Early View publication on www.interscience.wiley.com
(issue and page numbers not yet assigned;
citable using Digital Object Identifier – **DOI**)

phys. stat. sol. (a), 1–9 (2008) / **DOI** 10.1002/pssa.200723470

physica status solidi a
www.pss-a.com
applications and materials science

Thermoluminescence glow-peak shape methods based on mixed order kinetics

George Kitis[*,1], **Reuven Chen**[2], **and Vasilis Pagonis**[3]

[1] Aristotle University of Thessaloniki, Nuclear Physics Laboratory, 54124 Thessaloniki, Greece
[2] Raymond and Beverly Sackler School of Physics and Astronomy, Tel-Aviv University, Tel-Aviv 69978, Israel
[3] Physics Department, McDaniel College, Westminster, MD 21157, USA

Received 28 September 2007, revised 8 December 2007, accepted 13 December 2007
Published online 19 March 2008

PACS 78.60.Kn, 87.66.Sq

[*] Corresponding author: e-mail gkitis@auth.gr, Phone: +00 3023110998175, Fax: +00 312310998175

The peak shape methods used in thermoluminescence (TL) theory to evaluate the activation energy E, are based on first and second order kinetics equations. For the intermediate kinetic orders the peak shape methods are based on the empirical theory of general order kinetics. In the present work we derive peak shape methods based on the physically meaningful mixed order kinetics model. The derived equations are tested for their accuracy and are compared with other peak shape methods existing in the TL literature.

1 Introduction The basic phenomenological Thermoluminescence (TL) theory predicts two expressions for the description of experimental TL glow-peaks. These expressions are derived from the first order kinetics theory of Randall and Wilkins [1] and from the second order kinetics theory of Garlick and Gibson [2]. However, there are many reported experimental glow-peaks with a shape that does not correspond to first or second kinetics order, but rather to a kinetics order between the two. A purely empirical theory to describe these intermediate kinetics order was suggested by May and Partridge [3]. Chen et al. [4] suggested the use of mixed order kinetic theory to describe these cases of intermediate kinetic order.

The shape of a TL glow-peak plays an important role in basic research and in TL applications. In the case of basic TL research it is the basis of important and convenient methods for calculating the trapping parameters of distinct energy levels within the crystal. These methods are based on measurements of a few points on the glow-peak, as shown in Fig. 1.

Early work concentrated on the development of convenient expressions for calculating the activation energy E of trapping levels [5–7]. The term peak shape method is reserved in the TL literature for such methods, although there are other methods for finding E which are also based on the glow-peak shape (i.e. curve fitting methods) [8, 9]. Chen [10] summarized all pre-existing methods and gave a detailed methodology for deriving the coefficients of the expressions for first and second order kinetics.

For the case of intermediate kinetic orders the peak shape method coefficients were also evaluated by Chen [11] by (i) calculating the coefficients for first order kinetics, (ii) calculating the coefficients for second-order kinetics and (iii) using a linear interpolation method to obtain expressions for the intermediate kinetic orders as a function of the symmetry factor μ_g, which was found to be between 0.42 and 0.52 for first and second order kinetics. Recently, Kitis and Pagonis [12] provided a theoretical foundation for the Chen expressions for intermediate kinetics, by using the empirical model of general order kinetics, respectively. In the current status of TL theory, the region of intermediate kinetics order is described by empirical models.

Sunta et al. [13] tested the capability of the mixed and general order kinetics to fit synthetic glow-peaks derived from various phenomenological models, such as the one trap and one recombination centre model (OTOR), non interactive multi trap system (NMTS) and interactive multi-trap system (IMTS). They found that the mixed order kinetics model fits the NMTS and IMTS glow-peaks much more successfully than the general kinetics order. On the other hand, the mixed order kinetics fits poorly the TL

peaks produced by the OTOR model. Sunta et al. [13] attributed this result to the fact that the OTOR model is too simple and physically unrealistic. Their net conclusion was that mixed order kinetics is clearly superior to general kinetics order in the description of experimental TL glow-peaks.

The aim of the present work is to obtain new peak shape methods for evaluating the activation energy E, which are based on the physically meaningful model of mixed order kinetics.

2 Analytical mixed order TL expressions The mixed order kinetics equation as given by Chen et al. [4] (see also Chen and Kirsh [8], Chen and McKeever [9]), is:

$$I(T) = -\frac{\mathrm{d}n}{\mathrm{d}t} = n(n+C)\,s' \cdot \exp\left(-\frac{E}{kT}\right), \tag{1}$$

where n (cm^{-3}) is the concentration of electrons in traps, E (eV) is the activation energy, T (K) the temperature and C is the concentration of electrons trapped at some kind of deep traps. The solution of Eq. (1) for a linear heating rate β contains the well known exponential integral, which can be approximated by the following asymptotic series:

$$\int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right)\mathrm{d}T' \approx T\exp\left(-\frac{E}{kT}\right) \times \sum_{n=1}\left(\frac{kT}{E}\right)^{n}(-1)^{n-1}\,n!, \tag{2}$$

where T is larger from T_0 by at least a few degrees. By considering, for the sake of simplicity only two terms of the above asymptotic series, the quasi-analytical solution of Eq. (1) is:

$$I(T) = \alpha C^2 s' \cdot \exp\left(-\frac{E}{kT}\right)\cdot\frac{F(T)}{(F(T)-\alpha)^2}, \tag{3}$$

with

$$F(T) = \exp\left[\frac{Cs'kT^2}{\beta E}\cdot\exp\left(-\frac{E}{kT}\right)\cdot(1-\Delta)\right], \tag{4}$$

where $\alpha = n_0/(n_0 + C)$, $s' = s/(N + C)$, $\Delta = 2kT/E$, N (cm^{-3}) is the concentration of available electron traps, n_0 (cm^{-3}) the concentration of trapped electrons and s (s^{-1}) the frequency factor.

