Apparent anomalous fading of thermoluminescence associated with competition with radiationless transitions

R. Chen*, P.L. Leung, M.J. Stokes

Department of Physics and Materials Science, City University of Hong-Kong, Kowloon, Hong Kong

Abstract

Anomalous fading of thermoluminescence (TL) is the effect of a fading which is significantly faster than what is warranted by the trapping parameters which are evaluated from the features of the TL peak in question. A previous work suggested that in certain cases, apparent anomalous fading may be a normal fading in disguise. The idea was that, at least in some cases, radiationless transitions into competing recombination centers may yield a very narrow peak which, while using either the curve fit technique or the different peak shape method will result in very high values of effective activation energy E and frequency factor s which, in turn, will yield an apparent life-time orders of magnitude higher than the real one. The question has been raised whether this anomaly is observable only when the peak shape methods are utilized and in particular, can the same effect occur when the broadly used initial-rise method is applied. It is demonstrated in this work that under similar circumstances of competition, very high effective values of E and s are evaluated which result in very high life-times when the activation energy is evaluated by the initial-rise method. Thus, the explanation of apparent anomalous fading as being a normal decay in disguise, is extended to cases in which the initial-rise method is utilized for the parameter evaluation. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

An important feature of a thermoluminescence (TL) peak for its application in TL dosimetry and even more so, in TL dating is its stability with time. Every peak may undergo thermal fading which normally depends on the trapping parameters of the relevant peak and the temperature at which the sample is held

following its excitation, characteristically room temperature (RT). In the simplest case of first order kinetics, the relevant parameters are the activation energy E (eV) and the frequency factor s (s^{-1}), and the life-time for decay at temperature T (K) is $\tau = s^{-1}\exp(-E/kT)$ where k is the Boltzmann constant (eV K^{-1}). The trapping parameters E and s of a simple first-order peak can easily be evaluated by the temperature of the maximum and the shape of the peak (see, e.g., Chen and McKeever, 1997), and therefore, the expected decay time τ can be found easily. Thus, typically, a peak expected to occur, say, at 500 K, can be expected to be rather stable when the sample is held at room temperature ($\sim$300 K).

Quite a number of researchers have found that cer-

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* Corresponding author. School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel-Aviv, University, Ramat-Aviv, Tel-Aviv 69978, Israel. Tel.: +972-3-6408636; fax: +972-3-6429306.

E-mail address: chenr@ccsg.tau.ac.il (R. Chen).

tain peaks behaved in a different manner, and displayed anomalous fading. As early as 1950, Bull and Garlick (1950) reported that two UV excited peaks in diamond, occurring at 400 and 520 K, yield lower light levels if stored at 90 K for 6 h before glowing than if glowed immediately after excitation. Later, Hoogenstraaten (1958) reported the decay of light levels at low temperature in ZnS samples. He explained the effect as being due to the quantum mechanical tunneling of electrons from traps to empty activation centers. Schulman et al. (1969) reported the effect in CaF_2:Mn samples. Kieffer et al. (1971) found a similar effect in organic glasses. In all these cases, no temperature dependence of the anomalous fading was reported. As opposed to this, Wintle (1973, 1977) measured the anomalous fading in various minerals at different temperatures and discussed its implications regarding the dating of archaeological materials such as feldspars. Visocekas et al. (1983) studied the afterglow of $CaSO_4$:Dy and showed that after the initial irradiation, a weak afterglow is observed for a long period of time, with the same emission spectrum as that following TL. The peak used for dosimetry at ∼250°C decays down to LNT with time, at RT and below, practically independently of the temperature. The explanation given was that both the afterglow and anomalous fading in the material resulted from a quantum mechanical tunneling effect.

Further results on the anomalous fading of TL in zircon have been reported by Templer (1985, 1986) who concluded that in zircon and pumice samples, above room temperature, localized transitions are responsible for the anomalous fading whereas at lower temperatures, tunneling predominates. Hasan et al. (1986) reported the fading of TL in some meteorites and concluded that meteorites containing feldspars in the low form display anomalous fading. Tyler and McKeever (1988) studied the anomalous fading of TL in oligoclase and examined critically the conclusions of Hasan et al. (1986). Their conclusion is that the anomalous decay in this material is more closely described by the localized transition model of Templer, rather than by quantum mechanical tunneling. Fragoulis and Stoebe (1990) discussed the anomalous fading of TL of inclusions in quartz and suggested that the feldspar inclusions may account for a portion of the fading, but other inclusions probably participate in the fading. Visocekas et al. (1996) studied the tunneling effects in feldspars leading to anomalous fading.

