

A ONE TRAP, TWO LUMINESCENCE CENTRE TL MODEL

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Abstract — The differential equations governing the behaviour of a model of the TL process in the presence of two luminescence centres and only one thermally active electron trap have been solved numerically. An additional deep trap not communicating thermally with the conduction band is included. At low temperatures and, for glow curves, for low temperature rise rates the well known quasi-steady state regime applies. At sufficiently high temperatures, however, exhaustion of the electrons in the active trap may take place and the quasi-steady state conclusions may be no longer valid. The simultaneous influences of both luminescence centres must be taken into account. In the quasi-steady state regime the familiar methods of determining the activation energy E from the data are valid even in the presence of two luminescence centres, provided exhaustion effects are not present and provided the recombination rates for the two luminescence centres do not differ by too much.

INTRODUCTION

The most common model for thermo-luminescence (TL) in crystalline materials involves the thermal elevation of pre-trapped electrons from the trap sites into the conduction band. Once in the conduction band, the electrons either are captured by holes trapped in luminescence centres, with or without emission of photons, or are retrapped in empty electron traps. The probability of capture of an electron from the conduction band is the same for each one of a given type of luminescence centre, and the same is true for the retrapping by the empty traps, so that mass action laws may be applied in setting up differential equations for the rates of the various processes. Levy⁽¹⁾ has pointed out that in most real materials this model is not apt to be strictly valid since several types of electron traps are usually present and retrapping of electrons released from one type of trap into another must occur. Levy coined the phrase 'interactive kinetics' to describe this situation. However, the widespread use of variants of the simple one trap model makes it worthwhile to explore its properties in detail.

In quartz it is known that luminescence occurs in at least two regions of the spectrum, around 350–380 nm and around 470 nm. Yang and McKeever⁽²⁾ have attributed this luminescence to two recombination centres, involving Al (470 nm) and H (380 nm). Emission at 380 nm seems to occur in glow peaks below about 375°C, while the 470 nm mainly involves glow peaks at 375°C and above. In particular, we have noted that the Slowly Bleaching Peak in quartz, at 375°C for a ramp rate of 20°C.s⁻¹, emits strongly at 480 nm but also

somewhat less intensely at 350–380 nm. This has led to the suggestion⁽³⁾ of a model in which a single electron trap and two luminescence centres are connected by the conduction band. In this paper a study of this model is presented, involving to some extent the use of numerical solutions of the basic differential equations. The model does include additional trapped charges, but so situated that thermal excitation into and retrapping from the conduction band does not take place. The calculations cover glow curves and isothermal decay.

MODEL

Figure 1 illustrates the model. There are N active electron traps per unit volume and we assume that past exposure to ionising radiation has

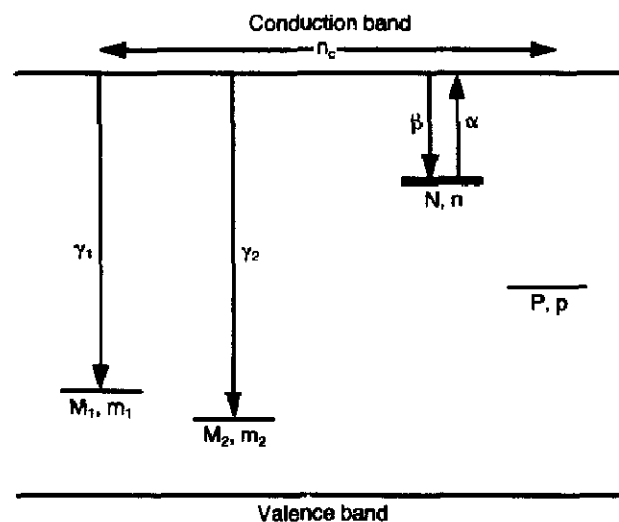


Figure 1. Schematic diagram of the model with two luminescence centres, one deep thermally disconnected electron trap, and one active electron trap.

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left $n_0 < N$ trapped electrons. The concentrations (M_1 and M_2) of both luminescent centres are assumed to exceed N , and there are initially m_{01} and m_{02} trapped holes. At temperature T electrons are ejected into the conduction band from the active trap at a rate given by $n\alpha$, where n is the instantaneous concentration of trapped electrons and α is given by the well known equation

$$\alpha = s \exp(-E/kT)$$

From the conduction band electrons are either retrapped with a rate $\beta n_c (N-n)$, where n_c is the concentration of electrons in the conduction band, or else are captured by the trapped holes in the luminescence centres with rates given by $\gamma_1 m_1 n_c$ and $\gamma_2 m_2 n_c$.