The condition for maximum is found by equating the derivative of Eq. (3) to zero, i.e.

$$\frac{\beta E}{kT_{\mathrm{m}}^2} = \frac{F_{\mathrm{m}}+\alpha}{F_{\mathrm{m}}-\alpha}\cdot Cs'\cdot\exp\left(-\frac{E}{kT_{\mathrm{m}}}\right), \tag{5}$$

where T_{m} is the temperature at glow-peak maximum intensity and F_{m} the value of $F(T)$ at $T = T_{\mathrm{m}}$.

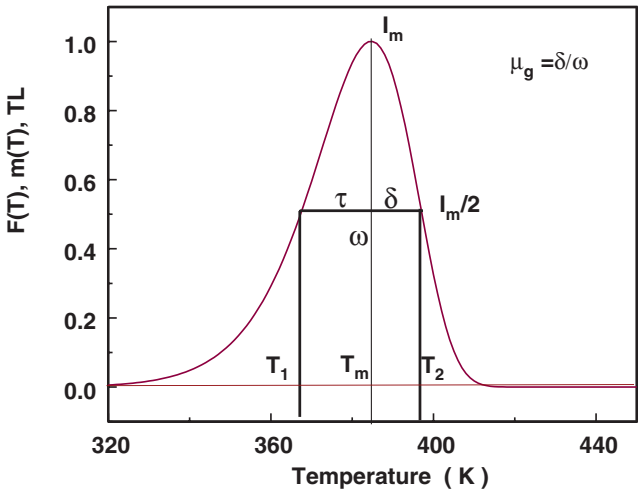

Figure 1 (online colour at: www.pss-a.com) Geometrical characteristics of a single glow-peak.

3 Geometrical characteristics of a single glow-peak The peak shape methods are based on certain characteristics of a single glow-peak, shown in Fig. 1, namely the peak maximum temperature T_{m}, and the temperatures at half maximum TL intensity T_1 and T_2 at the low and high temperature side of the glow-peak respectively. These quantities are used to define further the widths $\omega = T_2 - T_1$, $\delta = T_2 - T_{\mathrm{m}}$ and $\tau = T_{\mathrm{m}} - T_1$ as well as the symmetry factor of the glow-peak $\mu_{\mathrm{g}} = \delta/\omega$.

The derivation of the existing peak shape methods is based on the so-called triangle assumption, which can be expressed in three different ways, each one leading to an individual family of peak shape methods. In the form given by Chen [10] these are

$$\frac{\omega I_{\mathrm{m}}}{\beta n_0} = C_\omega\,, \tag{6}$$

$$\frac{\delta I_{\mathrm{m}}}{\beta n_{\mathrm{m}}} = C_\delta\,, \tag{7}$$

$$\frac{\tau I_{\mathrm{m}}}{\beta (n_0 - n_{\mathrm{m}})} = C_\tau\,, \tag{8}$$

with

$$n_{\mathrm{m}} = \int_{t_{\mathrm{m}}}^{\infty} I\,\mathrm{d}t\,, \tag{9}$$

where I_{m} is the peak maximum intensity, n_{m} the high temperature half integral of the glow-peak and C_ω, C_δ and C_τ are quantities, which characterize the degree by which the area of a single glow-peak approaches the area of a triangle. These quantities were found to vary extremely slowly for a given kinetic order and for a very wide range of kinetic parameters (E, s), and are called pseudo-constants. These pseudo-constants vary only a little for all glow-peaks derived using activation energies in the region of 0.1–1.6 eV and frequency factors in the region of 10^5–10^{13} s^{-1} [10].

Their values can be estimated as a function of the parameter α by producing synthetic glow-peaks using Eq. (3).

In order to derive the peak shape formulas using Eqs. (6)–(8), one has to evaluate the terms I_m/n_0, n_m/n_0 and I_m/n_m from the analytical TL expressions.

4 Derivation of the peak shape methods

4.1 Derivation of I_m/n_0 By considering Eq. (3) for $T = T_m$ we obtain

$$I_m = \alpha C^2 s' \cdot \exp\left(-\frac{E}{kT_m}\right) \cdot \frac{F_m}{(F_m - \alpha)^2}. \tag{10}$$

Using the condition for the maximum given by Eq. (5) and taking into account that $\alpha = n_0/(n_0 + C)$ one obtains after some algebra

$$\frac{I_m}{n_0} = (1-\alpha) \cdot \frac{\beta E}{kT_m^2} \cdot \frac{F_m}{F_m^2 - \alpha^2}. \tag{11}$$

4.2 Derivation of n_m/n_0 and I_m/n_m Solving Eq. (1) one obtains

$$\alpha \cdot \frac{n_m + C}{n_m} = \exp\left[\frac{Cs'kT_m^2}{\beta E} \cdot \exp\left(-\frac{E}{kT_m}\right) \cdot (1 - \Delta_m)\right] = F_m, \tag{12}$$

from which after some algebra it is found that

$$\frac{n_m}{n_0} = \frac{1-\alpha}{F_m - \alpha} = \mu_g'. \tag{13}$$

According to Halperin and Braner [7] the quantity n_m/n_0, which represents the ratio of the high temperature half integral of a glow-peak to the total integral is the integral symmetry factor μ_g' of a glow-peak, which differs very slightly from the commonly used geometrical symmetry factor μ_g defined above.

By dividing Eq. (11) by Eq. (13) one obtains

$$\frac{I_m}{n_m} = \frac{\beta E}{kT_m^2} \cdot \frac{F_m}{F + \alpha}. \tag{14}$$

4.3 Method based on the total width (ω) From Eq. (6) one obtains

$$\frac{I_m}{n_0 \beta} = \frac{C_\omega}{\omega}. \tag{15}$$

Using Eq. (11) one obtains

$$E_\omega = C_\omega \cdot \frac{kT_m^2}{\omega} \cdot \frac{1}{1-\alpha} \cdot \frac{F_m^2 - a^2}{F_m}. \tag{16}$$

From Eq. (13) it is found that

$$F_m = \frac{1 + \alpha(\mu_g' - 1)}{\mu_g'}. \tag{17}$$

Taking into account Eq. (17), Eq. (16) becomes

$$E_\omega = c_\omega \cdot \frac{kT_m^2}{\omega}, \tag{18}$$

where

$$c_\omega = C_\omega \cdot \frac{1}{\mu_g'} \cdot \frac{F_m + \alpha}{F_m}. \tag{19}$$

