Radiation Protection Dosimetry
Vol. 65, Nos. 1–4, pp. 63–68 (1996)
Nuclear Technology Publishing

A NEW LOOK AT THE MODELS OF THE SUPERLINEAR DOSE DEPENDENCE OF THERMOLUMINESCENCE

R. Chen†, G. Fogel† and C. K. Lee‡
†School of Physics and Astronomy
Raymond and Beverly Sackler Faculty of Exact Sciences
Tel-Aviv University, Tel-Aviv 69978, Israel
‡YSS Laboratory for TL
The Chinese University of Hong-Kong

INVITED PAPER

Abstract — Two types of model are usually employed for explaining the superlinearity (SL) of dose dependence of thermoluminescence (TL). One involves competition during excitation between trapping states, which causes the filling of the relevant trap or centre to be superlinear. The other model deals with competition during heating which may result in a strong SL, even if the filling of the trap and centre in question are linear with the dose. In the present work it is demonstrated that the two effects may occur in the same range in a model of one centre and two competing traps. The combined, very steep SL can thus be explained. In a model with one trap and two centres, TL follows approximately the filling of the active centre which is linear–superlinear–linear–saturation. Thus, in the case of two traps, SL results mainly from competition during heating whereas when two centres are involved, competition during excitation prevails.

INTRODUCTION

The dependence of thermoluminescence (TL) on the dose of excitation is of great importance. From the point of view of the applications in dosimetry and dating of archaeological and geological samples, a linear dose dependence is highly desirable. This is not always the case, and in situations of weak superlinearities some corrections have been suggested in the extrapolation utilised in evaluating the relevant dose[1]. In this particular case of TL from pottery samples, the dose dependence was superlinear at a relatively small initial range, followed by a long range of linear dependence. No specific theoretical account accompanied these experimental results. In some cases (see e.g. Zimmerman[2]), the typical behaviour has been an initial linear dose dependence, followed by a range of superlinearity. This, in turn, was followed by another linear range, after which a sublinear dose dependence occurred which was related to the approach to saturation. This behaviour was explained by Aitken *et al*[3] and, with more details, by Chen and Bowman[4] to be due to a superlinear filling of trapping states resulting from competition during the excitation with a competing trapping state that does not contribute directly to the measured TL.

A different kind of superlinearity, namely one which starts as of the very lowest doses has first been reported by Halperin and Chen[5] in semiconducting diamonds. This, however, was explained to be due to a multistage transition of electrons from the valence to the conduction band, and did not seem to be related to competition. Rodine and Land[6] reported a quadratic dose dependence of one of the TL peaks in ThO_2. They explained this qualitatively as resulting from competition during the heating. Kristianpoller *et al*[7] further developed this idea and gave it a mathematical form by which, using some assumptions, the quadratic dose dependence could be demonstrated in cases where the filling of both traps and centres was linear with the dose. They also demonstrated a somewhat more than quadratic dependence in dose ranges where the competitor approaches saturation.

Chen *et al*[8] reported a very strong superlinearity of the 110°C peak in β irradiated synthetic quartz. They adopted the previous theoretical model of Kristianpoller *et al*[7] and showed how the concept of competition during heating could, indeed, explain the strong superlinearity observed in synthetic quartz. Mische and McKeever[9] showed that the dose dependence in LiF, which goes linear–superlinear–saturation, can be explained by a model of competition during heating. In their model a distinction is made between the effect of nearest neighbour trap–centre pairs which are responsible for the linear part, and transitions through the conduction band in the presence of competitors, which is responsible for the superlinear behaviour. In a recent work Chen and Fogel[10] gave a theoretical account, based on the numerical solution of the appropriate differential equations. They found a dose dependence which started as a quadratic function (D^2) and turned to be more superlinear before getting linear and sublinear. All this occurred in a situation where the filling of the relevant trap and centre are nearly linear with the dose.

