which both include the restrictive assertion $m = n$.

Remembering the Garlick and Gibson's retrapping assumption, the first condition can be written as

$$mA_{\mathrm{m}} \ll (N-n)A_{\mathrm{n}}$$

and then the intensity is given by

$$I = -\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{mA_{\mathrm{m}}ns\exp\left(-\frac{E}{kT}\right)}{(N-n)A_{\mathrm{n}}} \tag{37}$$

Secondly, assuming that the trap is far from saturation, which means $N \gg n$, we obtain

$$I = -\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{mA_{\mathrm{m}}ns\exp\left(-\frac{E}{kT}\right)}{NA_{\mathrm{n}}} \tag{38}$$

Using the condition $m = n$ the last equation becomes

$$I = -\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{n^2sA_{\mathrm{m}}\exp\left(-\frac{E}{kT}\right)}{NA_{\mathrm{n}}} \tag{39}$$

which, with $s' = sA_{\mathrm{m}}/NA_{\mathrm{n}}$, is the Garlick and Gibson equation.

Assuming now equal recombination and retrapping probabilities $A_{\mathrm{m}} = A_{\mathrm{n}}$, as suggested by Wrezesinska [7], one obtains the same equation of Garlick and Gibson with $s' = s/N$:

$$I = -\frac{\mathrm{d}n}{\mathrm{d}t} = n^2s'\exp\left(-\frac{E}{kT}\right) \tag{40}$$

7. May-Partridge model

When the conditions of first or second order kinetics are not satisfied, one obtains the so called general order kinetics which deals with intermediate cases. May and Partridge (1964) [8] wrote an empirical expression for taking into account experimental situations which indicated intermediate kinetics processes. They started with the assumption that the energy level of traps is single, as already assumed for the first and second orders.

Let's assume that the number n of charge carriers present in a single energy level is proportional to n^{b}. Then, the probability rate of escape is:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -s'n^{\mathrm{b}}\exp\left(-\frac{E}{kT}\right) \tag{41}$$

where s' is the pre-exponential factor.

Equation 41 is the so called general order kinetics relation, and usually b is ranging in the interval between 1 and 2. The pre-exponential factor s' is now expressed in $\mathrm{cm}^{3(\mathrm{b}-1)}\mathrm{sec}^{-1}$. It has to be stressed that the dimensions of s' change with the order b. Furthermore, s' reduces to the pre-exponential factor of Garlick and Gibson equation when $b = 2$.

Rearranging Equation 41 we have:

$$\frac{\mathrm{d}n}{n^{\mathrm{b}}} = -s'\exp\left(-\frac{E}{kT}\right)\mathrm{d}t \tag{42}$$

which gives, by integration

$$n = n_0\left[1 + s'n_0^{\mathrm{b}-1}(b-1)t\exp\left(-\frac{E}{kT}\right)\right]^{\frac{1}{1-\mathrm{b}}} \tag{43}$$

Equation 43 can be rewritten as

$$n = n_0\left[1 + s''(b-1)t\exp\left(-\frac{E}{kT}\right)\right]^{\frac{1}{1-\mathrm{b}}}$$

with

$$s'' = s'n_0^{\mathrm{b}-1}$$

With this definition the difficulty with respect to the variation of dimensions has been bypassed. Any way, the frequency factor s'' is constant for a given dose and would vary when the dose is varied.

The intensity $I(t)$ is now given by:

$$I(t) = -\frac{\mathrm{d}n}{\mathrm{d}t} = s'n^{\mathrm{b}}\exp\left(-\frac{E}{kT}\right) = s''n_0\exp\left(-\frac{E}{kT}\right) \times\left[1 + s''(b-1)t\exp\left(-\frac{E}{kT}\right)\right]^{\frac{\mathrm{b}}{1-\mathrm{b}}} \tag{44}$$

Assuming a linear heating rate $\mathrm{d}T = \beta\mathrm{d}t$, we obtain from Equation 42:

$$n = n_0\left[1 + \frac{s''(b-1)}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)dT'\right]^{\frac{1}{1-\mathrm{b}}} \tag{45}$$

The intensity $I(T)$ is given by

$$I(T) = s''n_0\exp\left(-\frac{E}{kT}\right) \times\left[1 + \frac{s''(b-1)}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)dT'\right]^{-\frac{\mathrm{b}}{\mathrm{b}-1}} \tag{46}$$

It must be observed that two factors contribute to $I(T)$:

– the exponential factor which constantly increases with T;

– the factor included in brackets, decreasing as T increases.

So we have again the explanation of the bell shape of the glow-curve as experimentally observed.

To conclude, Equation 46 includes the second order case ($b = 2$). Equation 46, which is not valid for the case $b = 1$, reduces to the first order equation when $b \to 1$.

It must be stressed that Equation 41 is entirely empirical, in the sense that no approximation can be found which is able to derive Equation 41 from the set of differential equations governing the traffic of charge carriers and so, as a consequence, a physical model leading to general order kinetics does not exist.

The condition of the maximum emission for b-order kinetics can be looked from the general order Equation 46, making the derivative of its logarithm:

$$\frac{kT_M^2 bs''}{\beta E}\exp\left(-\frac{E}{kT_M}\right) = 1 + \frac{s''(b-1)}{\beta}\int_{T_0}^{T_M}\exp\left(-\frac{E}{kT'}\right)\mathrm{d}T' \quad (47)$$

The pre-exponential factor is then:

$$s'' = \left[\frac{kT_M^2 b\exp\left(-\frac{E}{kT_M}\right)}{\beta E} - \frac{(b-1)\int_{T_0}^{T_M}\exp\left(-\frac{E}{kT'}\right)\mathrm{d}T'}{\beta}\right]^{-1} \quad (48)$$

An interesting feature results from the equations giving the maximum conditions for the first-, second- and general-orders respectively:

$$\frac{\beta E}{kT_M^2} = s\exp\left(-\frac{E}{kT_M}\right) \quad (10)$$

$$\frac{\beta E}{2kT_M^2}\left[1 + \frac{s'n_0}{\beta}\int_{T_0}^{T_M}\exp\left(-\frac{E}{kT'}\right)\mathrm{d}T'\right] = s'n_0\exp\left(-\frac{E}{kT_M}\right) \quad (20)$$

$$\frac{kT_M^2 bs''}{\beta E}\exp\left(-\frac{E}{kT_M}\right) = 1 + \frac{s''(b-1)}{\beta}\int_{T_0}^{T_M}\exp\left(-\frac{E}{kT'}\right)\mathrm{d}T' \quad (47)$$

– Equation 10 does not include the initial concentration n_0, therefore the first order peak is not expected to shift as a function of the irradiation doses;

– on the contrary, owing to the dependence of the pre-exponential factors on n_0 for $b \neq 1$, and through it, on the excitation dose, one should expect T_M—from Equations 20 and 47—to be dose dependent.

The dependence of the T_M on the dose is an exciting property. A large effort has been dedicated the last 50 years for its experimental verification, without, however, undoubted success. Moreover, this property should have significant implication on the two main applications of TL: dosimetry and dating. For these reason this case of kinetics will be discussed in detail in a following section.

8. Zero order kinetics

Partridge and May [9] have reported some observations concerning an apparent kinetic order less than the first one ($b < 1$). They explained their experimental results by means of two competing processes: a first radiative order and a zero order without radiative transitions.

For such a model one can write:

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = c_1 n + c_2 \quad (49)$$

where $c_1$and c_2 are the first and the zero order rate constants respectively.

The integration of Equation 49 gets:

$$-\frac{1}{c_1}\ln(c_1 n + c_2) = t + k' \quad (50)$$

where k' is a constant of integration.

The TL intensity is given by

$$I = c_1 n \quad (51)$$

Combining Equations 50 and 51 one obtains

$$-\ln(I + c_2) = c_1 t + k'' \quad (52)$$

Partridge and May have reported that in isothermal decay experiments some data fitted Equation 52 better than an equation expressing order higher than the first one.

9. Braunlich–Scharman model

A more satisfactory physical interpretation of the TL kinetics can be based on a more complex description of the TL centers in the forbidden gap. Braunlich and Scharmann (1966) [10], wrote a set of differential equations describing the traffic of the charge carriers, during the thermal excitation, making reference to the energy level scheme proposed by Schon. This scheme contains one electron trap, one hole trap and retrapping transitions of the freed carriers back into their respective traps. The following Fig. 6 shows the band model used to describe the traffic of the carriers.