4.4 Method based on the high temperature half-width (δ) From Eq. (7) one obtains

$$\frac{I_m}{n_m \beta} = \frac{C_\delta}{\delta}. \tag{20}$$

Using Eq. (14)

$$E_\delta = c_\delta \cdot \frac{kT_m^2}{\delta}, \tag{21}$$

with

$$c_\delta = C_\delta \cdot \frac{F_m + \alpha}{F_m}. \tag{22}$$

4.5 Method based on the low temperature half-width (τ) Equation (8) can be re-written as

$$\frac{n_0}{n_m} - 1 = \frac{\tau}{C_\tau} \cdot \frac{I_m}{\beta n_m}. \tag{23}$$

Replacing the terms $I_m/\beta n_m$ and n_0/n_m from Eq. (11) and (13) respectively, one obtains after some algebra

$$E_\tau = C_\tau \frac{kT_m^2}{\tau} \cdot \frac{F_m - 1}{1-\alpha} \cdot \frac{F_m + \alpha}{F_m}. \tag{24}$$

Taking into account Eq. (17), Eq. (24) becomes

$$E_\tau = c_\tau \cdot \frac{kT_m^2}{\tau}. \tag{25}$$

With

$$c_\tau = C_\tau \cdot \frac{1 - \mu_g'}{\mu_g'} \cdot \frac{F_m + \alpha}{F_m}. \tag{26}$$

5 Results

5.1 Numerical Evaluation of geometrical characteristics The geometrical characteristics of the glow-peaks were evaluated by simulating synthetic glow-peaks using Eq. (3). The asymptotic series of Eq. (2) used to derive Eq. (3) was not used, since the software used contains the exponential integral as a built-in function.

The numerical simulation of synthetic glow-peaks was performed by using very broad regions of the trapping parameters, in order to cover as many practical cases as possible. The activation energy was varied between 0.7 eV and 2 eV, the frequency factor between 10^7 s^{-1} and 10^{21} s^{-1}. The mixed order parameter α was varied from 0.01 to 0.99.

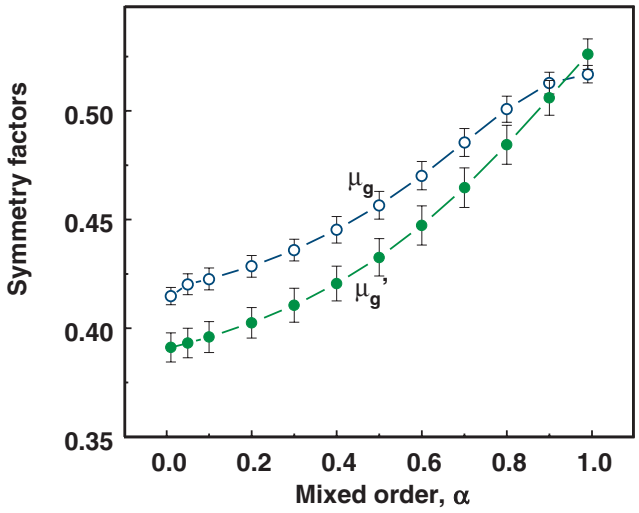

Figure 2 (online colour at: www.pss-a.com) Symmetry factors (a) Geometrical symmetry factor μ_g and (b) integral symmetry factor μ_g' as a function of the mixed order parameter α.

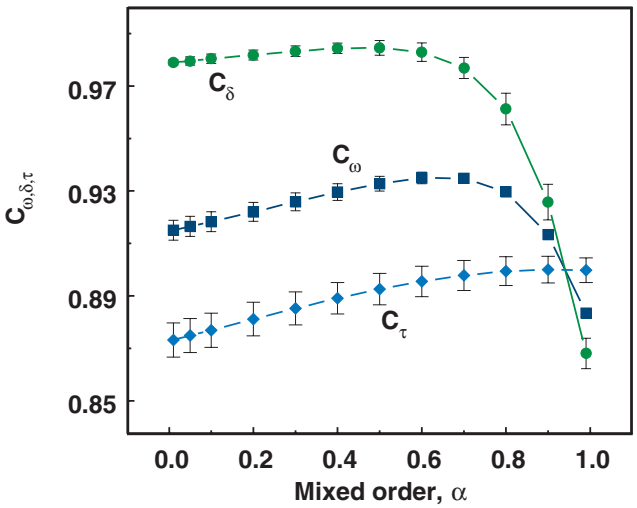

Figure 3 (online colour at: www.pss-a.com) Triangle assumption pseudo-constants as a function of the mixed order parameters α.

All the simulations were performed for $n_0 = N$, i.e. with the electron trap in saturation. The case of $n_0 \neq N$ will be studied in Section 5.8.

From each synthetic glow-peak the following quantities are evaluated: (i) The geometrical quantities shown in Fig. 1, (ii) the integral symmetry factor μ_g', (iii) the triangle assumption pseudo-constants C_ω, C_δ and C_τ, and (iv) the factor $(F_m + \alpha)/F_m$.

In order to ensure an accurate determination of the various parameters, a very small temperature step is necessary. In the present simulation the TL intensity was evaluated every 0.02 K.

5.2 Symmetry factors From the simulated synthetic glow-peaks both the geometrical symmetry factor μ_g and the integral symmetry factor μ_g' were evaluated. Their behaviour as a function of the mixed order parameter α is shown in Fig. 2. The main difference between μ_g and μ_g' is that the geometrical symmetry factor μ_g is saturated for α beyond 0.9, whereas the integral symmetry factor μ_g' is not. Their numerical values are listed in Table 1.

5.3 Evaluation of C_ω, C_δ and C_τ The behaviour of C_ω, C_δ and C_τ given by Eqs. (6)–(8), obtained from the simulation is shown in Fig. 3, whereas their numerical values are listed in Table 1. Looking at the results of Table 1 one can see why they are called pseudo-constants. For given mixed order parameter α, their variation over all (E, s) values used is 0.14%, 0.34% and 0.67% respectively. The parameters C_τ can be considered as pseudo-constant even over all the values of the mixed order parameter α.