More recently, Chen and Hag-Yahya (1997) raised the possibility that, in fact, anomalous fading may be in some instances just a normal fading in disguise. The idea has been that it is possible that due to competition of non-radiative centers, the visible TL peak will look significantly narrower than otherwise anticipated with the given activation energy E and the frequency

factor s of the peak. It has been demonstrated that using curve fitting or other shape methods for the evaluation of the activation energy, yielded under these circumstances very high values of the activation energy. This, in turn, yielded effective s values orders of magnitude higher than the "real" one; the result has been shown to be that the apparent life-time τ_{app} could be orders of magnitude higher than the real one τ. Thus, when one expects from the calculated parameters a long life-time, a short decay life-time is observed which may be referred to as "anomalous fading".

2. Extension of the model

A question has been raised about the generality of these conclusions (Aitken, 1998). As explained above, the unusually high activation energy evaluated resulted from the narrow form of the peak and the application of the shape method or the best-fit to such a narrow peak. One may ask what results should be expected if the initial-rise method is applied to such an artificially narrow glow peak. The initial-rise method is based on the assumption that practically independently of the details of the kinetics of the TL peak in question, a plot of $\ln(I)$ vs. $1/T$ in the initial-rise range should yield a straight line, the slope of which being $-E/k$, from which the activation energy E is readily evaluated. It is difficult to anticipate intuitively what can one get from the initial-rise method in which the features of the peak, had it been alone, can be masked by the interference of the competing radiationless center or centers. Very generally speaking, however, one can think that the narrow shape of the peak may mean that at the low temperature half of the peaks the TL intensity increases with temperature very fast which may result in an apparently high activation energy as a result of the high slope of the $\ln(I)$ vs. $1/T$ curve. In fact, the question can be divided into two parts: (1) Do we get a straight line on the $\ln(I)$ vs. $1/T$ curve at all? (2) Is the slope of this line large so that the apparent activation energy is high? If so, substituting in the equation for the maximum

$$\beta E/kT_m^2 = s \cdot \exp(-E/kT_m) \qquad (1)$$

would result in a very large value of the frequency factor s, and in turn, in a very high apparent life-time. In this very general sense, the initial-rise method measures a shape feature of the peak which therefore will, at least qualitatively behave in a similar way to the other shape methods, namely, will yield high activation energies for narrow peaks. It should be noted, however, that choosing the

"appropriate" initial-rise range is of great importance. For example, it may very well be that the initial-rise curve up to, say, 1% of the maximum may yield a straight line with a slope giving the original (low) activation energy. This may have no relevance in the experimental peak if the 1% level is too low to be measured. Thus, it is conceivable that, say, in the range of 1–5% of the maximum, a higher slope resulting in a higher apparent activation energy will be observed. Of course, at further high temperature, the slope decreases, which is similar to the situation in a "normal" TL peak beyond the initial-rise range.

In the following, we shall briefly repeat the model introduced by Chen and Hag-Yahya (1997), and will elaborate on the evaluation of the initial-rise activation energies and discuss the consequences concerning the apparent life-time.

Fig. 1 depicts the energy levels included in the model. M_1, M_2 and M_3 are the three recombination centers, the same symbols also stand for the concentrations (m^{-3}) of these three kinds of centers. m_1, m_2 and m_3 (m^{-3}) are the instantaneous concentrations of holes in these centers, respectively. The irradiation is assumed to produce electrons and holes at a rate of x $(m^{-3} s^{-1})$ in the conduction and valence bands, re-

