



## A NEW POSSIBLE INTERPRETATION OF THE ANOMALOUS FADING IN THERMOLUMINESCENT MATERIALS AS NORMAL FADING IN DISGUISE

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**Abstract**—A new possible explanation is given to the anomalous fading of thermoluminescence (TL), observed in some materials. It is suggested that anomalous fading may, in some cases, be normal fading in disguise. The existence of non-radiative centers which are competing with the radiative luminescence center may cause the occurrence of a very narrow TL peak. The apparent kinetics parameters, say  $E_{app}$  and  $s_{app}$  in first order kinetics, may appear to be much larger than the real values due to the narrowing of the peak. This, in turn, results in the expectation of a very long decay time,  $\tau_{app}$ , at, for example, room temperature. The real values of the parameters are, however, such that the loss of trapped carriers is orders of magnitude faster. The details of the model are given in terms of rate equations, as well as examples of numerical solutions during excitation followed by relaxation and then heating during the read-out phase. From these, the effective expected lifetimes were up to five orders of magnitude larger than that of the observable effect, which can explain, at least in some cases, the anomalous fading. © 1997 Elsevier Science Ltd

### 1. INTRODUCTION

It is well known that when an excited sample is held at a temperature somewhat below that of a thermoluminescence (TL) peak, a decay of the peak is expected with time, the decay being faster as the temperature approaches that of the maximum. This thermal decay of TL is obviously associated with the thermal probability of detrapping of carriers, normally given by  $\gamma(T) = s \cdot \exp(-E/kT)$ , where  $E$  is the activation energy of the trapped carrier (eV),  $k$  is the Boltzmann constant ( $\text{eV} \cdot \text{K}^{-1}$ ),  $T$  is temperature (K) and  $s$  is the frequency factor ( $\text{s}^{-1}$ ). This function,  $\gamma(T)$ , occurs in all the expressions describing the occurrence of the TL peak with an increasing heating function  $T(t)$ . It is obvious that if a sample is held at a constant temperature a little below that of the maximum,  $\gamma(T)$  will be large enough so that detrapping occurs at the given temperature. Thus, an effect of thermal fading is taking place since the expected TL that can be measured at a subsequent heating is expected to be lower than otherwise anticipated following a given excitation. This thermal fading is considered to be “normal”.

Many researchers found, however, that with certain materials, a decay of the expected TL occurs even when the sample is held at temperatures well below that of the TL peak; besides this, they found the decay was much faster than expected for the given trapping parameters and the temperature at which the sample is held. This effect was termed “anomalous” or “abnormal” fading. The first report on anomalous fading was given in 1950 for UV

stimulated TL in diamond (Bull and Garlick, 1950). Two peaks at 400 and 520 K, observed while heating the sample at  $2.5^\circ\text{C s}^{-1}$ , were found to yield lower light levels if stored at 90 K for 6 h before glowing than if glowed immediately. Another researcher who described this effect was Hoogenstraaten (1958) who reported the decay of light levels at low temperatures in ZnS samples doped with Cu, Co and Cl. He explained the effect of decay as due to the quantum mechanical tunneling of electrons from traps to empty activation centers. The effect of TL anomalous fading was discovered later in various materials. Schulman *et al.* (1969) reported the effect in  $\text{CaF}_2:\text{Mn}$  TL materials. Garlick and Robinson (1972) and Blair *et al.* (1972) found anomalous fading in lunar samples and, again, explained it by tunneling. Similar effects were found by Kieffer *et al.* (1971) in organic glasses. It is to be noted that in these measurements, no temperature dependence of the anomalous fading was reported. Wintle (1973) and (1977) measured the effect in various minerals at different temperatures and discussed its implications as regards the dating of archaeological samples. In particular, Wintle (1977) considered the phenomenon in feldspar samples in which the anomalous fading was temperature dependent. Wintle (1977) suggested three alternative possibilities to explain anomalous fading. (1) Defect diffusion which allows a non-radiative escape of trapped electrons when the diffusing defect encounters a trapping site. Wintle states, however, that it is difficult to explain the fading at very low temperatures (for example, RT) as being due to the diffusion of defects and this seems to suggest that diffusion is

usually not the cause of anomalous fading. (2) Direct transfer of an electron from a trap to an adjacent center, as suggested by Garlick and Robinson (1972). The temperature dependence, reported by Wintle (1977), of the anomalous fading in feldspars needs, however, a more complicated model. (3) One should consider whether anomalous fading can be caused by the reduction in the number of effective recombination centers with time.

