

# A model for non-monotonic dose dependence of thermoluminescence (TL)

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## Abstract

In the applications of thermoluminescence (TL) in dosimetry and archaeological and geological dating, a desirable dose dependence of TL intensity is a monotonically increasing function, preferably linear. It is well known that in many dosimetric materials, nonlinear dependence is observed. This may include a superlinear dependence at low doses and/or sublinear dose dependence at higher doses, where the TL intensity approaches saturation. In quite a number of materials, non-monotonic dose dependence has been observed, namely, the TL intensity reached a maximum value at a certain dose and decreased at higher doses. This effect is sometimes ascribed to 'radiation damage' in the literature. In the present work we show, both quasi-analytically and by using numerical simulation, that such dose dependence may result from a simple energy level scheme of at least one kind of trapping state and two kinds of recombination centres. One does not necessarily have to assume a destruction of trapping states or recombination centres at high doses. Instead, the main concept involved is that of competition which takes place both at the excitation stage and the read-out stage during the heating of the sample. This may explain the fact that the phenomenon in question, although very often ignored, is rather common. Cases are identified in which competition during excitation dominates, and others in which competition during read-out dominates.

## 1. Introduction

The dose dependence of thermoluminescence (TL) is usually an increasing function that, ideally, starts linearly and then goes sublinear when the TL intensity approaches a saturation value. For applications in dosimetry and archaeological and geological dating, one usually tries

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to exploit the linear dose range in order to determine the unknown dose imparted on the sample. In several materials, superlinear dose dependence has been reported (see e.g. chapter 4 in [1]), and it was usually explained to result from competition between transitions into trapping states or to recombination centres, either during the excitation by irradiation or during the heating of the sample or both. At high doses of excitation, the usually expected behaviour is that the dose dependence function goes sublinear while approaching saturation. The usual explanation for this is that trapping states and/or recombination centres are being filled to capacity so that further irradiation does not contribute to any further increase in the emitted TL.

In quite a number of publications, it is seen that for some TL peaks in different materials, the maximum TL intensity measured as a function of the excitation dose reaches a maximum and then decreases at higher doses. In some cases, the authors consider this as an unimportant fluctuation, and still term this rather unusual effect 'saturation'. In fact, quite often the set of measurements was terminated following one point of the decrease, and therefore it is hard to tell to what extent this reduction can go. In other cases, however, it is seen clearly that the intensity goes down quite significantly after having reached a maximum at a certain dose.

In the present work, we present a rather general model, without assuming a radiation damage or destruction of trapping states and/or recombination centres. This follows a recent work by Chen *et al* [2] in which non-monotonic behaviour was demonstrated by using numerical simulation of the excitation and read-out stages of TL. The main elements of the present model are the existence of (at least) one trapping state and two kinds of recombination centres. These seem to occur in practically any dosimetric material in use. The competition over charge carriers during both excitation and heating is considered using intuitive considerations, analytical derivation and more numerical simulation. Cases are identified in which either the competition during excitation or during heating dominates in being the reason for the non-monotonic dose dependence.

## 2. Experimental evidence

In the present section we give a brief account of the vast number of experimental results reported in the literature. It is interesting to note that this effect of a decrease in the TL intensity at high doses takes place in several materials including the most often used TL dosimetric materials, namely LiF and Al<sub>2</sub>O<sub>3</sub>, routinely used for dosimetry, and quartz, which is the main TL dating material. First reports on the effect are found in publications from the 1960s. Cameron *et al* [3] give a graph (previously presented by Schulman *et al*, 1967, in an unpublished report) of the dose dependence of TL in LiF (TLD-100) as a function of <sup>60</sup>Co  $\gamma$ -rays. They report on a rather broad range of linear dependence followed by a superlinear range after which a maximum value and a slight decline are seen. Similar results in LiF:Mg were given by Claffy *et al* [4]. Crittenden *et al* [5] describe the effect of TL decline in LiF:Mg, Ti irradiated by x-rays. Piesch *et al* [6] report on the  $\gamma$ -ray dose dependence of LiF ribbons and LiF-Teflon dosimeters of different thicknesses, and show in some of their samples a decrease in the intensity with the dose at relatively high doses. Jain *et al* [7] describe a significant decrease of the TL output of peak V in LiF, by a factor of  $\sim 2.5$  from the maximum, and ascribe it to 'radiation damage', a term which is later used by other investigators to describe the effect. They speculate that, at very high exposures, luminescence centres aggregate to form complex centres. Their graphs show that at very high doses, the dose-dependence curves tend to level off following a range of decrease in TL intensity. Kithara *et al* [8] also report on a quite significant decrease effect in  $\gamma$ -irradiated and thermal neutron irradiated LiF powder. Waligórski and Katz [9] show that in TLD-700 (<sup>7</sup>LiF), peak 5 decreases at high doses of <sup>60</sup>Co  $\gamma$ -exposure by a factor of  $\sim 20$  between 10<sup>3</sup> and 10<sup>5</sup> Gy. Moscovitch and Horowitz [10] show the effect in x-ray and  $\alpha$ -particle