spectively. The instantaneous concentration of electrons in the conduction band is denoted by n_c (m^{-3}) and that of the holes in the valence band by n_v (m^{-3}). B_1, B_2 and B_3 are the probabilities of capturing holes in M_1, M_2 and M_3, respectively, whereas A_{m1}, A_{m2} and A_{m3} are the three recombination probabilities of free electrons with captured holes. These may take place either during the excitation stage or during heating. As noted above, the transition into M_2 is considered to be radiative whereas those into M_1 and M_3 radiationless or radiative in a spectral range which is not measurable with the detecting device used. N (m^{-3}) denotes here the total concentration of electron trapping states and n (m^{-3}) its instantaneous filling. E (eV) and s (s^{-1}) are the activation energy and frequency factor of the electron trap and A $(m^3 s^{-1})$ the retrapping probability of electrons from the conduction band. All these magnitudes play a part in the excitation stage. As for the heating stage, it is obvious that no electron–hole production takes place during this stage which means that $x = 0$. Also, M_1, M_2 and M_3 are assumed to be rather far from the valence band, thus no holes are "raised" (energy-wise) into the valence band and therefore $n_v = 0$, thus B_1, B_2 and B_3 are irrelevant at this stage. As opposed to this, electrons from N may be thermally released into the conduction band and then, either
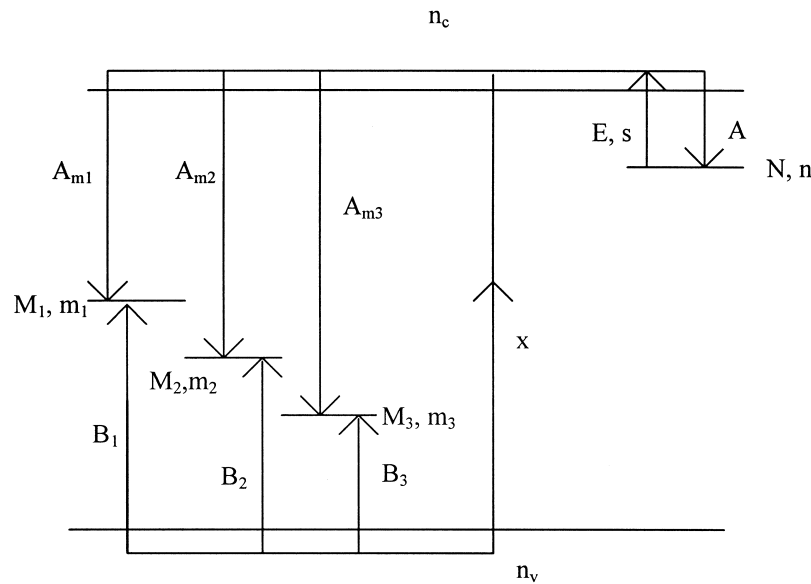

Fig. 1. Energy level model with one trapping state and three kinds of recombination centers. The transitions shown are those taking place during the excitation. The meaning of the different symbols are given in the text. In the heating stage, no electrons are raised from the valence into the conduction band, therefore $n_v = 0$ and B_1, B_2 and B_3 play no role; the source of electrons in the conduction band is the thermal raising from n, and transitions into M_1, M_2 and M_3 take place.

retrap or recombine with holes in M_1, M_2 and M_3. As pointed out earlier, it is assumed that the transitions into M_2 produce measurable photons whereas those into M_1 and M_3 are radiationless.

The set of simultaneous differential equations governing the process during the excitation stage is (see, Chen and Hag-Yahya, 1996)

$$dn_v/dt = x - B_1(M_1 - m_1)n_v - B_2(M_2 - m_2)n_v$$

$$- B_3(M_3 - m_3)n_v, \qquad (2)$$

$$dm_1/dt = -A_{m1} \cdot m_1 \cdot n_c + B_1(M_1 - m_1)n_v, \qquad (3)$$

$$dm_2/dt = -A_{m2} \cdot m_2 \cdot n_c + B_2(M_2 - m_2)n_v, \qquad (4)$$

$$dm_3/dt = -A_{m3} \cdot m_3 \cdot n_c + B_3(M_3 - m_3)n_v, \qquad (5)$$

$$dn/dt = A(N - n)n_c, \qquad (6)$$

$$dn_c/dt = dm_1/dt + dm_2/dt + dm_3/dt + dn_v/dt$$

$$- dn/dt. \qquad (7)$$

For a given set of the trapping parameters, this set of equations is numerically solved using the *ode23* solver in the MatLab package, for a time of excitation t_D. Thus, the dose of excitation is $D = x \cdot t_D$. Since at the end of the excitation we end up with $n_c \neq 0$ and $n_v \neq 0$, in order to follow the experimental conditions, the solution procedure is continued for a further period of relaxation time with $x = 0$ until the values of n_c and n_v are reduced to practically zero.

