CURVE FITTING METHODS IN THE ANALYSIS OF THERMALLY STIMULATED RELAXATION PHENOMENA

A. Mandowski, J. Świątek
Institute of Physics, Pedagogical University
ul. Armii Krajowej 13/15, 42-200 Częstochowa, Poland

INTRODUCTION

Due to mathematical complexity involved in the theoretical description of thermally stimulated relaxation (TSR) phenomena – *e.g.* thermoluminescence (TL), thermally stimulated conductivity (TSC), thermally stimulated exoelectron emission (TSEE), etc. – the analysis of the experimental data is very difficult. The situation even complicates when the measured spectrum consists of many overlapping peaks. To determine activation energies, frequency factors and other trap parameters from such spectra one has to deconvolute the curves for individual peaks attributed to particular trap levels. For these purposes, some approximate equations are used, usually based on the first or second order kinetics. These approximate models do not cover the variety of experimentally measured spectra. In crystalline solids it is usually assumed that trap levels have discrete distribution within the band gap. The most acceptable model [1,2] for the description of charge carriers kinetics during thermal stimulation is based on the following set of equations:

$$-\dot{n}_i = n_i \nu_i \exp\left(\frac{-E_i}{kT}\right) - n_c A_i (N_i - n_i), \qquad i=1..p, \tag{1a}$$

$$-\dot{m}_s = B_s m_s n_c, \qquad s=1..k, \tag{1b}$$

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

where E_i stands for the activation energy; N_i, n_i, and m_s denote the concentrations of trap states, electrons trapped in 'active' traps and holes trapped in RC. M stands for the number of electrons in the thermally disconnected traps (deep traps), *i.e.* traps that are not emptied during the experiment. A_i and B_s stand for the trapping and recombination probabilities, respectively, and ν_i is the frequency factor. Conductivity of the sample (TSC) is assumed to be proportional to n_c and luminescence (TL) is proportional to $(-\dot{m})$. TSC or TL spectrum usually consists of a series of peaks attributed to different trap levels of the material.

Many methods were developed for evaluating trap parameters from these spectra, unfortunately the set of equations (1) has no analytical solutions even for the simplest case of one trap level and one recombination centre. Therefore to analyse TSC and TL experiments one has to approximate eq. (1) to get analytical expressions. In the case of thermoluminescence, the most popular approximation is the general order kinetics (GOK) model [3,4,5]. Unfortunately, it was proved numerically that in many cases the model gives erroneous results [6]. In this paper we propose a new curve fitting algorithm for the analysis of the experimental data. The algorithm based on the fundamental kinetic equations allows to analyse a single peak, as well as to deconvolute complex curves.

QUASI-EQUILIBRIUM APPROXIMATION

Thermoluminescence

Recently Mandowski and Świątek [7] suggested to use approximate equations that can be written in the form of 'corrected initial rise' method. It was proved numerically that the validity of this approximation is not limited only to an initial part of a TL peak, but it usually covers the whole measurable TL curve. The first reported approximation is:

$$\frac{-E}{kT(t)} = \ln\left[\mathrm{L}\ (t)\right] + \ln\left\{\frac{1}{M+\mathrm{U}_{\ \infty}-\mathrm{U}\ (t)}\left[\frac{1}{\mathrm{U}_{\ \infty}-\mathrm{U}\ (t)}+L_1\right]\right\} + \ln(L_2), \qquad (2)$$

where the constants L_1 and L_2 are defined by:

$$L_1 = \frac{B - A}{AN + BM}, \tag{3}$$

$$L_2 = \frac{AN + BM}{\nu B}. \tag{4}$$

The variables L and U are defined as follows:

$$\mathrm{L}(t) \equiv -\dot{m}(t), \tag{5}$$

$$\mathrm{U}(t) \equiv \int_0^t \mathrm{L}(t')dt' = m_0 - m(t), \tag{6}$$

and $U_\infty = n_0$. L and U are directly proportional to observed TL intensity J and the area under TL curve respectively. It can be shown that the equation (2) is mathematically equivalent to a well-known quasi-equilibrium (QE) approximation of Kelly and Bräunlich [8] when deep trap levels are also taken into account. Typical application of the above equation (2) consists in such calculation of two unknown parameters L_1 and M occuring in the correction term

$$\Phi(T) = \ln\left\{\frac{1}{M + \mathrm{U}_\infty - \mathrm{U}(t)}\left[\frac{1}{\mathrm{U}_\infty - \mathrm{U}(t)} + L_1\right]\right\}, \tag{7}$$

that the plot of $\{\ln[J(T)] + \Phi(T)\}$ *vs.* $1/T$ gives a straight line. With all its simplicity and accuracy, this method can be used only to analyse a single, well separated peak. Therefore it cannot be applied to deconvolution.