irradiated LiF:Mg, Ti for doses above  $10^4$  Gy. Similar results are shown by Horowitz [11] for x-ray excitation. Mische and McKeever [12] report on the decline effect as of  $\sim 10^3$  Gy in  $\alpha$ ,  $\gamma$  and proton irradiated LiF samples. Piters and Bos [13] also discuss the effect in  $\beta$ -irradiated LiF:Mg, Ti. The measured quantity here is the integrated area of peaks 4 + 5, which reaches a maximum at  $\sim 20$  Gy.

The first report on non-monotonic dose dependence in quartz was also given in the 1960s by Ichikawa [14]. He found that out of four peaks in  $\gamma$ -irradiated natural quartz, the peak termed  $B_1$ , occurring at  $\sim 200^\circ\text{C}$ , reached a maximum at  $\sim 6 \times 10^4$  Gy and decreased at higher doses by at least a factor of 2.5. Durrani *et al* [15] reported on a significant decrease of the TL response as well as the TL sensitivity at doses  $> 10^7$  Gy in natural Brazilian quartz. In another paper, Durrani *et al* [16] reported such a decline above  $4 \times 10^4$  Gy of  $\gamma$ -radiation induced TL in natural quartz. David *et al* [17] showed the dose dependence of some TL peaks in  $\gamma$ -irradiated pink quartz, which revealed a decline following a maximum at  $10^3$ – $10^4$  Gy. Morris and McKeever [18] describe a model of three electron traps and two hole traps in quartz which explains a somewhat similar effect of the *residual* TL (following a given bleaching) as a function of the applied dose. In a recent paper, Yazici and Topaksu [19] report on the non-monotonic effect in 'peak 1' out of a series of four peaks in  $\beta$ -irradiated synthetic quartz.

Another material which exhibits non-monotonic behaviour is  $\text{CaSO}_4$ , nominally pure or doped with different impurities. Lakshmanan *et al* [20] and Srivastava and Supe [21] show a decline in the TL intensity at high  $\gamma$ -doses  $> 10^4$  Gy in  $\text{CaSO}_4:\text{Dy}$ . Natarajan *et al* [22] report on a decline of the peak intensity of a TL peak at 406 K following  $> 70$  h of self-irradiation in  $\text{CaSO}_4:^{241}\text{Am}$ , the excitation being equivalent to  $\sim 400$  Gy  $\text{h}^{-1}$  of  $\alpha$ -particles. Seshagiri *et al* [23] report TL peaks at 375, 400 and 440 K in  $\gamma$ -irradiated  $\text{CaSO}_4:\text{U}_2^{2+}$ . They suggest that the effect of self-irradiation is negligible, and show that the maximum takes place at  $\sim 4 \times 10^3$  Gy, after which the intensity reduces by a factor of  $\sim 2$  and levels off at higher doses, reaching a constant equilibrium value. Lewandowski and Mathur [24] give an account of the TL of  $\gamma$ -irradiated  $\text{CaSO}_4$ ,  $\text{CaSO}_4:\text{Dy}$  and  $\text{CaSO}_4:\text{Tm}$ . They measure the TL intensity integrated over a temperature range and get a maximum followed by a slight decline. They refer to this situation as 'saturation' and do not pursue the behaviour at higher doses. Yaskolko [25] describes the TL light sum in  $\text{CaSO}_4$  excited by UV light with photon energy significantly lower than the band gap. Yaskolko presents a model of two-stage photoexcitation, which can explain the slight decline following the maximum in this specific situation. Mathur *et al* [26] report on the dependence of TL in  $\text{CaSO}_4:\text{Dy}$  irradiated by protons. The maximum intensity of a TL peak at  $335^\circ\text{C}$  occurs at  $\sim 10^4$  Gy, and the intensity decreases by a factor  $\sim 7$  at  $\sim 10^6$  Gy. For a peak at  $475^\circ\text{C}$ , the maximum occurs at  $\sim 10^5$  Gy, and the following decline is by far less dramatic.

