

ON THE ANALYSIS OF THERMALLY STIMULATED PROCESSES

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Summary

Several methods are known for the evaluation of the main kinetic parameters related to a thermoluminescence (TL) curve: namely, the activation energy, the pre-exponential factor and the kinetic order. These methods can easily be applied, under certain conditions, to a series of related thermally stimulated phenomena which are governed by similar differential equations. These include thermally stimulated conductivity (TSC), thermally stimulated electron emission (TSEE), ionic conductivity (ITC) and thermally stimulated depolarization (TSD), thermal annealing (release of stored energy, measured thermally), partial thermo-remanent magnetization (PTRM), thermal desorption and evolved gas analysis (EGA), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The concept of a kinetic order which is neither first nor second is discussed as related to the various phenomena, as well as the temperature dependence of the pre-exponential factors. A special interest lies in performing simultaneous measurements of two (or more) of these effects, in particular, TL and TSC. A method is described for calculating the recombination probability from such simultaneous measurements and the cross-section for recombination therefrom.

1. Introduction

In a number of investigations, a certain property of a sample is measured as a function of temperature, when the sample is heated from a certain “low” temperature. The best known of such investigations are thermoluminescence (TL), sometimes referred to as thermally stimulated luminescence (TSL) and thermally stimulated conductivity (TSC). In TL, one excites a sample, usually by a suitable irradiation at a “low” temperature. During the subsequent heating, according to a certain scheme, the sample emits light in excess of the “black body” radiation, in the form of glow peaks. If the sample is sufficiently insulating these peaks may be accompanied by peaks in the dark conductivity (TSC peaks). A typical glow peak is shown in Fig. 1.

2. Analysis of the peaks with an energy band model

The appearance of a single TL peak can be explained by the aid of an energy level diagram as shown in Fig. 2. At least two energy levels, an electron trap (coactivator) and a hole center (activator), each belonging to a certain

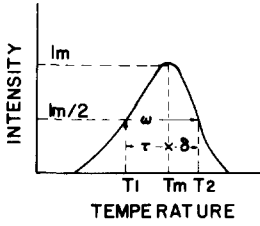


Fig. 1. A characteristic glow peak. The total half width ω , the low temperature half width τ , and high temperature half width δ are shown.

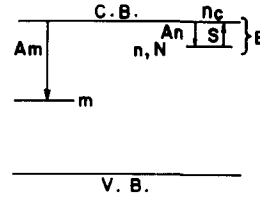


Fig. 2. Energy band model showing the thermal excitation from an electron trap and the possible retrapping and recombination processes.

impurity or defect in the sample are to be taken into account. While exciting the sample at a low temperature, an electron is raised, usually from the valence to the conduction band, and then it becomes trapped in the electron trap while the hole left behind is trapped in the hole center. While heating the sample, the electrons can (if E is small enough) be raised thermally to the C.B. from where they can either be retrapped, or recombine with a hole in m , and emit a photon.

The three differential equations governing the process are [1]:

$$I = -dm/dt = A_m m n_c, \quad (1)$$

$$-dn/dt = s n \exp(-E/kT) - A_n (N - n) n_c, \quad (2)$$

$$dn_c/dt = dm/dt - dn/dt, \quad (3)$$

where I is the TL intensity in photons/s, t is the time and T is the absolute temperature, E is the activation energy (eV), k is Boltzmann's constant (eV/K), s is the frequency (pre-exponential) factor (s^{-1}), m , n and n_c are the concentration of holes in the activator centers, electrons in the traps and electrons in the conduction band, respectively (cm^{-3}), N is the concentration of existing traps (cm^{-3}) and A_m , A_n are the "recombination probability" and "retrapping probability", respectively ($cm^3 s^{-1}$). According to Halperin and Braner [1],

$$A_m = v_e \sigma_m, \quad A_n = v_e \sigma_n, \quad (4)$$

where V_e is the thermal velocity of electrons and σ_m and σ_n are the cross-sections for recombination and retrapping, respectively. A_m and A_n are usually assumed to be temperature-independent, which is justified in view of the fast change of $\exp(-E/kT)$; a slight dependence on T can occur through $v_e \propto T^{1/2}$ and $\sigma_m, \sigma_n \propto T^\alpha$ [2]. In certain cases, one should take into account the possibility of a recombination probability which depends exponentially on temperature, $A_m \propto \exp(W/kT)$ which seems to be due to thermal quenching [3].

