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On the initial-occupancy dependence of some luminescence phenomena under the one-trap-one-recombination-center (OTOR) model

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ABSTRACT

We discuss the expected dependence of the maximum signal of a number of luminescence phenomena, used in dosimetry and archaeological and geological dating, on the initial occupancy of the relevant traps, n_0, within the OTOR (also called General One Trap (GOT)) model. This, in turn, has important bearing on the dose dependence of these phenomena. We discuss the dependence of the linearly-modulated optically-stimulated-luminescence (LM-OSL) as well as the non-linear optical stimulation (NL-OSL) on the initial concentration n_0 of trapped carriers. We also consider the behavior of CW-OSL and phosphorescence in a transformed form, as well as TL measured under hyperbolic and linear heating rates. Using an appropriate presentation, the maximum of the signal is seen to depend nearly linearly on n_0, which in many cases means nearly linear dependence on the dose, a property important for dosimetry and dating.

1. Introduction

Different luminescence phenomena are used for the evaluation of the absorbed dose in crystalline materials. These include thermoluminescence (TL) and its isothermal version, phosphorescence, as transformed in a manner suggested by Randall and Wilkins (1945) and further developed by Chen and Kristianpoller (1986). These authors suggested transforming the featureless decay function by plotting $y = L \cdot t$ as a function of $x = \ln t$. They showed that one gets a peak-shaped curve, similar to that of TL under a hyperbolic heating function. Also are included optically stimulated luminescence (OSL), either under continuous constant stimulation (CW-OSL) or under linearly-modulated stimulation (LM-OSL) (see e.g., Bulur, 1996). Recent work by Bos and Wallinga (2009) suggested the use of non-linearly modulated OSL (NL-OSL), including exponentially increasing OSL (EM-OSL), hyperbolically increasing OSL (HM-OSL) and reciprocally increasing OSL (RM-OSL).

Chen and Pagonis (2008) have shown that TL obtained with a hyperbolic heating function, phosphorescence transformed in a previously suggested manner and LM-OSL presented in a new way, repeated briefly below, can be cast into a unified form which has an important advantage when the first-order, second-order and general-order kinetics govern the read-out process. Chen and Pagonis have also shown that with the Bulur presentation of LM-OSL, whereas in the first-order kinetics, the dependence of the maximum signal is proportional to the initial trap concentration, n_0, the maximum of the signal behaved as $n_0^{b/(b-1)}$ with general-order kinetics, which for the important second-order case means an $n_0^{3/2}$ dependence. They suggested a manipulation of the LM-OSL data in which $y = t \cdot L(t)$ is plotted, where $L(t)$ is the LM-OSL signal as a function of $x = 2\ \ln t$. It has been shown that under these circumstances, in the new presentation of the LM-OSL, the dependence of the maximum of the LM-OSL is strictly linear with the initial carrier concentration of the trapped carriers for all the cases included in the general-order kinetics. In previous work (Chen et al., 2009), we have shown that the LM-OSL expected from the one-trap-one recombination-center (OTOR) model yields a nearly linear dependence on the initial concentration of trapped carriers which, in many cases, means a nearly linear dependence on the excitation dose. In the present work we show how the same ideas developed for LM-OSL can be used for CW-OSL and phosphorescence in a transformed form, as well as for TL measured using hyperbolic and linear heating rates. In particular, the expected dependence of these signals on the initial occupancy n_0 within

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the OTOR model is studied, which may, under the appropriate circumstances, represent the dose dependence of these luminescence phenomena. It should be noted, however, that Lawless et al. (2009) have shown that within the OTOR model, assuming that the quasi-steady condition holds, and that the dose D is much larger than the ratio $A_nN/(2A_m)$ where N is the concentration of the relevant trap and A_n/A_m the ratio between the retrapping and recombination probabilities, the occupancy concentration n_0 may depend on the dose D in a sublinear manner, sometimes as $D^{1/2}$.

2. Basic considerations for LM-OSL

In this section we very briefly repeat the main results of the previous work. Within the OTOR model there is one electron trapping state, n, and one kind of recombination center, m. For OSL, three simultaneous differential equations in n and m can be written which, along with the quasi-steady assumption (see e.g., Chen et al., 2009), yield

$$L = -\frac{\mathrm{d}m}{\mathrm{d}t} = f\frac{A_m mn}{A_m m + A_n(N-n)}, \tag{1}$$

where $A_m(\mathrm{cm}^3\ \mathrm{s}^{-1})$ and $A_n(\mathrm{cm}^3\ \mathrm{s}^{-1})$ are the recombination and retrapping probability coefficients, respectively, N is the total number of traps of a given kind and $f(\mathrm{s}^{-1})$ is the detrapping probability. If we denote the stimulating light intensity by $F(\mathrm{cm}^{-2}\ \mathrm{s}^{-1})$ and the optical cross section by $a(\mathrm{cm}^2)$, then $f = Fa$. In the OTOR model, assuming that no electrons are accumulated in the conduction band, the concentrations of electrons and holes are equal, $m = n$. In the case of CW-OSL, f is considered to be constant; in LM-OSL, it increases linearly with time, $f = f_0 t$, where $f_0(\mathrm{s}^{-2})$ is a constant. We obtain