Let us define new normalised variables for the TL intensity, the peak area and other symbols:

$$j_{\mathrm{TL}}(t) = \mathrm{L}(t)/n_0, \tag{8}$$

$$u(t) = \mathrm{U}(t)/n_0. \tag{9}$$

$$r = A/B, \tag{10}$$

$$\eta_0 = n_0/N. \tag{11}$$

$$\mu_0 = M/n_0. \tag{12}$$

$$\varepsilon(t) = \exp\left(-\frac{E}{kT(t)}\right). \tag{13}$$

Now, equation (2) may be written:

$$j_{TL}(t) = \frac{\nu\varepsilon(t)\left[\mu_0 + 1 - u(t)\right]\left[1 - u(t)\right]}{\mu_0 + r/\eta_0 + (1-r)\left[1 - u(t)\right]}. \tag{14}$$

Mathematically, the equation (14) is a non-linear integral equation with respect to $j(t)$.

Thermally Stimulated Conductivity

The same approximation written for TSC has the form:

$$\frac{-E}{kT(t)} = \ln\left[n_c(t)\right] + \ln\left\{\frac{K_1}{1 - \exp\left[B\left(S(t) - S_\infty\right)\right]} - 1\right\} + \ln(K_2), \tag{15}$$

where K_1 and K_2 denote:

$$K_1 = \frac{AN + BM}{A(N + M)}, \tag{16}$$

and

$$K_2 = \frac{A(N + M)}{\nu M}. \tag{17}$$

$S(t)$ and S_∞ denote areas under TSC curve [9]. These are defined as follows:

$$S(t) = \int_0^t n_c(t')dt'. \tag{18}$$

$$S_\infty \equiv \lim_{t\to\infty} S(t) = \frac{1}{B}\ln\left(1 + \frac{n_0}{M}\right). \tag{19}$$

Using the definitions (10)-(13) allows to write equation (15) in the form:

$$j_{TSC}(t) = \frac{\chi\nu\eta_0\varepsilon(t)\left[1 + \mu_0 - \mu_0\exp(\bar{B}S)\right]}{B\left[(1-r)\eta_0(1+\mu_0) + r(1+\eta_0\mu_0)\exp(\bar{B}S)\right]}, \tag{20}$$

where $j_{TSC}(t)$ denotes the TSC current $j_{TSC}(t) = \chi n_c(t)$, χ is a proportionality factor and $\overline{B} = \chi B$. Considering that S is represented by the integral (18), hence (20) is a non-linear integral equation.

THE ALGORITHM

Due to their mathematical complexity, equations (14) and (20) could not be applied directly to the analysis of a given TL or TSC curve. However, we can suggest a very effective algorithm for solving the equations. To write it together for both processes, we will denote intensities $j_{TL}(t)$ and $j_{TSC}(t)$ by $j(t)$. The areas $u(t)$ and $S(t)$ we will denote by $\sigma(t)$. Let us assume that fitting algorithm requires computation of $(k_{end}+1)$ values $j_k=j(t_k)$ for equidistant time intervals $\Delta t=t_{k+1}-t_k$. It is obvious to assume $j_0=0$ and $\sigma_0=\sigma(t_0)=0$. Then, subsequent values can be calculated from the following equation:

$$j_k = \Psi(\sigma_k), \tag{21}$$

where Ψ denotes the right-hand side of eqs. (14) and (20). The key point is the method of estimation of σ_k. Below, some formulae are suggested:

(i) σ_k not approximated

$$\sigma_k = \sigma_{k-1}. \tag{22}$$

(ii) rectangular approximation

$$\sigma_k = \sigma_{k-1} + j_{k-1}\Delta t. \tag{23}$$

(iii) trapezoidal approximation with derivative estimation

$$\sigma_k = \sigma_{k-1} + j_{k-1}\Delta t + \frac{j_{k-1} - j_{k-2}}{2}\Delta t = \sigma_{k-1} + \frac{3j_{k-1} - j_{k-2}}{2}\Delta t. \tag{24}$$

After calculating first estimation $j_k^{(1)}$, the following correction in the variable σ_k is required:

$$\sigma_k^{(2)} = \sigma_{k-1} + \frac{j_k^{(1)} + j_{k-1}}{2}\Delta t. \tag{25}$$

where $j_k^{(1)}$ denotes the previously calculated intensity. Using these methods, the process of calculating j_k and then correcting σ_k may be repeated many times to increase accuracy. Exclusively for eq. (14) an additional method may be suggested:

(iv) trapezoidal approximation

$$\sigma_k = \sigma_{k-1} + \frac{j_k + j_{k-1}}{2}\Delta t\,. \qquad (26)$$

Using the last method (iv) one needs to calculate j_k by solving quadratic equation.

NUMERICAL CALCULATIONS

To verify accuracy of the methods (i)-(iii), many TSC and TL curves were calculated for different trap parameters. In each case the results were compared to exact numerical solution of the basic set of differential equations (1). As the equations are of "stiff" type the numerical solutions were obtained by using the Gear method [10]. Typical examples for TSC are presented in Figs 1-4. A comparison of the three methods in Fig. 1 shows that the method (iii) is the most accurate . Relative numerical errors were defined as $(j_{acc} - j_{calc})/j_{max}$, where j_{acc} denotes the intensity calculated by solving eqs. (1), j_{calc} denotes the intensity calculated by one of the methods (i) - (iii) and j_{max} denotes the peak maximum.

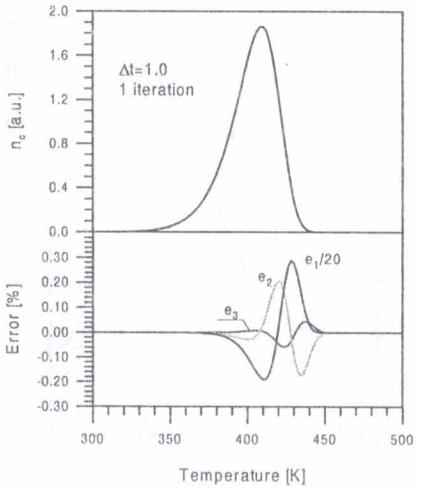

Figure 1. Comparison of various methods (i)-(iii) for one iteration. Curves e_1, e_2, e_3 represent relative errors of each of these methods. Trap parameters: E=0.9eV, $\nu=10^{10}s^{-1}$, β=1K/s, r=0, η_0=1, μ_0=1, χ=1. Computation step Δt=1.0s.

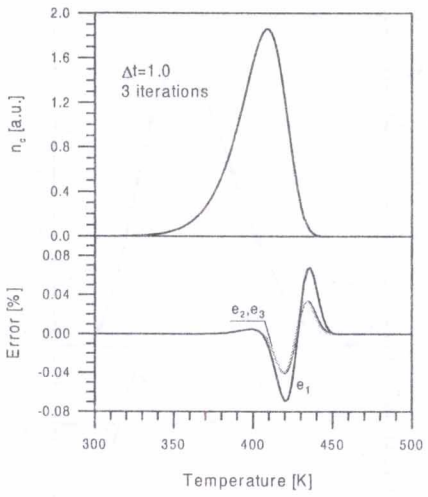

Figure 2. Comparison of various methods (i)-(iii) with three subsequent iterations using eqs. (12) and (16). Other parameters are the same as for Fig. 1.