In the present work the possible dependencies of the TL as well as the filling of traps and centres as a function of the dose are studied further. The different elements contributing to the superlinear dependence are discussed. These considerations are accompanied by numerical calculations simulating the dose dependence in two alternative models, namely, a model with one trap and two centres competing with each other, and a model with one centre and two competing traps. The numerical simulation followed the three stages taking place in the experiment, namely excitation, relaxation and heating. This way, the effects of superlinearity due to excitation and during heating may be mixed. However, this complication should be dealt with and understood since it may very well occur in the experiments.

It is to be noted that all these models are related to a uniform or nearly uniform excitation of the whole bulk of the sample, which is the case where irradiation is by UV light, X rays as well as β and γ excitations: this as opposed to excitation along tracks which is typical of heavy particle irradiation[11]. In the latter case, a different way of explaining superlinearity seems to be appropriate, although even in this case competition of non-irradiative centres appears to be essential. The possible relevance of the present considerations in the track model requires further study.

ELEMENTS OF SUPERLINEARITY

The model mentioned above of superlinearity due to competition during excitation (Suntharalingam and Cameron[12]) is shown in Figure 1. It is assumed in this somewhat naïve model that the measured TL is going to be proportional to the concentration in the active trap n_1. Here, n_2 plays the role of 'competitor during excitation'. Intuitively speaking, let us assume that the trapping probability A_2 into the competitor is larger than that into the active trap, A_1. At the low doses, both n_1 and n_2 grow linearly. The capacity of the competitor N_2, however, is relatively small and, therefore, at higher doses n_2 approaches saturation. More electrons are made available to n_1 and therefore n_1 is being filled faster. When n_2 is entirely saturated n_1 grows linearly but at a faster rate than at the low dose range. It is the intermediate dose range which is of great interest; when n_2 approaches saturation, n_1 is in the range of transition from small slope linearity to high slope linearity. In this range, the TL intensity is thus necessarily superlinear with the dose. A somewhat more quantitative account of this kind of superlinearity has been given by Chen and Bowman[4]. Using some conventional assumptions they found an approximate expression which demonstrated the initial linear dose dependence, followed by superlinearity which, in turn was followed by linearity and sublinearity.

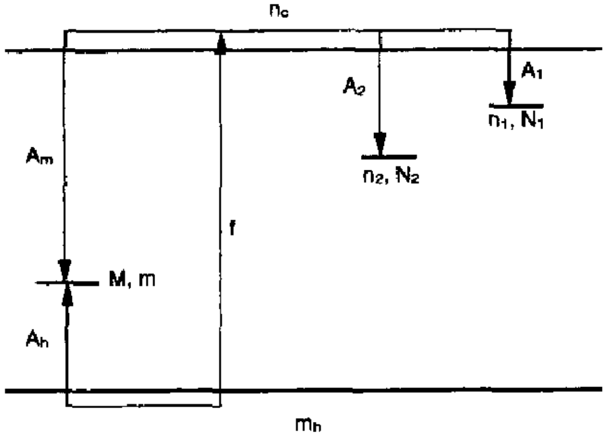

Figure 1. An energy level scheme for the model of two competing traps and one recombination centre. N_1 and N_2 (m^{-3}) are, respectively, the concentrations of the two kinds of traps. n_1 and n_2 (m^{-3}) are functions of time and denote the occupancies of the two trapping states. A_1 and A_2 ($m^3.s^{-1}$) are the trapping probabilities into n_1 and n_2. M (m^{-3}) is the concentration of relevant centres and m (m^{-3}) its instantaneous occupancy. f ($m^{-3}.s^{-1}$) is the rate of creation by the applied radiation of electrons and holes in the conduction and valence bands, respectively. n_c and m_h are the concentrations of electrons and holes in the conduction and valence bands, respectively. A_h ($m^3.s^{-1}$) is the probability of capture of holes in the centres and A_m ($m^3.s^{-1}$) is the recombination probability of free electrons with holes in centres.

