

DETERMINATION OF TRAP PARAMETERS FROM GENERALISED INITIAL RISE EQUATIONS

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Abstract — New generalised initial rise equations for TL (thermoluminescence) are derived and verified numerically. Unlike the classical Garlick–Gibson initial rise method these approximations cover not only the initial part but the whole range of the TL peak for most physically admissible trap parameters. Some new methods of determining trap parameters are proposed. Numerical tests show that applying generalised equations to experimental results allows determination of the activation energy with a very high accuracy.

INTRODUCTION

Thermally stimulated relaxation techniques are very well known methods for studying trap parameters, especially the activation energy E . During the TL (thermoluminescence) process a sample is excited at an appropriately low temperature T_0 . The excitation fills traps with carriers. During heating the probability of detrapping increases and the carriers (e.g. electrons) released from traps to the conduction band recombine, giving rise to the luminescence according to the equation:

$$J_{TL} = -\alpha dm_\lambda/dt \quad (1)$$

where m_λ stands for the number of holes in recombination centres characterised by the wavelength λ of the emitted light and α is the proportionality coefficient. For the sake of simplicity, it is often assumed that only one type of charge carrier, i.e. electrons, is involved in the conduction mechanism. TL spectra recorded in this way usually consist of a series of peaks attributed to trap levels of the material. Many methods were developed for evaluating trap parameters from a single TL peak. One of the simplest and most credible ones used for evaluating the activation energy is the so-called 'initial rise method'. In this method it is assumed that during linear heating, for a small initial part of TL peak, the following relation must hold⁽¹⁾:

$$\frac{-E}{kT} = \ln[J(T)] + \text{const} \quad (2)$$

where J is the measured intensity. Plotting the dependence $\ln[J(T)]$ against $1/T$ one gets a straight line with the slope $(-E/k)$. Although the equation is valid for various kinetic models, very often it is difficult to estimate its range of applicability. Usually it is assumed that the range is limited to one tenth of the maximum intensity of a peak. Nevertheless, in some specific cases, it was shown that the equation cannot be used even in this region⁽²⁾. In this work new generalised equations for TL are presented in the form:

$$\frac{-E}{kT} = \ln[J(T)] + \Phi(T) + \text{const} \quad (3)$$

where the function $\Phi(T)$ is the 'correction term'. It will be shown that in most cases the generalised Equation 3 can be successfully applied the whole TL peak with the fit error less than 0.1%.

THEORY

Basic equations

Charge carrier kinetics is described by the following set of equations⁽³⁾:

$$-\dot{n}_i = n_i D_i - n_c A_i (N_i - n_i) \quad i = 1 \dots p, \quad (4a)$$

$$-\dot{m} = B_s m_s n_c \quad s = 1 \dots k, \quad (4b)$$

$$\sum_{s=1}^k m_s = \sum_{i=1}^p n_i + n_c + M \quad (4c)$$

where

$$D_i = \nu_i \exp\left(\frac{-E_i}{kT}\right) \quad (5)$$

stands for the detrapping probability of an electron from the i^{th} trap level, having the energy depth E_i and characterised by the frequency factor ν_i . The remaining symbols have the following meaning: n_i stands for the concentration of electrons in the i^{th} trap level, n_c for the concentration of electrons in the conduction band, N_i for the total number of trapping states in this level, A_i and B_s for the trapping and recombination probabilities, respectively. M stands for the number of electrons in the thermally disconnected traps (deep traps), i.e. traps which are not emptying during the experiment, and k is the Boltzmann constant. In the following calculations we are dealing with only one type of trap and one type of recombination centre. Using the set of Equations 4 it can be proved that the following integral can be calculated analytically⁽⁴⁾:

$$S_{\infty} \equiv \int_0^{\infty} n_c(t') dt' = \frac{1}{B} \ln \left(1 + \frac{n_0}{M} \right) \quad (6)$$

The value S_{∞} is proportional to the total area under TSC (thermally stimulated conductivity) curve. To calculate the integral for an arbitrary value of t it is assumed that the integral $S(t)$ can be approximated by the following expression:

$$S(t) \equiv \int_0^t n_c(t') dt' = \frac{1}{B} \ln \left[1 + \frac{n_0 - n(t)}{M + n(t)} \right] \quad (7)$$