Visocekas *et al.* (1983) studied the afterglow in CaSO<sub>4</sub>: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 the 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 is that the afterglow and anomalous fading in the material result from a quantum mechanical tunneling effect.

### 2. THE MODEL

In a recent work, Chen and Hag-Yahya (1996) showed the possibility of explaining the occurrence of very high  $E$  and  $s$  values in some materials (e.g. peak V, in LiF) by assuming two competitors to the

luminescent center. The transitions into these centers are assumed to be radiationless and cause the measured peak to be anomalously narrow. This, in turn, makes the apparent values of  $E_{app}$  and  $s_{app}$ , evaluated by curve fitting or by the shape methods, to be much higher than the real ones, while the peak shape still looks like a normal first order peak as further explained below. In a simulation, they showed that with given values of  $E = 1.2$  eV and  $s = 2.5 \times 10^{11} \text{ s}^{-1}$ , effective values of  $E_{app} = 2.115$  eV and  $s_{app} = 5.6 \times 10^{20} \text{ s}^{-1}$  could be seen.

To illustrate this point, we consider a simple equation given by Chen (1969), which utilizes the full width of a single TL peak to evaluate the activation energy,

$$E = 2.29kT_m^2/\omega . \tag{1}$$

Here,  $\omega = T_2 - T_1$ , where  $T_1$  and  $T_2$  are the half intensity temperatures and  $T_m$  is the maximum temperature (all temperatures in K);  $k$  is the Boltzmann factor (eV·K<sup>-1</sup>); and the activation energy,  $E$ , is in eV. It is evident that if by any *artificial* means, the peak looks narrower than otherwise expected, the apparent activation energy evaluated by equation (1) will be larger than the real one. Similar results are expected with other *shape methods* for