The alternative model of competition during heating can be intuitively explained as follows (see Figure 2). Suppose a certain TL peak is related to a trap with initial concentration n_{10} and a centre with an initial concentration m_0. Normally, one would expect the TL intensity (measured either by the maximum intensity I_{max} or the area under the glow peak S) to be proportional to the smaller of the two (see e.g. Chen and Kirsh[13]). To put it in somewhat different words, S should be proportional to n_{10} or m_0 depending on whether the trap or centre is depleted first. It may happen, however, in the presence of a competitor with initial concentration n_{20} that, say, $n_{10}>m_0$ but n_{10} is depleted first since the released electrons may go either to the recombination centre or into the competitor. This leads to the dependence of the measured TL on n_{10} which, in turn, may depend linearly on the dose. In addition, the ratio of the total number of

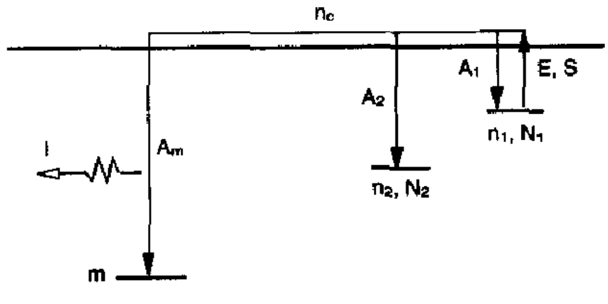

Figure 2. The transitions occurring during heating in the model shown in Figure 1. E (eV) is the activation energy of the active trap and s (s^{-1}) is the frequency factor of the trap. T (K) is the temperature and k ($eV.K^{-1}$) is Boltzmann's constant. The emitted light intensity I is directly related to the rate of change of holes concentration in centres, −dm/dt.

electrons going into the centre will be proportional to the relative concentration of the number of holes m_0 to the empty competitors $N_2 - n_{20}$. If the latter is far from saturation, then the measured TL is proportional to m_0 which, in turn, may be proportional to the dose. These two linear dependencies on the dose of n_{10} and m_0 in the same dose range combine to a quadratic dose dependence. The approximate expression given by Kristianpoller *et al*[7] was

$$S \cong (A_m/A_2N_2)m_0n_0 \quad (1)$$

which explained the quadratic dose dependence. As further shown by Chen *et al*[8], a better approximation is

$$S \cong \{A_m/[A_2(N_2 - n_{20})]\}m_0n_{10} \quad (2)$$

Since n_{20} is an increasing function of the dose, $N_2 - n_{20}$ is decreasing and since this factor appears in the denominator of the expression, it adds an increasing element to S with the dose. Thus, S is expected to be growing faster than quadratically with the dose.

It is to be noted that this extra effect is strong in the range where n_{20} approaches saturation. As described above, however, the range where n_{20} approaches saturation is that where competition during excitation plays an important role. This shows that in this region n_{10} by itself grows superlinearly with the dose, and therefore the measured TL may be more than quadratic for two different reasons. Here, the approach to saturation of the competitor may have effects both during the excitation and during heating. An important point to understand is

