A new look at the linear-modulated optically stimulated luminescence (LM-OSL) as a tool for dating and dosimetry

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Abstract

Optically stimulated luminescence (OSL) has been in use for dosimetry and dating in the last two decades. Since the OSL dependence on time is a featureless decaying function, a linear-modulation of the stimulating-light intensity has been suggested [Bulur, E., 1996. An alternative technique for optically stimulated luminescence. Radiat. Meas. 26, 701–709.], which resulted in a peak-shaped curve. The properties of this curve have been studied, assuming first-, second- and general-order kinetics. In a recent paper we have shown [Chen, R., Pagonis, V., 2008. A unified presentation of thermoluminescence (TL), phosphorescence and linear-modulated OSL (LM-OSL). J. Phys. D: Appl. Phys. 41, 035102 (1–6); that for general-order curves, the peak maximum cannot be expected to depend linearly on the dose of excitation. A new presentation of the LM-OSL has been suggested, in which the peak maximum is linear with the filling of trapping states, which, in turn, may be expected to be linear with the dose under appropriate conditions. In the present work, we report on results of numerical simulation of the LM-OSL, using the one trap-one recombination center (OTOR) model, dealing with the traffic of carriers between one trapping state, one kind of recombination center and the conduction and valence bands during excitation and read-out, and without making any simplifying assumptions. The process during optical read-out has been followed in the simulation that consisted of the numerical solution of the relevant sets of coupled differential equations, and also by analytical treatment. Sets of parameters leading to approximately first- and second-order kinetics, and to intermediate cases, have been used and the results presented in the original and the new ways are shown. The consequences concerning dating and dosimetry are discussed.

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1. Introduction

Optically stimulated luminescence (OSL) has been recognized as an important tool for dosimetry and for archaeological and geological dating (see e.g. Huntley et al., 1985). Bulur (1996) suggested changing the featureless OSL decay curve into a peak-shaped function by increasing the intensity of the stimulating-light linearly with time. For the linear-modulated OSL (LM-OSL) and first-order kinetics, the governing equation is

\[ L(t) = -\frac{dn_i}{dt} = (I_0/\theta) \frac{dn}{dn_i}(t), \] (1)

where \( L(t) \) is the emitted light intensity and \( t \) is the time, and where \( \theta \) (s) is the duration of the observation and \( a_0 \) (s⁻¹) is the probability of escape of electrons from the traps at a light intensity of \( I_0 \). The stimulating-light intensity here varies with time as \( I(t) = I_0/\theta \). The solution of this equation yields the intensity measured under these circumstances as a function of time

\[ I(t) = (a/\theta) n_0 I_0 \exp \left[ -\left( aI_0/2\theta \right) t^2 \right]. \] (2)

where \( n_0 \) is the initial occupancy of traps following excitation. This equation represents a peak-shaped function. As shown by Bulur (1996), the maximum intensity here is given by

\[ I_{\text{max}} = n_0 (aI_0/\theta)^1/2 \exp(-1/2). \] (3)

which is very useful in dosimetry applications since the maximum intensity is proportional to the initial concentration of trapped carriers \( n_0 \). This, in turn, is assumed to carry the information which concerns the absorbed dose. It is quite obvious that integration of Eq. (2) from 0 to infinity yields \( n_0 \). Thus, if one takes as the LM-OSL signal either the maximum intensity or the whole area under the

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curve, in the first-order case, the signal is proportional to the concentration following the excitation, \( n_0 \).

Bulur (1996) gave a similar treatment to LM-OSL governed by general-order kinetics. The governing equation here is

\[
L(t) = -dn/dt = \left( \gamma n_0 / \theta \right) tm^b, \tag{4}
\]

where \( \gamma \) is a constant. Bulur (1996) assumed that \( \gamma = \alpha/n_0^{b-1} \), where \( \alpha \) is the frequency factor. Bulur and Göksu (1999) changed this assumption to \( \gamma = \alpha/n^{b-1} \) where \( N \) is the concentration of trapping states, a similar assumption to that given by Rasheedy (1993) for general-order TL. Using the latter definition, the solution of Eq. (4) is

\[
L(t) = n_0^b \left( a_0 / \left( N^{b-1} \theta \right) \right) \left[ t / \left( N^{b-1} \theta \right) \right] \left\{ 1 + (b-1) \left[ a_0 n_0^{b-1} / \left( 2\theta N^{b-1} \right) \right] \right\} \times \left[ t^2 \right]^{-b/(b-1)}. \tag{5}
\]