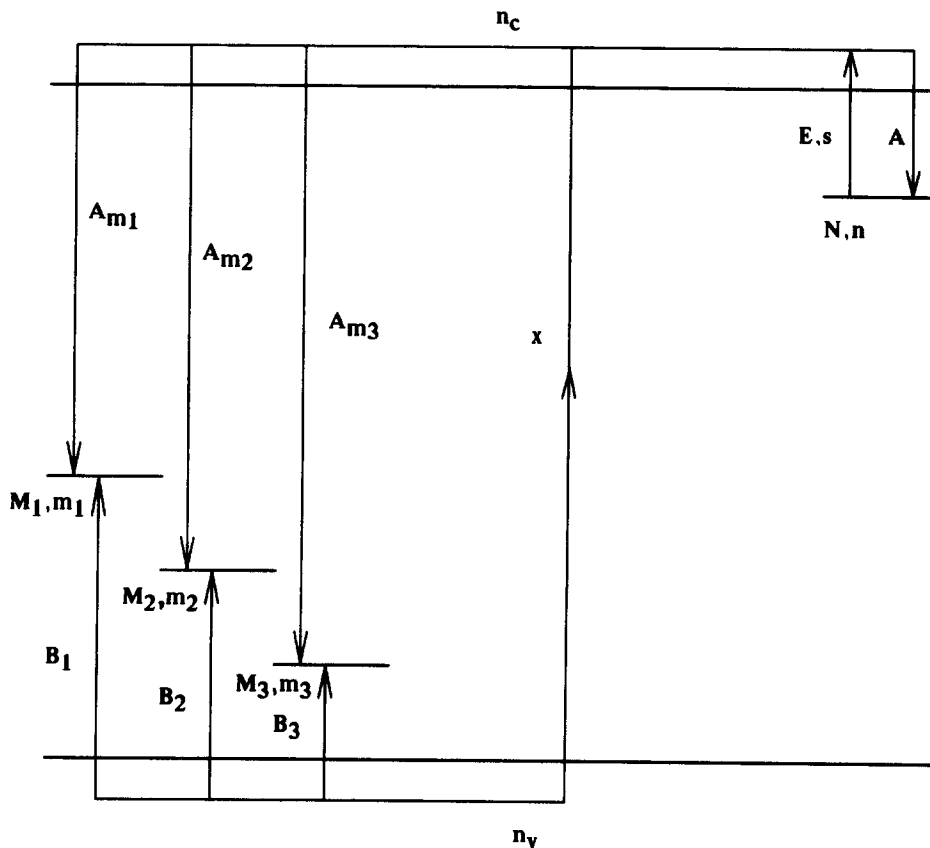


Fig. 1. Energy level model of one trapping state and three kinds of recombination centers. The transitions shown are those taking place during the excitation. The meaning of the different symbols is given in the text.

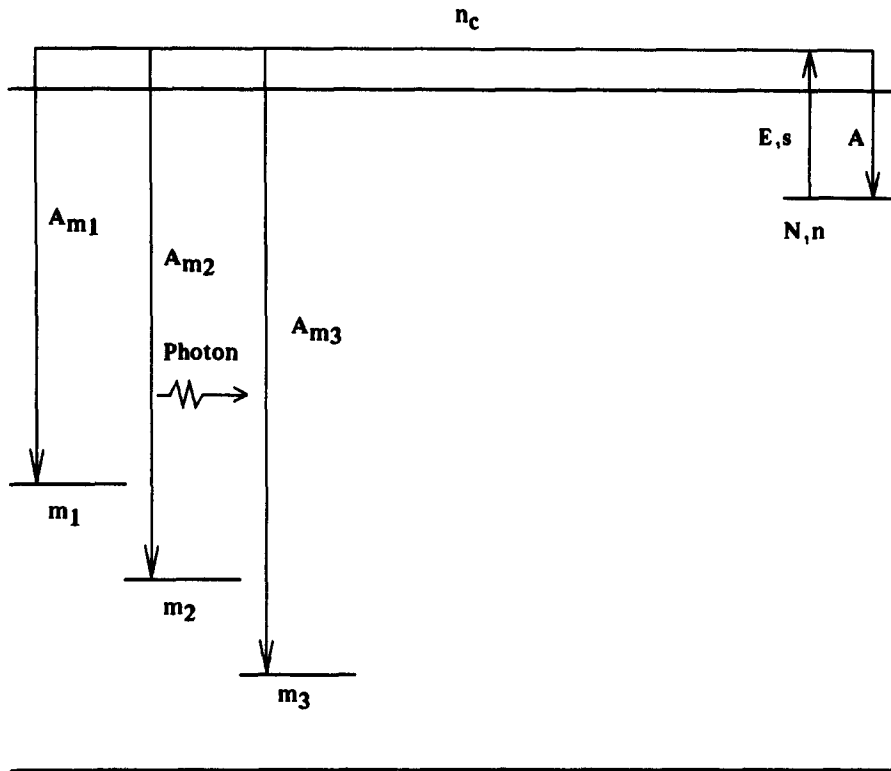


Fig. 2. Transitions during the heating of a sample with three recombination centers for the same model as Fig. 1. The meaning of the symbols are the same as Fig. 1.