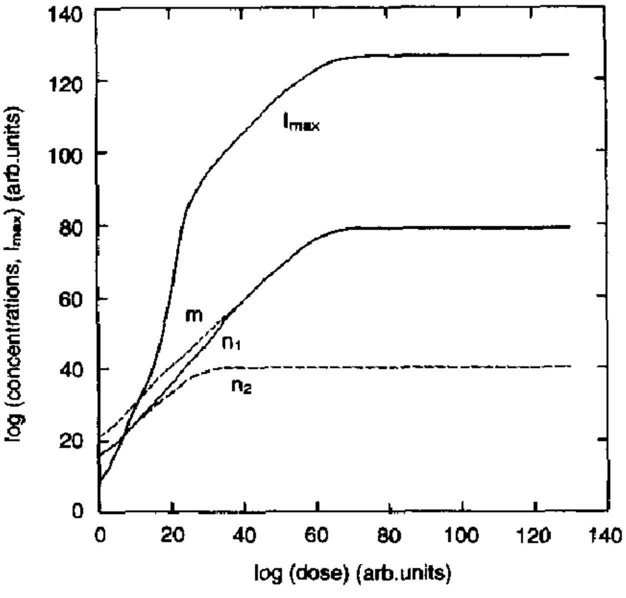

Figure 3. A sample result based on the model depicted in Figures 1 and 2 (Equations 4–12). The parameters used were $E = 1.0$ eV, $s = 10^{13}$ s^{-1}, $A_h = A_1 = A_m = 10^{-21}$ m^3.s^{-1}, $A_2 = 10^{-19}$ m^3.s^{-1}, $N_1 = 10^{23}$ m^{-3}, $N_2 = 10^{21}$ m^{-3}, $M = 1.01 \times 10^{23}$ m^{-3}, $f = 10^{21}$ m^{-3}.s^{-1}. The x axis gives, on a logarithmic scale, the time of irradiation, t_D in seconds, from which the relevant dose $D = ft_D$ is readily derived. The curves show the dose dependence of n_{10}, n_{20}, m_0, and I_{max}.

that under these circumstances the two effects of competition during excitation and heating are rather difficult to distinguish.

A somewhat similar situation occurs in the case of one trapping state n and two kinds of centres m_1, m_2, as shown in Figures 4 and 5. Let us assume that m_1 is the 'active' centre in the sense that during the heating stage, transitions into m_1 are measurable whereas m_2 behaves like a competitor, which means that transitions

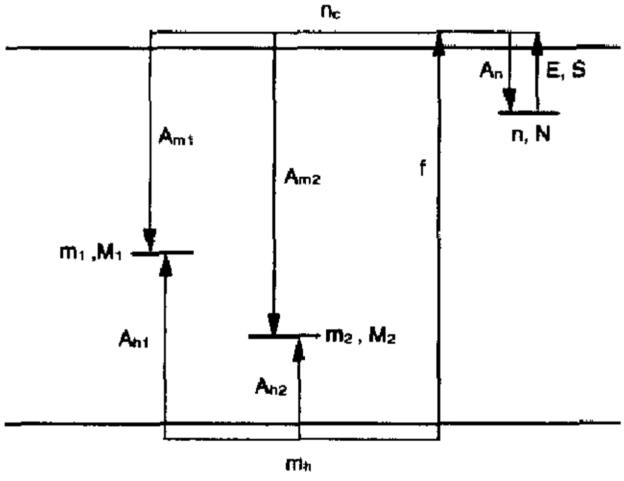

Figure 4. An energy level scheme for the model of two competing centres and one trapping state. M_1 and M_2 (m^{-3}) are the concentrations of the two centres and m_1, m_2 (m^{-3}) are their occupancies, respectively. A_{h1} and A_{h2} (m^3.s^{-1}) are the probabilities for capturing free holes from the valence band, and A_{m1}, A_{m2} (m^3.s^{-1}) are the recombination probabilities of free electrons. Here too, f (m^{-3}.s^{-1}) is the rate of creation of free electrons and holes in the conduction and valence bands, respectively. n_c and m_h (m^{-3}) are the concentrations of these free electrons and holes. N (m^{-3}) is the total concentration of traps and n (m^{-3}) its instantaneous occupancy. A_n (m^3.s^{-1}) is the trapping probability from the conduction band into the trap.

