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Computerized curve deconvolution analysis for LM-OSL

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Abstract

The computerized curve deconvolution analysis (CCDA) technique is well known in the case of thermoluminescence (TL). In the present work we investigate the application of CCDA to the linear modulated optically stimulated luminescence curves (LM-OSL). We derive single LM-OSL peak equations which are based on variables which can be extracted directly from the experimental OSL curve, for both first order and general order LM-OSL peaks. The similarities and differences between TL and OSL CCDA analysis are discussed. The resolution of the technique is also examined in the cases of synthetic curves consisting of two or four constituent components. Finally a new experimental procedure is suggested which can be used to separate composite LM-OSL curves into their constituent components

Keywords: Optically stimulated luminescence; OSL; Computerized curve deconvolulion; CCD

1. Introduction/scope

Experimental thermoluminescence (TL) and linear modulated optically stimulated luminescence (LM-OSL) curves usually consist of several overlapping peaks. The analysis and separation of these complex curves into their constituent components can be achieved using computerized curve deconvolution analysis (CCDA). In the case of TL glow curves this technique is well established and used routinely, but there have not been any systematic studies of the corresponding CCDA technique for LM-OSL curves.

In this paper the geometrical characteristics and symmetry factors of the peak-shaped LM-OSL curves are studied, and the similarities and differences between TL and OSL CCDA analysis are pointed out, for both first order and general order peaks. The study aims to define and evaluate variables which can be extracted directly from the experimental data and use them for improvement of the CCDA. Finally a new experimental procedure is suggested which can be used to separate composite LM-OSL curves into their constituent components.

2. Geometrical characteristics and symmetry factors

The shape of an LM-OSL peak is characterized by the maximum peak intensity I_{m}, the corresponding time t_{m}, and the times t_1 and t_2 at the half maximum OSL intensity. Using these points the quantities $\tau = t_{\mathrm{m}} - t_1$, $\delta = t_2 - t_{\mathrm{m}}$, $\omega = t_2 - t_1$ and the symmetry factor $\mu_g = \delta/\omega$ are defined, in analogy to the situation for TL peaks.

In the case of the TL glow-peaks, the derivation of the existing peak shape methods are 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 (1969) are

$$C_\omega = \frac{\omega I_{\mathrm{m}}}{n_0}, \quad C_\delta = \frac{\delta I_{\mathrm{m}}}{n_{\mathrm{m}}}, \quad C_\tau = \frac{\tau I_{\mathrm{m}}}{n_0 - n_{\mathrm{m}}}, \tag{1}$$

with

$$n_{\mathrm{m}} = \int_{t_{\mathrm{m}}}^{\infty} I \,\mathrm{d}t \tag{2}$$

The differential equation describing the first order OSL kinetics is

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -n\,\frac{\gamma}{T}\,t, \tag{3}$$

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where n is the concentration of electrons in traps, T the total illumination time, t the time and $\gamma = \sigma I_0$ with σ the cross and I_0 the illumination intensity.

By solving the last equation the following analytical expression for the OSL intensity $I(t)$ is derived, as well as the condition for the maximum intensity (Bulur, 1996):

$$I(t) = n_0 \gamma \frac{t}{T} \exp\left(-\frac{\gamma t^2}{2T}\right), \tag{4}$$

$$t_{\mathrm{m}} = \sqrt{\frac{T}{\gamma}}, \tag{5}$$

$$I_{\mathrm{m}} = \exp\left(-\frac{1}{2}\right) \frac{n_0}{t_{\mathrm{m}}}. \tag{6}$$

By combining Eqs. (1) and (6) one obtains

$$\frac{\omega}{t_{\mathrm{m}}} = 1.64872 C_\omega. \tag{7}$$

In a similar manner one obtains the corresponding equations for C_δ and C_τ

$$\frac{\delta}{t_{\mathrm{m}}} = C_\delta, \quad \frac{\tau}{t_{\mathrm{m}}} = 0.64872 C_\tau. \tag{8}$$

The differential equation describing the general order kinetics is

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{n^b}{N^{b-1}} \frac{\lambda}{T} t, \tag{9}$$

where b is the kinetic order and N the concentration of available electron traps.