The various concentrations of electrons and trapped holes during the thermally driven relaxation of the initial populations are governed by the differential equations

$$dn_c/dt = n\alpha - n_c [\beta (N-n) + \gamma_1 m_1 + \gamma_2 m_2] \quad (2.1)$$

$$dn/dt = -n\alpha + \beta n_c (N-n) \quad (2.2)$$

$$dm_1/dt = -\gamma_1 m_1 n_c \quad (2.3)$$

$$dm_2/dt = -\gamma_2 m_2 n_c \quad (2.4)$$

Equations 2.1–2.4 are consistent with the charge neutrality condition

$$n + n_c + p = m_1 + m_2 \quad (2.5)$$

In these equations p is the concentration of non-communicating trapped charge, which is constant with time or temperature. For glow curves with a linear temperature ramp rate b , dt is replaced by dT/b .

In order to display the behaviour of the model in a useful region of parameter space, we have selected a set of parameters based on that used, with a distribution of relaxation times missing here, to fit the Slowly Bleaching Peak in archaeological quartz⁽³⁾. These are listed in Table 1.

The actual values of β and the γ_i are controlled by the temperatures at which glow curve peaks occur and the peak shapes, and by the principle of detailed balance (see e.g. Simmons and Taylor⁽⁴⁾), which requires that

$$(\beta N) (N_c/N) = s \quad (2.6)$$

where N_c is the effective density of states in the conduction band. N_c should be of the order of 10^{19} cm^{-3} , while an experimentally detectable N

cannot be less than about 10^{12} . With the reasonable value for s above this implies that (βN) must be as large as 10^4 s^{-1} or larger. However, as shown below, the results are insensitive to multiplying β and the γ_i by a common factor as long as that factor is not too small. Since there is a positive advantage in the sense of ease of computation in working with as small values as possible, most of these computations were carried out with $(\beta N) = 3.5 \text{ s}^{-1}$, $\gamma_1 N = 1.3 \text{ s}^{-1}$, and $\gamma_2 N = 3.5 \text{ s}^{-1}$. For the purpose of exploring the properties of the model the parameters were allowed to vary, but this set defines the general region in parameter space in which we have worked. We have solved these equations iteratively by computer.

RESULTS

The quasi-steady state (QSS) approximation

At low enough temperatures α is very small and the rate of arrival of electrons to the conduction band is likewise small, resulting in a very small value at any time for n_c and therefore for dn_c/dt . Setting the latter equal to zero in Equation 2.1 results in the basic equation of the quasi-steady state approximation

$$n_c \approx n\alpha / [\beta (N-n) + \gamma_1 m_1 + \gamma_2 m_2] \quad (3.1)$$

The thermoluminescent intensity is proportional to $-dm/dt$, which can be written

$$-dm_i/dt = \gamma_i m_i (m_1 + m_2 - p) \alpha / [\beta (N+p) + (\gamma_1 - \beta) m_1 + (\gamma_2 - \beta) m_2] \quad (3.2)$$

Equations 3.1 and 3.2 illustrate the mutual influence of the two luminescence centres. Because of this interaction the factors that control the development of n_c with time and temperature and therefore the location and shape of the glow peaks are complex and in general cannot be expressed analytically but can only be dealt with by direct calculation, even when the QSS approximation is valid.

Isothermal decay

The isothermal decay curve is obtained by heating the specimen to a chosen temperature as rapidly as possible and observing the decay of the TL. There is thus an initial period of complex behaviour when the temperature is still rising before isothermal conditions prevail. Even if the chosen temperature could be attained instantaneously there is still an initial period in which the concentration of electrons in the conduction band rises from its initial zero. The time dependence of n_c during this idealised initial period is obtained from Equation 2.1 on the

Table 1. Representative parameters.