5.4 Practical forms of the peak shape equations The derived peak shape methods given by Eqs. (18), (21), (25) are not applicable to experimental glow-peaks. The reason

Table 1 Geometrical (μ_g) and integral (μ_g') symmetry factors for various values of the mixed-order parameter α. Errors in μ_g (1%), μ_g' (1.7%). The triangle assumption pseudo-constants C_ω, C_δ and C_τ for various values of mixed order parameters α. Errors in C_ω (0.14%), C_δ (0.34%) C_τ (0.67%). The values of the peak shape methods coefficients c_ω, c_δ, and c_τ for various values of mixed order parameters α. Errors in c_ω (1.2%), c_δ (0.19%) c_τ (2.3%).

α	μ_g	μ_g'	C_ω	C_δ	C_τ	c_ω	c_δ	c_τ
0.01	0.4148	0.3915	0.9150	0.9790	0.8732	2.3491	0.9829	1.3649
0.05	0.4203	0.3932	0.9165	0.9795	0.8749	2.3763	0.9993	1.3755
0.1	0.4227	0.3960	0.9183	0.9804	0.8769	2.4149	1.0216	1.3921
0.2	0.4285	0.4025	0.9220	0.9818	0.8812	2.4982	1.0716	1.4254
0.3	0.4360	0.4106	0.9259	0.9833	0.8853	2.5905	1.1305	1.4587
0.4	0.4453	0.4205	0.9296	0.9844	0.8891	2.6955	1.2000	1.4941
0.5	0.4566	0.4327	0.9327	0.9845	0.8926	2.8079	1.2820	1.5255
0.6	0.4702	0.4473	0.9350	0.9829	0.8955	2.9308	1.3779	1.5516
0.7	0.4855	0.4647	0.9348	0.9769	0.8978	3.060	1.4854	1.5734
0.8	0.5008	0.4844	0.9296	0.9612	0.8994	3.1863	1.5957	1.5893
0.9	0.5128	0.5060	0.9133	0.9257	0.9000	3.2869	1.6853	1.6003
0.99	0.5169	0.5261	0.8834	0.8681	0.8999	3.3286	1.7205	1.6062

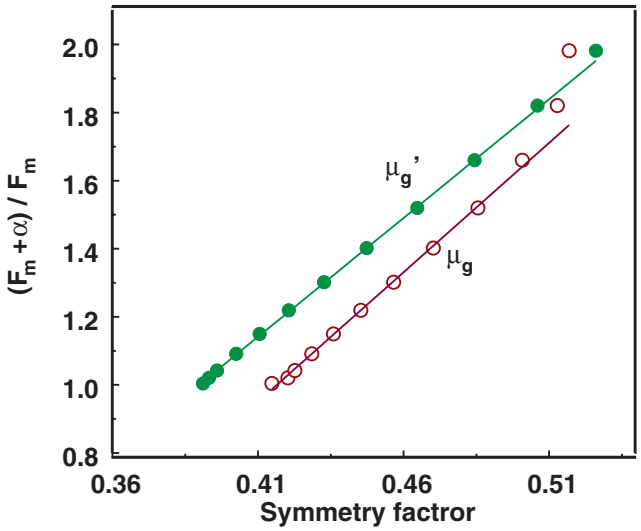

Figure 4 (online colour at: www.pss-a.com) Relation between the factor $(F_m + \alpha)/F_m$ and the symmetry factors μ_g and μ_g'.

is that the term $(F_m + \alpha)/F_m$, cannot be evaluated experimentally, whereas the triangle assumption pseudo-constants C_ω, C_δ and C_τ, are very difficult to evaluate experimentally. The peak shape methods given by Eqs. (18), (21), (25) can be brought into a useful practical form by either expressing the term $(F_m + \alpha)/F_m$, or the total coefficients c_ω, c_δ and c_τ given by Eqs. (19), (22), (26) as a function of experimentally measured quantities like μ_g' and μ_g. These attempts are described below.

5.5 Replacing the term $(F_m+\alpha)/F_m$ The term $(F_m + \alpha)/F_m$ is a common factor in the three families of peak shape methods given by Eqs. (18), (21), (25).

By evaluating this term for a wide range of parameters E and s, it was found that this factor depends nearly linearly on the symmetry factors μ_g' and μ_g as is shown in Fig. 4. It is clear that the linear correlation is excellent between this term and the integral symmetry factor μ_g', whereas in the case of the geometrical symmetry factor μ_g, there is a deviation from linearity as the mixed order parameter α approaches 1. So this relationship can be written as

$$\frac{F_m + \alpha}{F_m} = a_1 \mu_g' - b_1 \,, \tag{27}$$

where a_1 and b_1 are constants. Therefore, the peak shape methods can take the general form

$$E_\omega = C_\omega \cdot \frac{kT_m^2}{\omega} \cdot \frac{1}{\mu_g'} \cdot (a_1 \mu_g' - b_1) \,, \tag{28}$$

$$E_\delta = C_\delta \cdot \frac{kT_m^2}{\delta} \cdot (a_1 \mu_g' - b_1) \,, \tag{29}$$

$$E_\tau = C_\tau \cdot \frac{kT_m^2}{\tau} \cdot \frac{1 - \mu_g'}{\mu_g'} \cdot (a_1 \mu_g' - b_1) \,. \tag{30}$$

Table 2 Numerical values of the linear coefficients of Eqs. (30–32) as a function of the activation energy.