The next stage is to solve the relevant set of simultaneous differential equations during the heating stage, when the final values for the functions n, m_1, m_2, m_3, n_c and n_v calculated in the first stage are used as initial values for the next stage.

The set of simultaneous differential equations governing the process at the heating stage is given by

$$-dm_1/dt = A_{m1} \cdot m_1 \cdot n_c, \qquad (8)$$

$$-dm_2/dt = A_{m2} \cdot m_2 \cdot n_c, \qquad (9)$$

$$-dm_3/dt = A_{m3} \cdot m_3 \cdot n_c, \qquad (10)$$

$$dn/dt = -s \cdot n \cdot \exp(-E/kT) + A(N - n)n_c, \qquad (11)$$

$$dn_c/dt = dm_1/dt + dm_2/dt + dm_3/dt - dn/dt. \qquad (12)$$

The above-mentioned MatLab *ode23* solver is utilized to solve this set of equations, this time with the tem-

perature T changing linearly with time with a constant heating rate β. As pointed out above, only the recombination into m_2 is considered to be radiative. The intensity of the measurable thermoluminescence is therefore proportional to the rate of change of m_2, and the intensity of emitted light can be written as

$$I(T) = -dm_2/dt. \qquad (13)$$

Once a TL peak is thus simulated, an appropriate initial-rise range is chosen and the equivalent of plotting $\ln(I)$ vs. $1/T$ is performed. This is done by using the *fmins* multivariable minimization program from the MatLab package, applying it to the $\ln(I_i)$ vs. $1/T_i$ points in the chosen initial-rise range. With E as a minimization variable, the sum of squared differences between the $(\ln(I_i), 1/T_i)$ points as calculated by the solution of the differential equations, simulating the experimental results and a straight line is minimized. The $\ln(I_i)$ points are plotted as well as the calculated best-fitted straight line. Similarly to what one usually does with experimental results, the agreement between the simulated experimental results and the best straight line can be visually inspected, although a more objective criterion based on the sum of squares of the deviations at the final stage can also be easily devised.

3. Numerical results

The sequence of numerically solving the set of simultaneous differential equations (2)–(7) has been performed for chosen sets of the relevant parameters with a given excitation intensity x, followed by a relaxation period in which the same set is solved, when x is set to zero. Finally, the set (8)–(12) is numerically solved for a certain (constant) heating rate, yielding the expected TL intensity by Eq. (13). The sets chosen were such that the role of the competitors, in particular, the one which competes for electrons in the low temperature part of the measured peak, were appropriate , namely, that they have to change the shape of the measured peak but not to cause it to disappear. It turned out that using intuition in this choice of parameters was not a straight forward task since a change of any of the relevant parameters affected the results in both the excitation and heating phases in manners that were sometimes hard to predict. Basically, however, it was very easy to find examples in which the apparent initial-rise activation energy was found to be significantly higher than the real one. It is to be noted that the lines seen on the $\ln(I)$ vs. $(1/T)$ scale were in these cases convincingly straight lines with a slope yielding the high values of the activation energies.