The exactly analogous case of holes in traps and electrons in activator centers is also possible. In both cases, the TL peak can be accompanied by a TSC peak, the intensity of which is proportional to n_c . One can write

$$\sigma = e\mu n_c \quad (5)$$

where σ is the thermally stimulated conductivity, e is the electronic charge and μ is the mobility of electrons (or holes).

Another alternative that is to be considered is that, while heating the sample, electrons are raised to an excited state which is not the conduction band and recombine via tunneling with a hole in a center which should usually be in geometrical proximity to the trap. The equations in this case are slightly different. To complicate things further, glow peaks quite often overlap, which makes the analysis more difficult. This can be overcome, at least partly, by "thermal cleaning" [4].

3. Solution of the kinetic equations

The three simultaneous equations can be solved numerically [5,6] to give a TL and its corresponding TSC peak for a given set of parameters. One can, however, obtain valuable results by making the customary assumptions:

$$n_c \ll n, \quad |dn_c/dt| \ll |dn/dt|. \quad (6)$$

Basically, this means that electrons do not accumulate in the conduction band, but rather recombine or retrap rapidly. From (1), (2), (3) and (6) one obtains

$$I = -dm/dt = sn \exp(-E/kT) A_m m / [A_m m + A_n(N - n)]. \quad (7)$$

This equation can be solved for *certain* cases if additional assumptions are made. Assuming negligible retrapping, $A_m m \gg A_n(N - n)$ we obtain

$$I = -dm/dt = -dn/dt = sn \exp(-E/kT), \quad (8)$$

which is the original Randall–Wilkins [7] first-order (monomolecular) equation. Another well-known case is the second-order [8] (bimolecular) kinetics which occurs in either of the following two cases:

1. $m = n$, $A_n(N - n) \gg A_m m$ (dominating retrapping), and $N \gg n$ for which

$$I = -dn/dt = (sA_m/NA_n)n^2 \exp(-E/kT). \quad (9)$$

2. $m = n$, $A_n = A_m$ (equal retrapping and recombination probabilities) with the result

$$I = (s/N)n^2 \exp(-E/kT). \quad (10)$$

In both cases, we have $I = -dn/dt \propto n^2$.

One should remember that the relation between $A_n(N - n)$ and $A_m m$ is between functions (rather than constants) which, in certain cases, may

change when both m and n decrease. Thus, $A_m m \gg A_n(N - n)$ may cease to be true in the fall-off part of a peak. The relation $m = n$ seems to be obvious in the naïve approach taken so far. This is by no means necessarily so, since we would like to consider cases where deeper traps or low recombination probability centers store electrons (holes) which do not take part in the glow process. The term “bimolecular” is sometimes used as a synonym to “second order”.

In both cases we find

$$I = -dn/dt = s'n^2 \exp(-E/kT) \quad (11)$$

where s' is the “pre-exponential” factor which has units of $\text{cm}^3 \text{s}^{-1}$ and, therefore, should not be confused with the first-order frequency factor s .

It is to be stated at this point that both the first- and second-order cases are very special ones and definitely do not represent all the possibilities, even when only one trap and one center are involved.

Whereas the first-order peak is asymmetrical, having $\tau > \delta$, the second-order peaks are nearly symmetrical. The symmetry can be measured by the form factor introduced by Halperin and Braner [1] $\mu_g = \delta/\omega$. For first-order peaks one obtains $\mu_g = 0.42$ and for second-order peaks $\mu_g = 0.52$, practically irrespective of the values of E and the pre-exponential factor involved [9].

As mentioned, a peak may be of neither first nor second order. We can therefore speak about “intermediate” cases for which the peak is neither of the two. One of the possible features of such a general peak is a μ_g which differs from 0.42 or 0.52. Many investigators have found it useful to assume a general order equation of the form

$$I = -dn/dt = s'n^b \exp(-E/kT), \quad (12)$$

where b is not necessarily 1 or 2 but rather a number ranging between 0.6 and 3.0. Now, the units of the constant s' are $[s'] = \text{s}^{-1} \text{cm}^{3(b-1)}$.

Although certain investigators [10] described cases behaving like eqn. (12) with $b \neq 1$ and $b \neq 2$, such a generalised equation should only be considered for TL as an empirical equation since it is not derived directly from the three differential equations mentioned above. This approach is, however, widely used since real glow peaks can thus be closely approximated and the parameters E , $s(s')$ and b can be evaluated.