The same effect has also been discovered in the important dosimetric material  $\text{Al}_2\text{O}_3$ . A small effect was found by Wayne Cooke *et al* [27] in a UV excited TL peak at 270 K. A similar effect has been reported by a number of researchers in the more sensitive  $\text{Al}_2\text{O}_3:\text{C}$  material. Akselrod *et al* [28] reported a decrease in the TL output of  $\text{Al}_2\text{O}_3:\text{C}$  thin layer detector at  $> 15$  Gy of  $\beta$ -irradiation. Agersap Larsen *et al* [29] gave an account of a similar effect of a TL peak at  $\sim 430$  K in  $\gamma$ -irradiated  $\text{Al}_2\text{O}_3:\text{C}$ . An effect of the same nature though smaller was reported for a thermally stimulated conductivity (TSC) peak at  $\sim 480$  K. The same effect is described by Papin *et al* [30] for x-ray excited  $\text{Al}_2\text{O}_3:\text{C}$ , where the maximum is reached at  $\sim 10$  Gy. Chitambo *et al* [31] reported a very strong effect in which the main dosimetric peak at  $\sim 130^\circ\text{C}$  in  $\alpha$ - $\text{Al}_2\text{O}_3:\text{C}$  reaches a maximum at  $\sim 100$  Gy of  $\gamma$ -irradiation and decreases by a factor of  $\sim 4$  at  $\sim 450$  Gy. Further evidence for the non-monotonic effect dose dependence has been given by Bloom *et al* [32], who presented similar results of a maximum at  $\sim 15$  Gy of  $\beta$ -irradiation; the authors report on results of the same nature at about the same doses for optically stimulated

luminescence (OSL). Yukihara *et al* [33] gave an account on the dose dependence of samples of  $\text{Al}_2\text{O}_3:\text{C}$  from different batches. Whereas at lower  $\beta$  doses some superlinearity was observed, at doses of  $\sim 30$  Gy, the intensity of the 450 K peak reached a maximum and then declined at higher doses. These authors distinguish between the 'real' dose dependence and the sensitivity changes which are measured as the response to a small test-dose following a relatively high dose irradiation and annealing at  $\sim 500^\circ\text{C}$ . In both, the effect of reduction of the measured TL with  $\beta$ -dose is reported. The authors present a model which explains the observed effects in  $\text{Al}_2\text{O}_3:\text{C}$ , and is based on the occurrence of  $\text{F}/\text{F}^+$  centres known to exist in this material, as well as other traps/centres in  $\text{Al}_2\text{O}_3:\text{C}$ . The initial situation described is that of existing  $\text{F}^+$  centres. A number of reports are found in the literature on the non-monotonic dose dependence of other inorganic materials. The earliest one is by Halperin and Chen [34], who gave an account of the UV excited TL in semiconducting diamonds. Whereas for the main peak at  $\sim 250$  K lower than band-gap photon energies of the excitation light (300–400 nm) caused strong superlinear dose dependence followed by an approach to saturation, the secondary peak at  $\sim 150$  K increased linearly, reached a maximum and decreased at higher doses. Similar non-monotonic dependence of the same peak was found with 225 nm light excitation, which corresponds to band-to-band photon energy (5.5 eV), although the dose dependence of the main peak was different. Pradhan *et al* [35] report a similar  $\gamma$ -dose dependence in  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn}$ . Jain and Mitra [36] describe a rather strong decrease following the maximum of 'peak I' (out of four peaks) in natural and fired fluorites. Las and Stoebe [36] show the same kind of effect in UV excited MgO. Seshagiri *et al* [37] report on the dependence on the dose of three TL peaks in  $\text{SrSO}_4:^{239}\text{Pu}$ . In two out of the three, the TL intensity reached a maximum at  $\sim 5 \times 10^4$  Gy of  $\gamma$ -irradiation and reduced quite significantly at higher doses, reaching a constant equilibrium value.