Explanation of the symbols:

– n_c = concentration of electrons in CB,
– n_v = concentration of holes in VB,
– n = concentration of trapped electrons,
– N = concentration of electron traps,
– m = concentration of trapped holes,
– M = concentration of recombination centers (hole traps),
– A_n = retrapping probability for electrons in N,
– A_{mm} = recombination probability for electrons in M,

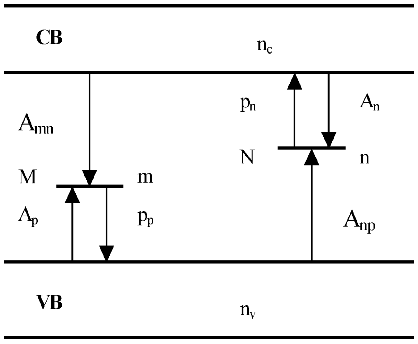

Figure 6 Braunlich model.

- A_p = retrapping probability for holes in M,
- A_{np} = recombination probability for holes in N,
- $p_n = s_n \exp(-(E_n/kT))$

is the thermal excitation probability for electrons from N to CB,

- $p_p = s_p \exp(-(E_p/kT))$

is the thermal excitation probability for holes from M to VB,

- E_n = electron trap activation energy,
- E_p = hole trap activation energy.

The set of the differential equations is:

$$\frac{dn_c}{dt} = np_n - n_c A_n(N-n) - n_c m A_{mn} \tag{53a}$$

$$\frac{dn_v}{dt} = mp_p - n_v A_p(M-n) - n_v n A_{np} \tag{53b}$$

$$\frac{dn}{dt} = -np_n + n_c A_n(N-n) - n_v n A_{np} \tag{53c}$$

$$\frac{dm}{dt} = -mp_p + n_v A_p(M-m) - n_c m A_{mn} \tag{53d}$$

Considering that, in the most general case, both recombination transitions are radiative, the total TL intensity is given by

$$I = -\frac{dn_c}{dt} - \frac{dn}{dt} = n_c m A_{mn} + n_v n A_{np} \tag{54}$$

The previous equation considers that the transitions of conduction electrons into traps and of holes from the valence band into recombination centers (hole traps) are non radiative.

Two parameters have now to be defined:

$$R_n = \frac{A_n}{A_{mn}} \tag{55a}$$

$$R_m = \frac{A_p}{A_{np}} \tag{55b}$$

which express the ratio of the retrapping probabilities compared to recombination for both electrons and holes.

The neutrality condition is given by

$$n_c + n = n_v + m \tag{56}$$

and furthermore, with the assumptions that

$$n_c \lll n, \quad n_v \lll m \tag{57}$$

the following relation is also valid:

$$n \approx m \tag{58}$$

Four cases are analyzed:

(a) $R_n \approx 0, \quad R_m \approx 0$
(b) $R_n \ggg 1, \quad R_m \ggg 1$
(c) $R_n \approx 0, \quad R_m \ggg 1$
(d) $R_n \ggg 1, \quad R_m \approx 0$

Case (a) concerns a situation where recombination prevails over trapping, case (b) considers that retrapping prevails over recombination and the two others cases are intermediate.

The quasi-equilibrium assumption is valid for both electrons and holes:

$$\frac{dn_c}{dt} = \frac{dn_v}{dt} \approx 0 \tag{59}$$

Case (a). The retrapping rate for both electrons and holes is very small. Then the retrapping terms can be neglected. Furthermore, taking into account the quasi-equilibrium condition the previous Equations (53a–d) become

$$\frac{dn_c}{dt} = np_n - n_c m A_{mn} \tag{60a}$$

$$\frac{dn_v}{dt} = mp_p - n_v n A_{np} \tag{60b}$$

$$\frac{dn}{dt} = -np_n - n_v n A_{np} \tag{60c}$$

$$\frac{dm}{dt} = -mp_p - n_c m A_{mn} \tag{60d}$$

Because $n \approx m$, from Equations 60a and 60b we obtain, taking into account relation (59)

$$n_c \approx \frac{p_n}{A_{mn}} \tag{61}$$

$$n_v \approx \frac{p_p}{A_{np}} \tag{62}$$

Equation 60c then reduces to

$$\frac{dn}{dt} = -n(p_n + p_p) \tag{63}$$

Considering a constant rate $\beta = dT/dt$, Equation 63 becomes

$$\frac{dn}{n} = -\frac{p_n + p_p}{\beta} dT \tag{64}$$

Integration of Equation 64 yields

$$n = n_0 \exp\left\{-\frac{1}{\beta}\int_{T_0}^{T} [p_\mathrm{n} + p_\mathrm{p}]\,\mathrm{d}T'\right\} \tag{65}$$

Going back to Equation 54, it can be rewritten, using Equations 61 and 62, as:

$$I = p_\mathrm{n} m + p_\mathrm{p} n \tag{66}$$

and using the relation (58) $n \approx m$

$$I = n(p_\mathrm{n} + p_\mathrm{p}) \tag{67}$$

which can be rewritten, using Equation 65

$$I = n_0[p_\mathrm{n} + p_\mathrm{p}] \exp\left\{-\frac{1}{\beta}\int_{T_0}^{T} [p_\mathrm{n} + p_\mathrm{p}]\,\mathrm{d}T'\right\} \tag{68}$$

which is similar to the Randall-Wilkins first order equation. Neglecting the transitions to the valence band, i.e., $p_\mathrm{p} = 0$, the Randall-Wilkins equation is obtained.

Case (b). The retrapping of charge carriers prevails over the recombination transitions. Equations (53a–d) become now

$$\frac{\mathrm{d}n_\mathrm{c}}{\mathrm{d}t} = np_\mathrm{n} - n_\mathrm{c} A_n (N - n) \tag{69a}$$

$$\frac{\mathrm{d}n_\mathrm{v}}{\mathrm{d}t} = mp_\mathrm{p} - n_\mathrm{v} A_\mathrm{p} (M - n) \tag{69b}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -np_\mathrm{n} + n_\mathrm{c} A_\mathrm{n} (N - n) - n_\mathrm{v} n A_\mathrm{np} \tag{69c}$$

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -mp_\mathrm{p} + n_\mathrm{v} A_\mathrm{p} (M - m) - n_\mathrm{c} m A_\mathrm{mn} \tag{69d}$$

Using now the quasi-equilibrium condition, Equation 59, and the neutrality condition in the form

$$\frac{\mathrm{d}n}{\mathrm{d}t} \approx \frac{\mathrm{d}m}{\mathrm{d}t} \tag{70}$$

from Equations (53a and c) we get, using $n \approx m$,

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -n(n_\mathrm{c} A_\mathrm{mn} + n_\mathrm{v} A_\mathrm{np}) \tag{71}$$

Equation 69a becomes

$$np_\mathrm{n} - n_\mathrm{c} A_\mathrm{n} (N - n) \approx 0 \tag{72}$$

Because $n \ll N$ (far from saturation), Equation 72 gives

$$n_\mathrm{c} \approx \frac{np_\mathrm{n}}{A_\mathrm{n} N} \tag{73}$$

Similarly, considering $m \ll M$, we obtain for n_v

$$n_\mathrm{v} \approx \frac{mp_\mathrm{p}}{A_\mathrm{p} M} \tag{74}$$

Substituting expressions (73) and (74) in Equation 71, and using again $n \approx m$, we obtain

$$\frac{\mathrm{d}n}{\mathrm{d}t} \approx -n^2\left(\frac{p_\mathrm{n} A_\mathrm{mn}}{A_\mathrm{n} N} + \frac{p_\mathrm{p} A_\mathrm{np}}{A_\mathrm{p} M}\right) \tag{75}$$