$$L = -\frac{\mathrm{d}n}{\mathrm{d}t} = f_0 t\frac{A_m n^2}{A_m n + A_n(N-n)}, \tag{2}$$

which is subjected to the initial condition $n = n_0$ at $t = 0$. This equation is integrated to yield

$$\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right) = \frac{1}{2}f_0 t^2. \tag{3}$$

Equation (3) can be rearranged to solve for t as a function of n,

$$t = \sqrt{\frac{2}{f_0}\left[\frac{A_m - A_n}{A_m}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right]}. \tag{4}$$

Combining Eqs. (2) and (4), the luminescence L can be found as a function of n alone,

$$L = \sqrt{2f_0\left[\frac{A_m - A_n}{A_m}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right]}\frac{A_m n^2}{A_m n + A_n(N-n)}. \tag{5}$$

We are also interested in the transformed luminescence, tL, which is found from Eqs. (4) and (5),

$$y = tL = 2\left[\frac{A_m - A_n}{A_m}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right]\frac{A_m n^2}{A_m n + A_n(N-n)}. \tag{6}$$

Now, t, L and tL, are all explicit functions of n in Eqs. (4–6). The method suggested by Chen et al. (2009) is to plot Lt as a function of $2\ln t$ and to choose a series of n values in the range $0 \le n \le n_0$. For each such value of n, Eqs. (4) and (5) can be used 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 tL vs. $2\ln t$. Chen et al. (2009) show how to transfer Eqs. (4-6) into a non-dimensionalized form where, instead of six quantities, there are only three normalized quantities. They also show the dependence of the peak of normalized transformed luminescence, tL/N on the normalized initial concentration, n_0/N for various values of the dimensionless quantity $\hat{A} = A_n/A_m$. This graph is repeated in Fig. 1 here, and shows that the maximum intensity of this representation of the LM-OSL is very close to linearity for a very wide range of values of the ratio A_n/A_m.

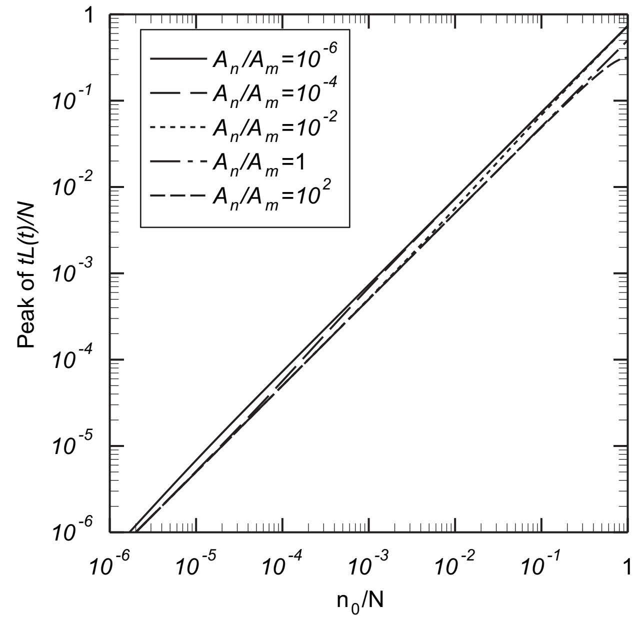

Fig. 1. The peak of the normalized transformed LM-OSL, tL/N, plotted against the normalized initial concentration, n_0/N for various values of $\hat{A} = A_n/A_m$. The slight changes in the y-axis for the other luminescence expressions are explained in the text.

3. The TL-like representation of phosphorescence and CW-OSL

For the case of CW stimulating light intensity, f is constant and Eq. (1), along with $n = m$, will be

$$L = -\frac{\mathrm{d}n}{\mathrm{d}t} = f\frac{A_m n^2}{A_m n + A_n(N-n)}. \tag{7}$$

Following the same procedures used to derive of Eqs. (3–6), we obtain the following set of analogous equations,

$$\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right) = ft. \tag{8}$$

$$t = \frac{1}{f}\left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right]. \tag{9}$$

$$y = Lt = \left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right]\frac{A_m n^2}{A_m n + A_n(N-n)}. \tag{10}$$

