

Comparison of some models for nonlinear fitting analysis of TSC measurements

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Abstract

Basic differential equations for thermally stimulated conductivity (TSC) measurement have no analytical solutions even for the simplest cases. Therefore, analysis of the obtained results is very difficult. The same equations are used also for thermoluminescence (TL). Nevertheless, TL analysis is much easier due to a number of approximate models, such as general order kinetics and mixed order kinetics. In this paper we discuss usefulness of the approximations in description of TSC with respect to determination of trap parameters using nonlinear curve fitting analysis. For this purpose appropriate equations were derived. The results are compared to the recently derived method based on the quasi equilibrium approximation. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thermally stimulated conductivity (TSC) is a measurement technique widely used for the investigation of charge carriers' traps in high-resistivity materials [1,2]. Initially, a sample under study is excited in any way—e.g., by high energy radiation (e.g. UV or X-ray). The excitation fills traps within energy gap with carriers. Then, increasing temperature, one releases charge carriers from traps. The free carriers may be recaptured by empty traps or may recombine with opposite ones. Most of these transitions go through the conduction band, thus they can be easily detected on

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conductivity curves. Calculating trap parameters from TSC curves is the main goal of TSC theory. Unfortunately, this key problem is still not solved satisfactorily, mainly due to mathematical complexity of the basic kinetic equations. Much more has been done in the field of thermoluminescence (TL) theory. TL is a related thermostimulated process where instead of conductivity one measures luminescence emitted during charge carriers' recombination. To analyse TL glow curves many approximate equations are used. The approximations are usually based on the assumption of first, second and general order kinetics (GOK) or mixed order kinetics (MOK). In this paper, we derive analogous expressions for TSC. The usability of the models is compared to the quasi-equilibrium (QE) approximation.

2. Theory

2.1. Fundamental equations for the simple model

In the framework of the most acceptable simple trap model charge carriers' kinetics is governed by the following set of differential equations [1,2]:

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

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

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

where

$$\varepsilon_i(t) = \exp \left[- \frac{E_i}{k_B T(t)} \right], \quad (2)$$

N_i , n_i , and m_s denote the concentrations of trap states, electrons trapped in 'active' traps and holes trapped in recombination centres, respectively. M stands for the concentration of electrons in the thermally disconnected traps (deep traps), i.e., traps that are not emptied during the experiment, n_c denotes the concentration of electrons in the conduction band. A_i and B_s stand for the trapping and recombination probabilities, respectively. E_i and v_i denote trap activation energy and its frequency factor, respectively. Luminescence intensity (i.e., the rate of radiative recombination) is proportional to $(-\dot{m})$, TSC is proportional to n_c . For the sake of simplicity we will assume the proportionality coefficients to be constant. The temperature is usually linearly dependent on time: $T = T_0 + \beta t$, where β is the heating rate. It is assumed in Eq. (1a)–(1c) that the system consists of p discrete trap levels and k recombination centres. Unfortunately, this set has no analytical solutions even for the simplest case of $p = 1$ and $k = 1$. Since all the approximations considered below deal with the simplest case the subscripts i and s will be omitted.

2.2. General order kinetics

In GOK model, it is assumed that during TL process the concentration of carriers in traps n decreases due to the following rule [3,4]:

$$J_{\text{TL}} = -\frac{dn}{dt} = v'n^b\varepsilon(t), \quad (3)$$

where J_{TL} is the measured TL intensity and b is a new parameter—the kinetic order. Usually, it is assumed that $b \in \langle 1, 2 \rangle$ however values out of this range were found also. The first part of this equation means actually the quasi equilibrium approximation, i.e.