E (eV)	a_1	b_1	a_2	b_2	a_3	b_3
0.7	6.7280	1.7093	8.7347	1.3824	6.9322	1.9698
0.8	6.7842	1.7083	8.8764	1.4042	7.004	1.9821
0.9	6.8311	1.7070	8.9849	1.4172	7.0615	1.9909
1.0	6.8855	1.7125	9.1211	1.4488	7.1249	2.0052
1.1	6.9276	1.7149	9.2406	1.4758	7.1795	2.0172
1.2	6.9646	1.7170	9.3409	1.4977	7.2262	2.0230
1.3	6.9912	1.7162	9.4173	1.5114	7.2606	2.0330
1.4	7.0179	1.7170	9.4110	1.5262	7.2941	2.0395
1.5	7.0472	1.7206	9.5827	1.5526	7.3357	2.0512
1.6	7.0626	1.7183	9.6194	1.5532	7.3520	2.0511
1.7	7.0867	1.7213	9.6897	1.5728	7.3841	2.0600
1.8	7.1004	1.7200	9.7280	1.5774	7.4008	2.0616
1.9	7.1140	1.7197	9.7675	1.5846	7.4181	2.0645
mean	6.9647 ±0.126	1.7155 ±0.005	9.3534 ±0.34	1.5003 ±0.07	7.2287 ±0.16	2.0268 ±0.032

The replacement of the term $(F_m + \alpha)/F_m$ can be tested using the values of C_ω, C_δ and C_τ from Table 1. It was found that the linear coefficients a_1 and b_1 depend slightly on the kinetic parameters E and s. Therefore they were studied separately as a function of the activation energy E. In addition, the mean values for the whole activation energy region (0.7–2 eV) were also calculated. Their values as a function of the activation energy E, as well as their mean values are listed in Table 2. As it is seen from Table 2, although the activation energy varies from 0.7 eV to 1.9 eV, the coefficients a_1 and b_1 vary by less than 2% and 0.3% respectively. However, even this low variation can cause a serious increase in the error of E. The results are shown in Fig. 5. Figure 5(a) shows the errors in E evaluated by Eq. (31) using the respective coefficients a_1, b_1 from Table 2. On the other hand Fig. 5(b) shows the errors in E evaluated by Eq. (28) when using the mean values of the coefficients a_1, b_1 from Table 2. The error in E is substantially increased when going from Fig. 5(a) to 5(b). The situation is similar for the δ based and the τ based methods. From the above results it is concluded that the term $(F_m + \alpha)/F_m$ was successfully approximated by Eq. (27).

The application of Eqs. (28)–(30) to experimental glow-peaks requires also a functional relation between the triangle assumption pseudo-constants and the integral symmetry factor μ'. However, as is shown in Fig. 3, it is rather complicated for C_ω, C_δ and rather simple for C_τ. A functional relation was not necessary, since the peak shape methods in their form given by Eqs. (28)–(30) can be applied by using the tabulated values of the relevant parameters as a function of μ_g', from Tables 1 and 2.

5.6 Evaluation of c_ω, c_δ and c_τ The values of the coefficients c_ω, c_δ and c_τ given by Eqs. (19), (22), (26) respectively, are listed in Table 1.

The above estimated values of the peak shape method coefficients should be useful for practical application, if an

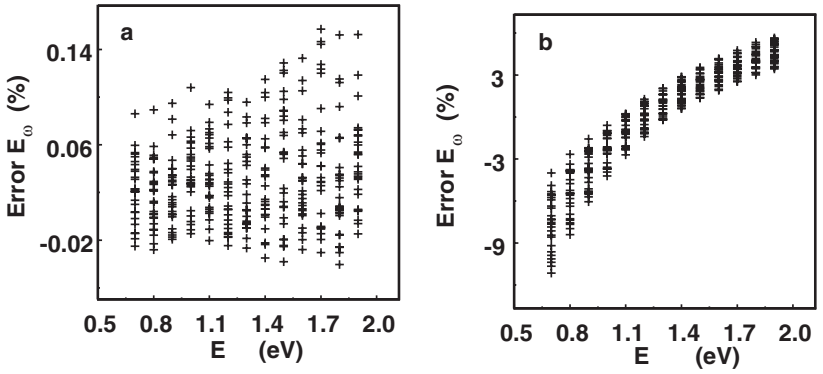

Figure 5 Errors in activation energy introduced by the replacement of the term $(F_m + \alpha)/F_m$ in Eq. (27). (a) Errors in the ω based peak shape methods when the coefficients in Eq. (28) are considered as a function of the activation energy. (b) Errors in the ω based peak shape methods when the coefficients in Eq. (28) are taken as the mean values over all activation energies.

analytical relationship as a function of μ_g' or μ_g can be found. Indeed, it was found that the coefficients c_ω, and c_δ, are linear functions of the geometrical symmetry factor μ_g, as is shown in Fig. 6(a). Therefore, a practical form of the ω and δ methods is:

$$E_\omega = (a_2\mu_g - b_2)\cdot\frac{kT_m^2}{\omega}, \quad (31)$$

$$E_\delta = (a_3\mu_g - b_3)\cdot\frac{kT_m^2}{\delta}. \quad (32)$$

Unfortunately, in the case of the τ method no good linear relationship exists between c_τ and μ_g, as shown in Fig. 6(b).

The linear coefficients in Eqs. (31), (32) are also activation energy dependent. Their values as a function of the activation energy as well as their mean values over the whole activation energy range are shown in Table 2. As is seen from the table, although the activation energy varies from 0.7 eV to 1.9 eV, the coefficients $a_{2,3}$ and $b_{2,3}$ vary by less than 4%. However, even this variation can cause a serious increase in the error of E. The results are shown in Fig. 7. Figure 7(a) shows the errors in E evaluated by Eq. (31) using the respective coefficients a_2, b_2 from Table 2. Figure 7(b) shows the errors in E evaluated by Eq. (31) using the mean values of the coefficients a_2, b_2 from Table 2. The error in E is substantially increased when going from Fig. 7(a) to (b). The situation is similar for the δ based Eq. (32).