Introducing a linear heating rate, we get by integration

$$n = \frac{1}{\left\{\frac{1}{n_0} + \frac{1}{\beta}\int_{T_0}^{T} \left[\left(\frac{A_\mathrm{mn} p_\mathrm{n}}{A_\mathrm{n} N}\right) + \left(\frac{A_\mathrm{np} p_\mathrm{p}}{A_\mathrm{p} M}\right)\right]\mathrm{d}T'\right\}} \tag{76}$$

and the TL intensity is given by

$$\begin{aligned} I &= -\frac{\mathrm{d}n}{\mathrm{d}t} \\ &= -\frac{1}{\left\{\frac{1}{n_0} + \frac{1}{\beta}\int_{T_0}^{T} \left[\left(\frac{A_\mathrm{mn} p_\mathrm{n}}{A_\mathrm{n} N}\right) + \left(\frac{A_\mathrm{np} p_\mathrm{p}}{A_\mathrm{p} M}\right)\right]\mathrm{d}T'\right\}^2} \\ &\quad \times \left(\frac{p_\mathrm{n} A_\mathrm{mn}}{A_\mathrm{n} N} + \frac{p_\mathrm{p} A_\mathrm{np}}{A_\mathrm{p} M}\right) \end{aligned} \tag{77}$$

This equation is similar to the second order equation given by Garlick and Gibson. It becomes identical to it by neglecting the probability for transitions into the valence band, i.e., supposing that $p_\mathrm{p} = 0$

Case (c). The new equations are now:

$$\frac{\mathrm{d}n_\mathrm{c}}{\mathrm{d}t} = np_\mathrm{n} - n_\mathrm{c} m A_\mathrm{mn} \tag{78a}$$

$$\frac{\mathrm{d}n_\mathrm{v}}{\mathrm{d}t} = mp_\mathrm{p} - n_\mathrm{v} A_\mathrm{p} (M - m) \tag{78b}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -np_\mathrm{n} + n_\mathrm{c} A_\mathrm{n} (N - n) - n_\mathrm{v} n A_\mathrm{np} \tag{78c}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -mp_\mathrm{p} + n_\mathrm{v} A_\mathrm{p} (M - m) - n_\mathrm{c} m A_\mathrm{mn} \tag{78d}$$

From Equations 78a and 78b we get

$$n_\mathrm{c} \approx \frac{p_\mathrm{n}}{A_\mathrm{mn}}, \quad n_\mathrm{v} = \frac{mp_\mathrm{p}}{A_\mathrm{p}(M - m)} \tag{79}$$

From (79) and (78d) we obtain

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -mp_\mathrm{n} \tag{80}$$

and then

$$m \approx m_0 \exp\left(-\frac{1}{\beta}\int_{T_0}^{T} p_\mathrm{n}\mathrm{d}T'\right) \tag{81}$$

The thermoluminescence intensity is

$$I = n_\mathrm{c} m A_\mathrm{mn} + n_\mathrm{v} n A_\mathrm{np} \tag{82}$$

which transforms in, using (79), $n \approx m$ and $M \gg m$

$$I = mp_{\mathrm{n}} + m^2 \frac{p_{\mathrm{p}} A_{\mathrm{np}}}{A_{\mathrm{p}} M} \tag{83}$$

and then, the explicit form for I is the following

$$\begin{aligned} I = {} & m_0 p_{\mathrm{n}} \exp\left(-\frac{1}{\beta}\int_{T_0}^{T} p_{\mathrm{n}} dT'\right) \\ & + \frac{m_0^2 p_{\mathrm{p}} A_{\mathrm{np}}}{A_{\mathrm{p}} M} \exp\left(-\frac{2}{\beta}\int_{T_0}^{T} p_{\mathrm{n}} \mathrm{d}T'\right) \end{aligned} \tag{84}$$

which is again the Randall-Wilkins equation for $p_{\mathrm{p}} = 0$.

Case (d). Equations (53a–d) reduce to

$$\frac{\mathrm{d}n_{\mathrm{c}}}{\mathrm{d}t} = np_{\mathrm{n}} - n_{\mathrm{c}} A_{\mathrm{n}} (N - n) \tag{85a}$$

$$\frac{\mathrm{d}n_{\mathrm{v}}}{\mathrm{d}t} = mp_{\mathrm{p}} - n_{\mathrm{v}} n A_{\mathrm{np}} \tag{85b}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -np_{\mathrm{n}} + n_{\mathrm{c}} A_{\mathrm{n}} (N - n) - n_{\mathrm{v}} n A_{\mathrm{np}} \tag{85c}$$

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -mp_{\mathrm{p}} + n_{\mathrm{v}} A_{\mathrm{p}} (M - m) - n_{\mathrm{c}} m A_{\mathrm{mn}} \tag{85d}$$

Assuming the quasi-equilibrium condition, $N \gg n, n_{\mathrm{v}}$ and n_{c} very small, i.e., $m \approx n$, we get from (85a)

$$n_{\mathrm{c}} \approx \frac{np_{\mathrm{n}}}{A_{\mathrm{n}} N} \tag{86}$$

and from (85b)

$$n_{\mathrm{v}} \approx \frac{p_{\mathrm{p}}}{A_{\mathrm{np}}} \tag{87}$$

Then

$$\begin{aligned} \frac{\mathrm{d}n}{\mathrm{d}t} & = -np_{\mathrm{n}} + n_{\mathrm{c}} A_{\mathrm{n}} (N - n) - n_{\mathrm{v}} n A_{\mathrm{np}} \\ & = -\frac{\mathrm{d}n_{\mathrm{c}}}{\mathrm{d}t} - \frac{p_{\mathrm{p}} n A_{\mathrm{np}}}{A_{\mathrm{np}}} = -np_{\mathrm{p}} \end{aligned} \tag{88}$$

from which, by integration

$$n = n_0 \exp\left(-\frac{1}{\beta}\int_{T_0}^{T} p_p \mathrm{d}T'\right) \tag{89}$$

The TL emission is then given by

$$I = n_{\mathrm{c}} m A_{\mathrm{mn}} + n_{\mathrm{v}} n A_{\mathrm{np}} \tag{90}$$

which transforms, using approximations (86), (87) and $n \approx m$, in the following expression

$$I = \frac{n^2 p_{\mathrm{n}} A_{\mathrm{mn}}}{A_{\mathrm{n}} N} + np_{\mathrm{p}} \tag{91}$$

Using Equation 89, we get the final expression for the intensity:

$$\begin{aligned} I = {} & \frac{n_0^2 A_{\mathrm{mn}} p_{\mathrm{n}}}{N A_{\mathrm{n}}} \exp\left(-\frac{2}{\beta}\int_{T_0}^{T} p_{\mathrm{p}} \mathrm{d}T'\right) \\ & + n_0 p_{\mathrm{p}} \exp\left(-\frac{1}{\beta}\int_{T_0}^{T} p_{\mathrm{p}} \mathrm{d}T'\right) \end{aligned} \tag{92}$$

This equation becomes again the Randall-Wilkins equation of the first order, ignoring the thermal release of trapped electrons, i.e., $p_{\mathrm{n}} = 0$.

10. Two-trap model (Sweet and Urquhart)

This model has been proposed by Sweet and Urquhart [11] to explain a situation where two peaks are so closely that they appear as only one peak.

Let us define the following symbols:

- $E_1, E_2 = (\succ E)$ = depth of two very closed traps (eV),
- N_1, N_2 = concentration of trapping centres (m^{-3}),
- n_1, n_2 = concentration of trapped electrons (m^{-3}),
- M = concentration of recombination centres (m^{-3}),
- m = concentration of trapped holes in recombination centres (m^{-3}),
- $n_{\mathrm{c}}, m_{\mathrm{v}}$ = concentration of free electrons in CB and free holes in VB (m^{-3}); both are assumed negligible,
- $A_{\mathrm{n1}}, A_{\mathrm{n2}}$ = trapping rate constants ($\mathrm{m}^3\ \mathrm{s}^{-1}$),
- A_{m} = recombination rate constant ($\mathrm{m}^3\ \mathrm{s}^{-1}$),
- $\gamma_1, \gamma_2 (= s_{\mathrm{i}} \exp(-\frac{E_{\mathrm{i}}}{kT}))$ = probability for electrons from trap to CB.

The following set of equations can be written:

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = -\gamma_1 n_1 + n_{\mathrm{c}} A_{\mathrm{n1}} (N_1 - n_1) \tag{93}$$

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = -\gamma_2 n_2 + n_{\mathrm{c}} A_{\mathrm{n2}} (N_2 - n_2) \tag{94}$$

$$\frac{\mathrm{d}n_{\mathrm{c}}}{\mathrm{d}t} + \frac{\mathrm{d}n_1}{\mathrm{d}t} + \frac{\mathrm{d}n_2}{\mathrm{d}t} = -A_{\mathrm{m}} n_{\mathrm{c}} m \tag{95}$$

The condition of charge neutrality is now:

$$m = n_{\mathrm{c}} + n_1 + n_2 \tag{96}$$

having considered $m_{\mathrm{v}} = 0$.