By solving Eq. (9) the following expressions are obtained (Bulur, 1996):

$$I(t) = n\left(\frac{n_0}{N}\right)^{b-1} \cdot \frac{\gamma t}{T} \cdot \left[\left(\frac{n_0}{N}\right)^{b-1} \cdot (b-1) \cdot \frac{\gamma t^2}{2T} + 1\right]^{b/b-1}, \tag{10}$$

$$t_{\mathrm{m}} = \sqrt{\frac{2T}{\gamma(b+1)} \cdot \left(\frac{N}{n_0}\right)^{b-1}}, \quad I_{\mathrm{m}} = 2\frac{n_0}{t_{\mathrm{m}}} \frac{1}{b+1} \left[\frac{2b}{b+1}\right]^{b/1-b}. \tag{11}$$

By manipulating these equations in a manner similar to the case of first order kinetics described above, the following expressions are derived for the pseudo-constants C_δ, C_τ and C_ω.

$$\frac{\omega}{t_{\mathrm{m}}} = C_\omega \frac{b+1}{2} \left(\frac{2b}{b+1}\right)^{b/b-1}, \tag{12}$$

$$\frac{\delta}{t_{\mathrm{m}}} = b C_\delta, \tag{13}$$

$$\frac{\tau}{t_{\mathrm{m}}} = C_\tau b \left[\left(\frac{2b}{b+1}\right)^{1/b-1} - 1\right]. \tag{14}$$

LM-OSL curves were numerically simulated using the general order Eq. (9). The region of γ values used, was between 0.01 and $0.4\,\mathrm{s}^{-1}$, in steps of 0.01. In order to obtain complete LM-OSL peaks a total stimulation time T of 1000 s was used for first order kinetics, which was gradually increased up to 4500 s for second order kinetics. During the simulation the following quantities were evaluated: total integral, the low side and high side half integrals, the peak maximum intensity I_{m}, the peak maximum time t_{m}, the low side and high side half maximum intensities t_1 and t_2, the widths ω, τ and δ, the symmetry factors δ/ω, n_{m}/n_0 and the pseudo-constants C_δ, C_τ and C_ω.

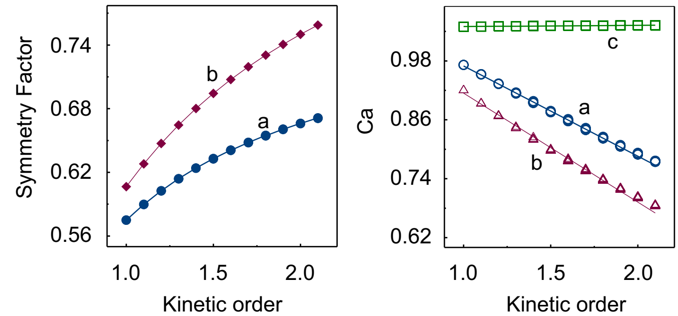

Fig. 1. Left-hand side: the symmetry factor of an LM-OSL peak as a function of kinetic order. (a) Geometrical symmetry factor δ/ω and (b) integral symmetry factor n_{m}/n_0. Right-hand side: the triangle assumption pseudo-constants C_α as a function of the kinetic order. (a) For C_ω, (b) for C_δ and (c) for C_τ.

Left-hand side of Fig. 1 shows the variation of the symmetry factors δ/ω and n_{m}/n_0 as a function of the kinetic order whereas the right-hand side shows the variation of the pseudo-constants C_ω, C_δ and C_τ as a function of the kinetic order.

3. Computerized curve deconvolution analysis (CCDA)

The experimental LM-OSL curves consist of more than one peak, which are usually overlapping. The separation of a complex OSL curve into its individual components is achieved by a CCDA. The single OSL peak models for the CCDA are those given by Eqs. (4) and (10). The free parameters of the CCDA are n_0 and γ for first order kinetics and n_0, b and γ for general order kinetics. The CCDA starts by assuming some initial guess values for the free parameters n_0, b and γ, which cannot be extracted directly from the experimental OSL curve. It is possible to transform the $I(n_0, b, \gamma, t)$ expressions into the expressions depending upon variables, which can be extracted directly from the experimental OSL curve, i.e., into the form $I(I_{\mathrm{m}}, t_{\mathrm{m}}, b, t)$.