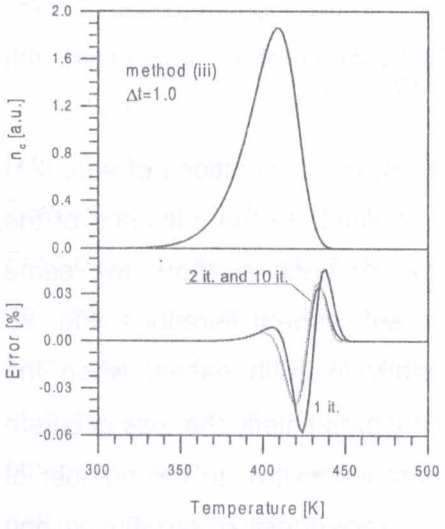

Figure 3. Illustration of the influence of the number of iterations on the accuracy of the method (iii). Other parameters are the same as for Fig. 1.

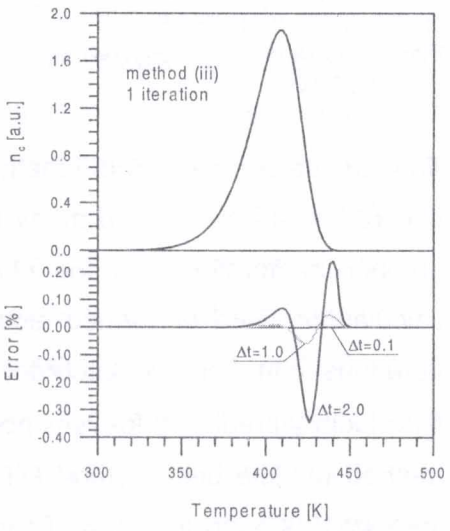

Figure 4. Illustration of the influence of the step of computation Δt on the accuracy of the method (iii). Other parameters are the same as for Fig. 1.

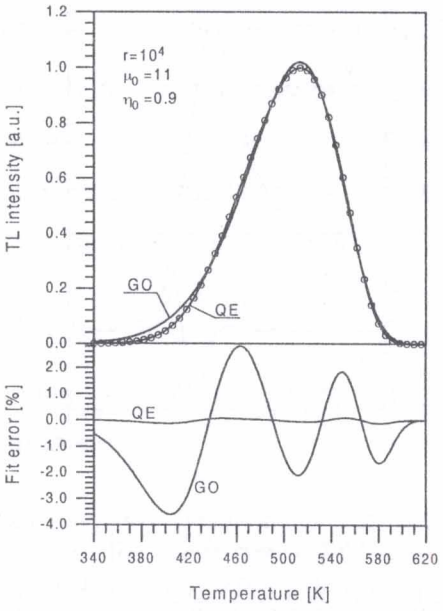

Figure 5. Application of GOK model and QE approximation (eq. 14) for fitting to numerically generated TL curve (O). Input parameters: E=0.9 eV, $\nu=10^{10}$ s^{-1}, $r=10^4$, $N=10^{15}$ cm^{-3}, $B=10^{-11}$ cm^3/s, $\mu_0=11$ and $\eta_0=0.9$.
Fitted parameters: $E_{GOK}=0.52$ eV, $E_{QE}=0.87$ eV.

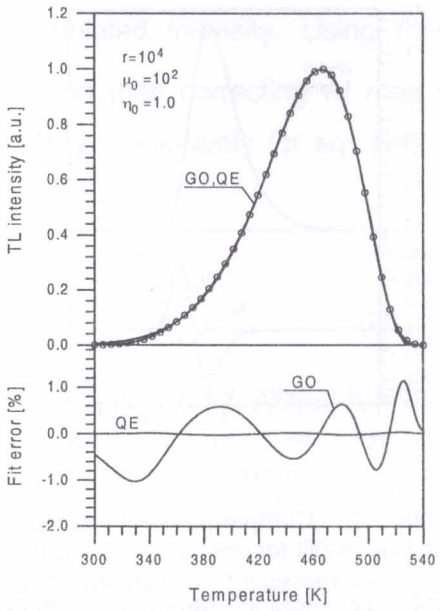

Figure 6. Application of GOK model and QE approximation (eq. 14) for fitting to numerically generated TL curve (O). Input parameters: E=0.9 eV, $\nu=10^{10}$ s^{-1}, $r=10^4$, $N=10^{15}$ cm^{-3}, $B=10^{-11}$ cm^3/s, $\mu_0=10^2$ and $\eta_0=1.0$.
Fitted parameters: $E_{GOK}=0.44$ eV, $E_{QE}=0.90$ eV.