Note that the general-order equation is merely an empirical presentation of cases intermediate in some sense between first and second order. An important special case is that of second-order kinetics, first suggested by Garlick and Gibson (1948), which takes place in cases of either dominating retrapping or of equal recombination and retrapping-probability coefficients (see e.g. P. 31 in Chen and McKeever, 1997). Here, we have for Eqs. (4) and (5) \( b = 2 \) and obtain

\[
L(t) = \frac{n_0^2 \left( a_0 / \left( N^{b-1} \theta \right) \right) t}{\left\{ 1 + \left[ a_0 n_0 / \left( 2N \theta \right) \right] t^2 \right\}^{2}} \tag{6}
\]

By equating the derivative of Eq. (5) to zero, one obtains

\[
t_{\text{max}} = \frac{2}{(b+1) \theta a_0 \left( N / n_0 \right)^{b-1}}. \tag{7}
\]

By inserting Eq. (7) into (5) one obtains

\[
L_{\text{max}} = 2 \left[ a_0 (b+1) / \theta n_0^{b-1} \right]^{1/2} \left[ 2b / (b+1) \right]^{-b/(b-1)} n_0^{(b+1)/2}. \tag{8}
\]

In a recent work, Chen and Pagonis (2008) have suggested a new presentation of LM-OSL results. Instead of the conventional way of plotting the LM-OSL intensity as a function of time, they suggested that the area under the phosphorescence decay graph into a peak-shaped curve suggested first by Randall and Williams (1945) and elaborated upon by Visocekas (1978) and Chen and Kristianpoller (1986). Chen and Pagonis (2008) showed that in the conventional presentation, the maximum intensity of the emitted signal can be expected to be superlinear with the initial concentration of trapped carriers, \( n_0 \), for general-order kinetics. From Eq. (8), we immediately see that

\[
L_{\text{max}} = n_0^{(b+1)/2} \frac{f}{\Gamma(b+1)}, \tag{9}
\]

where \( f = \Gamma(b+1) \) is the maximum of the curve, in the first-order case, the signal is proportional to the concentration following the excitation, \( n_0 \).

Thus, in the new presentation, when first-order or general-order kinetics, including the second-order case, governs the process, \( y_m \), the maximum of the \( y(x) \) curve must be linear with the initial concentration of carriers (following excitation by radiation). Note that this presentation is rather similar to the way of transforming the phosphorescence decay graph into a peak-shaped curve suggested by Chen and McKeever, 1997). Here, we have for Eqs. (4) and (5) \( b = 2 \) and obtain

\[
L(t) = \frac{n_0^2 \left( a_0 / \left( N^{b-1} \theta \right) \right) t}{\left\{ 1 + \left[ a_0 n_0 / \left( 2N \theta \right) \right] t^2 \right\}^{2}} \tag{6}
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2. The model

The model shown in Fig. 1 is the simplest possible one trap-one recombination-center (OTOR) for explaining the optically stimulated luminescence, including, of course, the LM-OSL. The meaning of the different magnitudes is given in the caption. The equations governing the process during the optical stimulation are

\[
L(t) = \frac{dm}{dt} = A_m m n_c. \tag{10}
\]

\[
\frac{dn}{dt} = A_m (N - n) n_c - f n, \tag{11}
\]

where \( m \) and \( n \) are the concentrations of electron trapping state and hole recombination centers; \( n \) and \( m \) are their instantaneous occupancies, respectively. \( f \) (s\(^{-1}\)) is the optical stimulation rate, such that the rate per cm\(^2\) per second is \( f \). Here, \( f = f_0 t \) where \( f_0 \) (s\(^{-1}\)) is constant. The instantaneous concentration of free electrons in the conduction band is \( n_c \) (cm\(^{-3}\)) and \( A_m, A_n \) are the recombination-probability and retrapping-probability coefficients, respectively.
Along the LM-OSL measurement, one may start with results immediately, namely of parameters, both in the original and new presentations. The maximum LM-OSL curve on read-out stage for different values of \( \frac{L}{C_0} \), during read-out, namely, linear modulation is achieved by increasing \( \frac{L}{C_0} \). To begin with, obviously the properties of the solution depend on the OTOR model, and substituting \( n = m \) and \( f = f_0 t \) we find

\[
L(t) = \frac{\text{d} n}{\text{d} t} = \frac{f_0 A_m n^2}{N A_n}.
\]

It appears more likely to get second-order kinetics with the dominating retrapping condition than with the equal probability coefficients. In any case, both Eqs. (18) and (19) are the same (with substitution of the relevant constants, \( \gamma / \theta = f_0 A_m / N A_n \)) as Eq. (4) with \( b = 2 \), and therefore Eq. (6) is its solution. Note that there are many intermediate cases in which \( A_m n \) is of the same order as \( A_n (N - n) \). These cannot be precisely presented by the ‘general-order’ equation.

