

INTERPRETATION OF VERY HIGH ACTIVATION ENERGIES AND FREQUENCY FACTORS IN TL AS BEING DUE TO COMPETITION BETWEEN CENTRES

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Abstract — Very high values, considered to be physically impossible, were reported for the activation energy E and the frequency factor s in some thermoluminescence (TL) peaks. In particular, peak 5 of LiF:Mg,Ti was reported to have $E = 2.0\text{--}2.2$ eV and $s = 10^{20}\text{--}10^{22}$ s $^{-1}$. If a peak shape method or curve fitting of a TL peak is utilised, there is an inverse relation between the width and the activation energy. Thus, if for a given TL peak, competition causes a narrowing of the peak, the effective activation energy is larger than expected. This, in turn, will cause the effective s to be significantly larger than the original one. In this study a model of one trap and three centres is considered, and the relevant simultaneous differential equations solved. Concentrating on the second peak, which looks like a first order peak and is very narrow, results in $E = 2.1$ eV and $s = 8 \times 10^{20}$ s $^{-1}$, for original parameters of $E = 1.2$ eV and $s = 2.5 \times 10^{11}$ s $^{-1}$.

INTRODUCTION

While dealing with the simplest form of a TL peak, namely, a first order kinetics peak, only two parameters, the activation energy E (eV) and the frequency factor s (s $^{-1}$) determine the shape of the peak. If the peak can be well separated from any neighbouring satellites, the property of its being of first order can easily be determined by its characteristic asymmetric form. Defining the shape factor $\mu = \delta/\omega$ where $\delta = T_2 - T_m$ and $\omega = T_2 - T_1$ and where T_m is the temperature of the maximum intensity and T_1 and T_2 the low and high half intensity temperatures respectively, the characteristic value of μ for first order is ~ 0.42 . A characteristic value of the frequency factor is $s \approx 10^{10} - 10^{13}$ s $^{-1}$ since, according to Mott and Gurney⁽¹⁾ s should be of the order of magnitude of the Debye frequency, which has to do with the number of times per second that the trapped electron interacts with the phonons. Indeed, most results reported by various authors over the years gave values of s in this range of $10^{10} - 10^{13}$ s $^{-1}$; sometimes lower values were reported which were explained as being the result of localised transitions⁽²⁾ or other complexities of the kinetics. Once the first order characteristics are established, a number of methods are available to evaluate the values of E and s . These include the initial rise method⁽³⁾, the peak shape methods⁽⁴⁾, the various heating rates methods⁽⁵⁾, the curve fitting methods⁽⁶⁾ and the isothermal decay methods⁽⁷⁾.

As an example of the family of peak shape methods, let us take⁽⁴⁾

$$E = 2.29kT_m^2/\omega \quad (1)$$

From this equation, it is obvious that there is an inverse relation between the activation energy E and peak width ω . A similar inverse relation is seen in all the other peak shape methods. It is therefore obvious that if we have in hand two first order peaks occurring at the same tem-

perature, with two different activation energies, the one with the larger activation energy will correspond to a narrower peak. Let us consider the well known equation for the maximum of a first order TL peak⁽⁷⁾

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

This can obviously be written as

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

For the two peaks occurring at the same temperature T_m , the narrower with the higher value of E will certainly possess a higher value of s . For an example in which the width ω is, say, reduced by one third in this comparison, the value of E will be larger by 50%, and as seen from Equation (3), the value of s will be larger by several orders of magnitude.