evaluating activation energies. Also, the *curve fitting methods* are utilizing the same features of the TL peak and, therefore, similar results are expected. Indeed, Chen and Hag-Yahya (1996) reported that under these circumstances, similar effective values of  $E$  are calculated from the shape methods and the best fit. Obviously, for a certain value of  $T_m$ , once we get a narrow peak with a high apparent value of  $E$ , denoted by  $E_{app}$ , the accompanying value of  $s_{app}$  will be orders of magnitude higher than the "normal". This can be seen from the condition for the maximum intensity in a first-order peak,

$$\beta E/(kT_m^2) = s \exp(-E/kT_m) \quad (2)$$

where  $\beta$  is the heating rate. This can be written as

$$s = \beta E/(kT_m^2) \exp(E/kT_m) \quad (3)$$

and since  $E$  appears in the exponent, a large apparent value,  $E_{app}$ , will result in an apparent value,  $s_{app}$ , orders of magnitude higher than the original value of  $s$ .

In the present work, we utilize similar ideas to give an alternative possible explanation of the anomalous fading. Again, we take a kinetic model of one trapping state and three kinds of recombination centers. We write the appropriate equations governing the processes which are taking place and solve them numerically. This is in order to demonstrate the possibility of getting high effective values of the activation energy and frequency factor as compared

to the real ones, which would explain the anomalous fading. The energy levels involved, and the transitions occurring during the excitation, are shown in Fig. 1. One trapping state is shown with an activation energy  $E$  (eV) and a frequency factor  $s$  ( $s^{-1}$ ). The concentration of this trap is  $N$  ( $m^{-3}$ ) and its instantaneous occupancy is  $n$  ( $m^{-3}$ ). Three recombination centers, with concentrations of  $M_1$ ,  $M_2$  and  $M_3$  ( $m^{-3}$ ) and occupancies  $m_1$ ,  $m_2$  and  $m_3$  ( $m^{-3}$ ), are assumed to participate in the process. During the excitation by external irradiation, the rate of pair production is  $x$  ( $m^{-3} s^{-1}$ ). The time during the excitation is denoted by  $t$ . Assuming a constant rate of excitation, the dose  $D$  of excitation is given by multiplying the rate,  $x$ , by the time of excitation  $t_D$ ,  $D = x \cdot t_D$ . The concentrations of free electrons and holes are  $n_c$  and  $n_v$  ( $m^{-3}$ ), respectively. The transitions of holes into the centers are governed by the probabilities  $B_1$ ,  $B_2$  and  $B_3$  ( $m^3 s^{-1}$ ) and recombinations during the excitation are also allowed, governed by  $A_{m1}$ ,  $A_{m2}$  and  $A_{m3}$  ( $m^3 s^{-1}$ ). In addition, retrapping of free electrons is allowed, associated with the retrapping probability  $A$  ( $m^3 s^{-1}$ ). The equations governing the process at the excitation stage are

$$dm_1/dt = -A_{m1} \cdot m_1 \cdot n_c + B_1(M_1 - m_1)n_v \quad (4)$$

$$dm_2/dt = -A_{m2} \cdot m_2 \cdot n_c + B_2(M_2 - m_2)n_v \quad (5)$$

$$dm_3/dt = -A_{m3} \cdot m_3 \cdot n_c + B_3(M_3 - m_3)n_v \quad (6)$$

$$dn/dt = A(N - n)n_c \quad (7)$$

$$\begin{aligned} \frac{dn_v}{dt} = & x - B_1(M_1 - m_1)n_v \\ & - B_2(M_2 - m_2)n_v - B_3(M_3 - m_3)n_v \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{dn_c}{dt} = & \frac{dm_1}{dt} + \frac{dm_2}{dt} \\ & + \frac{dm_3}{dt} + \frac{dn_v}{dt} - \frac{dn}{dt} \end{aligned} \quad (9)$$

The numerical solution of these simultaneous differential equations was performed by the use of a fifth order Runge-Kutta algorithm [see, for example, Zonneveld (1970)].

Following the excitation, a relaxation period is simulated. At the end of the excitation, non-zero concentrations of electrons in the conduction band and holes in the valence band are expected. In order to follow the normal experimental procedure, we should consider the relaxation time until the conduction and valence bands are practically empty. This is done numerically by solving the set of equations (4)–(9) while setting the excitation intensity,  $x$ , to zero. The numerical solution is performed using the same algorithm.