$$n_c \ll n, \quad (4)$$

$$\left| \frac{dn_c}{dt} \right| \ll \left| \frac{dn}{dt} \right|. \quad (5)$$

The second part replaces Eq. (1a). The GOK, being very popular in practical applications (mainly dosimetric), was also criticised by many authors due to non-physical character the kinetic order b as well as a bad accuracy in some cases [5–7]. For $b = 1$ the solution is known as the Randall–Wilkins (RW) approximation [8]:

$$J_{\text{TL}} = \chi v' n_0 \varepsilon(t) \exp \left[-\frac{v' n_0}{\beta} \int_0^t \varepsilon(t') dt' \right], \quad (6)$$

where n_0 denotes initial concentration of charge carriers in traps and χ is the proportionality coefficient. This is ‘first-order’ or ‘monomolecular’ kinetics. It was found that many observed TL curves obey this simple equation. Fitting algorithms constructed for RW model require only three unknown parameters per peak—i.e., E , v' and χ . For $b \neq 1$ the solution is:

$$J_{\text{TL}} = \chi v' (n_0)^b \varepsilon(t) \left[1 + (b-1) v' n_0^{(b-1)} \int_0^t \varepsilon(t') dt' \right]^{-b/(b-1)}. \quad (7)$$

It contains four fitting parameters. The model is physically justified only in two limiting cases: $b = 1$ that corresponds to RW model and $b = 2$ derived by Garlick and Gibson [9] (‘second-order’ or ‘bimolecular’ kinetics). Moharil [5] and Opanowicz [6] pointed out that the kinetic order is usually non-constant during a thermally stimulated process. Lewandowski and McKeever [10] and Lewandowski et al. [11] suggest using a kinetic order function instead of the kinetic order constant. Combining (1b) and (1c) together with QE conditions (4) and (5) we have

$$n_c = \frac{-\dot{n}}{B(n + n_c + M)} \cong \frac{-\dot{n}}{B(n + M)}. \quad (8)$$

Solving (3) with respect to n and substituting the result to (8) we get

$$n_c = \frac{v'n_0^b}{B} \varepsilon(t) \{ n_0 [W(t)]^{-1/(b-1)} + M \}^{-1} [W(t)]^{-b/(b-1)}, \quad (9)$$

where

$$W(t) = 1 + v'n_0^{b-1}(b-1) \int_0^t \varepsilon(t') dt'. \quad (10)$$

As the measured, TSC intensity is proportional to n_c : $J_{TSC} = \chi n_c$, finally, for $b \neq 1$ we obtain

$$J_{TSC} = \frac{\chi v' n_0^{b-1}}{B} \left\{ 1 + \frac{M}{n_0} [W(t)]^{1/(b-1)} \right\}^{-1} [W(t)]^{-1} \varepsilon(t). \quad (11)$$

Similarly, for $b = 1$, solving Eq. (1a)–(1c) and substituting the result to (8) we get

$$J_{TSC} = \frac{\chi v'}{B} \left\{ 1 + \frac{M}{n_0} \exp \left[v' \int_0^t \varepsilon(t') dt' \right] \right\}^{-1} \varepsilon(t). \quad (12)$$

2.3. Mixed order kinetics

The model is defined as follows:

$$J_{TL} = -\frac{dn}{dt} = v'n(n+c)\varepsilon(t), \quad (13)$$

where c is a constant. Similarly, as for GOK model, the equation is easy solvable analytically:

$$J_{TL} = v'c^2 \alpha \frac{V(t)}{[V(t) - \alpha]^2} \varepsilon(t), \quad (14)$$

where $\alpha = n_0/(n_0 + c)$ and

$$V(t) = \exp \left[cv' \int_0^t \varepsilon(t') dt' \right]. \quad (15)$$

The definition (13) also includes non-explicit QE assumptions. Using again Eq. (8) we get the following expression for TSC:

$$J_{TSC} = \frac{\chi v' c^2 \alpha}{BM} \frac{V(t)}{[V(t) - \alpha][V(t) + \gamma]} \varepsilon(t), \quad (16)$$

where $\gamma = \alpha(c - M)/M$.