Assuminig a linear heating rate $T = T_{\mathrm{i}} + \beta \cdot t$, where T_{i} is the initial temperature and $\beta = \mathrm{d}T \mathrm{d}t$.

In order to solve numerically the previous equations, the following approximations are assumed:

$$n_{\mathrm{c}} \lll n_1, \frac{\mathrm{d}n_{\mathrm{c}}}{\mathrm{d}t} \lll \frac{\mathrm{d}n_1}{\mathrm{d}t} \tag{97}$$

$$n_{\mathrm{c}} \lll n_2, \frac{\mathrm{d}n_{\mathrm{c}}}{\mathrm{d}t} \lll \frac{\mathrm{d}n_2}{\mathrm{d}t} \tag{98}$$

Inserting (97) and (98) in Equation (96) one gets

$$m = n_1 + n_2 \tag{99}$$

Then, using Equations 95 and 96, we obtain

$$-\frac{\mathrm{d}m}{\mathrm{d}t} = -\frac{\mathrm{d}n_\mathrm{c}}{\mathrm{d}t} - \frac{\mathrm{d}n_1}{\mathrm{d}t} - \frac{\mathrm{d}n_2}{\mathrm{d}t} = A_\mathrm{m} n_\mathrm{c} m \tag{100}$$

Equation 99 can be rewritten as

$$\frac{\mathrm{d}m}{\mathrm{d}t} \approx \frac{\mathrm{d}n_1}{\mathrm{d}t} + \frac{\mathrm{d}n_2}{\mathrm{d}t} \tag{101}$$

and then, inserting (101) into Equation 100, we obtain

$$\frac{\mathrm{d}n_\mathrm{c}}{\mathrm{d}t} \approx 0 \tag{102}$$

Inserting now (102) in Equation 95 we get

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} + \frac{\mathrm{d}n_2}{\mathrm{d}t} + A_\mathrm{m} n_\mathrm{c} m = 0 \tag{103}$$

Equations 93 and 94 can be now written as

$$\begin{aligned}\frac{\mathrm{d}n_1}{\mathrm{d}t} + \frac{\mathrm{d}n_2}{\mathrm{d}t} &= -\gamma_1 n_1 - \gamma_2 n_2 + n_\mathrm{c} A_\mathrm{n1}(N_1 - n_1) \\ &\quad + n_\mathrm{c} A_\mathrm{n2}(N_2 - n_2)\end{aligned}$$

which can be rearranged, using (99) and (103), as

$$\begin{aligned}A_\mathrm{m} n_\mathrm{c}(n_1 + n_2) &= \gamma_1 n_1 + \gamma_2 n_2 - n_\mathrm{c} A_\mathrm{n1}(N_1 - n_1) \\ &\quad - n_\mathrm{c} A_\mathrm{n2}(N_2 - n_2)\end{aligned} \tag{104}$$

from which

$$n_\mathrm{c} = \frac{\gamma_1 n_1 + \gamma_2 n_2}{A_\mathrm{m}(n_1 + n_2) + A_\mathrm{n1}(N_1 - n_1) + A_\mathrm{n2}(N_2 - n_2)} \tag{105}$$

Because the glow-curve intensity is given by the decrease of the trapped holes during recombination, the TL intensity is

$$I(T) = -c\frac{\mathrm{d}m}{\mathrm{d}t} \tag{106}$$

Using Equations 99 and 100 and taking $c = 1$, Equation 106 becomes

$$\begin{aligned}I(T) &= A_\mathrm{m} n_\mathrm{c} m = A_\mathrm{m} n_\mathrm{c}(n_1 + n_2) \\ &= \frac{A_\mathrm{m}(n_1 + n_2)(\gamma_1 n_1 + \gamma_2 n_2)}{A_\mathrm{m}(n_1 + n_2) + A_\mathrm{n1}(N_1 - n_1) + A_\mathrm{n2}(N_2 - n_2)}\end{aligned} \tag{107}$$

It has to be stressed that Equation 107 becomes the equation of the first-order model by setting equal to zero the parameters with subscript 2 and considering that recombination dominates, i.e., $A_\mathrm{m} n_1 \gg A_\mathrm{n1}(N_1 - n_1)$. Equation 107 gives also the second order model considering the retrapping assumption and assuming to be far from the trap saturation, i.e., $N_1 \gg n_1$.

Equation 107 has been solved numerically for fitting experimental results obtained from the study of ZnS. The parameters used for the best fit are

$$\begin{aligned}&s_1 = s_2 = 3 \times 10^{15} s^{-1},\ \frac{N_1}{n_1} = 64, \\ &\frac{N_2}{n_2} = 100,\ E_1 = 18\ \text{meV},\ E_2 = 22.5\ \text{meV}, \\ &\frac{A_\mathrm{n1}}{A_\mathrm{m}} = \frac{A_\mathrm{n2}}{A_\mathrm{m}} = 90\end{aligned}$$

11. Mixed first and second order kinetics

The common assumption leading to kinetics orders larger than 1 is the $m = n$. This assumption seems to be the less probable to occur in a real material which contains, in principle, many kinds of defects and impurities. So, it has been suggested that in the real case the most appropriate assumptions should be the following [12]:

$$m = n + n_\mathrm{c} + C \tag{108}$$

where C represents the number of trapped electrons or holes not taking part in the TL process (i.e., charges located in deep traps or in low probability recombination centers). Relation (108) is equivalent to the charge neutrality.

Assuming as usual n_c negligible compared to m or n and considering $A_\mathrm{m} = A_\mathrm{n}(\sigma = 1)$, the TL intensity is now given by

$$I(t) = -\frac{\mathrm{d}n}{\mathrm{d}t} = \left(\frac{s}{C + N}\right) n(n + C)\exp\left(-\frac{E}{kT}\right) \tag{109}$$

If retrapping is dominating $A_\mathrm{n}(N - n) \gg A_\mathrm{m} m$. Furthermore, if the trap is far from saturation, $N \gg n$, we also have

$$I(t) = -\frac{\mathrm{d}n}{\mathrm{d}t} = \left(\frac{s A_\mathrm{m}}{N A_\mathrm{n}}\right) n(n + C)\exp\left(-\frac{E}{kT}\right) \tag{110}$$

Both previous equations can be written as

$$I(t) = -\frac{\mathrm{d}n}{\mathrm{d}t} = s' n(n + C)\exp\left(-\frac{E}{kT}\right) \tag{111}$$

where s' is a constant ($\mathrm{cm}^3\ \mathrm{s}^{-1}$).

Equation 111 can be considered as a combination of the first and second order kinetics.

The solution of Equation 111, considering a linear heating rate, is the following:

$$n = \frac{C}{\left\{-1 + \frac{1}{\alpha}\exp\left[\frac{Cs'}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)\mathrm{d}T'\right]\right\}} \tag{112}$$

where

$$\alpha = \frac{n_0}{n_0 + C}$$

The TL intensity as a function of temperature is then

$$I(T) = \frac{s'C^2\alpha \exp\left[\frac{Cs'}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)\mathrm{d}T'\right]\exp\left(-\frac{E}{kT}\right)}{\left\{\exp\left[\frac{Cs'}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)\mathrm{d}T'\right]-\alpha\right\}^2} \tag{113}$$

This expression behaves like $\exp(-E/kT)$ at low temperatures, similarly to the first, second and general orders. At higher temperatures the shape depends on the value of α.

For $\alpha = 0(n_o \ll C)$ the shape of Equation 113 tends to the one of the first order; for $\alpha = 1(n_o \gg C)$ it tends to a second order.

