ON THE APPLICATION OF QUASI-EQUILIBRIUM CONDITIONS TO THE NUMERICAL ANALYSIS OF SIMULTANEOUS TL/TSC MEASUREMENTS

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ABSTRACT

Thermally stimulated relaxation (TSR) phenomena are analysed on the basis of several analytical approximations. These approximations - e.g. the general order kinetics (GOK) model and the mixed order kinetics (MOK) are usually oversimplified with respect to the real phenomena under study. Therefore, the application of these equations often leads to erroneous results or misleading interpretations. Some recent papers have shown the advantage of using certain formulae directly derived from the simple trap model to the analysis of thermoluminescence (TL) and thermally stimulated conductivity (TSC) experiments. These equations allow to construct very fast and efficient algorithms to determine trap parameters by application of nonlinear fitting methods. The only disadvantage of this approach is a relatively high number of unknown parameters. To overcome the difficulty we applied the equations to simultaneous TL/TSC measurements, which are closely related phenomena. Using some previously derived relations it was possible to reduce the number of parameters of the model. To test the accuracy of the method the fitting algorithm was applied to a series of computer generated TL/TSC curves calculated from the simple trap model equations.

INTRODUCTION

Thermally stimulated relaxation (TSR) phenomena are important tools in characterising high-resistivity materials (for review see Chen and McKeever, 1997). Using thermoluminescence (TL), thermally stimulated conductivity (TSC) or other methods one is able to get information concerning trap structure of the dielectrics under study. Unfortunately, the kinetics of the basic TSR processes is complex. This makes the analysis of the experimental data very difficult. Recently, it was shown by many authors (e.g. see Mandowski and Świątek, 1999a and Sunta et al. 1999a) that some classical approximations (e.g. general order kinetics - GOK) are not so accurate as it was believed earlier. For example - the GOK model would give very inaccurate results when applied to numerical fitting of the model to experimental

data. The error in estimation the activation energy would be greater than 50%. In crystalline solids, it is usually assumed that trap levels have discrete distribution within the band gap. The most acceptable model for the description of charge carriers kinetics during thermal stimulation is based on the following set of equations:

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

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

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

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 recombination centres (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 v_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 this paper, we propose a new curve fitting algorithm for the analysis of the TL/TSC simultaneous measurements.

QUASI-EQUILIBRIUM APPROXIMATION

TL

Recently Mandowski and Świątek (1996) suggested using 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 usually it covers the whole measurable TL curve. The first reported approximation is:

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

where the constants L_1 and L_2 are defined by:

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

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

The variables L and U are defined as follows:

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

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

and $U_\infty = n_0$. L and U are directly proportional to observed TL intensity J_{TL} and the area under TL curve respectively. It can be shown that the equation (2) is mathematically equivalent to the well-known quasi-equilibrium (QE) approximation of Kelly and Bräunlich (1972) when deep trap levels are also taken into account. The validity of QE conditions were questioned by Lewandowski and McKeever (1992), however more detailed numerical calculations showed later that their objections were not justified by others (Opanowicz and Przybyszewski 1995, Mandowski and Świątek 1996, Sunta et al. 1999b, 1999c). Contrary, it was shown that QE conditions hold for most typical trap parameters. Let us define new normalised variables for the TL intensity, the peak area and other symbols:

$$\Phi_1(T) = \ln\left\{\frac{1}{M + U_\infty - U(t)}\left[\frac{1}{U_\infty - U(t)} + L_1\right]\right\}, \tag{7}$$

$$u(t) = U(t)/n_0. \tag{8}$$

$$r = A/B, \tag{9}$$

$$\eta_0 = n_0/N. \tag{10}$$

$$\mu_0 = M/n_0. \tag{11}$$

$$\varepsilon(t) = \exp\left(-\frac{E}{kT(t)}\right). \tag{12}$$

Now, equation (2) may be written:

$$j_{TL}(t) = \frac{v\varepsilon(t)[\mu_0 + 1 - u(t)][1 - u(t)]}{\mu_0 + r/\eta_0 + (1-r)[1-u(t)]}. \tag{13}$$

Mathematically, equation (13) is a non-linear integral equation with respect to $j_{TL}(t)$.