Finally, in a small number of works, the non-monotonic dependence of TL intensity on the excitation dose in organic materials has been described. Charlesby and Partridge [38] report on the effect starting at  $\sim 10^4$  Gy in  $\gamma$ -irradiated polyethylene. They show that the maximum intensity behaviour differs from peak to peak, and for each peak it is different between the visible and UV components of the luminescence. In a later paper, Charlesby and Partridge [39] discuss a similar effect in UV-irradiated polyethylene. Wintle [40] gives a theoretical account for the effect for this specific material and irradiation, postulating that here, indeed, one can speak about 'radiation damage'. He assumes that ionized centres are destroyed at a rate proportional to the dose-rate, and allows for the destruction of the un-ionized but excited centres by a separate bimolecular reaction. Further work on the effect in UV-irradiated polyethylene has been given by Partridge [41]. He explains the non-monotonic behaviour by a model of a double excitation mechanism followed by competition for the ejected electrons between shallow traps and radiation-produced alkyl radicals, with electrons in shallow traps also being untrapped by the incident radiation. Hama *et al* [42] give an account of TL in electron beam irradiated polycarbonate. The  $\alpha$  and  $\beta$  peaks are shown to reach a maximum at  $\sim 2 \times 10^4$  Gy and then decrease at higher doses. The authors suggest that this indicates that luminescence centres are destroyed by the irradiation. Pietrzak and Leszczyński [43] report on the  $\gamma$ -irradiated TL in aliphatic–aromatic polyamides. They show that a maximum is reached at  $\sim 2.4 \times 10^4$  Gy, and the TL intensity decreases significantly to  $\sim 20\%$  of the maximum value at  $\sim 3 \times 10^5$  Gy. Vanderschueren *et al* [44] describe a smaller effect following a maximum in UV-irradiated polycarbonate doped with triphenyl methane and xanthene dyes.

### 3. The model and analytical considerations

Chen *et al* [2] demonstrated that by using the two-trap, two-centre model and choosing appropriate sets of trapping parameters, two main kinds of non-monotonic behaviour could

be observed in numerical simulations. One kind of behaviour is where the maximum TL increases with the applied dose up to a maximum intensity and then declines to a certain intermediate intensity where it levels off and then remains constant. The relevant radiative recombination centre population at the end of the irradiation, denoted below by  $m_2$ , behaves in practically the same way, namely, reaching a maximum at the same dose and decreasing to a plateau level. The similarity between the two curves indicates that the TL intensity follows the occupancy of the radiative centre. Obviously, the latter results from competition during excitation, and thus, the non-monotonic dose behaviour of TL results from competition during excitation, and competition during heating has only minor influence on the dose dependence under these circumstances. In the present work, we demonstrate that rather similar results can be reached in the system with two kinds of recombination centres, but only one kind of trapping state. Figure 1 depicts an energy level system with two trapping states and two kinds of recombination centres. Although some of the relevant results may be reached with only one trapping state, in other cases the effect of competition with another trapping state is also of importance, and therefore, the more general situation of having two trapping states is shown. Transitions taking place during the excitation are shown in the figure by solid lines, whereas those that occur during heating by dashed lines.

### 3.1. Competition during excitation

*3.1.1. Governing equations.* The set of simultaneous differential equations governing the process during excitation in the case where two kinds of centres but only one trapping state exist is