3. Theory

In Section 4, we present numerical solutions of Eqs. (13–15) for sample sets of the five parameters: \( A_m, A_n, f_0, n_0 \) and \( N \). In this section, we use the quasi-steady assumption to develop an analytical solution. Then, we develop scaling laws that reduce the number of parameters that must be studied. The value of this reduction will be shown in the plots presented in Section 4. Starting with Eq. (16) of the OTOR model, and substituting \( n = m \) and \( f = f_0 t \) we find

\[
L = -\frac{\text{d} n}{\text{d} t} = f_0 t \frac{A_m n^2}{A_m n + A_n (N - n)}.
\]

which is subjected to the initial condition of \( n = n_0 \) at \( t = 0 \). This can be immediately integrated

\[
A_m - A_n \ln \left( \frac{n_0}{n} \right) + A_n \left( \frac{1}{n} - \frac{1}{n_0} \right) = \frac{1}{2} f_0 t^2.
\]

Equation (21) can be rearranged to solve for \( t \) as a function of \( n \),

\[
t = \sqrt{\frac{2}{f_0} \left[ \frac{A_m - A_n \ln \left( \frac{n_0}{n} \right)}{A_m} + A_n \left( \frac{1}{n} - \frac{1}{n_0} \right) \right]}.
\]

Combining Eqs. (20) and (22), the luminescence \( L \) can be found as a function of \( n \) alone,

\[
L = \sqrt{\frac{2 f_0}{A_m} \left[ \frac{A_m - A_n \ln \left( \frac{n_0}{n} \right)}{A_m} + A_n \left( \frac{1}{n} - \frac{1}{n_0} \right) \right]} \frac{A_m n^2}{A_m n + A_n (N - n)}.
\]

We are also interested in the transformed luminescence, \( t_l \), which is found from Eqs. (22) and (23),

\[
y = t_l t = 2 \left[ \frac{A_m - A_n \ln \left( \frac{n_0}{n} \right)}{A_m} + A_n \left( \frac{1}{n} - \frac{1}{n_0} \right) \right] \frac{A_m n^2}{A_m n + A_n (N - n)}. \quad (24)
\]

Now, we have \( t, L \), and \( t_l \) all as explicit functions of \( n \) in Eqs. (22–24). In order to create plots of \( L \) as a function of \( t \) and of \( t_l \) as a function of \( 2t_l n \), we choose a series of \( n \) in the range \( 0 \leq n \leq n_0 \). For each such value of \( n \), we can use Eqs. (22) and (23) to compute the values of time \( t \) and luminescence \( L \) which occur when the density reaches \( n \). This provides a point for use on a plot of \( L \) vs. \( t \). Similarly, by choosing various values of \( n \), we can create the transformed plot of \( t_l \) vs. \( 2t_l n \).
\[ \tilde{A} = \frac{A_m}{A_m} \]

Using these variables, Eqs. (22–24) can be rewritten as

\[ \tilde{t} = \sqrt{2 \left[ (1 - \tilde{A}) \ln \left( \frac{\tilde{n}_0}{\tilde{n}} \right) + \tilde{A} \left( \frac{1}{\tilde{n}} - \frac{1}{\tilde{n}_0} \right) \right]} \]

\[ \tilde{L} = \sqrt{2 \left[ (1 - \tilde{A}) \ln \left( \frac{\tilde{n}_0}{\tilde{n}} \right) + \tilde{A} \left( \frac{1}{\tilde{n}} - \frac{1}{\tilde{n}_0} \right) \right] \frac{\tilde{n}^2}{\tilde{n} + \tilde{A} (1 - \tilde{n})}} \]

\[ \tilde{L} = 2 \left[ (1 - \tilde{A}) \ln \left( \frac{\tilde{n}_0}{\tilde{n}} \right) + \tilde{A} \left( \frac{1}{\tilde{n}} - \frac{1}{\tilde{n}_0} \right) \right] \frac{\tilde{n}^2}{\tilde{n} + \tilde{A} (1 - \tilde{n})} \]

Whereas the right-hand sides of Eqs. (22–24) depend on six quantities, \( A_m, A_m f_0, N, n_0 \) and \( n \), in Eqs. (29–31), the right-hand sides depend on only three quantities, \( \tilde{n}, \tilde{n}_0 \) and \( \tilde{A} \). The use of these new equations is discussed below.