At this point it is useful to discuss the accuracy of the experimental evaluation of both the geometrical and integral symmetry factors μ_g and μ_g' respectively. Obviously an accurate determination of both requires clean isolated glow-peaks. However, in practice even isolated glow-peaks can have some type of shoulders at both low and high temperatures. The low temperature shoulders can be removed successfully by a proper annealing procedure. However, this is impossible for shoulders at the high temperature part. In these cases, of course, there is an unavoidable increase of the error, which depends on the contribution of the shoulder. At first look it may seem that the influence of the shoulder would be higher on the integral symmetry factor μ_g', rather than on the geometrical symmetry factor μ_g. However, the final accuracy is more or less the same, because the geometrical symmetry factor depends on three points of the glow-peak, the T_m, T_1, and T_2 the errors of which are propagated to the value of $\mu_g = (T_2 - T_m)/(T_2 - T_1)$, whereas the integral symmetry factor depends only on one point, T_m, which is determined more accurately than T_1 and T_2.

5.7 Properties of the factor $(F_m+\alpha)/F_m$ A very interesting observation is that the values of the term $(F_m + \alpha)/F_m$, which will be called b_{mix}, have a role in the mixed order kinetics similar to the kinetic order b of the general order kinetics. In principle this is concluded from the following fact.

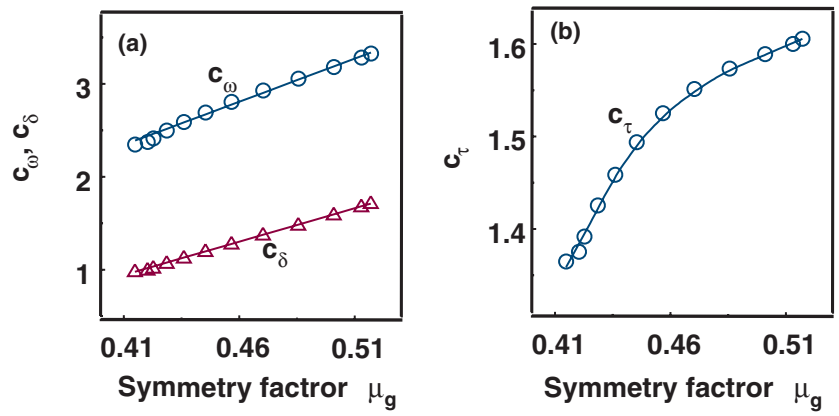

Figure 6 (online colour at: www.pss-a.com) (a) Relationship between the total coefficient values of the ω and δ based peak shape methods as a function of the geometrical symmetry factor μ_g. (b) Relationship between the total coefficient value of the τ based peak shape method as a function of the geometrical symmetry factor μ_g.

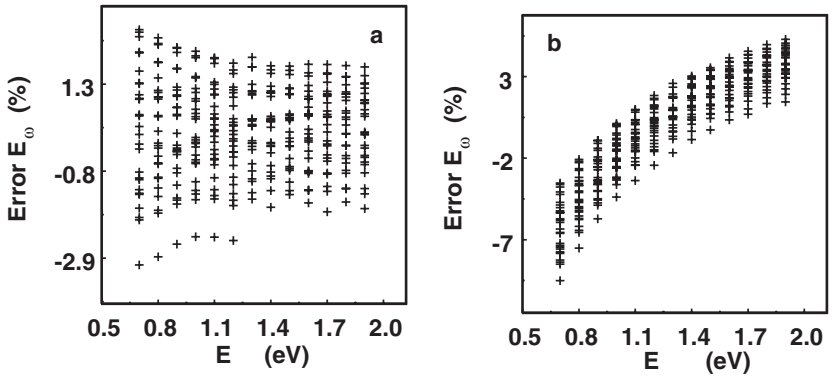

Figure 7 Errors in activation energy introduced by the replacement of the term c_ω by its linear dependence on μ. (a) Errors in the ω based peak shape methods when the coefficients in Eq. (31) are considered as a function of the activation energy. (b) Errors in the ω based peak shape methods when the coefficients in Eq. (31) are considered as a mean values over all activation energies.

The δ family of peak shape methods for the case of general order kinetics is given by the equation [9]

$$E_{\delta G} = C_{\delta G} \cdot b \cdot \frac{kT_m^2}{\delta_G}. \tag{33}$$

The respective method for mixed order kinetics is given by Eq. (21) which is re-written in the form below:

$$E_{\delta M} = C_{\delta M} \cdot b_{mix} \cdot \frac{kT_m^2}{\delta_M}, \tag{34}$$

where, the index M is for mixed order and the index G for general order kinetics. Since both methods must give the same E, i.e. $E_{\delta G} = E_{\delta M}$, it is easily found that

$$\frac{b_{mix}}{b} = \frac{C_{\delta G}}{C_{\delta M}} \cdot \frac{\delta_M}{\delta_G}. \tag{35}$$

Obviously $\delta_M = \delta_G$, and the triangle assumption pseudo-constants, although not equal, differ by less than 5%, so it is concluded that Eq. (35) is very close to unity so that $b_{mix} \sim b$. This relationship was further studied and the results are shown in Fig. 9(a–c). In Fig. 9(a, b) one can see the be-haviour of b, b_{mix} as a function of the mixed-order parameter α and the symmetry factor μ', respectively, whereas in Fig. 9(c) one can see the ratio of b_{mix} over b as a function of the mixed-order parameter α. In the worst case shown in Fig. 9(c) the difference between the two parameters is of the order of 5%. The interesting result here is that the empirical general order parameter b is found to be almost equal to the physically meaningful parameter b_{mix}.

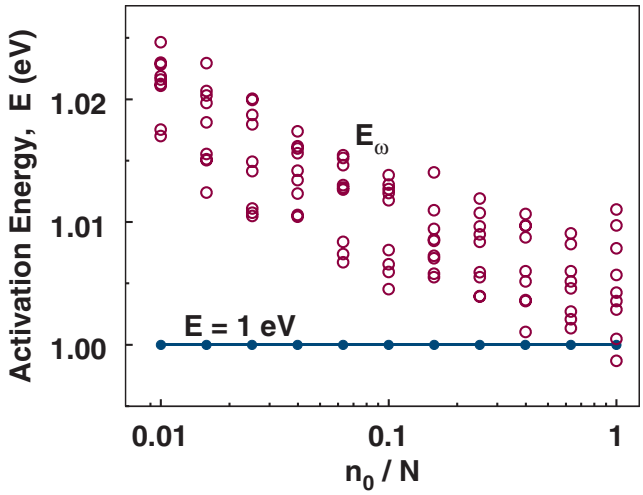

Figure 8 (online colour at: www.pss-a.com) Errors in activation energy as a function of the trap occupancy n_0/N.