$$\frac{dm_1}{dt} = -A_{m1}m_1n_c + B_1(M_1 - m_1)n_v, \quad (1)$$

$$\frac{dm_2}{dt} = -A_{m2}m_2n_c + B_2(M_2 - m_2)n_v, \quad (2)$$

$$\frac{dn}{dt} = A_n(N - n)n_c, \quad (3)$$

$$\frac{dn_c}{dt} = X - A_{m1}m_1n_c - A_{m2}m_2n_c - A_n(N - n)n_c, \quad (4)$$

$$\frac{dn_v}{dt} = X - B_2(M_2 - m_2)n_v - B_1(M_1 - m_1)n_v. \quad (5)$$

Here,  $M_2$  ( $\text{m}^{-3}$ ) is the concentration of the radiative hole centres with instantaneous occupancy of  $m_2$  ( $\text{m}^{-3}$ ),  $M_1$  ( $\text{m}^{-3}$ ) is the concentration of non-radiative hole centres with instantaneous occupancy of  $m_1$  ( $\text{m}^{-3}$ ), and  $N$  ( $\text{m}^{-3}$ ) is the concentration of the electron trapping state with instantaneous occupancy of  $n$  ( $\text{m}^{-3}$ ).  $n_c$  and  $n_v$  are the concentrations ( $\text{m}^{-3}$ ) of electrons and holes in the conduction and valence bands respectively.  $X$  ( $\text{m}^{-3} \text{ s}^{-1}$ ) is the rate of production of electron-hole pairs, which is proportional to the excitation dose-rate, and  $B_1$  and  $B_2$  ( $\text{m}^3 \text{ s}^{-1}$ ) are the trapping coefficients of free holes in centres 1 and 2 respectively.  $A_{m1}$  and  $A_{m2}$  ( $\text{m}^3 \text{ s}^{-1}$ ) are the recombination coefficients for free electrons with holes in centres 1 and 2, and  $A_n$  ( $\text{m}^3 \text{ s}^{-1}$ ) is the retrapping coefficient of free electrons into the trapping state  $N$ . It should be noted that, in some instances, the occurrence of a competing trapping state is of importance with regard to the non-monotonic dose dependence, in which case equation (3) is replaced by two similar equations, one with  $n_1$ ,  $N_1$  and  $A_{n1}$  and the other with  $n_2$ ,  $N_2$  and  $A_{n2}$  [2] (see also the next subsection). If we denote the time of excitation by  $t_D$ ,  $D = Xt_D$  is the total concentration of electrons and holes produced, which is proportional to the total dose imparted. It should be mentioned that, at the end of the excitation, free electrons and holes remain in the

conduction and valence bands, respectively. In order to simulate the experimental situation properly, one has to consider a relaxation time following the excitation and prior to the heating stage, during which practically all the free carriers relax and end up in the traps and centres. It should be noted that the relaxation process is important because the carriers can build up to significant levels during excitation, and relaxation is needed to provide the time necessary for them to decay back toward zero. The analytical model to be presented here, however, is for slow excitation rates,  $X$  (with high doses achieved by long exposure times). Because  $X$  is small, the free carrier concentrations are always small (see equations (12) and (13) below), and there is no need for considering the relaxation process (see also the discussion concerning the numerical results at the end of section 4).

It is quite obvious from equation (3) that  $n$  is an increasing function of time, and therefore of dose  $D$ , which approaches saturation,  $n \rightarrow N$ , at large doses. The behaviour of the centres is more complex. If  $M_1 + M_2 < N$ , then, in general, it is found that both  $m_1$  and  $m_2$  will approach saturation at large doses,  $m_1 \rightarrow M_1$  and  $m_2 \rightarrow M_2$ . For the other case of  $M_1 + M_2 > N$ , however, it is generally found that neither centre becomes full regardless of dose. Further, in this case, at large dose, it is found that the sum ( $m_1 + m_2$ ) monotonically increases with dose and approaches a limiting value of  $m_1 + m_2 \rightarrow N$ . The main point in this respect, however, is that although  $m_1 + m_2$  is an increasing function of the dose, approaching saturation, this may not be the case with  $m_1$  and  $m_2$  separately. Due to the rather complex competition processes taking place during excitation, which involve the transitions of holes from the valence band into  $M_1$  and  $M_2$ , the recombination of electrons with these holes and the retrapping of electrons into  $N$ , the distribution of holes between  $m_1$  and  $m_2$  at the end of relaxation may be such that one of them will increase, say, superlinearly with the dose whereas the other will reach a maximum and decrease at higher doses. If the latter happens to be the radiative centre, the measured TL intensity may follow this behaviour, reach a maximum at a certain dose and then decrease at higher doses.