The next stage is that of the heating. The transitions involved are shown in Fig. 2. The trapped electrons are now thermally raised into the conduction band and may recombine with the three centers  $M_1$ ,  $M_2$  and  $M_3$ . Also, retrapping of electrons with empty electron trapping states may take place. The equations governing the process are given by:

$$- \frac{dm_1}{dt} = A_{m1} \cdot m_1 \cdot n_c \quad (10)$$

$$- \frac{dm_2}{dt} = A_{m2} \cdot m_2 \cdot n_c \quad (11)$$

$$- \frac{dm_3}{dt} = A_{m3} \cdot m_3 \cdot n_c \quad (12)$$

$$\frac{dn}{dt} = -s \cdot n \cdot \exp(-E/kT) + A(N - n) \cdot n_c \quad (13)$$

$$\frac{dn_c}{dt} = \frac{dm_1}{dt} + \frac{dm_2}{dt} + \frac{dm_3}{dt} - \frac{dn}{dt} \quad (14)$$

Here too, the numerical solution is performed using the same fifth order Runge-Kutta algorithm.

Only the transitions into one of the recombination centers,  $m_2$ , is assumed to be measurable whereas the two others are assumed to be radiationless. Thus, the intensity of emitted visible thermoluminescence is proportional to the rate of change of  $m_2$  and assuming the proportionality factor to be unity (which sets a certain set of units to the emitted light), we can write the emitted light  $I(T)$  as

$$I(T) = - \frac{dm_2}{dt} \quad (15)$$

### 3. NUMERICAL RESULTS

The parameters chosen for the trapping state are  $E = 0.7$  eV and  $s = 10^6$  s<sup>-1</sup>. The decay time at room temperature for these traps is  $\tau = s^{-1} \exp(E/kT) = 5.75 \times 10^5$  s, which is just under a week. The other parameters chosen are: the retrapping probability,  $A = 1 \times 10^{-22}$  m<sup>3</sup> s<sup>-1</sup>; the three recombination probabilities,  $A_{m1} = 1.2 \times 10^{-18}$  m<sup>3</sup> s<sup>-1</sup>,  $A_{m2} = 2.8 \times 10^{-19}$  m<sup>3</sup> s<sup>-1</sup>,  $A_{m3} = 7.5 \times 10^{-20}$  m<sup>3</sup> s<sup>-1</sup>; the trapping probabilities for holes into the recombination centers,  $B_1 = 1 \times 10^{-21}$  m<sup>3</sup> s<sup>-1</sup>,  $B_2 = 1.1 \times 10^{-21}$  m<sup>3</sup> s<sup>-1</sup>,  $B_3 = 1.2 \times 10^{-21}$  m<sup>3</sup> s<sup>-1</sup>; the total concentration of traps,  $N = 1.2 \times 10^{21}$  m<sup>-3</sup>; and the concentrations of the three centers are chosen to be  $M_1 = M_2 = M_3 = 4 \times 10^{20}$  m<sup>-3</sup>. The radiation intensity in the appropriate units is  $x = 5 \times$