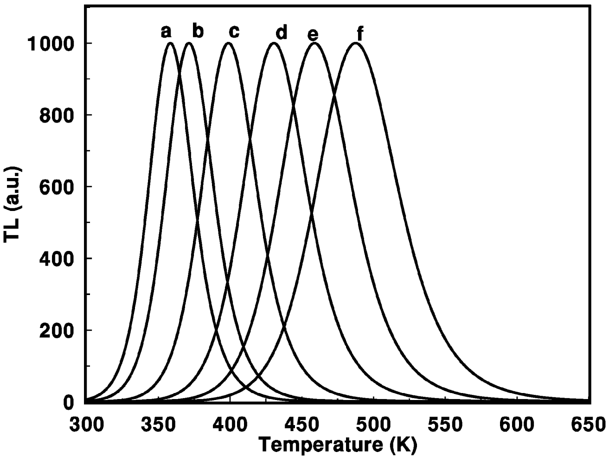

Figure 7 Glow-peaks for various n_0 normalized to the same peak height in order to show the effects of the n_0 on the glow-peak shape and peak maximum: (a) $n_0 = 1$, (b) $n_0 = 0, 3$, (c) $n_0 = 0, 03$, (d) $n_0 = 3.10^{-3}$, (e) $n_0 = 5.10^{-3}$, and (f) $n_0 = 10^{-4}$.

The special case of the second—general order kinetics

According to Equations 19 and 46 the peak maximum temperature T_M depends on the n_0. In practical situations this means that T_M depends on the dose. The dependence of the T_M on the dose is an exciting property. It has become the main criterion for accepting or not an experimental glow peak as a peak with $b > 1$, although other criteria, like the glow peak shape (symmetry factor) and its isothermal decay properties, exists. This fact is the source of a great controversy in the literature of the last 50 years, where one can find an enormous amount of articles, which report experimental glow peaks with $b > 1$ based on both symmetry factor and isothermal decay data. However, one cannot find one article, which reports glow peaks with $b > 1$, due to the dependence of its T_M on dose. Moreover, if $b > 1$ is obtained from peak shape and isothermal decay data, the conclusion is not totally accepted (or it is rejected), if the dependence of the T_M on dose is not further established.

Another fact, which (at the best of our knowledge) has never been discussed in literature, is the possible implication of the dependence of T_M on dose on the main TL applications; namely dosimetry and dating.

Due to the importance of the above subjects, they will be discussed in detail. Initially, a simulation will be performed, which reproduces the most basic properties of the glow-peaks with $b > 1$. Based on the simulation results the implications to dosimetry and dating will be examined. Finally, an interpretation will be given of why the behavior of experimental glow peaks with $b > 1$ is not in agreement to the prediction of the theory.

12. Simulation

Using Equation 46, synthetic glow-peaks were simulated keeping the value of s constant and varying the value of n_0 from 10^{-4} up to 1 (this mean $N = 1$ and the variation is of the n_0/N). The aim is to study a dose variation over four order of magnitudes. The trapping parameters used are $E = 1$ eV, $s = 10^{13}$ s^{-1} and $b = 1.2$, 1.4,1.6,1.8 and 2. In experimental situations the reference position of a glow-peak is that induced by the lowest possible dose i.e., the dose which corresponds to the lowest detectable limit (LDL) for this glow-peak. This fact is crucial for the general order kinetics, where a variation of the T_M as a function of dose is expected. In the present simulation assuming $n_0 = 10^{-4}$ as the lowest possible dose, the selected E and s values induce a glow-peak with peak maximum T_M at about 200°C, which is, usually, preferred for practical dosimetry.

13. General properties

Fig. 7, shows a set of glow-peaks as a function of n_0, normalized to the same peak height in order to see clearly the shift as well as possible changes of the glow-peaks shape.

Fig. 8, shows the behaviour of T_M versus the n_0 (dose). This is a reproduction of the very known and multiple discussed property of the general order kinetics. It is seen that for a variation of the n_0 by four order of magnitudes, the T_M shifts to lower temperature by 135 K for $b = 2$. This is a dramatic shift, which

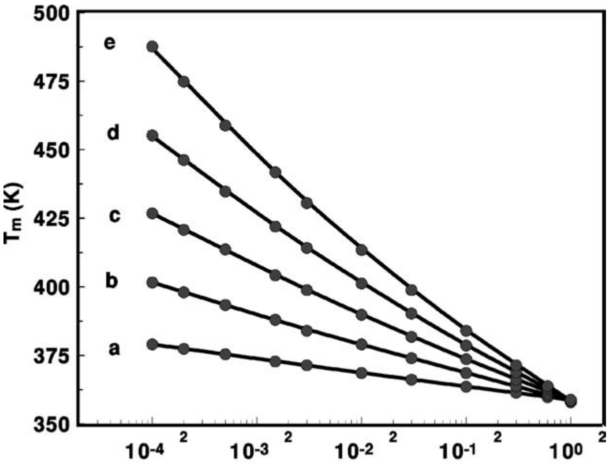

Figure 8 Behaviour of the peak maximum temperature as a function of the initial concentration of the trapped electrons, n_0 for variouskinetic orders b. (a) 1.2, (b) 1.4, (c) 1.6, (d) 1.8, and (e) 2.

could have an influence in the applications of the TL in dosimetry and dating (see discussion below). On the other hand the variations in peak shape and T_M would give the impression that different set of E and s values correspond to the glow-peak at each dose. However, the above variations are due to the fact that in the general order kinetic Equation 46, the frequency factor and the initial concentration n_0 act like an effective frequency factor, which for $N = 1$ is $s'' = s' n_0^{b-1}$. Note that the readout heating rate, β, must be considered stable and equal to 1, otherwise it contributes to the effective frequency factor (s_{eff}). The set of E and s values used for the derivation of the glow peaks in Fig. 7, can be reproduced by performing a curve fitting procedure. All the synthetic glow-peaks obtained were fitted using two general order TL glow-peak algorithms. The one, which doses not contain the frequency factor like that of Kitis *et al.* [13]. The second with the original function given by Equation 46, where the pre-exponential factor was considered as a single valued s_{eff}.

The curve fitting procedure was performed using the MINUIT program [14]. The accuracy of the fit was tested by using the Figure Of Merit (FOM)[15]. The fitting with the algorithm by Kitis *et al.* [13] gives directly the values of E and T_M, because they are the free parameters of the fitting. This curve fitting procedure reproduces exactly the value of the activation energy (1 eV). The FOM values obtained were very low, of the order of 10^{-5}, which insures an almost perfect fit. The values of s_{eff} obtained directly (as a free parameter) from the fitting are equal (as it has to be) to the values of $s'' = s' n_0^{b-1}$.

From the curve fitting procedure, except the values of T_M, as a function of n_0, the temperatures T_2, T_1, which correspond to the half maximum intensity and the Full Width at Half Maximum FWHM $= T_2 - T_1$, were also evaluated. Using these data and applying the peak shape method of Chen [16] the activation energy was evaluated. The peak shape method gave values of as a function of n_0 equal to the original $E = 1$ eV.

Fig. 9, shows the behaviour of the FWHM as a function of n_0. So, one can see that in case of general order kinetics the glow—peak becomes narrower as the n_0 (i.e., the dose) increases.

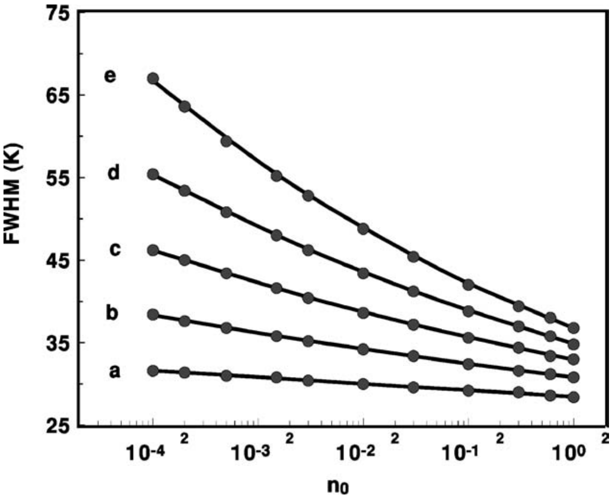

Figure 9 Behaviour of the FWHM as a function of the initial concentration of the trapped electrons, n_0 for various kinetic orders b: (a) 1.2, (b) 1.4, (c) 1.6, (d) 1.8, and (e) 2.