Equation (10) is the same as Eq. (6), except for the factor 2 in the latter. Equations (6) and (10) will be shown below to be special cases of a more general time dependent stimulating light intensity function. It is important to note that since Eq. (10) is practically the same as Eq. (6), the conclusions concerning the n_0 dependence of the maximum hold for the present case as well. In addition to the strictly linear dependence of the signal for first and second-order situations (as well as in the cases of general-order kinetics), in all the OTOR cases, the n_0 dependence of the signal is nearly linear for all values of A_n/A_m as shown in Fig. 1. The practical advantage over the LM-OSL case is that the experiment is usually simpler since there is no need for linear modulation. One only has to manipulate the OSL decay data and the conclusion of near linearity is the same for LM-OSL and the TL-like presentation. One should note, however, that in order to reach a constant level, a certain period of time is required. The stimulating light intensity is, in fact, a step function which may not be easy to realize. Therefore, in analyzing ultra-fast OSL components, trying to use CW-OSL may be problematic.

Exactly the same conclusions can be reached for the decay of phosphorescence within the OTOR model. In Eq. (7) we have to replace the constant stimulating light intensity f by $\gamma = s\cdot\exp(-E/kT)$, where s and E are the relevant frequency factor and activation energy and T is the temperature. Since in the phosphorescence measurement the temperature is kept unchanged, this factor is a constant. Thus, Eqs. (7–10) remain exactly the same for the case of phosphorescence, with γ replacing f throughout.

4. NL-OSL

As mentioned above, a non-linear stimulation intensity was mentioned as another possibility for OSL. Let us concentrate on a power law dependence, $f = f_0 t^k$ where k is any power, integer or a fraction, and f_0 has the appropriate units so that f has the dimensions of s^{-1}. Equation (2) is now slightly changed,

$$L(t) = -\frac{dn}{dt} = f_0 t^k \frac{A_m n^2}{A_m n + A_n(N-n)}. \tag{11}$$

where f_0 has the appropriate units so that $f_0 t^k$ has units of s^{-1}. This integrates directly to yield

$$\left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right] = \frac{1}{k+1} f_0 t^{k+1}, \tag{12}$$

From Eq. (11) we obtain

$$t\cdot L(t) = f_0 t^{k+1} \frac{A_m n^2}{A_m n + A_n(N-n)}, \tag{13}$$

and by comparing Eqs. (12) and (13) one gets

$$Lt = (k+1)\left[\frac{A_m - A_n}{A_m}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right]\frac{A_m n^2}{A_m n + A_n(N-n)}. \tag{14}$$

This is the same as Eq. (6), except for the factor $k + 1$ that replaces the factor of 2. Obviously, Eq. (6) is a special case of Eq. (14), applicable to the LM-OSL case, where $k = 1$, and Eq. (10) is the special case applicable to phosphorescence and CW-OSL, both for the general OTOR case, with $k = 0$.

Another stimulation mode, mentioned by Bos and Wallinga (2009) with regard to the first-order NL-OSL is the exponential mode which can be written as

$$f(t) = f_0 e^{\alpha t}, \tag{15}$$

for which, Eq. (2) can be changed to

$$L(t) = f_0 e^{\alpha t} \frac{A_m n^2}{A_m n + A_n(N-n)}. \tag{16}$$

By integration,

$$\left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right] = \frac{1}{\alpha} f_0 e^{\alpha t}, \tag{17}$$

from which,

$$L(t) = \frac{1}{\alpha}\left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right]\frac{A_m n^2}{A_m n + A_n(N-n)}, \tag{18}$$

where the right-hand side is the same as that in Eq. (14) except that $1/\alpha$ replaces $(k + 1)$. Note that here, on the left-hand side we have $L(t)$ and not $tL(t)$.

Going one step further, we can consider any monotonically non-decreasing stimulation mode $f(t)$. This can include the above mentioned cases, along with the hyperbolically increasing stimulation intensity (HM-OSL) and the reciprocal stimulation function mentioned by Bos and Wallinga (2009) as well as other possibilities. In full analogy to the previous cases, we obtain the general relationship

$$\frac{\int_0^t f(t')dt'}{f(t)} L(t) = \left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right] \times \frac{A_m n^2}{A_m n + A_n(N-n)}. \tag{19}$$

It can readily be seen that the case of constant stimulation intensity and phosphorescence, as well as all the mentioned monotonically increasing stimulation functions, are included in Eq. (19). In these cases, the function of t preceding $L(t)$ in Eq. (19) can be easily evaluated as shown above. With other stimulation functions, the evaluation of $\int_0^t f(t')dt'/f(t)$ may not be as easy. Note that the expression $\int_0^t f(t')dt'/f(t)$ has dimensions of time. While comparing Eq. (19) on one hand and Eqs. (6), (10) and (14) on the other hand, the expression $\int_0^t f(t')dt'/f(t)$ can be considered as a "generalized time" for the present purpose.