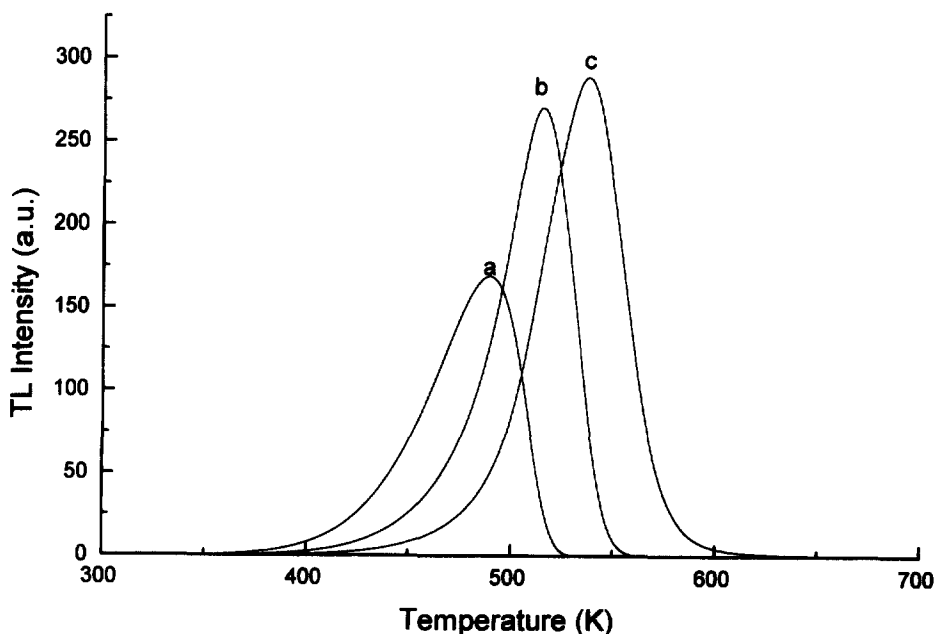


Fig. 3. The rates of transitions into the three competing centers as a function of temperature: (a)  $-dm_1/dt$ ; (b)  $-dm_2/dt$  and (c)  $-dm_3/dt$ , as calculated by the numerical solution of the sets of simultaneous differential equations. The values of the parameters chosen for the calculation are given in the text.

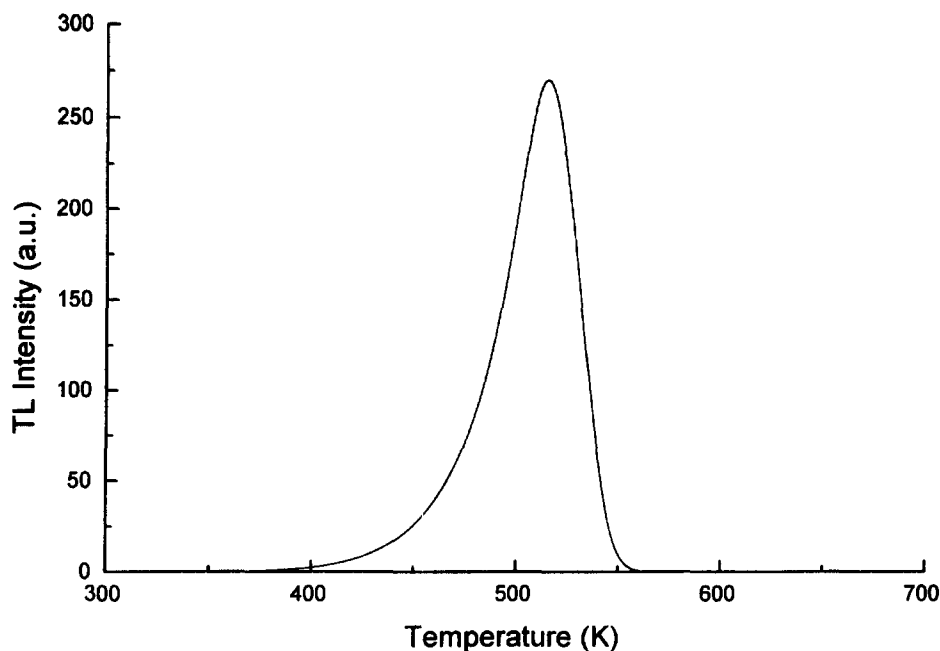


Fig. 4. Curve (b) from Fig. 3 which is assumed to be the only radiative, measurable TL emission. The chosen parameters are the same as Fig. 3.