2.4. Quasi equilibrium approximation

Recently, it was found [7,12] that using only the QE approximation (4) and (5) it is possible to write the following equation for TSC current:

$$J_{\text{TSC}}(t) \equiv \chi n_c = \frac{\chi v \eta_0 \varepsilon(t) [1 + \mu_0 - \mu_0 \exp(\bar{B}S(t))]}{B[(1-r)\eta_0(1+\mu_0) + r(1+\eta_0\mu_0)\exp(\bar{B}S(t))]}, \quad (17)$$

where $\bar{B} = \chi B$, $r = A/B$, $\eta_0 = n_0/N$, $\mu_0 = M/n_0$, and

$$S(t) = \int_0^t n_c(t') dt'. \quad (18)$$

Considering that $S(t)$ is represented by the integral (18), hence (17) is a non-linear integral equation. However, we can suggest very effective formula for calculating $J_{\text{TSC}}(t)$. To calculate TSC intensities $j_k = J_{\text{TSC}}(t_k)$ at equidistant time intervals t_k , we have to calculate iteratively $j_k = \Psi(t_k, S_k)$ where Ψ denotes the right-hand side of Eq. (17) and

$$S_k = S_{k-1} + \frac{3j_{k-1} - j_{k-2}}{2} \Delta t. \quad (19)$$

Initial conditions are obvious: $j_0 = j_1 = 0$, $S_0 = S(t_0) = S_1 = S(t_1) = 0$. After calculating first estimation $j_k^{(1)}$ one needs to correct the variable S_k as follows:

$$S_k^{(2)} = S_{k-1} + \frac{j_k^{(1)} + j_{k-1}}{2} \Delta t. \quad (20)$$

The correction loop may be repeated several times, however excellent results are achieved also for a single run (Fig. 1). The high accuracy allows using relatively long computational steps (Fig. 2).

3. Conclusions

Approximate TSC equations were derived based on GOK and MOK models. As one can see in the corresponding Eqs. (11) and (16) the resulting curves depend on 5 parameters. These are $\{E; b; M/n_0; \chi/B; v\eta_0^b\}$ for GOK and $\{E; cv'; \alpha; \gamma; \chi v' c^2 \alpha / BM\}$ for MOK. The same number of parameters is required for the quasi-equilibrium approximation (17), because for $r \neq 1$ the equation may be written as

$$J_{\text{TSC}}(t) = \frac{A_1 \varepsilon(t) [1 + \mu_0 - \mu_0 \exp(\bar{B}S)]}{[1 + A_2 \exp(\bar{B}S)]}, \quad (21)$$

where $A_1 = \chi v \eta_0 / [B(1-r)\eta_0(1+\mu_0)]$ and $A_2 = r(1+\eta_0\mu_0) / [(1-r)\eta_0(1+\mu_0)]$. Thus, the unknown parameters are $\{E; \mu_0; \bar{B}; A_1; A_2\}$. For $r = 1$ the set of parameters

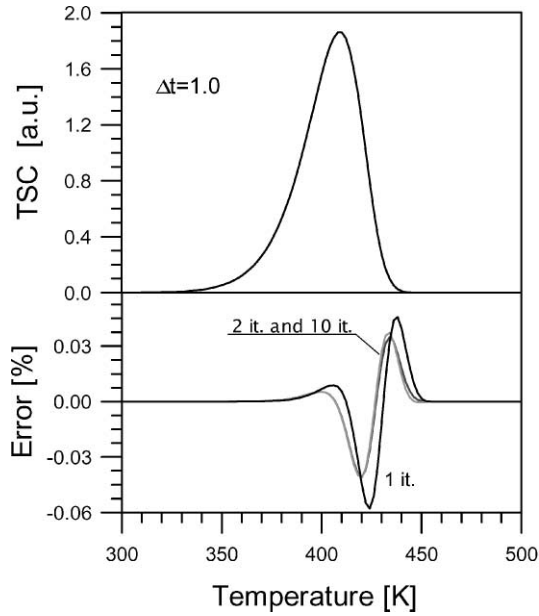


Fig. 1. Illustration of the influence of the number of iterations on the accuracy of the QE method (20)–(21). Curve parameters: $E = 0.9 \text{ eV}$, $\nu = 10^{10} \text{ s}^{-1}$, $\beta = 1 \text{ K/s}$, $r = 0$, $\eta_0 = 1$, $\mu_0 = 1$, $\chi = 1$. Computation step $\Delta t = 1.0 \text{ s}$.