5.8 Case of $n_0 \neq N$ The results presented up to now concerned the case of a saturated trap i.e. $n_0 = N$. However, a complete picture requires to examine the cases of a non saturated trap i.e. $n_0 \neq N$. This case was studied for $E = 1$ eV, $s = 10^{12}$ s^{-1} and n_0/N varying by two orders of magnitude between 0.01 and 1. The results concerning the application of the peak-shape methods given by Eqs. (31), (32) are shown in Fig. 8. As can be seen the dependence on n_0/N is between 0% and 2.5%. It is observed that the dependence of the error on n_0/N seems to be systematic. It must also be noticed that these systematic variations enable the improvement of the results. For example, by inserting a factor of 0.9875 in front of Eqs. (31), (32), the error will be reduced from 0–2.5 % to ±1.25%.

5.9 Comparison with other peak shape methods The peak shape methods derived in the present work will be compared with the existing peak shape methods like those of Chen [11] and those suggested by Kitis and Pagonis [12]. The comparison method adopted has the following steps.

Step 1: Synthetic mixed order glow-peaks are derived using Eq. (3).

Step 2: The integral symmetry factor μ_g' is evaluated for each glow-peak

Step 3: Using the value of μ_g' the kinetic order b of a general order glow-peak having the same μ_g' is evaluated by an iteration method using the following equation suggested by Kitis and Pagonis [12]:

$$\mu_g' = \left[\frac{b}{1+(b-1)\,\Delta_m}\right]^{\frac{1}{1-b}}, \tag{36}$$

where $\Delta_m = 2kT_m/E$. The accuracy of Eq. (36) depends only on the number of terms in the asymptotic series approxi-

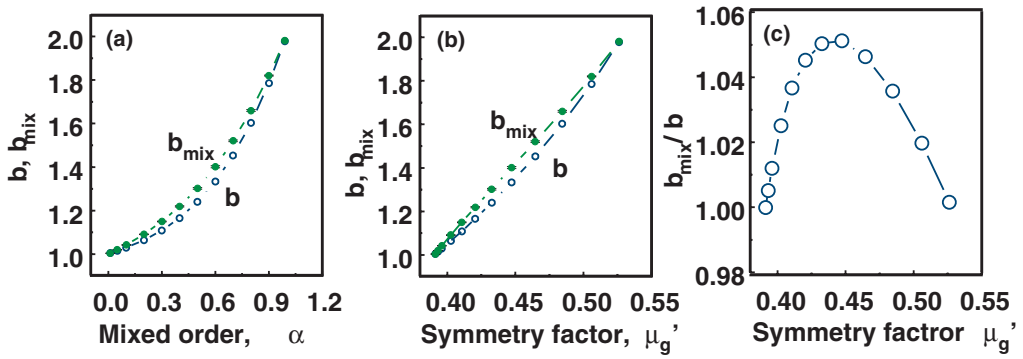

Figure 9 (online colour at: www.pss-a.com) Behaviour of the general order kinetics b and the mixed order parameter b_{mix} (a) as a function of mixed order parameter α and (b) as a function of the integral symmetry factor μ_g'. (c) The ratio of b_{mix}/b as a function of the integral symmetry factor μ_g'.

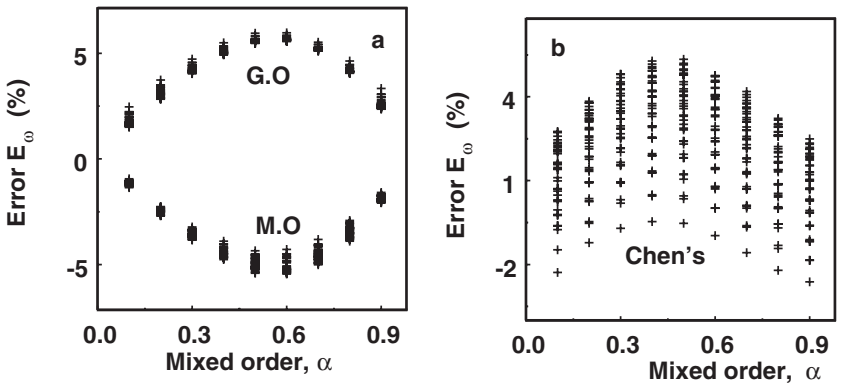

Figure 10 (a) G.O. represents the errors in E when general order peak shape methods are applied to mixed order glow-peaks and M.O. represents the errors in E when mixed order peak shape methods are applied to general order glow-peak. (b) Chen's represents the errors in E when the Chen's peak shape method is applied to mixed-order glow-peaks.

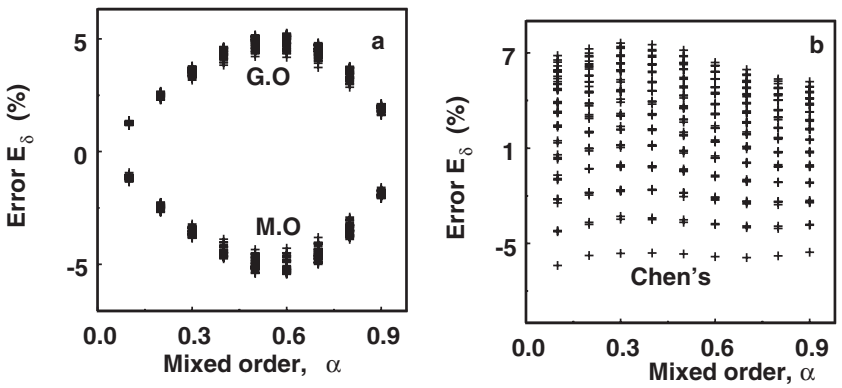

Figure 11 As in Fig. 10, for the δ method.