In a number of published TL peaks, values of s have been reported that are much higher than the expected 'physical' values of up to $\sim 10^{13}$ s $^{-1}$. The most well known case is that of peak V in LiF:Mg,Ti (TLD-100). The experimental values of E and s appearing in the literature vary a lot, depending on the method used for evaluation of the parameters. Sometimes, even using the same methods by different authors resulted in significantly different results. Zimmerman *et al.*⁽⁸⁾, Blak and Watanabe⁽⁹⁾, Johnson⁽¹⁰⁾ and Yossian *et al.*⁽¹¹⁾, using isothermal decay methods, found values of $E \approx 1.25$ eV and $s \approx 4 \times 10^{10}\text{--}2 \times 10^{12}$ s $^{-1}$. On the other hand, Taylor and Lilley⁽¹²⁾ reported an activation energy of 2.06 eV and a frequency factor of 2×10^{20} s $^{-1}$ for the isothermal decay results in peak V. As for the method of different heating rates, Gorbics *et al.*⁽¹³⁾ reported $E = 2.4$ eV and $s = 1.7 \times 10^{24}$ s $^{-1}$, whereas Pohlit⁽¹⁴⁾ reported the exceedingly high values of $E = 3.62$ eV and $s = 10^{42}$ s $^{-1}$ and Taylor and Lilley found $E = 2.06$ eV and $s = 2 \times 10^{20}$ s $^{-1}$. Fairchild *et al.*⁽¹⁵⁾ suggested that the kinetics of this peak and other peaks with unusually

large s values might actually be complex and the apparent first order behaviour is a special case (or approximation) of a more complex kinetics situation. For the specific case of peak V, McKeever⁽¹⁶⁾ suggested that the TL here is related to trimer dissociation, where the trimers may have originated during heating. McKeever proposes that the activation energy of peak V is the sum of the trimer binding energy and a term related to the release of charge from the dissociated dipoles. Finally, an international effort to compare results of the glow curve in LiF by numerical deconvolution of the glow curve⁽¹⁷⁾, showed practically unanimously the same very high value of E and s in peak V.

In the present work, an alternative method is offered for the occurrence of such unusually high values of E and s .

THE MODEL

As discussed with relation to Equation 1, it is obvious that if, for any reason, a TL peak is very narrow, its effective activation energy becomes very large. Once this happens, Equations 2 and 3 show that if the activation energy E is very high, the effective frequency

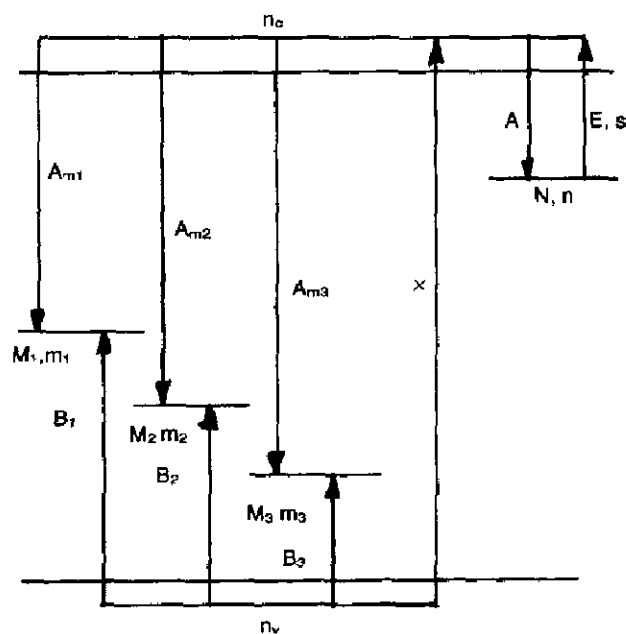


Figure 1. Schematic energy level diagram of one trapping state and three kinds of recombination centres. E (eV) is the activation energy of the trap and s (s^{-1}) the frequency factor. A ($m^3 \cdot s^{-1}$) is the trapping (retrapping) probability, N (m^{-3}) is the total concentration of traps and n (m^{-3}) its instantaneous occupancy. M_1 , M_2 and M_3 (m^{-3}) are the concentrations of the three centres and m_1 , m_2 and m_3 their instantaneous occupancies, respectively. B_1 , B_2 and B_3 ($m^3 \cdot s^{-1}$) are the trapping probabilities of free holes into the three centres respectively and A_{m1} , A_{m2} and A_{m3} ($m^3 \cdot s^{-1}$) the recombination probabilities of free electrons into these centres, respectively. n_e and n_v (m^{-3}) are the instantaneous concentrations of free electrons and holes respectively, and x ($m^{-3} \cdot s^{-1}$) the production rate of electron-hole pairs due to irradiation. The arrows indicate transitions during the excitation.