$E/k = 1.683 \times 10^4 \text{ K}$	$n_0/N = 0.330$
$s = 5.1 \times 10^{11} \text{ s}^{-1}$	$m_{10}/N = 0.510$
$p/N = 0.197$	$m_{20}/N = 0.017$
$\gamma_1/\gamma_2 = 0.371$	$\beta/\gamma_1 = 2.69$

assumption that during the initial rise the values of n , m_1 and m_2 do not depart appreciably from their initial values, n_0 , m_{01} and m_{02} , resulting in Equation 3.3

$$n_c = (n_0 \alpha / b'_0) [1 - \exp(-b'_0 t)] \quad (3.3)$$

where

$$b'_0 = [\beta (N - n_0) + \gamma_1 m_{01} + \gamma_2 m_{02}] \quad (3.4)$$

The time constant of this initial rise is b'_0^{-1} , independent of temperature, and the same for m_1 and m_2 .

After the initial rise, the beginning value of n_c is given by

$$n_{c0} = n_0 \alpha / b'_0 \quad (3.5)$$

The quasi-steady state approximation requires that dn_c/dt be much less than dn/dt and dm/dt . A very small value for n_{c0}/n_0 ensures that the quasi-steady state approximation holds throughout the isothermal decay. From Equation 3.5 the QSS approximation is valid when α is much smaller

than b'_0 . As a practical matter the approximation appears to be valid when the ratio α/b'_0 is less than about 0.01, a requirement that is met for all experimentally useful temperatures with our values of E/k and s .

Our computations show that during isothermal decay in the quasi-steady state regime both m_i are functions of $x = \alpha t$, and not independent of either time or temperature. For a single luminescence centre this can be shown directly, but with two luminescence centres present it rests on the numerical results. That is

$$m_i/N = f_i(x)$$

where $x = \alpha t$, so that

$$dm_i/dt = \alpha df_i/dx \quad (3.6)$$

For isothermal relaxation this means that the TL divided by α follows a 'universal' curve when plotted as a function of $x = \alpha t$, independently of the temperature. This is the basis of the technique of Visocekas (PhD thesis, Paris 1978 — cited in Reference 5, p. 175) for determining E . The time t_c to some characteristic point on the curve of $(TL)t$ against t is identified for several temperatures (Visocekas suggested the peak). Then $\ln(t_c)$ will be linear in T^{-1} in kelvins with slope E/k as long as the QSS approximation is valid.

Equations 2.3 or 2.4 lead to Equation 3.7

$$m_i(x) = m_{oi} \exp[-\gamma_i \int_0^x (n_c/\alpha) dx] \quad (3.7)$$

Equation 3.7 implies that since the m_i are functions of x and not of T and t independently, so also is n_c/α . These 'universal' curves are valid as long as the QSS approximation is valid. When it is not, for small values of b'_0 , each temperature dictates a separate decay curve.

This situation is illustrated by Figure 2 ($b'_0 = 30.7$). The isothermal decays for both m_1 and m_2 are well described by 'universal' curves. The curves for m_1 and m_2 are very similar, but are shifted with respect to each other along the x axis. The relationship between the curves for the two luminescence centres can be derived from Equation 3.8

$$[m_1(x)/m_{01}]^{\gamma_1^{-1}} = [m_2(x)/m_{02}]^{\gamma_2^{-1}} \quad (3.8)$$

As $x \rightarrow \infty$ this equation combined with

$$m_{\infty 1} + m_{\infty 2} = p$$

determines the final distribution of the remaining holes between the two luminescence centres in case p is positive.

The presence of electrons in non-communicating traps ($p > 0$) increase the rate of isothermal decay. Physically, this increase in relaxation rate is brought about by the

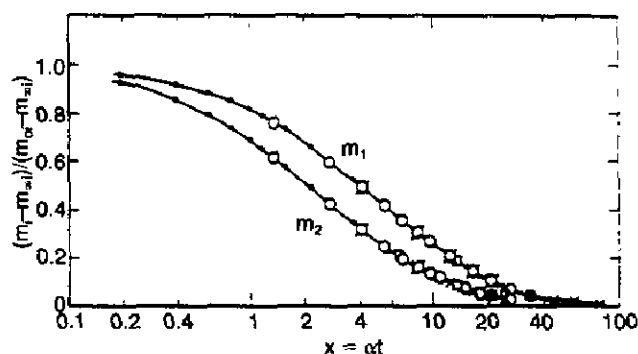


Figure 2. Isothermal decay curves for m_1 and m_2 at three temperatures for large b'_0 (30.7 s^{-1}): (●) 533 K, (○) 568 K, and (×) 590 K, and (□) 600 K. The parameters of Table 1 were used except that βN , $\gamma_1 N$ and $\gamma_2 N$ were multiplied by 10 to ensure the validity of the QSS approximation.