4. Application to other phenomena

A large number of other phenomena are being researched using exactly the same mathematical equations, some with more theoretical justification and others with less. The differences between the mathematical representations of these phenomena are usually minor. They include, in addition to TL and TSC the following: thermally stimulated electron emission (TSEE), ionic thermoconductivity (ITC) and related phenomena, thermal annealing, partial thermo-remanent magnetization (PTRM), thermal desorption and evolved gas

analysis (EGA), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

For a linear heating rate $T = T_0 + \beta t$ the solution of the above mentioned general order equation is

$$I = s'n_0^b \exp(-E/kT) \left\{ 1 + [(b-1)s'n_0^{b-1}/\beta] \int_{T_0}^T \exp(-E/kT')dT' \right\}^{-b/(b-1)}. \quad (13)$$

This includes the well-known second-order case for $b = 2$. Writing $s = s'n_0^{b-1}$, we have

$$I = sn_0 \exp(-E/kT) \left\{ 1 + [(b-1)s/\beta] \int_{T_0}^T \exp(-E/kT')dT' \right\}^{-b(b+1)}. \quad (14)$$

s now has the units of s^{-1} and in this sense it is similar to the frequency factor in the first-order case. The present s depends, however, on the initial concentration n_0 and, therefore, on the excitation dose.

For $b = 1$ one obtains the well-known first-order equation:

$$I = sn_0 \exp(-E/kT) \exp \left[-(s/\beta) \int_{T_0}^T \exp(-E/kT')dT' \right]. \quad (15)$$

Although most investigators analysed the phenomena assuming solutions like eqns. (13)–(15), other cases are sometimes to be taken into account. For example, considering a TSC peak corresponding to the second-order TL one, we should remember that $n_c = I/A_m m$. Since $\sigma = e\mu n_c$ and assuming that μ is temperature-independent, we have [11]

$$\sigma = (e\mu s'n_0/A_m) \exp(-E/kT) \left[1 + (s'n_0/\beta) \int_{T_0}^T \exp(-E/kT')dT' \right]^{-1} \quad (16)$$

This cannot be analysed in the previous way since no general order accounts for this case in which $\mu_g \approx 0.8$. The exact similarity in shape between TL and TSC peaks exists only when $\tau = \text{const.}$, which means $A_m m = \text{const.}$

5. Calculation of the kinetic parameters

One certainly wishes to deduce parameters related to impurities or defects in a sample by the use of the glow curves. Even in the simplified model, three parameters exist, namely, E , s and b , whereas eight parameters are involved in the differential eqns. (1)–(3). A method for finding a certain parameter means finding a property of the glow curve which is sensitive to one parameter and insensitive to the others. For example, in the well-known initial rise

method, one plots $\ln I$ versus $1/T$ and obtains a straight line in the initial rise range, the slope of which is $-E/k$. Thus, E can be found practically irrespective of the other parameters or of the exact mechanism. Two other groups of methods for evaluating E are also quite well known. One group uses the value T_m , the temperature at the maximum and the magnitudes τ , δ and ω explained in reference to eqn. (1) (c.f. Fig. 1). The other group uses the changes in the peak temperature or maximum intensity due to changes in the heating rate.

Urbach [12] gave an empirical equation $E(\text{eV}) = T_m(\text{K})/500$ which has been shown to be correct to an accuracy of a multiplicative factor of 2.

Lushchik [13] gave the equation $E_{\delta_1} = kT_m^2/\delta$ for first-order and $E_{\delta_2} = 2kT_m^2/\delta$ for second-order. Halperin and Braner [1] found

$$E_{\tau_1} = 1.71(kT_m^2/\tau)(1 - 1.58\Delta) \quad (17)$$

where $\Delta = 2kT_m/E$ for first-order and a similar equation with other constants for second-order. Chen [9] found

$$E_{\omega_1} = 2.52kT_m^2/\omega - 2kT_m \quad (18)$$

for first-order and a similar equation with other constants for second-order.

He also suggested corrections to the equations of Lushchik, and Halperin and Braner to make them non-iterative and more accurate. This was done using numerical calculations in the following ranges of E and s : $0.1 \text{ eV} \leq E \leq 2.0 \text{ eV}$ and $10^5 \text{ s}^{-1} \leq s \leq 10^{13} \text{ s}^{-1}$.