By manipulating expressions (10), and (11) we obtain the desired expression which depends on the experimentally determined quantities:

$$I(t) = I_{\mathrm{m}} \frac{t}{t_{\mathrm{m}}} \left[\frac{b-1}{2b} \frac{t^2}{t_{\mathrm{m}}^2} + \frac{b+1}{2b}\right]^{b/1-b}. \tag{15}$$

The corresponding equation for first order kinetics is

$$I(t) = 1.6487 I_{\mathrm{m}} \frac{t}{t_{\mathrm{m}}} \exp\left[-\frac{t^2}{2t_{\mathrm{m}}^2}\right]. \tag{16}$$

The CCDA of complex spectra is widely used for TL glow-curves. However, two major problems exist. The first problem

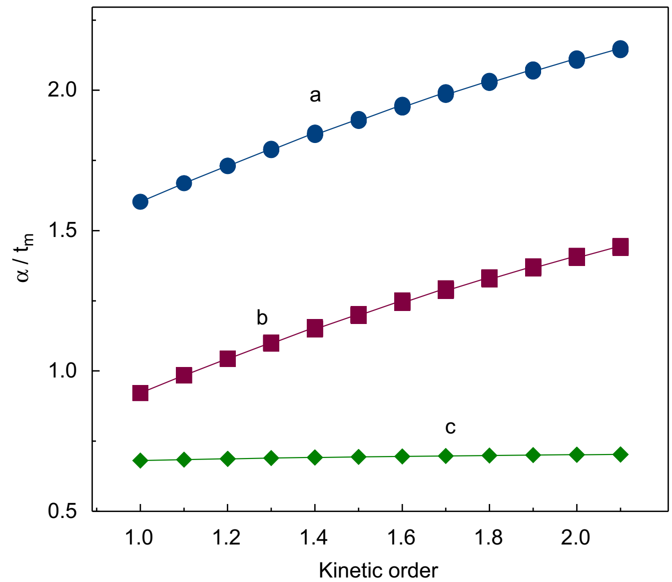

Fig. 2. The quantities $\alpha/t_{\rm m}$ as a function of the kinetic order. (a) $\omega/t_{\rm m}$, (b) $\delta/t_{\rm m}$ and (c) $\tau/t_{\rm m}$.

Table 1
Numerical values of the quantities $\omega/t_{\rm m}$, $\delta/t_{\rm m}$ and $\tau/t_{\rm m}$ for various kinetics orders

b	$\omega/t_{\rm m}$	$\delta/t_{\rm m}$	$\tau/t_{\rm m}$
1	$1.6023 \pm 1 \times 10^{-4}$	$0.9214 \pm 1 \times 10^{-4}$	$0.6809 \pm 5 \times 10^{-5}$
1.1	$1.6681 \pm 1 \times 10^{-4}$	$0.9838 \pm 1 \times 10^{-4}$	$0.6843 \pm 5 \times 10^{-5}$
1.2	$1.7295 \pm 2 \times 10^{-4}$	$1.0423 \pm 2 \times 10^{-4}$	$0.6872 \pm 6 \times 10^{-5}$
1.3	$1.7868 \pm 1 \times 10^{-4}$	$1.0970 \pm 2 \times 10^{-4}$	$0.6898 \pm 6 \times 10^{-5}$
1.4	$1.8405 \pm 2 \times 10^{-4}$	$1.1484 \pm 2 \times 10^{-4}$	$0.6921 \pm 7 \times 10^{-5}$
1.5	$1.8905 \pm 2 \times 10^{-4}$	$1.1967 \pm 2 \times 10^{-4}$	$0.6942 \pm 7 \times 10^{-5}$
1.6	$1.9381 \pm 2 \times 10^{-4}$	$1.2416 \pm 3 \times 10^{-4}$	$0.6960 \pm 9 \times 10^{-5}$
1.7	$1.9828 \pm 3 \times 10^{-4}$	$1.2851 \pm 2 \times 10^{-4}$	$0.6977 \pm 9 \times 10^{-5}$
1.8	$2.0248 \pm 3 \times 10^{-4}$	$1.3256 \pm 3 \times 10^{-4}$	$0.6993 \pm 1 \times 10^{-4}$
1.9	$2.0646 \pm 3 \times 10^{-4}$	$1.3639 \pm 3 \times 10^{-4}$	$0.7006 \pm 1 \times 10^{-4}$
2	$2.1022 \pm 3 \times 10^{-4}$	$1.4003 \pm 3 \times 10^{-4}$	$0.7019 \pm 1 \times 10^{-4}$

is the existence of very closely spaced glow-peaks, which is a common problem to any kind of spectrum and the second problem is that at every peak maximum temperature $T_{\rm m}$ correspond, theoretically, an infinite number of (E, s) pairs. The main consequence of these two problems is that it is almost impossible in the case of TL to define and to evaluate some kind of resolution.