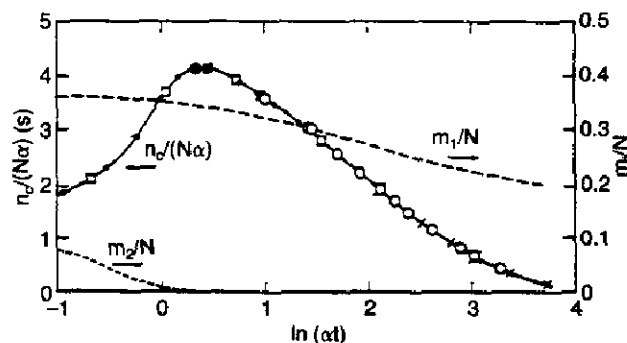


Figure 3. Isothermal decay curve of $n_c/(\alpha N)$ in the two-centre model when $\gamma_2 \gg \gamma_1$. $E/k = 1.683 \times 10^4 \text{ K}$, $s = 5.1 \times 10^{11} \text{ s}^{-1}$, $\beta N = 35 \text{ s}^{-1}$, $\gamma_1 N = 13 \text{ s}^{-1}$, $\gamma_2 N = 1300 \text{ s}^{-1}$, $n_0/N = 0.330$, $m_{01}/N = 0.362$, $m_{02}/N = 0.165$, $p/N = 0.197$. (●) 533 K, (□) 550 K, (○) 568 K, (×) 590 K.

accompanying increase in m_1 and/or m_2 , operating through Equations 2.3 and 2.4.

With two luminescence centres n_c during isothermal decay does not necessarily decrease monotonically with x . It can be shown that the initial value of d^2n_c/dt^2 can be positive if

$$n_0 (\gamma_1^2 m_{01} + \gamma_2^2 m_{02}) > (\gamma_1 m_{01} + \gamma_2 m_{02}) \times (\beta N + \gamma_1 m_{01} + \gamma_2 m_{02}) \quad (3.9)$$

In that case n_c first rises to a maximum and then decreases, as shown in Figure 3. Physically, this occurs when the two values of γ_i are very different, so that the holes in one luminescence centre almost all recombine before the concentration of those in the other changes appreciably, n_c increasing in the process. The TL for the recombination centre that reacts more slowly will also rise initially and approximately follow the course of n_c . These effects illustrate well the way the presence of one luminescence centre influences the behaviour of the other.

Glow curves

Because experimentally the measurement of glow curves always starts at relatively low temperatures, the QSS approximation is always valid at the beginning of a glow curve. At sufficiently high temperatures, on the other hand, the rate of ejection of electrons from the traps could become so large that $n < n_c^{(6)}$, violating the conditions of the QSS approximation and producing instead the exhaustion regime. Thus during the course of a glow curve run the system would pass from the quasi-steady state regime to the exhaustion regime. This appears to happen at temperatures low enough to affect the peak of the glow curve when b'_0 from Equation 3.4 is numerically less than or approximately equal to b , the rate of rise of the temperature in $K.s^{-1}$ during the glow curve run. However, for any realistic set of parameters $b'_0 \gg b$ and the QSS approximation is valid at all experimental temperatures.

With two luminescence centres electrons are captured from the same pool in the conduction band by the two centres. Given the course of n_c as a function of temperature the peak temperatures of the glow peaks are determined solely by their respective values of γ_i , since from Equations 2.3 and 2.4 it follows that

$$(dn_c^{-1}/dt)_{T_m} = \gamma_i \quad (3.10)$$

is the condition for the glow curve maximum and therefore defines T_m for peak i .

The two separate peaks, stemming from different luminescence centres, can be expected to emit light of different spectral character so that in principle the two glow peaks should be measurable

separately⁽³⁾. Then in general the ratio γ_1/γ_2 can be found experimentally from glow curve data by combining Equations 2.3 and 2.4 to yield

$$(d \ln m_1 / dt) / (d \ln m_2 / dt) = \gamma_1 / \gamma_2 \quad (3.11)$$

where the logarithmic derivatives can be estimated with the help of the 'light sums', the areas under the glow curves from the temperature in question to the high temperature end of the glow peak.