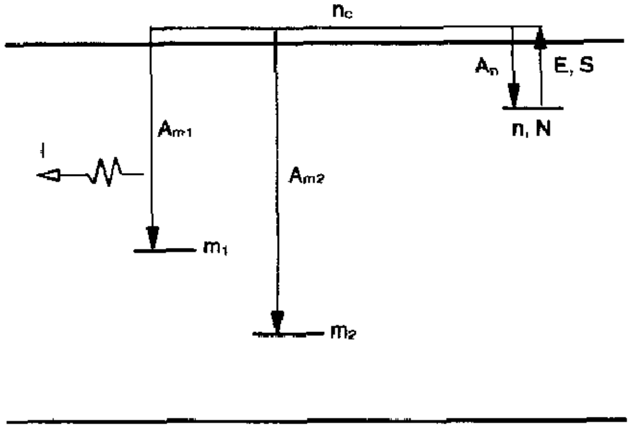

Figure 5. The transitions occurring in the same model shown in Figure 4 during heating. E (eV) and s (s^{-1}) are the activation energy and frequency factor of the trap. It is assumed that the measured emission is only from m_1, and therefore, the TL intensity I is directly related to $-dm_1/dt$.

from the conduction band into m_2 are either radiationless or radiative in spectral ranges not measurable by the system in hand. The same approximations leading to Equation 2 above will lead here to

$$S \cong [A_{m1}/(A_{m2}m_{02})]\, m_{01}n_0 \quad (3)$$

The consequences concerning the dose dependence, however, are entirely different from the previous case. If, for example, n_0 and m_{20} behave in a certain dose range in a similar manner, say, both grow linearly with the dose, the measured TL dependence on the dose will behave in the same way as m_{01}. If due to competition during excitation, m_{01} goes superlinearly with the dose, so will the measured TL. If in the same region, m_{20} is sublinear with the dose, the superlinearity of TL will be stronger in this range. As opposed to the previous case, however, this kind of trap and centre filling may account for a behaviour that starts linearly, gets superlinear and at higher doses approaches saturation. This, of course, as opposed to the previous case where the initial dose dependence was expected to be quadratic, and at higher doses became even more superlinear before starting its approach to saturation.

Since these conclusions are based on simplifying assumptions, they should be supported by numerical calculations demonstrating the two kinds of possible behaviour. This will be done by choosing particular sets of parameters for each of the two different models. Of course, the advantage is that no simplifying assumptions are required here, and the results are dependent only on the choice of the sets of kinetic parameters.

NUMERICAL RESULTS

Figures 1 and 2 are associated with the excitation and heating phases of the same energy level configuration, namely, a situation with two trapping states and one kind of centre. The set of simultaneous differential equations governing the excitation in the model depicted in Figure 1 is:

$$-dm/dt = A_m n_c m - A_h m_h(M - m) \quad (4)$$

$$dm_h/dt = f - A_h m_h(M - m) \quad (5)$$

$$dn_1/dt = A_1 n_c(N_1 - n_1) \quad (6)$$

$$dn_2/dt = A_2 n_c(N_2 - n_2) \quad (7)$$

$$dm/dt + dm_h/dt = dn_c/dt + dn_1/dt + dn_2/dt \quad (8)$$

where the different quantities are defined in the caption of Figure 1. The assumption is made here that the excitation is performed at a temperature low enough for no charge carriers to be released thermally. This set of equations is solved numerically using a conventional algorithm (see, e.g., Chen *et al*[14], and Chen and Fogel[10]). The dose of excitation D is defined as $D = f.t_D$ where t_D is the total length of excitation time. The relaxation period following the excitation is simulated by setting $f = 0$ and taking the initial values for the functions n_1, n_2, m, n_c, and m_h as the final values at the end of excitation. This procedure is now continued until n_c and m_h decay to negligible values.