4. Numerical results

In order to check the dependence on the initial concentration, \( n_0 \), of the original as well as the revised LM-OSL curves, we chose sets of parameters, and solved numerically Eqs. (13–15) for different values of the initial traps and centers occupancy, \( n_0 = m_0 \), using the Matlab ode23s solver. Alternatively, we used Eqs. (29–31) and proceeded as explained below. The figures shown below are of the simulation, but the results of both methods were exactly the same. The exact agreement of the two approaches is related to the choice of parameters such that the quasi-steady assumption for free carriers prevails. We then changed the value of the initial occupancies, and observed the variations in the peak shape. This has been done for cases of first order, second order of the two types mentioned above and for intermediate cases. Throughout the simulation process, we monitored the values of \( A_m m \) and \( A_m (N - n) \), and compared them in order to see whether the conditions mentioned above are fulfilled. We have also monitored the values of \( n_t \) and \( n \) in order to verify that the quasi-steady condition holds.

Fig. 2 shows the results of the simulation for the set of parameters given in the caption. Here, \( A_m \) is 5 orders of magnitude larger than \( A_m \), and first-order kinetics can be expected. Indeed, \( mAm \) is found to be 3–4 orders of magnitude larger than \( A_m \) in the simulations. The result is a peak in the LM-OSL curve, which does not shift with the change of the initial value of \( n_0 \). As seen in the graph, the maximum intensity doubles from one curve to the next, as expected when \( n_0 \) varies by factors of 2. Fig. 3 shows the same results in the new way suggested by Chen and Pagonis (2008). The peaks here are very similar in shape to first-order TL peaks. As expected, the maxima are linearly dependent on \( n_0 \).

Fig. 4 shows the results of simulations with the parameters given in the caption. Here, \( A_m \) is larger than \( A_m \), and along with \( N \) being significantly larger than \( n \), \( A_m (N - n) \gg A_m m \), and the second-order kinetics results. Like in TL, the peak shifts to lower values of \( t \) for higher values of \( n_0 \). As for the maximum intensity, it is readily seen to increase superlinearly with \( n_0 \). For example, while going from curve (a) to (e), \( n_0 \) increases by a factor of 16, and \( L_{\text{max}} \) by \( \sim 64 \), which, indeed is \( 16^{3/2} \). Fig. 5 shows the same results in the new presentation. The peaks are symmetric, similarly to second-order TL peaks. As expected from the work by Chen and Pagonis (2008), the maximum intensity here is proportional to the value of \( n_0 \). Similar simulations have been performed with \( A_m = A_m \) (not shown here). As expected, here, irrespective of the relation between \( A_m m \) and \( A_m (N - n) \), the second-order behavior is seen.

Fig. 6 shows the LM-OSL results of an intermediate case, the relevant parameters are given in the caption. Here, for the lowest value of \( n_0 \), \( A_m (N - n) \) is about an order of magnitude larger than \( A_m m \), whereas for the highest value, the former is smaller than the latter. The peak shifts here with the value of \( n_0 \), pointing to a non-first-order behavior. The ratio of \( L_{\text{max}} \) between the largest to smallest \( n_0 \) is here ~48, which is rather superlinear, behaving like \( \sim n_0^{3/2} \). Fig. 7 depicts the same results in the new presentation. Here, the dependence on \( n_0 \) is somewhat more than linear. The ratio between the maximum intensities is 18.38 for the change of \( n_0 \) by a factor of 16.

In the present work, we are dealing with single LM-OSL peaks, but in dosimetry and dating, it is common that a number of peaks occur. If there is some overlapping of components but peaks are
separated sufficiently, integration over certain interval may be used so as to maximize counts but at the same time to isolate as much as possible the different peaks. We have studied the behavior of such an area on $n_0$ in our simulations for the set of parameters used in Figs. 6 and 7, where the dependence on $n_0$ is strongly superlinear. We have taken the area under the curve from $t_m - dt$ to $t_m + dt$ where $t_m$ is the time of maximum of the LM-OSL signal and $dt$ a selected time interval. For each value of $dt$, the value of $x$ in the approximate dependence $n_0^x$ has been determined. The results are shown in Table 1 and discussed below.