The situation is different in case of the LM-OSL spectrum. The reason is that as it is seen from Eqs. (5) and (11) the time maximum $t_{\rm m}$ depends on one parameter only and not of two as in the case of TL. Therefore, for a given total stimulation time T, the respective $t_{\rm m}$ there corresponds to one and only one peak.

In the case of the OSL curves, in addition to the above discussed property, the constant values of the previously presented quantities $\omega/t_{\rm m}$, $\delta/t_{\rm m}$ and $\tau/t_{\rm m}$ could have a significant contribution on accurate application of the deconvolution analysis (Fig. 2 and Table 1). The reason is very simple. In all experimental LM-OSL inclination points exist, indicative for respective values of $t_{\rm m}$. Knowing the value of $t_{\rm m}$, then using the values $(\omega, \delta, \tau)/t_{\rm m}$ from Eqs. (7), (8) (12)–(14) one can evaluate the whole peak inside the LM-OSL curve. This is a very useful practical knowledge since it can help to drive the deconvolution toward the correct solution.

Another significant difference between TL and OSL in the deconvolution analysis is that in the case of TL it is not valid to accept that the best fit of a complex TL glow-curve corresponds to the lowest possible number of glow-peaks. However, in the case of OSL, the best fit with the lowest possible number of peaks could very well lead to the real solution. Therefore, the resolution is the main problem in the CCDA of LM-OSL.

4. A preliminary resolution study

This study is as follows. A synthetic first order LM-OSL peak is numerically produced using Eq. (4) with $\gamma = 0.04\,{\rm s}^{-1}$, $n_0 = 10^5\,{\rm cm}^{-3}$ and $T = 400\,{\rm s}$. This peak has $t_{\rm m} = 100\,{\rm s}$ and $I_{\rm m} = 600$ a.u. That single OSL peak is then fitted with two first order LM-OSL peaks by varying both their $t_{\rm m}$ and $I_{\rm m}$. The set of peak maximum intensities studied was $I_{\rm m2}/I_{\rm m1} = 0.1$, 0.2, 0.34, 0.5, 0.71 and 1. For each value of $I_{\rm m2}/I_{\rm m1}$ the values of $t_{\rm m1}$ was left to vary above $t_{\rm m} = 100\,{\rm s}$ whereas the value of $t_{\rm m2}$ was left to vary below $t_{\rm m}$. The goodness of fit was tested by using the figure of merit (FOM). Here one has to decide which values of FOM are acceptable. Usually, in the cases of experimental TL glow-curves the fit is acceptable for FOM% values less than 2%. However, in the present case since we deal with synthetic peaks, we will use an acceptable value of FOM% less than 1%. Initially, the synthetic OSL peak derived by Eq. (4) was fitted using the modified expression given by Eq. (16). The resulting FOM% was 10^{-4}%, i.e., the agreement between the two first order expressions is excellent. The results of this study are shown in Fig. 3. The horizontal line represents the 1% FOM.

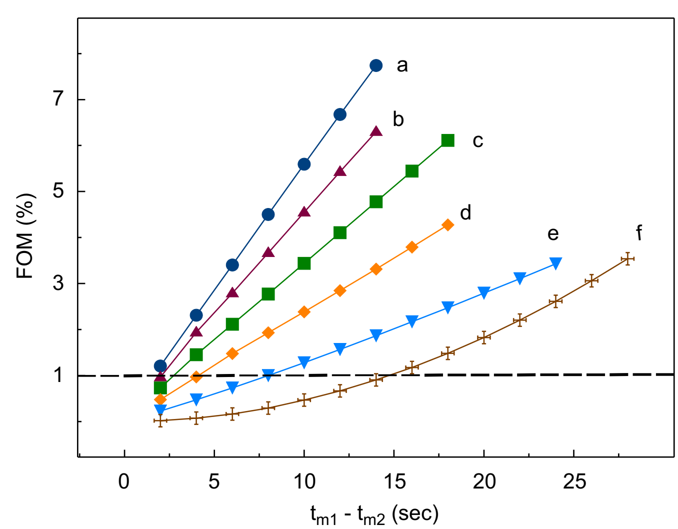

Fig. 3. FOM(%) values from the fitting a single LM-SOL curve using two components as a function of their $t_{\rm m}$ difference for various values of $I_{\rm m1}/I_{\rm m2}$ (a) 0.1, (b) 0.2, (c) 0.34, (d) 0.6, (e) 0.71 and (f) 1.