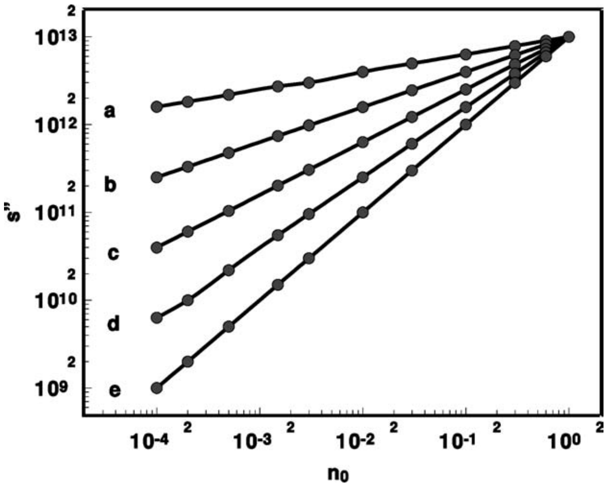

Figure 10 The s'' as obtained by Equation $s'' = s' n_0^{b-1}$, as a function of the initial concentration of the trapped electrons, n_0 for various kinetic orders b: (a) 1.2, (b) 1.4, (c) 1.6, (d) 1.8, and (e) 2.}

Fig. 10, shows the values of the s'', as it is obtained from the curve fitting described above and from Equation $s'' = s' n_0^{b-1}$, as a function of the n_0 for various kinetic orders. The numerical values are shown in Table 1.

The exact evaluation of the frequency factor is a very important task because it is used to evaluate the half—life of the trapping state, which is a necessary property for the practical applications.

In the case of general (and second) order kinetics the pre-exponential factor is given by the Equation 48, which can be rearranged, using the integral approximation [16], in the following expression

$$s' = \frac{\beta E \exp\left(\frac{E}{kT_M}\right)}{n_0^{b-1} k T_M^2}\left[1 + \frac{2kT_M(b-1)}{E}\right]^{-1} \qquad (114)$$

Table I shows the results concerning the frequency factor evaluation. Columns 2–6 gives the values of s'' as obtained from the curve fitting procedure using Equation 46. As it was stated above these values are exactly the same with those obtained from Equation $s'' = s' n_0^{b-1}$. The last column gives the values of s'' as obtained using Equation 114, which are almost equal to the original value of $s = 10^{13}$, differentiated slightly due to the last term, in brackets, of Equation 114.

The half-life of a trap, for a general-order process, is given by

$$t_{1/2} = \frac{n_0^{1-b}}{s'(1-b)}\left[1 - \frac{1}{2^{1-b}}\right]\exp\left(\frac{E}{kT_S}\right) \qquad (115)$$

The above equation can be rearranged inserting in it the explicit expressions for s' given by Equation 114. So, the half-life is given by

$$t_{1/2} = \frac{\exp\left(\frac{E}{kT_S}\right)}{(1-b)}\left[1 - \frac{1}{2^{1-b}}\right]\left[\frac{kT_M^2}{\beta E \exp\left(\frac{E}{kT_M}\right)}\right] \times \left[1 + \frac{2kT_M(b-1)}{E}\right] \qquad (116)$$

TABLE I Columns $b = 1.2$–2, s'' were obtained from the curve fitting procedure using Equation 46. Last column s'' as obtained using $s'' = s' n_0^{b-1}$ for all values of n_0 and b, which are same with those obtained from Equation 114 for all n_0 and b.

N_0	$b = 1.2$	$b = 1.4$	$b = 1.6$	$b = 1.8$	$b = 2$	Eq. 114
1×10^{-4}	1.58×10^{12}	2.51×10^{11}	$3.98. \times 10^{10}$	6.31×10^{9}	1.0×10^{9}	9.76701^{12}
2×10^{-4}	1.82×10^{12}	3.31×10^{11}	6.03×10^{10}	1.00×10^{10}	2.0×10^{9}	9.80331^{12}
5×10^{-4}	2.18×10^{12}	4.78×10^{11}	1.04×10^{11}	2.20×10^{10}	5.0×10^{9}	9.87411^{12}
1.5×10^{-3}	2.40×10^{12}	7.42×10^{11}	2.02×10^{11}	5.50×10^{10}	1.5×10^{10}	9.79001^{12}
3×10^{-3}	2.72×10^{12}	9.79×10^{11}	3.06×10^{11}	9.58×10^{10}	3.0×10^{10}	9.83601^{12}
1×10^{-2}	3.98×10^{12}	1.58×10^{12}	6.30×10^{11}	2.51×10^{11}	1.0×10^{11}	9.85211^{12}
3×10^{-2}	4.96×10^{12}	2.46×10^{12}	1.22×10^{12}	6.05×10^{11}	3.0×10^{11}	9.88531^{12}
1×10^{-1}	6.30×10^{12}	3.98×10^{12}	2.51×10^{12}	1.58×10^{12}	1.0×10^{12}	9.84201^{12}
3×10^{-1}	7.86×10^{12}	6.18×10^{12}	4.86×10^{12}	3.81×10^{12}	3.0×10^{12}	9.79711^{12}
6×10^{-1}	9.03×10^{12}	8.15×10^{12}	7.36×10^{12}	6.64×10^{12}	6.0×10^{12}	9.81861^{12}
1	1.00×10^{13}	1.00×10^{13}	1.00×10^{13}	1.00×10^{13}	1.0×10^{13}	9.82431^{12}

The new Equation 116 does not contains directly the n_0, but gives the half-life as a function of the peak maximum temperature T_M.

Using the above Equations 115 and 116 the half-life was evaluated during simulation at Room Temperature (RT) and at the peak maximum temperature.

Fig. 11, shows the half life at the peak maximum temperature as a function of the initial concentration of the trapped electrons, n_0. The half life was evaluated by Equation 115.

Fig. 12, shows the half life at the peak maximum temperature as a function of the initial concentration of the trapped electrons, n_0. The half life was evaluated by Equation 116.

Comparing the results of Figs 11 and 12 it is seen that there are great difference between the two estimations. This means that one has to be careful in evaluating the half life in case of general order kinetics. Obviously the results of Fig. 11 are the wrong ones. The reason is in the fact that for any glow-peak the half-life at peak maximum temperature should be much lower the time needed to record the glow-peak during the TL readout with a linear heating rate. For example a glow-peak with a FWHM equal to 35°C needs less than 100 s to be recorded using a heating rate of 1°C/s. Therefore, a half-life of 10^5 s (curve e) at the peak maximum position means that the respective glow-peak can not be recorded with the usual TL readout procedure. On the other hand Equation 116 gives the correct values of the half life at peak maximum position, because these values are compatible with the TL readout procedure.

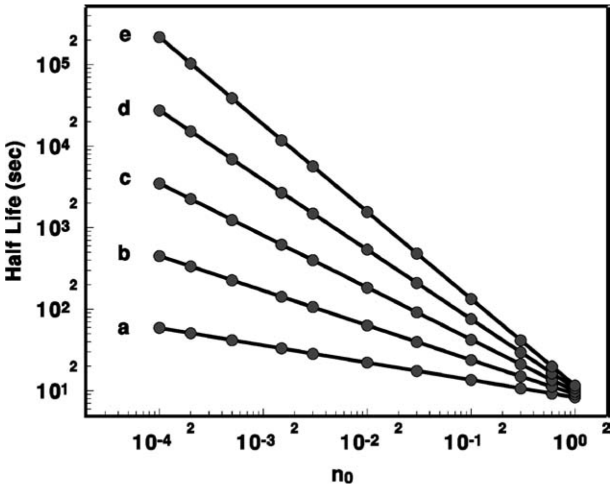

Figure 11 Half-life at the peak maximum temperature as a function of the initial concentration of the trapped electrons, n_0 as it was obtained from Equation 115 for various orders of kinetics b: (a) 1.2, (b) 1.4, (c) 1.6, (d) 1.8, and (e) 2.