The next step of the TL behaviour during the heating stage is governed by the set

$$dn_1/dt = -s\exp(-E/kT)n_1 + A_1(N_1 - n_1)n_c \quad (9)$$

$$dn_2/dt = A_2(N_2 - n_2)n_c \quad (10)$$

$$I = -dm/dt = A_m.m.n_c \quad (11)$$

$$dm/dt = dn_1/dt + dn_2/dt + dn_c/dt \quad (12)$$

The results of a sample run are shown in Figure 3 with the parameters chosen given in the caption. In the dose range shown, the dose dependence of n_{10} is linear first, goes superlinear when n_{20} approaches saturation, and becomes linear again when n_{20} reaches saturation. At higher doses, n_{10} itself approaches saturation. m_0 starts linearly with the dose, and approaches saturation at high doses. The calculated maximum TL intensity I_{max} starts quadratically with the dose, as expected in the range where the competitor is far from saturation. At higher doses, the dependence gets much more superlinear as a result of the two reasons mentioned above, both related to the approach of n_{20} to saturation.

As explained above semi-analytically, namely, with a number of simplifying assumptions, the competition between two centres in a model with one trap and two centres is not the same as in the case of one centre and two traps. In order to support this, a numerical calculation of the process in this model has been performed. Figure 4 shows the energy level diagram of a case with two recombination centres m_1 and m_2 and one trapping state n. The meaning of the parameters is given in the caption. The excitation is simulated again by inserting pairs of free electrons and holes at a rate of f per second per m^3 for different periods of time resulting in different applied doses. It is assumed that the measured TL is related to the transition during the heating into m_1. This implies that the transition into m_2 is radiationless or radiative in a spectral range to which the detector in hand is not sensitive.

The equations governing this process during the excitation are

$$dm_h/dt = f - A_{h1}m_h(M_1 - m_1) - A_{h2}m_h(M_2 - m_2) \quad (13)$$

$$dm_1/dt = A_{h1}m_h(M_1 - m_1) - A_{m1}m_1\, n_c \quad (14)$$

$$dm_2/dt = A_{h2}m_h(M_2 - m_2) - A_{m2}m_2\, n_c \quad (15)$$

$$dn/dt = A_n(N - n)n_c \quad (16)$$

$$dm_1/dt + dm_2/dt + dm_h/dt = dn/dt + dn_c/dt \quad (17)$$

The dose D is, again, $D = ft_D$ where t_D is the duration of the excitation. Again, the same set of equations with $f = 0$ governs the process during the relaxation time.

Figure 5 depicts the transitions taking place during the heating stage with the same trap and centres as in

Figure 4. The set of differential equations governing the process in this stage is

$$I = -\,dm_1/dt = A_{m1}m_1n_c \quad (18)$$

$$-\,dm_2/dt = A_{m2}m_2n_c \quad (19)$$

$$-\,dn/dt = sn\exp(-E/kT) - A_n(N-n)n_c \quad (20)$$

$$dn/dt + dn_c/dt = dm_1/dt + dm_2/dt \quad (21)$$

The meaning of the different symbols is given in the figure caption. This set has been solved numerically following the simulation of the excitation and relaxation stages. Figure 6 gives the results of a sample run of solving the sets (13–17) and (18–21) sequentially; the chosen parameters are given in the caption. It is seen that the dependence of n_0 on the dose is linear. m_{20} starts linearly and goes to saturation at a certain dose. m_{10} also starts linearly, but at the range where m_{20} approaches saturation, it gets superlinear before going back to linearity. The main point to emphasise here, however, is that I_{max} representing the maximum of the measured TL follows more or less exactly the dependence of m_{10} on the dose. The reason for that seems to be that none of the two elements leading to superlinearity mentioned in relation to the previous model exists here. Thus, a Suntharalingam and Cameron[12] type of superlinearity is demonstrated here under circumstances somewhat different from those originally suggested.