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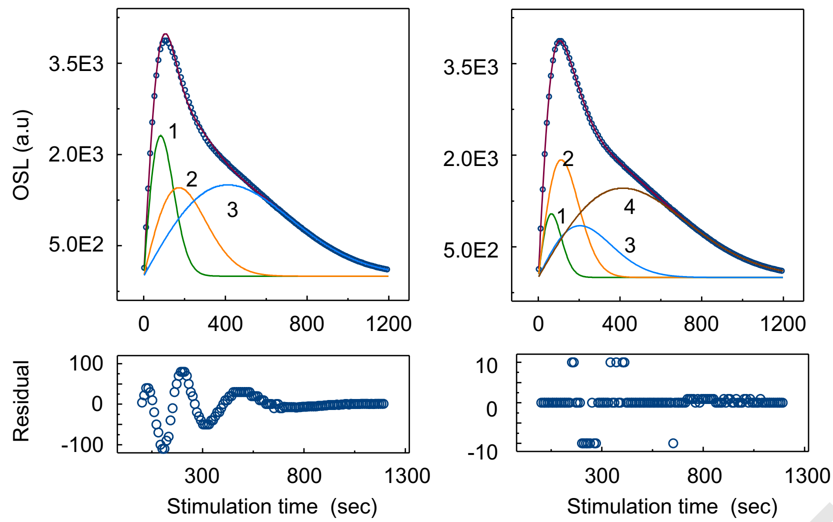

Fig. 4. Left-hand side: Fitting with three components and right-hand side: fitting with four components.

Fig. 3 shows the possibility of resolving two very closely spaced peaks depends on the distance between their peak positions t_{m1}, t_{m2} as well as on their relative intensities I_{m1} and I_{m2}. From Fig. 4 it is concluded that when the relative intensities are far from being equal (curve a) the CCDA can resolve them, even if their distance is less than 5 s. However, as the relative intensities tend to become equal (from curve a to curve f) the resolution becomes poorer. For example when $I_{m1} = I_{m2}$ the CCDA resolves them only when their distance becomes greater than 15 s.

5. CCDA of a synthetic composite LM-OSL curve

Despite the advantages mentioned above, the deconvolution of a composite LM-OSL curve remains a difficult problem even if the individual peaks overlap little. The reason is unavoidable in most overlapping cases, which has its origin in the fact that every LM-OSL peak starts always from the earlier stimulation time ($t = 0$). So, in the region of low stimulation times there is always a substantial contribution from all peaks. The deconvolution example given below is a synthetic composite LM-OSL consisting of four components. Their t_m values were selected to be quite apart but their relative intensities were selected so that the final LM-OSL curve contains a very high degree of overlapping.

The deconvolution of the synthetic curve is shown in Fig. 4. Initially the curve fitting was applied by using fixed parameters values for t_m and I_m. The FOM(%) of 10^{-4} is the reference FOM. In a next step looking for the best fit with the lowest possible number of peaks, the curve fitting was attempted using two and three components. In the case of two components the fit fails giving an FOM(%) = 7. The case of fitting with three components is shown in the left-hand side Fig. 5 along with the residual, i.e., the difference between the fitted curve and its fit. The FOM(%) obtained was 1.4, which is quite good but clearly not acceptable for a theoretical study with an expected FOM(%) of 10^{-4}. The last case of the fitting with four