factor should be orders of magnitude higher in order to permit the maximum TL to occur at the given temperature T_m . In the present model, we would like to demonstrate the possibility of getting a very narrow glow peak which would appear as a first order curve as far as its shape and symmetry properties are concerned, which would result in the high effective E and s values. For this, the possibility of having competing centres is used, the transition into which are either non-radiative or are radiative in a spectral range which is not measurable with the detecting device utilised. Yet another possibility is that the TL peak or peaks related to the competitors are measurable, but are separable from the peak in question by the deconvolution employed for separating the apparently single peak.

Using one such competing centre indeed caused the measurable peak to be narrower than without the competitor; however, the shape of the peak was significantly distorted, and it did not look like a first order curve at all. In order to get a narrow peak at the desired temperature with nearly first order features, it had to be assumed that two recombination centres existed, one with a larger recombination probability than that of the peak of interest, and the other with a lower one.

Figure 1 shows an energy level diagram with one trapping state, and given parameters E and s for the activation energy and frequency factor. Three recombination centres denoted by the labels 1, 2, and 3 are shown, and the meaning of the different parameters are given in the caption. The differential equations governing the transitions during the excitation period are

$$dm_1/dt = -A_{m1}m_1n_e + B_1(M_1 - m_1)n_v \quad (4)$$

$$dm_2/dt = -A_{m2}m_2n_e + B_2(M_2 - m_2)n_v \quad (5)$$

$$dm_3/dt = -A_{m3}m_3n_e + B_3(M_3 - m_3)n_v \quad (6)$$

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

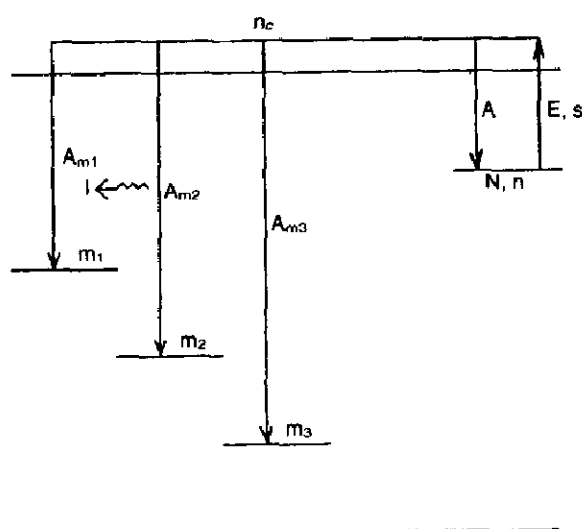


Figure 2. Transitions occurring in the same energy level scheme as in Figure 1 during the heating phase. The measurable TL is due to the recombinations of free electrons into centre No. 2.

$$dn_v/dt = x - B_1(M_1 - m_1)n_v - B_2(M_2 - m_2)n_v - B_3(M_3 - m_3)n_v \quad (8)$$

$$dn_c/dt = dm_1/dt + dm_2/dt + dm_3/dt + dn_v/dt - dn/dt \quad (9)$$

This set of simultaneous differential equations is solved numerically for a period of time t_D , and the dose of excitation is defined as $D = xt_D$. The final values of m_1 , m_2 , m_3 , n , n_v and n_c are used as initial values for the next stage of relaxation. This is a period of time in which x is set to zero and the simultaneous equations are solved to simulate the period of time between the end of irradiation and the beginning of the heating stage. The run of this stage is continued until n_c and n_v are reduced to negligible values.