To increase accuracy of the methods (i)-(iii), the calculations of eqs. (21) and (25) can be repeated many times. To illustrate the influence of the number of iterations on the correctness of each method, the same calculations were performed also with 3 subsequent iterations (Fig. 2). Iterations can improve accuracy especially in such cases, when the introductory prediction for σ_k is poor. It concerns chiefly the less accurate method (i). The best method (iii) is almost insensitive to the number of iterations as seen in Fig. 3. To increase preciseness of calculation one has to decrease the step of computation Δt. As it is shown in Fig. 4, even calculating TSC with rather high step Δt=2s, the relative error we obtain is less than $4\cdot10^{-3}$. Decreasing the step down to 0.1s results in excellent accuracy of $10^{-5}..10^{-6}$ that is comparable to the accuracy of the quasi-

equilibrium approximation itself. Almost the same results were obtained for TL. The method (iv) appeared to be as high accurate as the method (iii). These superior properties allow to apply the quasi-equilibrium equation for determination of trap parameters from TSR curves by using non-linear fitting techniques. Preliminary results show that the activation energy can be determined this way with a very low error. A comparison of GOK and QE fitting results is presented in Figs. 5,6. In most applications the theoretical curve can be determined with the computation step Δt=2s or higher. Therefore the curve fitting algorithm is very fast.

CONCLUSIONS

Theoretical analysis of TSR data is difficult due to complexity of the basic set of kinetic equations (1). Many approximations developed for this purpose – based on the assumption of first- or second-order kinetics [11,12] – are oversimplified, some other – *e.g.* based on the assumption of general order kinetics [4,5] – contain some non-physical parameters. In this paper a new numerical method for the calculation of TL and TSC curves with the quasi-equilibrium approximation was proposed. Very good properties of this approximation were proved in some earlier papers [6,7]. The advantages of using the quasi-equilibrium model are indisputable. First of all one uses a physical model having all its parameters clearly defined. Furthermore, its accuracy is excellent and justified numerically. Numerical methods proposed here allow calculation of TL or TSC with a high computation step Δt and a very high accuracy. When applied to a fitting program, it allows to use high steps at the begining of the calculations and then, when a first approximation is achieved Δt may be decreased to get the best accuracy. Such an algorithm allows to analyse a single peak, as well as to deconvolute complex curves.

REFERENCES

1. R. Chen and S.W.S. McKeever, *Theory of Thermoluminescence and Related Phenomena.*, Singapore: World Scientific, 1997.
2. R. Chen and Y. Kirsch, *Analysis of Thermally Stimulated Processes*, Pergamon Press, Oxford, 1981
3. C.E. May and J.A. Partridge, Thermoluminescence kinetics of alpha-irradiated halides, *J. Chem Phys.* 40(5), pp. 1401-1409, 1964.
4. R. Chen, Glow curves with general order kinetics, *J. Electrochem. Soc.* 116, pp. 1254-1257, 1969.
5. R. Chen, Review: Methods for kinetic analysis of thermally stimulated processes, *J. Mater. Sci* 11, 1521-1541, 1976
6. A. Mandowski, J. Świątek, On the numerical deconvolution of thermoluminescence spectra, in *International Conference of Solid State Crystals'98: Single Crystal Growth, Characterization and Applications*, ed. Andrzej Majchrowski and Jerzy Zieliński, Proc. SPIE 3724, 203-208, 1998
7. Mandowski and J. Świątek, Determination of Trap Parameters from Generalised Initial Rise Equations, *Radiat. Prot. Dosim.* 65(1-4), pp. 55-58, 1995.
8. Mandowski and J. Świątek, A method for determining the density of deep traps by using the simultaneous TL/TSC measurement, *J. Phys. D: Appl. Phys.* 25, 1829-1833, 1992
9. C.W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations.* Englewood Cliffs: Prentice-Hall, 1971
10. J.T. Randall, and M.H.F. Wilkins, Phosphorescence and electron traps: I. The study of trap distributions, *Proc. Roy. Soc.* A 184, pp. 366-389, 1945.
11. G.F.J. Garlick, and A.F. Gibson, The electron trap mechanism of luminescence in sulphide and silicate phosphors, *Proc. R. Soc. London*, Sect. A 60, p. 574, 1948.