In a typical example, we chose the parameters as follows:

$E = 0.7 \, \text{eV}; \quad s = 10^6 \, \text{s}^{-1}; \quad A = 10^{-20} \, \text{m}^3 \, \text{s}^{-1};$

$N = 1.2 \times 10^{21} \, \text{m}^{-3}; \quad A_{m1} = 10^{-17} \, \text{m}^3 \, \text{s}^{-1};$

$A_{m2} = 10^{-18} \, \text{m}^3 \, \text{s}^{-1}; \quad A_{m3} = 10^{-19} \, \text{m}^3 \, \text{s}^{-1};$

$B_1 = 10^{-21} \text{m}^3 \, \text{s}^{-1}; \quad B_2 = 1.1 \times 10^{-21} \, \text{m}^3 \, \text{s}^{-1};$

$B_3 = 1.2 \times 10^{-21} \text{m}^3 \, \text{s}^{-1}; \quad M_1 = 5 \times 10^{19} \, \text{m}^{-3};$

$M_2 = 4 \times 10^{19} \, \text{m}^{-3}; \quad M_3 = 3 \times 10^{19} \, \text{m}^{-3}.$

The resulting curve is shown in Fig. 2. Choosing as an initial-rise range 425–434 K, the plot of $\ln(I)$ as a function of $1/T$ has been drawn, and is shown in Fig. 3. The straight line received yields a slope from which an apparent activation energy of 1.5 eV is found. Combining this value with the temperature of the maximum T_m yields by the use of Eq. (1) an apparent value of $s = 6.5 \times 10^{15} \, \text{s}^{-1}$. Combining these yield the apparent life-time $\tau_\text{app} = s_\text{app} \exp(E_\text{app}/kT)$ where T is taken to be room temperature 296 K (23°C). This life-time of 5.2×10^9 s (227 years) is obviously significantly higher than the real lifetime at 296 K where the E and s values are the original ones of 0.7 eV and $10^6 \, \text{s}^{-1}$, re-

spectively, which is 8.3×10^5 s (~10 days). The former, high value of the life-time may look to the experimentalist measuring the results as the real expected value whereas the latter, real and much shorter life-time may look as associated with anomalous fading. Thus, as suggested in the previous work by Chen and Hag-Yahya (1997) (with relation to the shape method and the full curve best fit), the apparent anomalous fading may be interpreted, at least in some cases, as normal decay in disguise.

4. Conclusions

The examples shown in the previous section demonstrate the possibility that apparent high values of the activation energy can be evaluated by the initial-rise method when the situation is that of a competition between radiative and non-radiative centers. While associated with the equation of the maximum (1), a high value of the frequency factor is evaluated and both of these combined yield a very high apparent life-time τ_app. Thus, the apparent anomalous fading can be explained as being a nor-
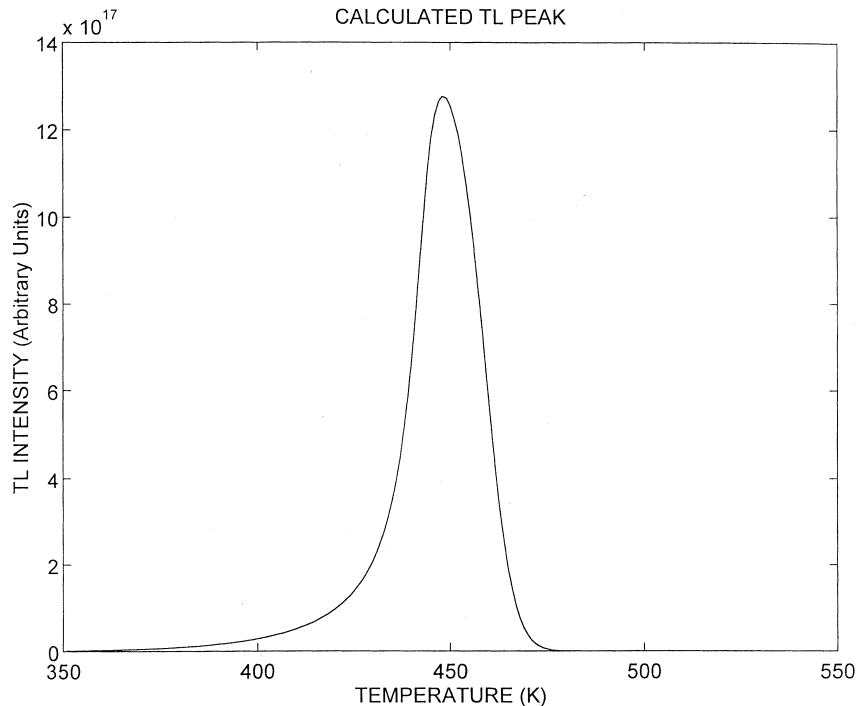

Fig. 2. A simulated TL peak calculated by sequentially solving the sets of simultaneous differential equations governing the process at excitation, relaxation and heating. The values of the trapping parameters chosen are given in the text; the TL assumed to be measurable is from the luminescent center whereas the two competing non-luminescent centers influence the results indirectly.