The transitions occurring during the heating are shown in Figure 2. Of course, the same energy scheme should be used here as in the first two stages with the same parameters. The equations governing this stage are

$$I_1(t) = -dm_1/dt = A_{m1}m_1n_c \quad (10)$$

$$I_2(t) = -dm_2/dt = A_{m2}m_2n_c \quad (11)$$

$$I_3(t) = -dm_3/dt = A_{m3}m_3n_c \quad (12)$$

$$-dn/dt = sn \exp(-E/KT) - A(N - n)n_c \quad (13)$$

$$dn_c/dt = dm_1/dt + dm_2/dt + dm_3/dt - dn/dt \quad (14)$$

NUMERICAL RESULTS

The simultaneous sets of equations have been numeri-

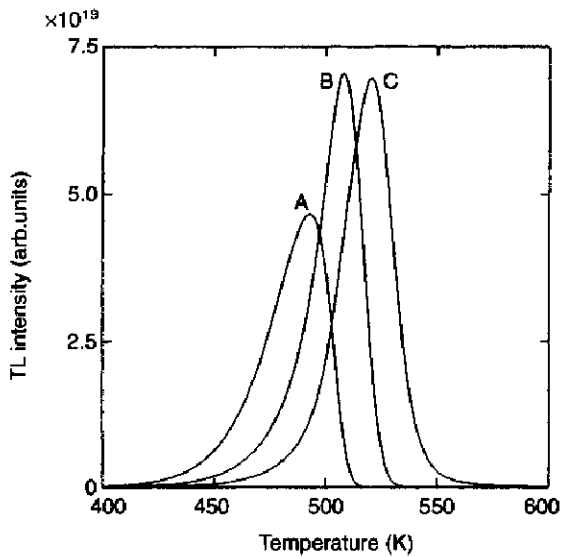


Figure 3. The rates of recombination into centres 1, 2 and 3 are shown in curves A, B and C respectively. The parameters used are: $E = 1.2$ eV; $s = 2.5 \times 10^{11} \text{ s}^{-1}$; $A = 10^{-22} \text{ m}^3 \cdot \text{s}^{-1}$; $N = 1.2 \times 10^{21} \text{ m}^{-3}$; $A_{m1} = 1.2 \times 10^{-18} \text{ m}^3 \cdot \text{s}^{-1}$; $A_{m2} = 2.8 \times 10^{-19} \text{ m}^3 \cdot \text{s}^{-1}$; $A_{m3} = 7.5 \times 10^{-20} \text{ m}^3 \cdot \text{s}^{-1}$; $B_1 = 1.0 \times 10^{-21} \text{ m}^3 \cdot \text{s}^{-1}$; $B_2 = 1.1 \times 10^{-21} \text{ m}^3 \cdot \text{s}^{-1}$; $B_3 = 1.2 \times 10^{-21}$; $M_1 = M_2 = M_3 = 4 \times 10^{20} \text{ m}^{-3}$. For the excitation: $n_0 = m_{10} = m_{20} = m_{30} = n_{c0} = n_{v0} = 0$; $x = 10^{21} \text{ m}^{-3} \cdot \text{s}^{-1}$; $t_D = 35 \text{ s}$; $T_0 = 300 \text{ K}$. For the heating: $\beta = 6 \text{ K} \cdot \text{s}^{-1}$; $T_i = 300 \text{ K}$; $T_f = 600 \text{ K}$.

cally solved using the fifth order Runge-Kutta method. The results of $I_1(T)$, $I_2(T)$ and $I_3(T)$ are shown in curves A, B and C of Figure 3, respectively. The parameters chosen are given in the figure caption. As mentioned already, it is assumed that only curve B is measurable, and in this sense it represents peak V of LiF (TLD-100), or any other peak with unusually high values of E and s. This peak looks like a 'normal' first order peak with the symmetry factor $\mu \approx 0.42$. However, while using Equation 1 for evaluating the activation energy, one gets $E = 2.236$ eV. Substituting this value into Equation 3 yields $s = 9.3 \times 10^{21} \text{ s}^{-1}$. These values should be compared with the original ones inserted into Equation 13 which are $E = 1.2$ eV and $s = 2.5 \times 10^{11} \text{ s}^{-1}$.

Although Equation 1 is related only to the half width method, it is quite obvious that similar values will be found using the best fit to a first order curve. Figure 4 shows such a fit where the squares represent points from the simulation (curve B of Figure 3) and the solid line is the best fitted first order curve. Apart from a small deviation in the range 450–480 K, the fit is very good. The effective parameters found are $E = 2.115$ eV and $s = 5.6 \times 10^{20} \text{ s}^{-1}$.