5. Thermoluminescence with a hyperbolic heating rate

Similar to the previous case, the following expression can be written for TL

$$L = -\frac{dn}{dt} = s\exp(-E/kT)\frac{A_m n^2}{A_m n + A_n(N-n)}, \tag{20}$$

where the temperature T is a function of time. The initial condition for $t = 0$ is again $n(0) = n_0$. By integration,

$$\left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right] = s\int_0^t \exp(-E/kT(t'))dt'. \tag{21}$$

The hyperbolic heating function, frequently mentioned in the literature (see e.g., Stammers (1979) and Chen and McKeever (1997)), can be written as

$$\frac{1}{T(t)} = \frac{1}{T_0} - \frac{t}{\beta'}, \tag{22}$$

where β' has units of K s. Using Eq. (22), the integration in Eq. (21) can be performed exactly to yield

$$\left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right] = \frac{sk\beta'}{E}\left[e^{-E/kT} - e^{-E/kT_0}\right]. \tag{23}$$

Since the exponent is a rapidly increasing function of temperature, the second exponent can be neglected for any T larger than T_0 even by only a few degrees. Equation (23) is now integrated to

$$\left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right] = \frac{sk\beta'}{E}e^{-E/kT}. \tag{24}$$

By substituting Eq. (24) in Eq. (20), we get

$$L = \frac{E}{k\beta'}\left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right]\frac{A_m n^2}{A_m n + A_n(N-n)}. \tag{25}$$

Again, except for the constant coefficient, the expression on the right-hand side is exactly the same as in Eqs. (6), (10), (14) and (18).

6. Thermoluminescence with a linear heating function

For the linear heating function,

$$T = T_0 + \beta t, \tag{26}$$

where β is the constant heating rate, we get from Eq. (21)

$$\left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right] = (s/\beta)\int_0^T \exp(-E/kT)\mathrm{d}T. \tag{27}$$

The integral on the right-hand side can be written as

$$\int_0^T \exp(-E/kT)\mathrm{d}T = \exp(-E/kT)\cdot f(T,E), \tag{28}$$

and if we choose the asymptotic series method for evaluating the integral,

$$f(T,E) = T\sum_{i=1}\left(\frac{kT}{E}\right)^i(-1)^{i-1}i!. \tag{29}$$

Note that other approximate expressions may replace the right-hand side of Eq. (29). From Eqs. (27) and (28),

$$s\exp(-E/kT)\cdot f(T,E) = \beta\left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right]. \tag{30}$$

Substituting Eq. (30) into Eq. (20) yields

$$L\cdot f(T,E) = \beta\left[\frac{A_m - A_n}{A_n}\ln\left(\frac{n_0}{n}\right) + \frac{A_n N}{A_m}\left(\frac{1}{n} - \frac{1}{n_0}\right)\right]\frac{A_m n^2}{A_m n + A_n(N-n)}. \tag{31}$$

For given values of n_0, E, β and A_n/A_m, Eq. (30) yields values for $s\exp(-E/kT)f(T,E)$ for any chosen value of n, and for a given E, it can be numerically inverted to get $T(n)$. Substituting T into $f(T,E)$ results in an expression of L as a function of n and all the given parameters, which can be maximized to yield the maximum of the TL intensity for any given n_0. The right-hand side of Eq. (31) is exactly the same expression as in the previous cases (e.g., Eq. (6) in the LM-OSL case described above, with β replacing 2) whereas to evaluate the left-hand side a reasonable approximation of $f(T,E)$ is required, which depends on an evaluation of the activation energy E.

7. Conclusion

We have shown that several luminescence phenomena, namely, LM-OSL, TL-like presentation of phosphorescence and CW-OSL, NL-OSL with different stimulation modes and TL under hyperbolic and linear heating rates can be given in a unified form within the OTOR model. Based on our previous work (Chen et al., 2009), it is concluded that in all these phenomena, when presented in an appropriate manner, the maximum signal depends nearly linearly on the initial occupancy of the traps, n_0, as shown in Fig. 1. This, as compared with the "general-order" kinetics where at least for a revised representation of the LM-OSL, it has been shown that the dependence is strictly linear. This, in turn, may be translated into a near linear dose dependence in cases where the initial occupancy (following the appropriate irradiation) is linear with the excitation dose.

It should be noted that in Fig. 1, $t\cdot L(t)/N$ is plotted against n_0/N, as previously suggested for the LM-OSL case. The same should be done for the TL-like representation of phosphorescence and CW-OSL as well as the $\sim t^k$ dependence of the stimulation intensity. For TL measured with a hyperbolic heating rate, and for NL-OSL measured with an exponential mode of stimulation, L should be plotted as a function of n_0/N. More complicated cases are those of the general stimulation mode where the left-hand side of the expression derived is $((\int_0^t f(t')\mathrm{d}t')/(f(t)))L(t)$ and where TL is measured with a linear heating rate it is $L\cdot f(T,E)$.

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