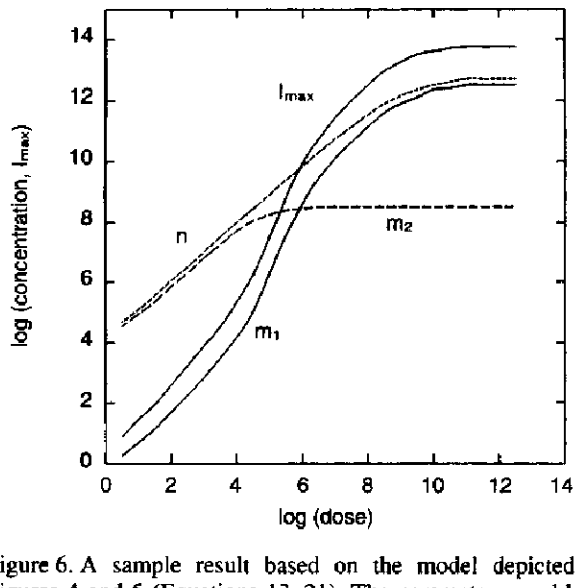

Figure 6. A sample result based on the model depicted in Figures 4 and 5 (Equations 13–21). The parameters used here were $E = 1.0$ eV, $s = 10^{13}\ s^{-1}$, $f = 10^{21}\ m^{-3}.s^{-1}$, $A_{m1} = A_{m2} = 10^{-21}\ m^3.s^{-1}$, $A_n = 2\times10^{-21}\ m^3.s^{-1}$, $M_1 = 9\times10^{23}\ m^{-3}$, $M_2 = 10^{23}\ m^{-3}$, $A_{h1} = 10^{-21}\ m^3.s^{-1}$, $A_{h2} = 10^{-20}\ m^3.s^{-1}$, $N = 10^{24}\ m^{-3}$. Here too, the x axis gives t_D, the duration of irradiation, to which the excitation dose is proportional by $f\,t_D$. The curves show the dose dependencies of m_{10}, m_{20}, n_0 and I_{max}.

CONCLUSION

The main points addressed in the present work can be summed up as follows.

(1) It is inadequate to consider the two kinds of competition separately. In this respect, the recent arguments in the literature (see, e.g., Mische and McKeever[9], Rosenkrantz and Horowitz[15]) on which kind of competition occurs in specific cases may not be entirely justified since both types may contribute to the observed superlinearity in the same material and under the same experimental conditions.

(2) The superlinear effect due to competition during heating has two elements. One has to do with the final result being proportional to both the concentrations of charge carriers in traps and centres in the presence of a strong competitor. Thus, if each of them is proportional to the dose, the total dose dependence is quadratic. In addition, in the dose range where the competitor approaches saturation, the reduction in competition causes some extra superlinearity (more than quadratic behaviour).

(3) The numerical solutions of the sets of simultaneous differential equations enable us to bypass the possible problems of artefacts due to the approximations made. Thus, if a certain behaviour is observed, we can be sure that it is a net effect of the model in hand, and therefore, can be compared with the relevant experimental results. On the other hand, the numerical results are associated with the chosen sets of parameters, and it is rather difficult to draw general conclusions. It is felt, however, that it is of prime importance to be able to demonstrate that the experimentally observed behaviours can, indeed, be associated with these models. It is appropriate to mention here a recent paper by Lee and Chen[16] who used the opposite way, namely, reached some conclusions concerning superlinearity by making approximations, thus getting semi-analytical results.

(4) As opposed to what one might have thought, it has been found, both from analytical considerations and numerical results, that there is a big difference between a situation with a competition of two trapping states and a competition between two centres. In the former, a typical behaviour is an initially quadratic dose dependence followed by stronger superlinearity before saturation effects set in. In the latter, a typical dependence is an initial linear range followed by moderate superlinearity, and, in turn, back to linearity and saturation. It appears that the main difference between a trap competitor and a centre competitor is that, in the former case, $N_2 - n_2$ which competes with m_{10} on released electrons, decreases with the dose. In the latter case, m_{20} which is the relevant competitor, increases with the dose.