This can be done by analogy with a similar expression for limited heating cycles⁽⁴⁾. When the sample, at the time t , is rapidly cooled to a 'low' temperature T_0 , the exact value of $S(t)$ is given by:

$$S^{(e)}(t) = \frac{1}{B} \ln \left[1 + \frac{n_0 - n^{(e)}(t)}{M + n^{(e)}(t)} \right] \quad (8)$$

where $n^{(e)}(t)$ denotes the concentration of carriers in traps, after cooling the sample. It is obvious that $n^{(e)}(t)$ should be closely related to $n(t)$. The approximation (Equation 7) allows us to determine $n(t)$

$$n(t) = (M + n_0) \exp[-BS(t)] - M \quad (9)$$

and its derivative:

$$-\dot{n}(t) = B n_c (M + n_0) \exp[-BS(t)] = B n_c (n + M) \quad (10)$$

These equations, together with the basic set (Equations 4) allow us to derive analytical solutions for TL without doing any other approximations.

The first approximation for TL

Let us define new variables:

$$\mathcal{L}(t) \equiv -\dot{m}(t) \quad (11)$$

$$\mathcal{U}(t) \equiv \int_0^t \mathcal{L}(t') dt' = m_0 - m(t) \quad (12)$$

Assuming the proportionality factor $\alpha = 1$ in Equation 1 it can be seen that \mathcal{L} denotes TL intensity and \mathcal{U}_{∞} denotes the total area under TL curve. Now, using the approximations of Equations 9 and 10 with the basic set of Equations 4, the following 'generalised initial rise formula' is produced:

$$\frac{-E}{kT(t)} = \ln[\mathcal{L}(t)] + \ln \left\{ \frac{1}{M + \mathcal{U}_{\infty} - \mathcal{U}(t)} \left[\frac{1}{\mathcal{U}_{\infty} - \mathcal{U}(t)} + L_1 \right] \right\} + \ln(L_2) \quad (13)$$

where L_1 and L_2 are constants:

$$L_1 = \frac{B - A}{AN + BM} \quad (14)$$

$$L_2 = \frac{AN + BM}{\nu B} \quad (15)$$

If this equation is correct, then plotting the dependence $\ln[J(T)] + \Phi_1(T)$ against $1/T$ produces a straight line with the slope $(-E/k)$. Because the areas under the TL curve may be directly determined from experimental data, hence the correction term

$$\Phi_1(T) = \ln \left[\frac{1}{M + \mathcal{U}_{\infty} - \mathcal{U}(t)} \left(\frac{1}{\mathcal{U}_{\infty} - \mathcal{U}(t)} + L_1 \right) \right] \quad (16)$$

depends only on two unknown parameters M and L_1 . Possible applications of Equation 13 to experimental results will be discussed later. Equation 13, in the special case $M = 0$, coincides with the solution obtained by Maxia *et al*⁽⁵⁾ and Aramu and Maxia⁽⁶⁾.

The second approximation for TL

Although using Equation 9 as a consequence of the approximation (Equation 7) is quite natural, yet using also its derivative (Equation 10) may be somewhat ambiguous. It can be proved that the second assumption may be omitted, however, in the final equation:

$$\frac{-E}{kT(t)} = \ln[\mathcal{L}(t)] + \Phi_2(T) + \ln(\bar{L}_3) \quad (17)$$

the correction term $\Phi_2(T)$ has a more complex form:

$$\Phi_2(T) = \ln \left\{ \frac{1}{M + \mathcal{U}_{\infty} - \mathcal{U}(t)} \left[\frac{1}{\mathcal{U}_{\infty} - \mathcal{U}(t)} \left(\frac{d[\ln(\mathcal{L}(t))]}{dt} + \frac{\mathcal{L}(t)}{M + \mathcal{U}_{\infty} - \mathcal{U}(t)} + \bar{L}_1 \right) + \bar{L}_2 \right] \right\} \quad (18)$$

and depends on three unknown parameters, M , \bar{L}_1 and \bar{L}_2 . In the above equations \bar{L}_1 , \bar{L}_2 and \bar{L}_3 are constants:

$$\bar{L}_1 = AN + BM \quad (19)$$

$$\bar{L}_2 = B - A \quad (20)$$

$$\bar{L}_3 = 1/(B\nu) \quad (21)$$

Special cases

Analysis of Equation 13 shows that for some cases the correction term can be simplified. Below, two special cases are considered. The first is $M \gg \mathcal{U}_{\infty} = n_0$. In this case the correction term depends weakly on M , and holds $|L_1| \ll [\mathcal{U}_{\infty} - \mathcal{U}(t)]^{-1}$. This way Equation 13 simplifies to:

$$\frac{-E}{kT(t)} = \ln[\mathcal{L}(t)] - \ln[\mathcal{U}_{\infty} - \mathcal{U}(t)] + \ln(L') \quad (22)$$

where

$$L' = \frac{AN + BM}{\nu BM} \quad (23)$$

Here the linearisation procedure is straightforward because no additional parameters are needed. The plot $\ln\{\mathcal{L}(t)/[\mathcal{U}_\infty - \mathcal{U}(t)]\}$ against $(1/T)$ should give a straight line with the slope $(-E/k)$. The second case is $M \ll n_0$ and $A \equiv B$. Now, Equation 13 reduces to

$$\frac{-E}{kT(t)} = \ln[\mathcal{L}(t)] - 2\ln[\mathcal{U}_\infty - \mathcal{U}(t)] + \ln(L_2) \quad (24)$$

The constant L_2 is defined by Equation 15. In this case to linearise a TL spectrum one should plot the dependence $\ln\{\mathcal{L}(t)/[\mathcal{U}_\infty - \mathcal{U}(t)]^2\}$ against $1/T$.

NUMERICAL VERIFICATION

To check the range of validity of the equations obtained, numerical calculations were performed to compare the new approximations (Equations 13 and 17)

with exact solutions of the differential Equations 4 and classical Garlick–Gibson initial rise method (Equation 2). The exact solutions were calculated using the Gear algorithm for stiff differential equations⁽⁷⁾. Typical results are presented in Figures 1(a) and 1(b). The second plot on the graph represents linearised dependence in the form of Equations 2 and 3. The third plot represents relative errors of each approximation. For almost all calculated TL spectra the first (Equation 13) and the second approximations (Equation 17) coincided. A slight difference between these two solutions was observed only for extremely low values of the recombination coefficient B within the small initial region of the TL peak (cf. spectrum w1 in Figure 1(b)). In most cases, calculated for a wide range of trap parameters, the range of applicability of the new equations covered the whole range of the TL peak with an excellent accuracy. The only exceptions were observed for extremely low values of the recombination coefficient $B < 10^{-13} \text{ cm}^3 \cdot \text{s}^{-1}$. However, even in those cases, up