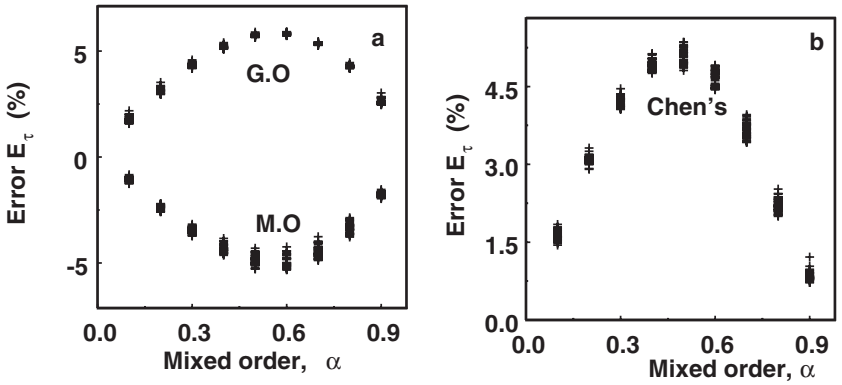

Figure 12 Same as Figs. 10 and 11, for the τ method.

mation of the exponential integral given by Eq. (2). For a given Δ_m the kinetic order b can be evaluated to any desired accuracy, depending upon the number of iterations.

Step 4: Once the kinetic order b is evaluated then the corresponding general order glow-peak is derived using the same (E, s) values.

Having thus both kinds of glow-peaks the peak shape methods are applied to them as following.

The general order peak shape methods of Chen [11] and of Kitis and Pagonis [12] are applied to mixed order glow-peaks, whereas the mixed order peak shape methods derived in the present work are applied to the general order glow-peaks. The degree to which the E values found by peak shape methods agree with the input E values is a measure of the agreement between general and mixed order glow-peaks.

The results are shown in Figs. 10–12 for the ω, δ and τ peak shape methods respectively. The basic conclusion from these results for all families of peak shape methods is that when the general order kinetics peak shape methods by Kitis and Pagonis [12] are applied to mixed order glow-peaks they overestimate the value of E in a manner depending upon the mixed order parameters α. On the other hand when the mixed order peak shape methods are applied to a general order glow-peak they underestimate the E in a manner depending upon the mixed order parameters α. The differences between general and the mixed-order peak shape methods, reflects exactly qualitatively and quantitatively the relation between the mixed order term b_{mix} and the kinetic order b shown in Fig. 9(c). The above relation between mixed order peak shape methods and the general order peak shape method by Kitis and Pagonis is not followed by the general order peak shape methods of Chen [11] in the case of the ω and δ methods and it is followed very well by the τ method.

6 Conclusions In this paper we derive new peak-shape methods for evaluating the activation energy E of a TL glow-peak, which are based on the physically meaningful mixed order kinetics model.

In their original form given by Eqs. (18), (21), (25) the peak shape equations are not very useful for analyzing experimental glow-peaks. However, this form should be very useful in testing the quality of glow-peaks generated during the numerical simulation of various TL phenomena, where all relevant parameters can be evaluated during the simulation. The reason is that as it was shown by Sunta et al. [13], the mixed order kinetics model is much more successful than the general order kinetics model in describing glow-peaks resulting from physical models like NMTS and IMTS. The peak shape methods derived here can be used for fast and accurate peak quality test within the simulation.

The peak shape equations given by Eqs. (28)–(30) are expressed as a function of the integral symmetry factor μ_g'. However in this form these equations are of limited practical use, since they contain the triangle assumption pseudo-constants C_ω, C_δ and C_τ. Nevertheless, they can be applied to experimental glow-peak by using the tabulated values of C_ω, C_δ and C_τ as a function of μ_g' from Tables 1 and 2.

Finally, the forms given by Eqs. (31), (32) are useful in practice, since they are expressed as a function of the geometrical symmetry factor μ_g. The error in the activation energy is $\pm 1.5\%$ when the slight dependence of the coefficients in Eqs. (31), (32) is taken into account (Fig. 7(a)) and $\pm 3.5\%$ when it is not (Fig. 7(b)).

It has been found that the term $b_{mix} = (F_m + \alpha)/F_m$, of mixed order kinetics is very similar to the general order kinetics parameter b, as shown in Fig. 9(a, b). From this similarity it was found that the physically meaningful mixed order kinetics differs from the empirical general order kinetics parameter by less than 5% in the worst case, as is shown in Fig. 9(c).

Finally, the application of the mixed-order peak shape method to general-order kinetics glow-peak and the application of the general-order kinetics glow-peaks on mixed order kinetics glow-peaks gave errors (see Figs. 10–12), which follow qualitatively and quantitatively their behaviour shown in Fig. 9(c).

References

[1] J. T. Randall and M. H. F. Wilkins, Proc. R. Soc. Lond. A **184**, 390 (1945).
[2] G. F. J. Garlick and A. F. Gibson, Proc. Phys. Soc. Lond. **60**, 574 (1948).
[3] C. E. May and J. A. Partridge, J. Chem. Phys. **40**, 1401 (1964).
[4] R. Chen, N. Kristianpoller, Z. Davidson and R. J. Visocekas, Lumin. **23**, 293 (1981).
[5] L. I. Grossweiner, J. Appl. Phys. **24**, 1306 (1953).
[6] C. B. Lushchik, Dokl. Akad. Nauk SSSR **101**, 641 (1955).
[7] A. Halperin and A. A. Braner, Phys. Rev. **117**, 408 (1960).
[8] R. Chen and Y. Kirsh, Analysis of thermally stimulated processes (Pergamon Press, 1981), p. 167.
[9] R. Chen and S. W. S. McKeever, Theory of Thermoluminescence and related phenomena (World Scientific), 1997.
[10] R. Chen, J. Appl. Phys. **40**, 570 (1969).
[11] R. Chen, J. Electrochem. Soc. **116**, 1254 (1969).
[12] G. Kitis and V. Pagonis, Nucl. Instrum. Methods B **262**, 313 (2007).
[13] C. M Sunta, W. E. F Ayta, J. F. D Chubaci, and S. Watanabe, Radiat. Meas. **35**, 47 (2002).