An important quantity in the determination of the peak temperature and shape is the ratio

$$R_0 = \frac{\beta N}{\gamma_1 m_{01} + \gamma_2 m_{02}} \quad (3.12)$$

As pointed out by Levy⁽¹⁾, R_0 acts as the 'order' parameter in the general order formulation of glow peaks⁽⁵⁾. As R_0 passes from zero to large values the glow curves pass continuously from first to second order character. Multiplication of β and the γ_i by a common factor has no effect on the computed temperature and shape of either peak for a wide variation in γ_1/γ_2 , as long as the QSS approximation is valid. The activation energy E/k directly influences the peak temperature but not the shape factor $\mu_g^{(5)}$. In these calculations the width of the peaks increased linearly with the peak temperature. The degree of saturation n_0/N and non-communicating trapped charge concentration p/N were also found to influence peak temperatures and shapes.

As in the case of isothermal decay, the behaviour of the two peaks was found to depend on the relative values of γ_1 and γ_2 . If they were not too different, within approximately an order of magnitude of each other, the behaviour resembled in some respects that of a system with a single luminescence centre. The two peaks had about the same shape, with the higher temperature peak usually the broader. That they do not really constitute a single system, however, was shown by a computation in which the degree of saturation n_0/N was varied, the corresponding holes being distributed in the luminescence centres in the same proportion as shown in Table 1, after subtraction of p/N from m_{01}/N . The peak temperatures and shapes for two peaks varied with n_0/N in roughly the same way, but whereas one peak became broader as n_0/N increased, the other became narrower.

On the other hand when γ_1 and γ_2 differ by several orders of magnitude, the two peaks are distorted in the region of overlap between them (Figure 4(a)). The high temperature side of the low temperature peak drops precipitously because n_c , the concentration of electrons in the conduction band, is maintained at a high level by the trapped electrons not yet expended in the high temperature

peak. Conversely the low temperature side of the high temperature peak is depressed initially because n_c is kept low until the low temperature peak is finished (Figure 4(b)). This interaction between the two peaks, mediated by the conduction band electron population, can interfere with the use of both the initial rise and the Hoogenstraaten⁽⁷⁾ methods of determining E.

CONCLUSIONS

- a) The behaviour of the model can be understood on the basis of two regimes. At low temperatures and, for glow curves, when the temperature ramp rate is small, the quasi-steady state regime applies, and Equation 3.1 is a valid approximation to use. At high temperatures, and for high ramp rates, the exhaustion regime may be encountered, where the thermally connected electron traps are essentially empty.
- b) Even in the quasi-steady state regime, each glow curve cannot be treated independently of the other. The influences of both luminescence centres simultaneously must be recognised, and Equations 3.1 and 3.2 must be applied consistently.
- c) In isothermal decay in the QSS regime, n_c/α , m_i , and $\alpha^{-1}(dm_i/dt)$ all are described by 'universal' curves with $x = \alpha t$ as the independent variable.
- d) When the γ_1 and γ_2 differ by several orders of magnitude interaction between the two luminescence centres, mediated by the conduction electrons, becomes apparent. In isothermal decay, this can result in the slower decaying luminescence exhibiting a maximum in the TL decay curve. In the glow curve distortion of the peaks in the region of overlap can occur.
- e) Even with several luminescence centres, but in the absence of a distribution of activation energies, the familiar methods of determining E from the experimental data are valid, although with restrictions. The isothermal decay method and the Hoogenstraaten method depend on the system being in the quasi-steady state regime without exhaustion effects, whereas the initial rise method, operating as it does at lower temperatures, is not so vulnerable to exhaustion effects. Both the latter methods can be invalidated if γ_1 and γ_2 differ by several orders of magnitude.