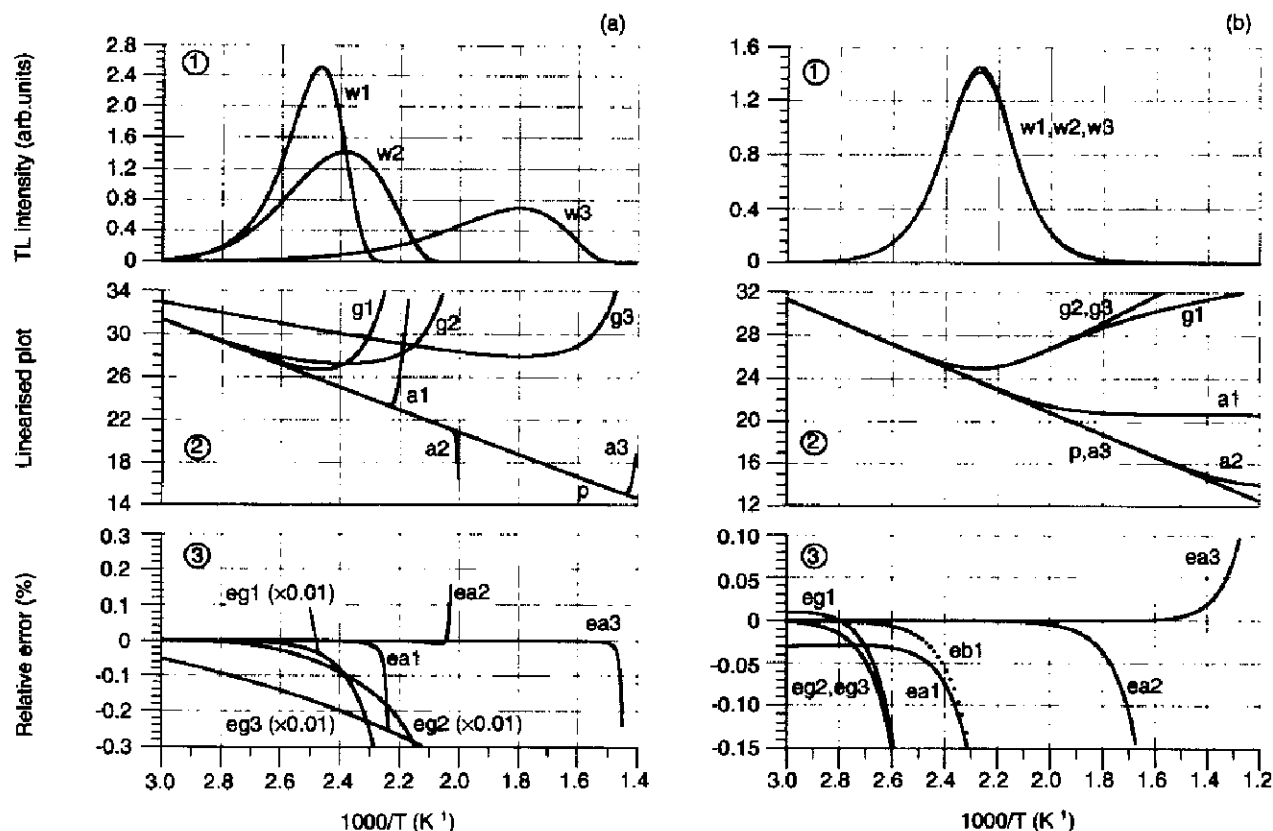


Figure 1. The comparison of the classical initial rise method (the curves g on the diagrams 2) calculated from Equation 2 with the new generalised approximations (the curves a) calculated from Equations 13 and 17. The TL spectra (denoted as w) are presented on the diagrams 1. Line p represents the 'ideal' dependence $y(1/T) = E/kT + \text{const}$. The respective relative errors are plotted on the diagram 3: eg for the Garlick–Gibson method; ea for the first approximation (Equation 13); and eb (...) for the second approximation (Equation 17). The first and the second initial rise approximations coincide except for a small initial part of the spectrum w_1 on the diagram (b). On the diagram (a) the spectra 1, 2 and 3 are calculated for different re trapping coefficients $r \equiv A/B$: $r = 0$ for curve 1, $r = 10$ for curve 2 and $r = 10^4$ for curve 3. The recombination coefficient is $B = 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$. The three almost identical spectra on the diagram (b) were calculated for the re trapping coefficient $r = 1$ and $B = 10^{-14}, 10^{-11}, 10^{-8} \text{ cm}^3 \cdot \text{s}^{-1}$ for curves 1, 2 and 3 respectively. The other trap parameters for all the spectra of (a) and (b) are the same: $E = 0.9 \text{ eV}$, $\nu = 10^{10} \text{ s}^{-1}$, $N = 10^{15} \text{ cm}^{-3}$ and $M = 0$.

to the maximum of a peak the fit was excellent, with an error less than 0.2%.

DISCUSSION

New approximate equations can be applied to the evaluation of trapping parameters, especially the activation energy E , from TL spectra. The 'generalised initial rise' method is accurate even in the case when the classical method fails in the initial part of the peak, giving the 'false straight line' (e.g. curve g3 on the second plot in Figure 1(a)). Numerical calculations show that the first approximation (Equation 13) is effi-

cient for most TL spectra. Any differences between them are usually negligible. Since the Equation 13 is more simple than 17 it is suggested that Equation 13 be used in analysis of experimental results. The simplest way is try to use one of the special Equations 22 or 24. In case these are not appropriate the general formula (Equation 13) should be applied. Determination of activation energy can be achieved by fitting the 'correction term' which depends only on two unknown parameters. However using simultaneous TSC/TL experiment parameters B and M can be easily determined^(4,8,9) so, in this case, the fitting term would depend only on a single parameter.

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