TSC

The same approximation written for TSC has the form (Mandowski and Świątek, 1999b):

$$\frac{-E}{kT(t)} = \ln[n_c(t)] + \ln\left\{\frac{K_1}{1 - \exp[-B\Delta(t)]} - 1\right\} + \ln(K_2), \tag{14}$$

where K_1 and K_2 denote:

$$K_1 = \frac{AN + BM}{A(N+M)}, \tag{15}$$

and

$$K_2 = \frac{AN + BM}{vM}. \tag{16}$$

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

$$S(t) = \int_0^t n_c(t') dt'. \tag{17}$$

$$S_\infty \equiv \lim_{t \to \infty} S(t) = \frac{1}{B} \ln\left(1 + \frac{n_0}{M}\right). \tag{18}$$

Using definitions (7)-(12) allows writing equation (14) in the form:

$$n_c(t) = \frac{\nu \eta_0 \varepsilon(t)[1 + \mu_0 - \mu_0 \exp(\beta S)]}{B[(1-r)\eta_0(1+\mu_0) + r(1 + \eta_0\mu_0)\exp(\beta S)]}, \tag{19}$$

where $n_c(t)$ is a quantity that is proprtional to the TSC current J_{TSC}. Considering that S is represented by the integral (17), hence (19) is also a non-linear integral equation.

TL/TSC equation

Experimentally measured TL and TSC intensities are proportional to the previously defined variables: $J_{TL} = j_{TL}/\chi_L$ and $J_{TSC} = n_c/\chi_c$, where χ_L and χ_c are constants. Comparing the basic equations (13,19) and using some earlier derived relations between TL and TSC (Mandowski and Świątek, 1992) one comes to the following equation:

$$\frac{-E}{kT(t)} = \ln[n_c(t)] + \ln\left\{\frac{K_1}{1 - \exp[-B\Delta(t)]} - 1\right\} + \ln(K_2), \tag{20}$$

where $R(t)$ defines the ratio:

$$R(t) = \frac{j_{TL}}{J_{TSC}} \tag{21}$$

and δ, R_0 and K_3 are constants:

$$\delta = \frac{1 - r}{1 + \frac{r}{\omega}} \tag{22}$$

$$R_0 = \frac{B\mu_0\chi_c}{\chi_L} \tag{23}$$

$$K_3 = \frac{B\chi_c}{\nu}\left(1 + \frac{r}{\omega}\right) \tag{24}$$

In the above equations $\omega = \mu_0\eta_0 \equiv M/N$ denotes the relative concentration of deep traps. For an arbitrary TL/TSC measurement data the plot of the right-hand side of eq. (20) should give a straight line against $(1/kT)$. As the measure of linearity one may choose the correlation coefficient, which in the case of eq. (13) depends only on two parameters: δ and R_0. Therefore, it is easy to fit the parameters to optimize the correlation coefficient r_c.

NUMERICAL VERIFICATION

For a given one trap - one recombination centre system the ratio $R(t)$ is a decreasing function (fig. 1). To check the validity and usefulness of eq. (20) we applied the method to a computer generated TL/TSC curves. By using Monte Carlo optimization method, the best values of δ and R_0 were found (for which the correlation coefficient is closest to -1). The slope of the fitted function gave us the activation energy E. For all tested curves, the agreement was excellent. Several best values found in the cycle of 10^6 Monte Carlo trials are listed in table 1. Typical variation of the correlation coefficient r_c with δ and R_0 can be seen in fig.2. Although the changes are only slight - here the plot of r_c^4 was done. Sharp boundaries indicate allowed range of fitted parameters. The picture gives also a good explanation for why did we choose the Monte Carlo method instead of many other ones (e.g. the steepest descent or similar gradients methods). Simply the range of parameters is easier to be kept under control. In fig. 3 it is shown the dependence of the estimated activation energy on the correlation coefficient found during a single run of the Monte Carlo algorithm for the same data as in fig. 1 and the table 1. Looking at the diagram it is obvious that a reasonable value of the activation energy could be determined by averaging several of the best points of the plot. Such an average is presented also in table 1.
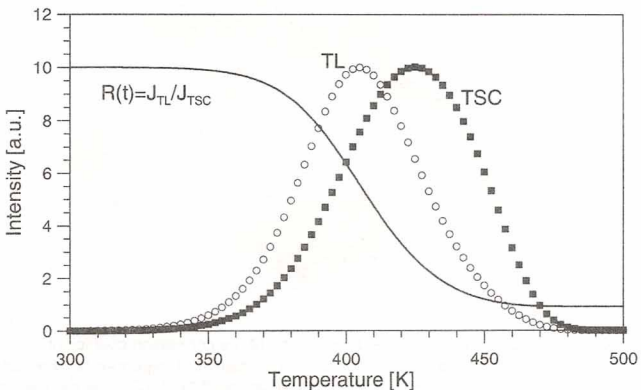