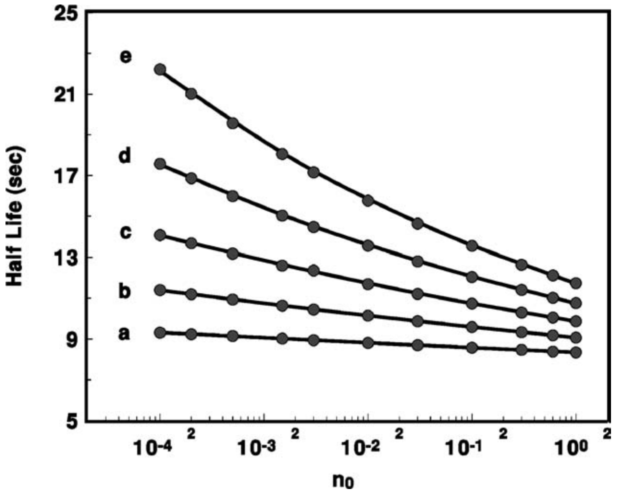

Figure 12 Half-life at the peak maximum temperature as a function of the initial concentration of the trapped electrons, n_0 as it was obtained from Equation 116 for various orders of kinetics b: (a) 1.2, (b) 1.4, (c) 1.6, (d) 1.8, and (e) 2.

Fig. 13, shows the half live at the Room temperature as a function of the initial concentration of the trapped electrons, n_0. for various kinetic orders. The half live was evaluated, by Equation 115.

Fig. 14, shows the half live at the Room temperature as a function of the initial concentration of the trapped electrons, n_0. for various kinetic orders. The half live was evaluated, by Equation 116.

Comparing the results of Figs 13 and 14 it is seen that there are large differences. According to what is said for the two previous figures the correct values are those of Fig. 14.

14. Discussion

The most important fact is the possible influence of the properties of a general order peaks, presented above, to the two main application of the TL. Namely, Dosimetry and TL dating. To the best of our knowledge these cases are never discussed in literature.

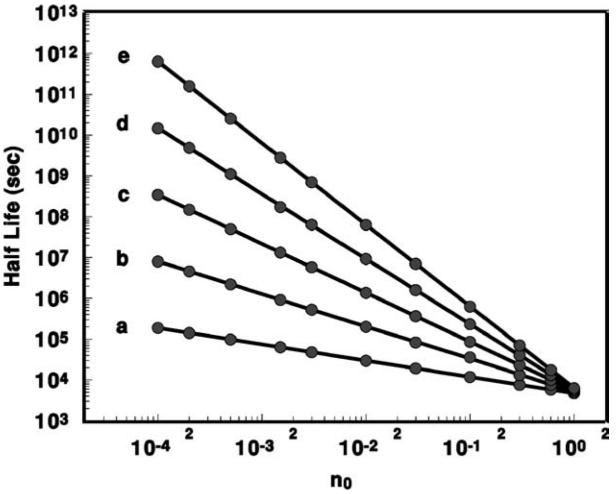

Figure 13 Half-live at the room temperature as a function of the initial concentration of the trapped electrons, n_0 for various kinetic orders as it was evaluated from Equation 115: (a) 1.2, (b) 1.4, (c) 1.6, (d) 1.8, and (e) 2.

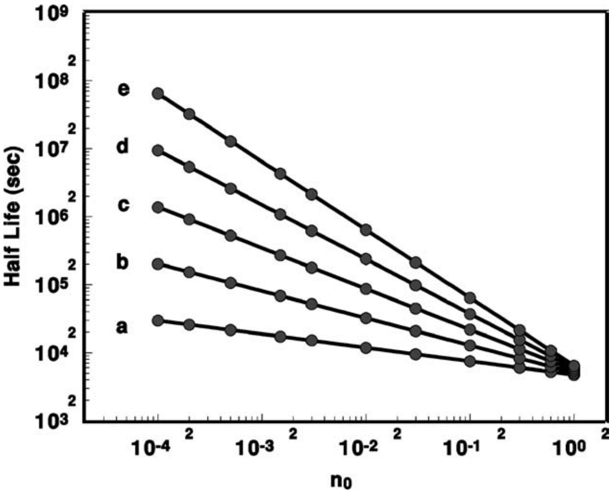

Figure 14 Half- live at the room temperature as a function of the initial concentration of the trapped electrons, n_0 for various kinetic orders as it was evaluated from Equation 116. (a) 1.2, (b) 1.4, (c) 1.6, (d) 1.8, and (e) 2.

14.1. Implication to dosimetry

In most cases the practical dosimetric glow-peaks of a TL dosimeters are between 420–520 K (150–250°C). Let say that for the lowest value of $n_0 = 10^{-4}$ of the present simulation corresponds to the dose of the Lowest Detectable Limit (LDL). Let also take as an example the second order kinetics, $b = 2$. For $n_0 = 10^{-4}$ the glow-peak appears at 488 K (215°C), with a half life at room temperature more than two years. Let also assume a glow-peak would accepted as a dosimetric glow-peak if its half-life at room temperature is greater than one month (2.6×10^6 s)(In fact this a very short practical half life). For an increase of n_0 from 10^{-4} to 5×10^{-4} (i.e., 5 LDL) the half life drops below 1 month according to Equation 115. This means that this glow-peak is not any more capable for dosimetry. For the case of Equation 116 it happens after $n_0 = 3 \times 10^{-3}$ (i.e., 30 LDL).

Obviously, this conclusion could be obtained without the need of special evaluations by observing the shift of the T_M shown in Fig 8. A dose variation by a factor of 10 shifts the T_M to lower temperature by about 30–40°C. This means that if one measured 100 μGy using a dosimetric peak at 150°C, he cannot probably measure a dose of 10 μGy using the same peak. The above, very simple, examples makes clear that a second order glow-peak is rather not useful for wide dosimetric purposes.

14.2. Implication to dating

The implications of a general order glow-peak, if any, on the TL dating are very different. The TL dating method is in fact the application of the dosimetric method on the Natural Thermoluminescence (NTL) glow-curve shown by a material of archaeological interest. The NTL glow-curve consist only from the high temperature glow-peaks from 250–450°C, because the lower temperature glow-peaks are eliminated during a time interval equal to the radiation age of the archaeological material. The Equivalent beta dose, ED_β, i.e., a beta dose, which induces TL equal to NTL, is usually in the dose interval 10–50 Gy. If the NTL glow-curve consist of general order glow-peaks then its temperature position for doses much lower that the ED_β will be higher i.e., above 400 or 450°C. However, this (although without any practical interest and influence) is rather an advantage, because at these higher temperature the half life will by larger. The influences must be searched in the Additive dose procedure (ADP), which leads to the ED_β evaluation. The ADP consist of giving increasing doses on the already existing natural dose, in order to obtain a calibration TL versus dose curve, from which the ED_β is obtained. The dose region of the additive beta doses are usually within an order of magnitude. However, even this dose variation could cause a temperature shift of the laboratory induced TL towards the lower temperatures relative to the position of the NTL. This temperature shift, however, can not cause any problems to the TL dating procedure, because the glow-peaks used for dosimetry are already at very high temperatures and the time between the laboratory irradiation and readout is too short (usually minutes).

15. Treatment of the experimental data

The number of crucial details which have been so far discussed, at the best of our knowledge, has never presented in literature although it is very important for the experimental understanding of the general order kinetics.

The basic property of general order kinetics, which has to be verified experimentally, is the shift of the peak maximum T_M towards the lower temperature as the dose increases as it is clearly shown in Fig. 8.

The procedure usually used is [17–19]:

1. Plot of the T_M of a glow-peak as a function of the delivered dose.
2. Evaluation of the kinetic parameters E and s of the glow-peak.
3. Simulation like that of the present work to evaluate the behaviour of T_M as a function of dose (in arbitrary units).
4. The net conclusion is arisen by comparing the experimental and simulated results.

The procedure described by the above steps 1–4, could lead to confusions if one does dot take into account that the theoretical predictions hold only when the TL dose response is closely linear i.e., when: dose $= n_0 =$ TL. However, in the most experimental cases the linear region is only a restricted part of the whole TL dose response curve. In the non-linear parts of the TL dose response curves the n_0 is not a linear function of dose. However, the TL is proportional to n_0. Therefore, in experimental cases, one can see the expected behaviour of the T_M, by plotting the T_M versus the TL and not the T_M versus the delivered dose. However, it is not easy in most cases to put a non linear behaviour of TL on x-axis, so it is not possible to plot T_M versus TL in order to have a presentation of T_M versus n_0. In order to solve this problem at the best, a good presentation is to plot in close relation both TL and T_M versus dose and to compare their behaviour. The expected behaviour which is in agreement with the expectations of the theory should be a specular behaviour respect to the dose axis. It will be shown below in detail what is the meaning of the term specular behaviour, by considering some examples of TL dose response curves for which a kinetic order of $b = 2$ is assigned. The cases selected are:

1. Linear-superlinear-sublinear TL dose response
2. Strong sub-linear TL dose response

The results are shown in Figs 15 and 16. In both figures the upper ones show the TL dose response curves. Curve (a) shows theline of linearity, whereas curve (b) the non-linear TL dose response. The down figures show, in one to one correspondence with the upper figures, the behaviour of T_M as a function of dose. The dependence of the behaviour of the T_M on the form of the TL dose response curve is obvious. The mirror behavior mentioned above means that the curves (a) and (b) of the are the mirror likes relative to the dose axis of the respective curves of the upper figures. Therefore, if one compares the experimental behaviour of T_M versus dose, in a non-linear TL dose response case, with a simulated behaviour based on a linear increase of n_0, as it is done in the references [17–19] then an erroneous conclusion could be emerge.