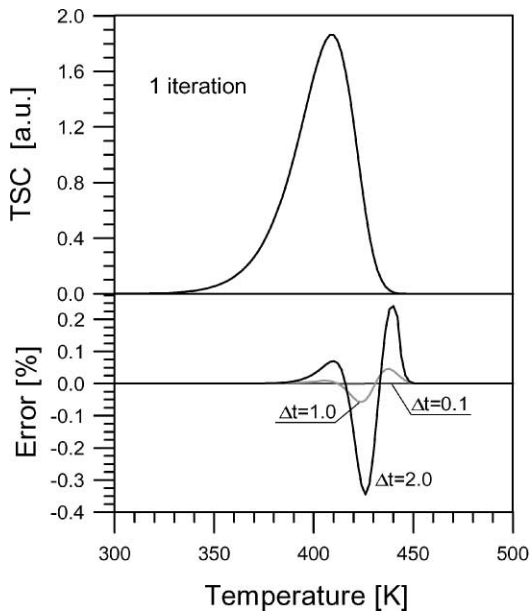


Fig. 2. Illustration of the influence of the step of computation Δt on the accuracy of the QE method. Other parameters are the same as for Fig. 1.

reduces to four. To effectively apply a given formula to nonlinear fitting analysis, it is important that the whole curve must be quickly calculated for a given set of parameters. Eqs. (11) and (16) are fully analytical, however, calculation of TSC intensity in this case takes much more time than using QE Eq. (17) together with the iteration procedure defined by Eqs. (19)–(21). This is due to the integral appearing in Eqs. (11) and (16). The next advantage of the QE approximation over GOK and MOK is the accuracy. It was proved numerically [13], that QE conditions hold in most cases. Both GOK and MOK use the QE assumptions (4) and (5), however, in addition, the models replace the first kinetic equation (1a) with its simplified versions (3) and (13). Consequently, GOK and MOK are less accurate than QE. Another benefit of the QE equation is that all parameters have precise and well-defined sense. On the contrary, parameters b and c in GOK and MOK models are only formal. For all these reasons, the QE model is the superlative for determining trap parameters from experimentally collected TSC data.

References

- [1] R. Chen, S.W.S. McKeever, *Theory of Thermoluminescence and Related Phenomena*, World Scientific, Singapore, 1997.
- [2] S.W.S. McKeever, *Thermoluminescence of Solids*, Cambridge University Press, Cambridge, 1985.
- [3] C.E. May, J.A. Partridge, *J. Chem. Phys.* 40 (1964) 1401–1409.
- [4] R. Chen, *J. Mater. Sci.* 11 (1976) 1521–1541.
- [5] S.V. Moharil, *Phys. Stat. Solidi A* 73 (1982) 509–514.
- [6] A. Opanowicz, *Phys. Stat. Solidi A* 116 (1989) 343–348.
- [7] A. Mandowski, J. Świątek, *Radiat. Prot. Dosim.* 84 (1999) 123–126.
- [8] J.T. Randall, M.H.F. Wilkins, *Proc. R. Soc. A* 184 (1945) 366–389.
- [9] G.F.J. Garlick, A.F. Gibson, *Proc. R. Soc. London Sect. A* 60 (1948) 574.
- [10] A.C. Lewandowski, S.W.S. McKeever, *Phys. Rev. B* 43 (1991) 8163–8178.
- [11] A.C. Lewandowski, B.G. Markey, S.W.S. McKeever, *Phys. Rev. B* 49 (1994) 8029–8047.
- [12] A. Mandowski, J. Świątek, in: A.A. Konsta (Ed.), *Proc. of ISE'10, IEEE, Athens, 1999*, pp. 359–362.
- [13] A. Mandowski, J. Świątek, *Radiat. Prot. Dosim.* 65 (1995) 55–58.