The six equations for the τ , δ and ω methods can be summed up as

$$E_\alpha = c_\alpha(kT_m^2/\alpha) - b_\alpha(2kT_m), \quad (19)$$

where E_α stands for E_τ , E_δ and E_ω and α stands for τ , δ and ω , respectively, and where b_α and c_α are given in Table 1. The comparative advantages and disadvantages of the τ , δ and ω methods have been discussed by Chen [9]. The equations have been shown [14] in a semi-empirical way to be extendable to cases with $b \neq 1$ and $b \neq 2$ in the range $0.7 \leq b \leq 2.5$ by using the measured value of $\mu_g = \delta/\omega$ as an extrapolation parameter as follows:

$$\begin{aligned} c_\tau &= 1.51 + 3(\mu_g - 0.42) & b_\tau &= 1.58 + 4.2(\mu_g - 0.42) \\ c_\delta &= 0.98 + 7.3(\mu_g - 0.42) & b_\delta &= 0 \\ c_\omega &= 2.52 + 10.2(\mu_g - 0.42) & b_\omega &= 1 \end{aligned} \quad (20)$$

TABLE 1

	first-order			second-order		
	τ	δ	ω	τ	δ	ω
c_α	1.51	0.98	2.52	1.81	1.71	3.54
b_α	1.58	0	1	2	0	1

The reason for using μ_g as an extrapolation parameter is that, as shown in Fig. 3, μ_g depends strongly on b and hardly depends on E and s . In regard to the applicability of eqns. (19) and the coefficients given in (20), it should be mentioned that they have been successfully used [6] (especially the τ method) for synthetic peaks computed by the three differential equations (1)–(3).

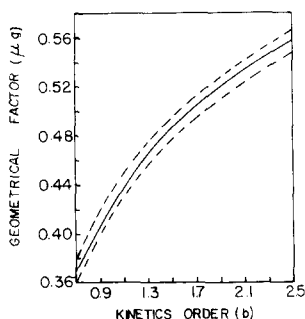


Fig. 3. Dependence of the geometrical factor μ_g on the kinetic order b . The dotted lines represent the highest and lowest μ_g found for a given b , the solid line gives average values.

In cases where the order is known, one can get an equation for the maximum condition by differentiating the appropriate expression for I and equating the derivative to zero. For first-order, for example, this yields

$$\beta E/(kT_m^2) = s \exp(-E/kT_m). \quad (21)$$

One can use this equation to evaluate s once E is found. This equation can also be written as $\beta E/(ks) = T_m^2 \exp(-E/kT_m)$. This shows that if β increases, T_m increases as well, since the right-hand side is a monotonically increasing function of T_m . The changes in T_m with β can be used to evaluate E by repeating the experiment with various heating rates. Plotting $\ln(\beta/T_m^2) = f(1/T_m)$ should give a straight line, the slope of which is $-E/k$. This is known to be true for first-order kinetics and linear heating rates. It is, however, also correct for non-linear heating rates when β_m , the instantaneous heating rate at the maximum, replaces β [15]. The same method has also been proved to be correct, to a very good approximation, to the second-order case and the "intermediate" ($-dn/dt \propto n^b$) order cases [15].

In another TSP case, namely, thermal annealing, it has been shown [16] that the process is governed by various equations of the form $-dn/dt \propto F(n)$ where $F(n)$ is not necessarily n^b . Even in this case, if $F(n)$ is a well-behaving function, it was shown that the above-mentioned various heating rates (VHR) method is applicable. Another variant of the VHR method [16] uses the variations of the maximum intensity I_m with the heating rate β_m .

In several cases [2], it has been shown that the pre-exponential factor s' (or s) is temperature-dependent i.e. $s' \propto T^a$ with $-2 \leq a \leq 2$. This occurs in practically all the thermally stimulated phenomena. For all three methods for

evaluating E (initial rise, symmetry, VHR) it has been shown [9,15,17] that a correction of the form $E_c = E - akT$ should be made to the otherwise accepted values. Various methods of curve fitting [18], usually employed with the aid of a computer, should be mentioned. These may yield directly the values of E , s' and b .