Fig.1. Typical TL and TSC glow curves and the ratio R(t)=TL/TSC calculated in the framework of the simple trap model defined by eqs. (1)

Table 1. Several cases with the best values of the correlation coefficient r_c found during the Monte Carlo optimization calculations. The number of trials was 10^6

correlation coefficient r_c	$E \pm \Delta E$ [eV]	δ	R_0
-0.999999807	0.91290 ± 0.00005	-5.183E-0003	1005
-0.999999718	0.90612 ± 0.00006	-2.935E-0003	1001
-0.999999268	0.87137 ± 0.00010	1.282E-0002	992
-0.999999239	0.87307 ± 0.00010	1.140E-0002	990
-0.999999212	0.92762 ± 0.00011	-1.118E-0002	1009
Average values:	0.898 ± 0.012	0.001 ± 0.005	999 ± 4
Input values:	0.9	0.0	-

It should be noted that no considerable differences were found due to the range of the temperatures in which the basic equation (20) were fitted. Nonetheless, somewhat bigger errors were noticed while exploring the equation only in the linear region of $R(t)$ (e.g. within a narrow region near the TL maximum - see fig.1).
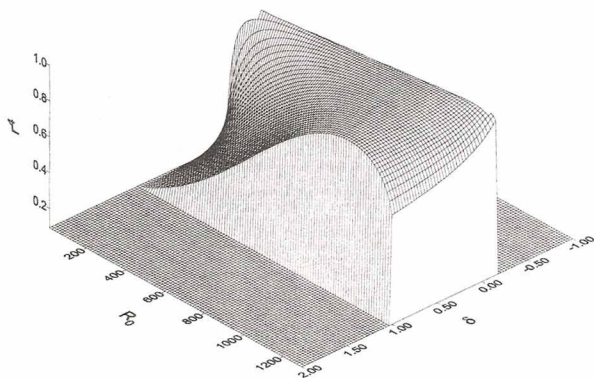

Fig. 2. 3-D representation of the dependence of the correlation coefficient r_c on the fitting parameters δ and R_0. To illustrate more clearly the dependence, the surface represents the fourth power of the correlation coefficient r_c^4. The diagram was calculated for the data presented in fig. 1
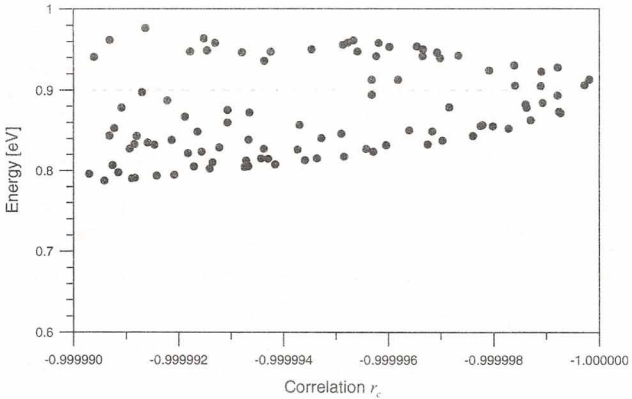
Fig. 3. The dependence of the estimated activation energy on the correlation coefficient r_c found by the Monte Carlo "best fit" algorithm. The dotted line represents the true (input) value E=0.9 eV

CONCLUSIONS

A new equation for simultaneous TL/TSC measurement was presented (20). It is valid for a single trap and a single recombination centre system (with a series of "deep traps") under quasi-equilibrium conditions. Analogous considerations relating simultaneous TL/TSC measurements were presented also in earlier papers (e.g. Bindi et al. 1994, Opanowicz 1999) however the method presented here is presumably the most accurate and simplest one with respect to the estimation of the activation energy. Numerical calculation shows that it is easy applicable to any TL/TSC measurements in every case when the single-level trap approximation is valid. The method requires calculation of only two unknown parameters: δ and R_0, therefore, the fit is easy to be performed, and the obtained results are credible.

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