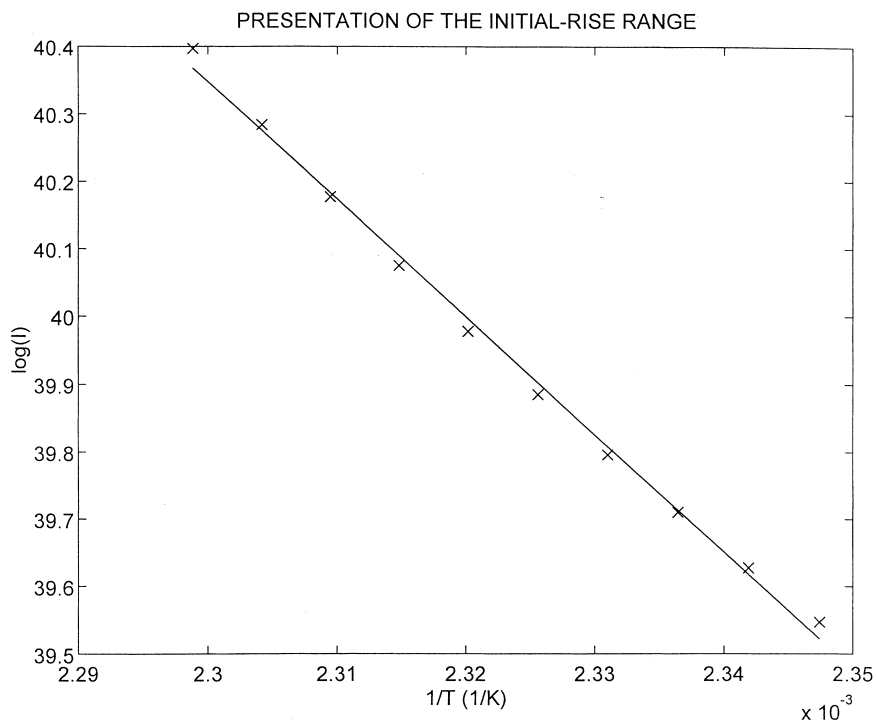PRESENTATION OF THE INITIAL-RISE RANGE

Fig. 3. A plot of $\ln(I)$ vs. $(1/T)$ in the temperature range of 425–434 K. The source results of TL intensity vs. temperature are taken from the same simulation as in Fig. 2.

mal fading in disguise; one observes an apparent simple first order peak with high apparent values of the activation energy and the frequency factor, and as a result, the expected life-time is very long. The fading is associated, of course, with the original lower values of E and s which lead to a low life-time which erroneously is referred to as being anomalous. These results are qualitatively similar to those previously reported by Chen and Hag-Yahya (1997) who evaluated the activation energy by the shape methods or the full curve fitting. It is to be noted that the agreement here is rather limited. Although in both cases the measured real life-time is significantly shorter than the apparent one under the same conditions of competition, the values of the activation energies by the different methods are not necessarily the same. Therefore, the frequency factors evaluated are not necessarily the same, and hence, the apparent life-times may not be the same.

A note should be made about an effect reported by Wintle (1975) which, in a sense, is inverse to the one mentioned here. Wintle reports that under certain circumstances, a thermal quenching occurs which has to do with the decrease of luminescence efficiency with temperature increase. This phenom-

enon causes the initial-rise method of trap depth determination to yield artificially low results which erroneously implies thermal instability of a peak which, in fact, is suitable for dating.

In summation, we can say that the possibility has been demonstrated of observing an apparent anomalous fading of TL due to the competition of radiationless centers. We have shown here that if one evaluates the activation energy using the initial-rise method, a much higher stability of the TL peak at RT could erroneously be predicted than the real one, hence an apparent anomalous fading is being reported when the real, lower life-time is observed.

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