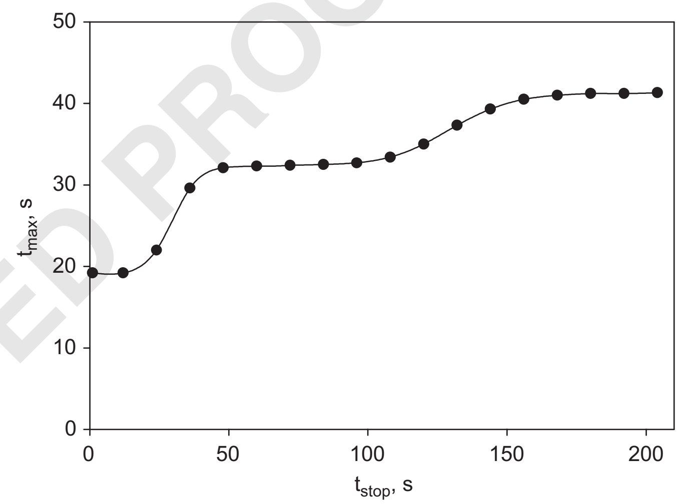

Fig. 5. Results of simulating the t_m–t_{stop} procedure for LM-OSL in quartz using the model by Bailey (2001).

components is shown in the right hand side of Fig. 4 along with the respective residuals. In this case the guess values of all free parameters were set equal. The resulting FOM(%) was 10^{-2}, whereas the expected values of the t_m and I_m for each component where obtained very satisfactory. However, even in this case the FOM(%) of 10^{-2} is far from the expected value of 10^{-4}. It was found that if the parameters t_m and I_m of even one component are well known then the resulting FOM(%) is improved to the order of 10^{-4}, implying that the fitting has attained the correct solution.

6. The t_{max}–t_{stop} experimental procedure

A new experimental procedure is suggested which can be used to separate composite LM-OSL curves into their constituent components. The procedure is analogous to the well-known T_m–T_{stop} technique of analysis for composite TL glow

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curves and similar to ratio of unbleached and partially bleached LM-OSL curves (Agersnap-Larsen et al., 2000). In the new procedure the sample is bleached for a time period t_{stop}, then the complete LM-OSL signal is measured and the time t_m for the maximum LM-OSL intensity is recorded. The process is repeated for a gradually increasing bleaching time t_{stop}, and a graph of t_m vs. t_{stop} is produced. Possible changes in the sensitivity of the sample are monitored in each step and corrected for by using the 110 °C TL peak of quartz.

This program simulates a t_m–t_{stop} experiment for LM-OSL in quartz using the comprehensive quartz model by Bailey (2001). The model consists of nine energy levels, four of which are designated as electron traps and four levels represent hole traps/recombination centers. The steps in the simulation are as follows:

(1) "Natural sample" as described in the Bailey (2001, p. 24, Section 2.5) paper.
(2) Give the natural sample a dose of 10 Gy at room temperature.
(3) Bleach the sample (blue LM-OSL) for $t_{stop} = 12$ s at a temperature of 20 °C.
(4) Measure blue LM-OSL for 200 s at the same temperature of 20 °C. Record the time t_{max} for the maximum of the LM-OSL.
(5) Repeat steps 2–4 using a different aliquot and by changing the bleaching time in step 3 to 24, 36, 48, etc. up to a maximum of 180 s. There may be some sensitivity change for each cycle, but it should not be very critical for our results.
(6) Repeat the whole process for a different OSL temperature in steps 3 and 4 (20, 40, 60, etc. up to 200 °C), to see how the shape of the t_m–t_{stop} graph changes with OSL-temperature.

The new procedure produces a t_m–t_{stop} graph which is analogous to the T_m–T_{stop} graph for TL studies, and a "staircase" shape in this graph identifies individual LM-OSL components. The procedure can be repeated at different excitation temperatures to study the temperature dependence of the LM-OSL components.

The comprehensive quartz model of Bailey (2001) is used to simulate the new t_m–t_{stop} procedure, and the results of the simulation are shown in Fig. 5. The model contains three energy levels which are optically sensitive, and these correspond to the three "steps" shown in Fig. 5.

7. Conclusions

The CCDA analysis can be very effective in the case of complex LM-OSL. The main advantage is that, for a given total stimulation time T, the respective t_m corresponds to one and only one peak whereas in the case of TL at every peak maximum T_m correspond, theoretically, to an infinite number of single glow-peaks. Applying the CCDA to synthetic complex LM-OSL curves it was found that even in cases of highly overlapped peaks the exact knowledge of even one component can lead to the correct deconvolution of the complex curve. For this reason a new technique, analogous to the well-known T_m–T_{stop} in TL is suggested in order to find the individual characteristics of each peak needed for the CCDA.

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