Let us consider the LM-OSL peak intensity in a more general way. For fixed initial concentration $n_0$ and fixed rate-constant ratio $A$, we can find, via Eq. (30), the value of concentration $\bar{n}$ which maximizes the LM-OSL luminescence $L$. This was done using the numerical function maximizer fminbound from the package in SciPy (scientific Python). The value of the maximum luminescence $\bar{L}$ can be plotted as shown in Fig. 8 as a function of $n_0$ for different values of $\bar{A}$. This log–log plot has a slope of 1.5 for large values of $A_0/A_m$, and is more than unity even for smaller values, which shows that the response of the LM-OSL maximum is superlinear except when kinetics are first-order; the response is linear only when $\bar{n}_0 \gg \bar{A}$, i.e. $n_0 A_m \gg N A_m$.

The transformed LM-OSL can be studied similarly. We start by finding the values of $\bar{n}$ which maximize Eq. (31) for fixed values of $\bar{n}_0$ and $\bar{A}$. This was done again with the same numerical maximizer. The values of $\bar{L}$ found from the maximizer are plotted against $\bar{n}_0$ on a log–log scale in Fig. 9. Note that the peak of the transformed intensity, $\bar{L}$, depends on only two parameters, $\bar{n}_0$ and $\bar{A}$. Since Fig. 8 shows the peak plotted against $\bar{n}_0$ for various values of $\bar{A}$, this plot includes the entire parameter space. From Fig. 9, it is clear that the transformed LM-OSL peak intensity is mostly linear with $n_0$. Note that, unlike usual LM-OSL, the peak intensity of the transformed LM-OSL is independent of the experimental value of $f_0$, though its position depends on $f_0^{0.5}$, as can be seen in Eq. (22).
The peak of luminescence as plotted against normalized initial concentration

<table>
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<th>50</th>
<th>75</th>
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<td>1.390</td>
<td>1.375</td>
<td>1.350</td>
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5. Discussion

In this work, we have studied the LM-OSL curves in their original and revised versions, by solving numerically the governing set of coupled differential equations, and by analytical means, using the one trap-one recombination-center model. By choosing sets of parameters leading to first-order kinetics, namely, dominating recombination, we have seen the characteristic behavior, i.e. that the LM-OSL peak maximum does not shift with the initial occupancy of traps. In addition, the shape of the new presentation resembled a first-order TL peak as expected and the maximum intensity depended linearly on $n_0$. The second-order case was seen either by having dominating retrapping or, alternatively, with the recombination and retrapping-probability coefficients being equal; in the former case, the trap has to be far from saturation. In both cases, the initial-concentration dependence of the original presentation was like $n_0^{1.5}$, and that of the revised one was linear, as expected. As for the intermediate cases, depending on the parameters chosen, intermediate dependencies on $n_0$ could be found. In the specific example shown in Figs. 6 and 7, in the original LM-OSL presentation, the initial-concentration dependence of the maximum could be given by $\sim n_0^{1.05}$ in the example given, a very weak superlinearity as compared to the expected linearity for any value of $b$ in the general-order presentation. The results of Fig. 9 show that the near-linear dependence of the transformed LM-OSL on $n_0$ takes place generally within the OTOR situation. However, one should not be surprised that there are slight deviations from linearity since one cannot expect the results of the simulation to fit exactly into the general-order framework.

It should be pointed out that the dependence of $n_0$ on the dose, which is very relevant to the dose dependence of the LM-OSL signal in its two presentations, has not been dealt with here. In cases where the trap occupancy is linear with the dose, the dependency of the LM-OSL maximum on the dose is, obviously, the same as that of $n_0$ discussed here. Other dependencies of $n_0$ can sometimes be expected, and will be discussed elsewhere. If, for example, $n_0(D)$ is a square-root function (Lawless et al., in press), this should be combined with the dependence of the LM-OSL signal on $n_0$. Thus,

![Fig. 8](image1)

![Fig. 9](image2)

Fig. 8. The peak of luminescence as plotted against normalized initial concentration $n_0/N$ for various values of $A = A_0/A_m$.

Fig. 9. The peak of the normalized transformed luminescence, $n_0/N$, plotted against the normalized initial concentration, $n_0/N$ for various values of $A = A_0/A_m$. 

Table 1

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<thead>
<tr>
<th>$\Delta t$ (s)</th>
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cases where the latter depends linearly on the dose, the signal will go like $D^{3/2}$, whereas if $n_0(D) \propto D^{3/2}$, the LM-OSL maximum may go like $D^{3/4}$. Obviously, the question of whether the LM-OSL maximum is linear with the excitation dose is of great importance for dosimetry and dating. Therefore, before using the procedure for dose evaluation, the dose dependence of the specific material under study should be established.

Acknowledgement

We would like to thank the anonymous referees for some important comments and suggestions which improved this work significantly.

References