6. Simultaneous measurements of TL and TSC

Simultaneous measurements of TL and TSC have quite frequently been performed. Let us consider only one of the three mentioned differential equations, eqn. (1), writing now A instead of A_m

$$I(t) = -dm/dt = Amn_c \quad (1')$$

This equation merely states that the TL intensity equals (more precisely, is proportional to) $-dm/dt$, and this, in turn, is proportional to m and n_c . This is expected to be correct for cases where more than a single trap is responsible for the electrons (holes) in the band, if transitions into only one recombination center are measured. Even if more than one recombination center is involved, one can improve the situation by using a suitable filter to isolate one kind of transition from the others [19]. Supposing that $n_c(t)$ is a known function (as measured by TSC for example), and assuming that A is a constant one obtains

$$I(t) = Am_0 n_c(t) \exp\left(-A \int_0^t n_c(t') dt'\right). \quad (22)$$

Writing this equation for two arbitrary points t_1 and t_2 and dividing one by the other we obtain

$$I(t_2)/I(t_1) = [n_c(t_2)/n_c(t_1)] \exp\left(-A \int_{t_1}^{t_2} n_c(t) dt\right). \quad (23)$$

All the quantities in this equation are measurable except for A which can thus be evaluated (Fig. 4).

Since $A = \sigma_m v$, one can evaluate σ_m by using the known value of the thermal velocity v . It is to be noted that for the evaluation of A in this way, one needs only relative values of $I(t)$ whereas for $n_c(t)$ an absolute measurement is needed (in the integral only). One can now differentiate eqn. (22), set the derivative to zero and obtain the condition for the maximum of the TL peak:

$$(dn_c/dt)_{\max} = A[n_c(t_{\max})]^2. \quad (24)$$

An important feature of eqn. (24) is that m_0 does not appear in it, which means that if a certain excitation changes m_0 , T_m does not shift. This resembles the simple first-order case. On the other hand, excitation that changes the initial trap filling may change $n_c(t)$ and therefore would influence

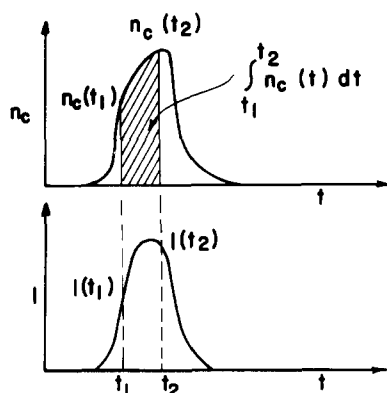


Fig. 4. Schematic illustration of a simultaneous measurement of $I(t)$ and $n_c(t)$ curves. The parameters needed for the evaluation of A are shown.

T_m , usually shifting it to a lower temperature similar to the second-order case.

Since the right-hand side of eqn. (24) is always positive, we have $(dn_c/dt)_{\max} > 0$ and this means that the TL maximum occurs at a lower temperature than its $n_c(T)$ counterpart. This may not be the case if $A = \sigma_m v$ is an increasing function of temperature [20]. It has been shown that σ_m may depend on temperature like T^α with $-4 \leq \alpha \leq 0$, but $v \propto T^{1/2}$ and therefore $A = A' T^a$ with $-7/2 \leq a \leq 1/2$. The condition for the occurrence of the TL maximum at a temperature higher than the TSC one is

$$A_m T_m n_{cm} < a\beta_m, \quad (25)$$

where A_m is now the recombination probability at the maximum. This inequality will be obeyed quite rarely. However, if one compares, the TL peak with the TSC peak, one should also take into account the dependence of the mobility on temperature. Since $\sigma = e\mu n_c$ and if [2] $\mu = \mu' T^b$, one obtains the condition for inversion:

$$A_m T_m \sigma_{\max} < c\beta_m, \quad (26)$$

where $c = a - b$ and $A_m = (A'/\mu'c)T_m^c$. For $b = -1.5$, for example, we find $-2 \leq c \leq 2$ and for the higher possible values of c , the inequality can hold more easily.

7. Final remarks

Several other aspects of TL, TSC and other thermally stimulated processes are of importance. More information can be achieved by making the following measurements:

(1) Dependence on the dose of excitation, which can be linear, superlinear ($I_m \propto D^n$ for $n > 1$) or sublinear (including saturation effects).

(2) The area under a glow curve can be measured, in absolute units if possible, which yields information on n_0 or m_0 as the case may be.

(3) The limiting (saturation) value of n_0 can give in certain cases the magnitude of N .

(4) The related effect of phosphorescence decay at a constant temperature can add some information [21].

(5) Effects of bleaching, enhancement, pre-bleaching and pre-enhancement, i.e. changes in TL due to subsequent illumination by two different wavelengths (or, for example, γ -rays followed by u.v. or visible light), can sometimes give more information on the processes involved.

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