*3.1.2. Centre kinetics: qualitative considerations.* The reason that the population of a centre may decline with dose at high doses can be understood by examining the two competing processes which fill and deplete a centre. Considering for specificity centre  $m_2$ , hole capture, represented by the term  $B_2(M_2 - m_2)n_v$  on the right-hand side of equation (2), always acts to increase the population of  $m_2$ . By contrast, electron capture, represented by the term  $A_{m_2}m_2n_c$ , always acts to decrease  $m_2$ . The usual initial condition is that the centre is empty:  $m_2 = 0$ . In this case, electron capture is initially zero and, initially, therefore  $m_2$  increases due to hole capture. Suppose the alternate case happens and, for some reason,  $m_2$  is initially large, say:  $m_2 \rightarrow M_2$ . In this case, the hole capture becomes small as  $(M_2 - m_2) \rightarrow 0$  and electron capture will dominate over hole capture and  $m_2$  will consequently decrease. This is the key difference between centres and traps. While trap populations may approach saturation,  $n \rightarrow N$ , at large doses, centre populations may not. Electron capture by centres prevents this from happening. Furthermore, as we discuss in more detail below, it is possible, at high doses, for electron capture to become stronger relative to hole capture and actually drive  $m_2$  down as the dose increases.

To clarify the nature of the competition between filling the centre by hole capture and depleting it by electron capture, we can rearrange equation (2) as follows:

$$\frac{dm_2}{dt} = n_c \left( A_{m_2} + B_2 \frac{n_v}{n_c} \right) \left[ \frac{B_2 M_2 \frac{n_v}{n_c}}{A_{m_2} + B_2 \frac{n_v}{n_c}} - m_2 \right]. \quad (6)$$

This can be rewritten as

$$\frac{dm_2}{dt} = \frac{m_{2QS} - m_2}{\tau_2} \quad (7)$$

where we have defined two useful abbreviations:

$$m_{2QS} = \frac{B_2 M_2 \frac{n_v}{n_c}}{A_{m2} + B_2 \frac{n_v}{n_c}}, \quad (8)$$

$$\tau_2 = \frac{1}{n_c(A_{m2} + B_2 \frac{n_v}{n_c})}. \quad (9)$$

It is important to note that equations (6) and (7) are equivalent to equation (2). The terms have merely been rearranged to make qualitative discussion easier. For simplicity, suppose that the ratio of free holes to free electrons,  $\frac{n_v}{n_c}$ , remains constant in time during the excitation dose. In this case, the quantity  $m_{2QS}$  is also a constant in time, and equation (7) shows that the centre population  $m_2$  will asymptotically approach the constant quantity  $m_{2QS}$ . Note that this conclusion is independent of the initial condition: it does not matter whether the centre is initially empty,  $m_2 = 0$ , or initially full,  $m_2 = M_2$ . In either case, equation (7) shows that, as time progresses,  $m_2$  will approach  $m_{2QS}$ . This approach occurs over the timescale  $\tau_2$ .

In general, as excitation progresses, the ratio  $\frac{n_v}{n_c}$  is not constant. Suppose  $\frac{n_v}{n_c}$  happens to increase with time as the excitation progresses. From equation (8), it follows that  $m_{2QS}$  will also be increasing with time. Inspection of equation (7) leads to the conclusion that at long times (high doses),  $m_2$  will also increase. In the usual case with centre  $m_2$  initially empty,  $m_2 = 0$ ,  $m_2$  will increase over the entire excitation period from beginning to end as long as  $\frac{n_v}{n_c}$  (and hence  $m_{2QS}$ ) is increasing.

An increase in the ratio  $\frac{n_v}{n_c}$  means that free holes are becoming more plentiful relative to free electrons. This means that hole capture,  $B_2(M_2 - m_2)n_v$ , which attempts to increase  $m_2$ , becomes stronger relative to electron capture,  $A_{m2}m_2n_c$ , which attempts to decrease  $m_2$ . Thus it is not surprising that an increasing  $\frac{n_v}{n_c}$  drives  $m_2$  to increase.

The opposite case, with  $\frac{n_v}{n_c}$  decreasing with time (dose), is far more interesting here. In the usual case with  $m_2$  initially empty, equation (7) shows that  $m_2$  will initially increase. With  $\frac{n_v}{n_c}$  decreasing with time,  $m_{2QS}$  will decrease while  $m_2$  is increasing until these two meet. At the instant that  $m_{2QS}$  drops to the level of  $m_2$ ,  $m_2$  stops increasing and  $\frac{dm_2}{dt} = 0$ , as per equation (7). If  $m_{2QS}$  continues to decrease, it will drop below the value of  $m_2$ , and equation (7) shows that  $m_2$  will then start dropping. This is just the effect that is of interest to explain the excitation-driven form of the non-monotonic dose effect. A decreasing ratio  $\frac{n_v}{n_c}$  means that free electrons are becoming more plentiful relative to free holes, and this increases the importance of electron capture relative to hole capture. Electron capture decreases  $m_2$ , and this is what makes possible a decreasing  $m_2$  at high doses.