$10^{20} \text{ m}^{-3} \text{ s}^{-1}$  and the irradiation time is 200 s. The simultaneous equations governing the process during the excitation and heating are solved numerically in three stages, excitation, relaxation (in which the excitation intensity,  $x$ , is set to zero) and simulated emission of the TL, which is followed while mimicking the heating of the sample at a heating rate of  $5 \text{ K s}^{-1}$ .

Figure 3 depicts the curves of  $-dm_1/dt$ ,  $-dm_2/dt$  and  $-dm_3/dt$  (curves a, b and c). As suggested above, only the middle curve is assumed to be measurable. Figure 4 shows only curve b; this looks exactly like a simple TL peak. The maximum temperature here is found to be 515 K ( $242^\circ\text{C}$ ). The symmetry factor is defined as  $\mu_g = \delta/\omega$  where  $\delta = T_2 - T_m$ ,  $\omega = T_2 - T_1$  and where  $T_m$  is the maximum temperature and  $T_1$ ,  $T_2$  are the low and high temperatures at half intensity. Here, the value found is  $\mu_g = 0.424$ , which is typical of first order kinetics. Using the equation for evaluating  $E$  from a first order kinetics peak yields  $E_{\text{app}} = 1.3 \text{ eV}$ . Using the equation for the maximum of a first order peak results in the apparent frequency factor to be  $s_{\text{app}} = 1.6 \times 10^{12} \text{ s}^{-1}$ . With these values, the apparent lifetime at RT is found to be  $\tau_{\text{app}} = s_{\text{app}}^{-1} \times \exp(E_{\text{app}}/kT) = 4.3 \times 10^9 \text{ s}$  or  $\sim 137 \text{ y}$ . The ratio between the apparent and real lifetimes is  $\approx 10^4$ .

In a similar calculation, the activation energy chosen was  $E = 0.8 \text{ eV}$  with all the other parameters kept the same. In this case, the lifetime expected at room temperature is  $\tau = s^{-1} \exp(E/kT) = 2.75 \times 10^7 \text{ s}$ , which is about 45 weeks. When the calculation is carried out in a similar way to that discussed above, solving the same sets of equations numerically, we

found a peak at 584 K ( $311^\circ\text{C}$ ) which looks like a first order peak, with a shape factor of 0.425. The apparent activation energy and frequency factor found here are, respectively,  $E_{\text{app}} = 1.5 \text{ eV}$  and  $s_{\text{app}} = 2 \times 10^{12} \text{ s}^{-1}$ , yielding  $\tau_{\text{app}} = 7.9 \times 10^{12} \text{ s}$ , or  $\sim 2.5 \times 10^5 \text{ y}$ . The ratio between the apparent and real lifetimes is  $\tau_{\text{app}}/\tau \approx 3 \times 10^5$ . It is obvious that this is a demonstration of a situation in which one would expect no decay of the peak at any measurable length of time, but an observable decay of  $\sim 4.5\%$  per two weeks can be found.

#### 4. CONCLUSION

An alternative possibility for explaining anomalous fading as normal fading in disguise has been presented. The explanation is within the framework of the conventional kinetic theory, pertaining to transitions between trapping states and recombination centers without resorting to the quantum-mechanical tunneling effect which appears to be the reason for anomalous fading in some of the materials in which the effect occurs. In this case, the thermal detrapping associated with the  $E$  and  $s$  parameters of the TL peak in question is normal. However, the shape of the peak may be changed due to competition with non-radiative transitions. It has been shown that if the peak gets narrow due to competition of the radiative center with non-radiative centers, the apparent  $E_{\text{app}}$  and  $s_{\text{app}}$  values will be significantly larger than the original ones, and therefore, the apparent lifetime,  $\tau_{\text{app}}$ , will be orders of magnitude larger than the measured decay lifetime  $\tau$ . Two numerical examples are presented, in which the resulting glow peak looks like a genuine

first-order peak, but with apparent lifetimes 4–5 orders of magnitude larger than the real ones. This may be, in some cases, an explanation for anomalous fading. It is to be noted that this explanation can apply only to those cases where the anomalous fading is temperature dependent.

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