(5) The apparent discrepancy between the theoretical dependence which starts quadratically and gets more superlinear at higher doses, and the more than cubic initial dose dependence in the 110°C peak in synthetic quartz can be explained easily. It is very plausible that the initial expected quadratic dependence cannot be observed due to an insufficient sensitivity of the measuring system in the low dose range.

(6) As stated by Mische and McKeever[9], under the circumstances of a competing luminescence centre, no superlinearity is expected. This is, more or less, confirmed here, as far as competition during heating is concerned. The only superlinearity possible seems to be that related to the superlinear filling of the centres involved; the measured TL follows practically the same pattern.

REFERENCES

1. Tite, M. S. *Thermoluminescence Dating of Ancient Ceramics: A Reassessment.* Archaeometry **9**, 155–169 (1966).
2. Zimmerman, J. *The Radiation Induced Increase of TL Sensitivity of the Dosimetry Phosphor LiF (TLD-100).* J. Phys. C: Solid State Phys. **4**, 3277–3291 (1971).
3. Aitken, M. J., Thompson, J. and Fleming, S. J. *Pre-Dose Effects in TL and in Luminescence During Irradiation.* In: Proc. 2nd Int. Conf. on Luminescence Dosimetry, Gatlinburg. CONF-680920, pp. 364–370 (Springfield, VA: NTIS) (1968).
4. Chen, R. and Bowman, S. G. E. *Superlinear Growth of Thermoluminescence Due to Competition during Irradiation.* Eur. PACT J. **2**, 216–230 (1978).
5. Halperin, A. and Chen, R. *Thermoluminescence of Semiconducting Diamonds.* Phys. Rev. **148**, 839–845 (1966).
6. Rodine, E. T. and Land, P. L. *Electronic Defect Structure of Single Crystal ThO_2 by Thermoluminescence.* Phys. Rev. B4, 2701–2724 (1971).
7. Kristianpoller, N., Chen, R. and Israeli, M. *Dose Dependence of Thermoluminescence Peaks.* J. Phys. D: Appl. Phys. **7**, 1063–1072 (1974).
8. Chen, R., Yang, X. H. and McKeever, S. W. S. *The Strongly Superlinear Dose Dependence of Thermoluminescence in Synthetic Quartz.* J. Phys. D: Appl. Phys. **21**, 1452–1457 (1988).
9. Mische, E. F. and McKeever, S. W. S. *Mechanisms of Superlinearity in Lithium Fluoride Thermoluminescence Dosemeters.* Radiat. Prot. Dosim. **29**, 159–175 (1989).
10. Chen, R. and Fogel, G. *Superlinearity in Thermoluminescence Revisited.* Radiat. Prot. Dosim. **47**, 23–26 (1993).
11. Horowitz, Y. S. *Mathematical Modelling of TL Supralinearity for Heavy Charged Particles.* Radiat. Prot. Dosim. **33**(1/4), 75–81 (1990).
12. Suntharalingam, N. and Cameron, J. R. *TL Response to Radiation with Different LET.* Phys. Med. Biol. **14**, 397–410 (1969).
13. Chen, R. and Kirsh, Y. *Analysis of Thermally Stimulated Processes* (Oxford: Pergamon Press) p. 195 (1981).
14. Chen, R., McKeever, S. W. S. and Durrani, S. A. *Solution of the Kinetic Equations Governing Trap Filling. Consequences Concerning Dose Dependence and Dose-Rate Effects.* Phys. Rev. **B24**, 4931–4944 (1981).
15. Rosenkrantz, M. and Horowitz, Y. S. *Alpha Particle Induced TL Supralinearity in TLD-100: Dependence on Vector Properties of the Radiation Field.* Radiat. Prot. Dosim. **47**, 27–30 (1993).
16. Lee, C. K. and Chen, R. *Explanation of the Superlinear Behaviour of Thermoluminescence by Considering the Residual Holes in the Recombination Centers before Irradiation.* J. Phys. D: Appl. Phys. **28**, 408–414 (1995).