A suggestion in order to extract a conclusion about the kinetic order of a glow-peak based on the behaviour of its T_M versus dose is:

1. Plot TL versus dose response curve
2. Plot T_M versus dose
3. compare the plots as in the case of Figs 15 and 16. If the “mirror like” behaviour relative to the dose axis is obtained, then a conclusion about first of higher order kinetics can be extracted.

Alternatively on can use the following procedure.

1. Plot of TL versus dose curve.
2. Normalization of the TL versus dose over the TL in the saturation region in order the higher value to be equal to 1.

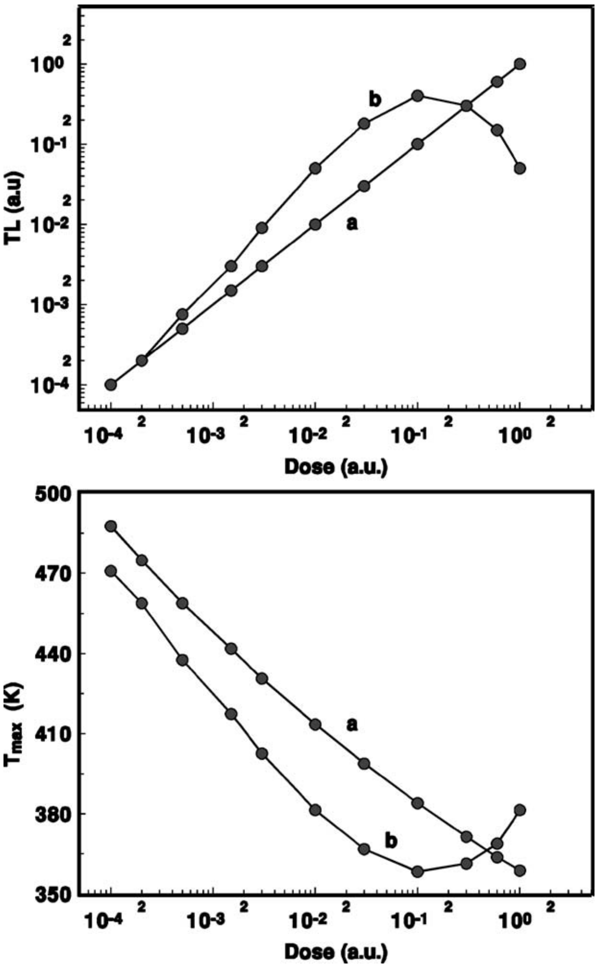

Figure 15 Case of a linear-superlinear-sublinear TL dose response. Upper: (a) A linear TL versus dose response curve, and (b) A non-linear TL dose response curve. Down: The behaviour of T_M as a function of dose. Curves (a) and (b) are in one to one correspondence with the upper curves.

3. The values of TL in fractions of the higher TL value 1, obtained from the previously noticed normalization, can be now used as the n_0 values, with which the simulation through a general or second order kinetic equation must be done.
4. Plot experimental and simulated T_M versus dose.
5. Compare the TL and T_M versus dose as in the cases of Figs 15 and 16.
6. If the simulation is performed with the correct E, s and b values then the simulated and experimental T_M versus dose behaviours coincide, otherwise only a qualitative agreement will be obtained.

16. Model dependent behaviour

The whole problem of T_M versus dose in general order kinetics is not yet exhausted. There is another very important parameter. This parameter has to do with the model of the TL dose response curve. The non-linear dose response models are of three main categories. (I) Models which are based on a competition during excitation (irradiation). (II) Models with competition during recombination (readout heating) and (III) mixed models i.e., model which suppose a primary non-linear response during excitation and a final non-linear response during recombination.

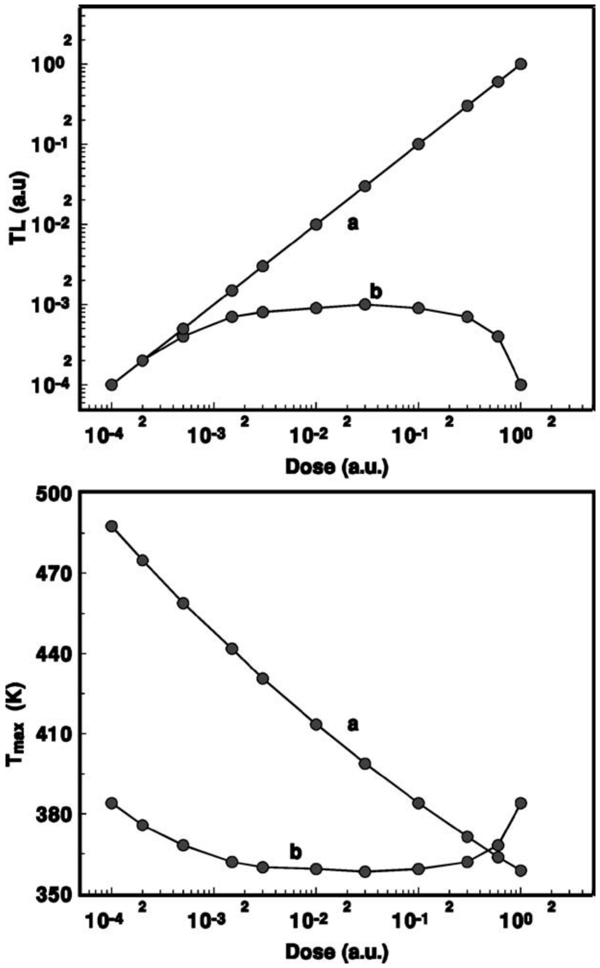

Figure 16 Case of a sublinear TL dose response. Upper: (a) A linear TL versus dose response curve, and (b) A non-linear TL dose response curve. Down: The behaviour of T_{M} as a function of dose. Curves (a) and (b) are in one to one correspondence with the upper curves.

The theoretical simulation presented in the preceding sections does not take in to account non-linearities. The additional simulation presented in this subsection assumes non-linearities, which (this must be noticed) are compatible, only, with the models involving competition during excitation. It is very difficult to predict what happens in cases the non-linearity is due to a competition during recombination. However, some arguments could be given. During irradiation a number of the existing traps, N, are filled at a concentration of n_0. During the readout the trapped electrons are released. In these models the recombination of the released electrons are competed by a competitor deep trap. This means that only a percentage of the trapped electrons n_0 arrive at recombination centres and gives TL. Experimentally this means that the emitted TL correspond to a restricted number of the n_0 caused by irradiation and then released during the readout. The question is what one has to suppose for the behaviour of T_{M}? Is in these cases the behaviour of T_{M} as a function of dose and even as a function of TL, representative of its kinetic order?

In the competition during heating model of superlinearity the final degree of superlinearity and therefore the shape of TL dose response curve depend upon the behaviour as a function of dose of the concentration of trapped electrons $n(D)$, the concentration holes in the recombination centres, $m(D)$ and the concentration of the competing centres $n_{\mathrm{c}}(D)$, during the excitation (irradiation) stage. The behaviour of T_{M} versus doses could be predicted if one find the correct behaviour of $n(D)$ and $m(D)$.

According to what was discussed in the previous sections, the lack of the experimental verification of the dependence of the T_{M} on dose could be attributed to the method of analysis of experimental data, which was not the appropriate. In the preceding section a method of analysis is proposed, which is able to confirm this property. If the proposed method of analysis fails, also, to confirm the experimental verification of this property then a revision of the analytical expressions for second and general order kinetics is necessary.

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