The E and s effective values have also been evaluated from the simulated decay by three other methods, the isothermal decay, the initial rise and the various heating rates method. In the isothermal decay, the effective values found were $E = 2.29$ eV and $s = 8.6 \times 10^{20} \text{ s}^{-1}$, this in good agreement with that of peak V in LiF as given by Taylor and Lilley⁽¹²⁾ and in disagreement with the other authors mentioned above. With the initial rise method, values close to the 'real' ones were found, namely, $E = 1.21$ eV and $s = 3.3 \times 10^{11} \text{ s}^{-1}$. This can be

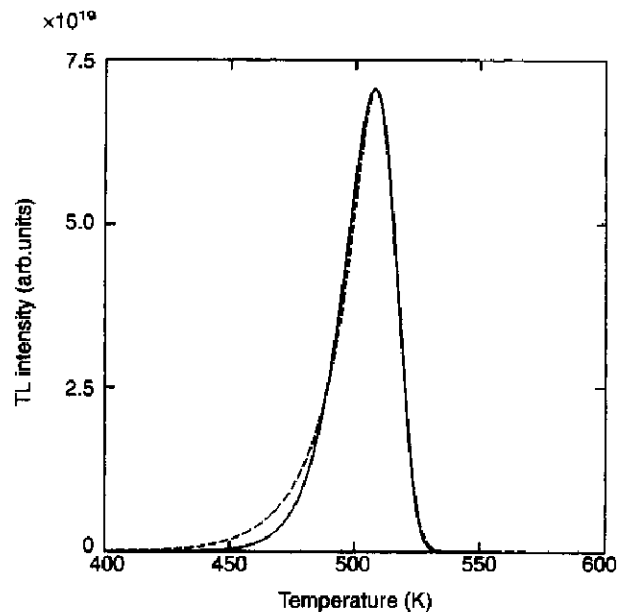


Figure 4. Curve B from Figure 3, simulated by the solution of the simultaneous differential equations given by the dashed line. The best fitted first order curve is shown as the solid line.

compared to the values given for peak V by Miller and Babe⁽¹⁸⁾ of $E = 1.59$ eV and $s = 1.3 \times 10^{16}$ s⁻¹, a rather poor agreement; however, the experimental result is still much closer to that found here from the simulated peak than to the very high values found by the peak shape and curve fitting methods. Finally, evaluating the parameters by utilising the various heating rates method was also tried, and again, values were found which are very close to the original ones, namely, $E = 1.197$ eV and $s = 2.43 \times 10^{11}$ s⁻¹, compared with the very high values quoted in the introduction. We cannot explain this discrepancy, but should mention that some suspicious disagreement occurred between the impossibly huge values reported by Pohlit⁽¹⁴⁾ on one hand, and by Gorbics *et al*⁽¹³⁾ and Taylor and Lilley⁽¹²⁾, with the 'regular' high values on the other hand. It is known that the various heating rates method may yield erroneous experimental results due to bad thermal contact between the sample and the temperature measuring device, and because of thermal gradients within the sample.

CONCLUSION

In this work, it has been shown that TL peaks, occur-

ring in a certain temperature range, may be very narrow due to competition of recombination centres, the transitions into which do not produce measurable light emission. Analysis of these curves by the standard peak shape and curve fitting methods yields very high activation energies, and non-physically high frequency factors, quite similar to those found in peak V of LiF (TLD-100). The procedure here has been to choose a set of parameters related to a model of one trap, one active centre and two competing centres, and solve the sets of simultaneous differential equations for the excitation, relaxation and heating stages. From the numerical results, the transitions into the active centre as a function of temperature are treated separately and analysed as being a single first order peak. Effective results of $E \sim 2.2$ eV and $s \sim 10^{21}$ s⁻¹ are found from peak shape methods and from best fit should be considered as a demonstration that the unusually high values of E and s found in peak V of LiF and other materials, can be explained as being only effective values associated with competing centres. For another example of very high values of E and s , for example, Azorin *et al*⁽¹⁹⁾.

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