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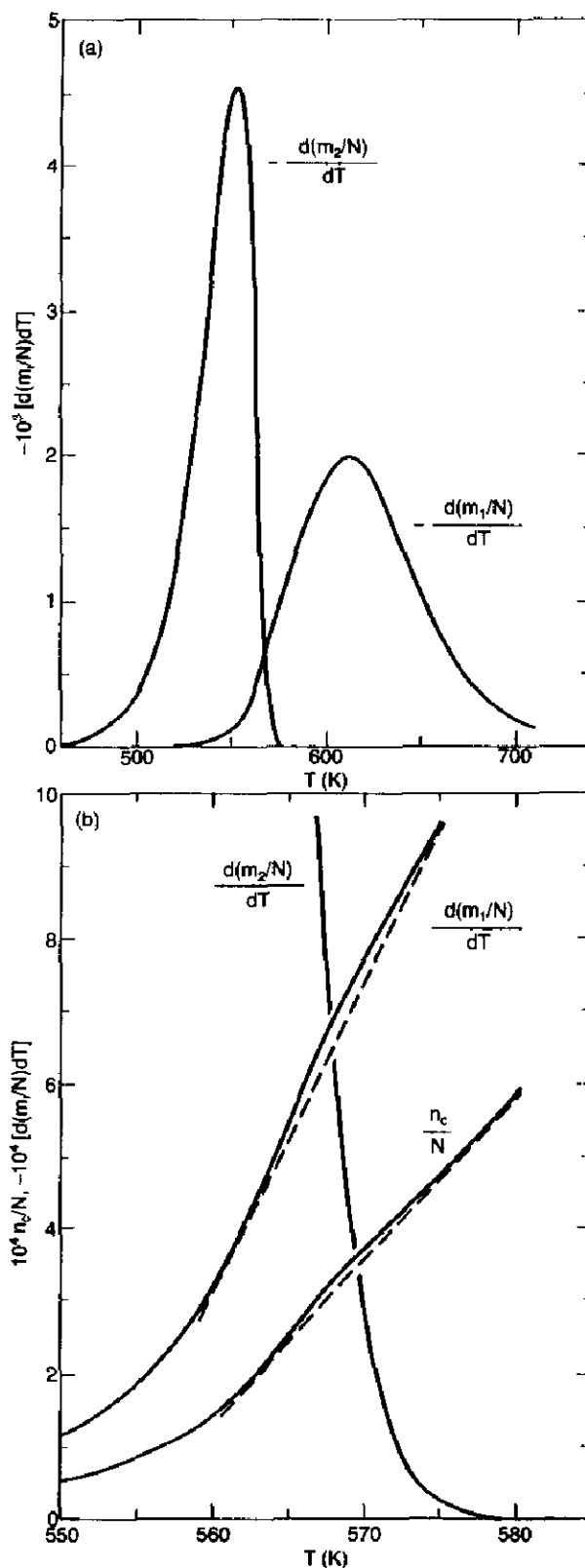


Figure 4.(a) Glow curves for the two-centre model when $\gamma_2 \gg \gamma_1$, $E/k = 1.683 \times 10^4$ K, $s = 5.1 \times 10^{11} \text{ s}^{-1}$, $\beta N = 35 \text{ s}^{-1}$, $\gamma_1 N = 13 \text{ s}^{-1}$, $\gamma_2 N = 1300 \text{ s}^{-1}$, $n_0/N = 0.330$, $m_{01}/N = m_{02}/N = 0.165$, $p/N = 0$. (b) Expanded section of Figure 4(a). The dotted lines are straight lines to reveal the curvature in the plots.

REFERENCES

1. Levy, P. W. *Thermoluminescence in Systems not Subject to the Usual Approximations for First and Second Order Kinetics*. *Radiat. Effects* **72**, 259 (1983).
2. Yang, X. H. and McKeever, S. W. S. *The Pre-dose Effect in Crystalline Quartz*. *J. Phys. D: Appl. Phys.* **23**, 237 (1990).
3. Hornyak, W. F., Chen, R. and Franklin, A. D. *The TL Characteristics of the 375 °C Electron Trap in Quartz*. *Phys. Rev. B* **45**, 8036 (1992).
4. Simmons, J. G. and Taylor, G. W. *Non-Equilibrium Steady-state Statistics and Associated Effects for Insulators and Semiconductors Containing an Arbitrary Distribution of Traps*. *Phys. Rev. B* **4**, 502 (1971).
5. Chen, R. and Kirsh, Y. *Analysis of Thermally Stimulated Processes* (Oxford: Pergamon Press) (1981).
6. Kelly, P. Laubitz, M. J. and Braunlich, P. *Exact Solutions of the Kinetic Equations Governing Thermally Stimulated Luminescence and Conductivity*. *Phys. Rev. B* **4**, 1960 (1971).
7. Hoogenstraaten, W. Phillips. *Electron Traps in ZnS Phosphors*. *Res. Repts.* **13**, 515 (1958).