If  $m_2$  is starting from the usual initially empty state,  $m_2 = 0$ , it follows from the above discussion that two conditions are necessary for  $m_2$  to decrease with increasing excitation time (dose). They are:

- (1) The excitation must last long enough that  $m_2$  grows to equal  $m_{2QS}$ . This likely takes an excitation time of at least the order of  $\tau_2$ .
- (2) The ratio  $\frac{n_v}{n_c}$  continues to decrease after the instant of time when  $m_2 = m_{2QS}$ .

Unless specified otherwise, the following discussion will assume the usual initial condition of  $m_2 = 0$ .

The above conclusions raise the immediate question: when can we expect  $\frac{n_v}{n_c}$  to decrease with increasing dose? A simple answer that applies to the case of most interest to us will be derived in the next subsection.

3.1.3. *Necessary condition for excitation-driven decline in  $m_2$ .* The discussion above found two necessary conditions for the centre population  $m_2$  to decline at high dose, which can cause an excitation-driven non-monotonic effect. In this subsection, we reduce the second condition to a simple quantitative form for the case of most interest to us. As discussed in a previous section, for a two-centre problem,  $m_1 + m_2 = n$  is strictly increasing with time (or dose). If  $m_2 \gg m_1$ , then  $m_2$  will likely have to increase so that the sum  $m_1 + m_2$  is increasing. Since we are studying the non-monotonic effect, this case would not be interesting. So, let us consider the case  $m_2 \ll m_1$ . We can reach this case by assuming  $M_2$  and its associated rate constants,  $B_2$  and  $A_{m_2}$ , are small so that  $M_2 \ll M_1$ ,  $A_{m_2}m_2 \ll A_{m_1}m_1$ , and  $B_2(M_2 - m_2) \ll B_1(M_1 - m_1)$ . Under this assumption of small  $m_2$ , the conservation conditions for free electrons, equation (4), and free holes, equation (5), become

$$\frac{dn_c}{dt} = X - A_{m_1}m_1n_c - A_n(N - n)n_c, \quad (10)$$

$$\frac{dn_v}{dt} = X - B_1(M_1 - m_1)n_v. \quad (11)$$

For slow enough excitation, the usual quasi-steady assumption applies. This can be stated as  $|dn_c/dt| \ll n_c/\tau_c$  and  $|dn_v/dt| \ll n_v/\tau_v$ , where  $\tau_c = 1/(A_{m_1}m_1 + A_n(N - n))$  and  $\tau_v = 1/(B_1(M_1 - m_1))$ . Equations (10) and (11) yield

$$n_c = \frac{X}{A_{m_1}m_1 + A_n(N - n)}, \quad (12)$$

$$n_v = \frac{X}{B_1(M_1 - m_1)}. \quad (13)$$

It follows that the ratio of interest is

$$\frac{n_v}{n_c} = \frac{A_{m_1}m_1 + A_n(N - n)}{B_1(M_1 - m_1)}. \quad (14)$$

For the case  $m_2 \ll m_1$ , it follows from conservation of charge that  $n \simeq m_1$ , so

$$\frac{n_v}{n_c} = \frac{A_{m_1}n + A_n(N - n)}{B_1(M_1 - n)}, \quad (15)$$

or, after slight rearrangement,

$$\frac{n_v}{n_c} = \frac{A_n N}{B_1 M_1} \frac{1 - (1 - \frac{A_{m_1}}{A_n}) \frac{n}{N}}{1 - \frac{N}{M_1} \frac{n}{N}}. \quad (16)$$

The only variable with time in the above equation is  $n$ , and  $n$  always increases with dose. Thus, it is clear from equation (16) that the ratio  $\frac{n_v}{n_c}$  will only decrease with increasing dose if

$$1 - \frac{A_{m_1}}{A_n} > \frac{N}{M_1}, \quad (17)$$

or

$$\frac{A_{m_1}}{A_n} + \frac{N}{M_1} < 1. \quad (18)$$

If the parameters of the problem satisfy equation (18), then it is possible for  $m_2$  to decrease with dose, providing a non-monotonic effect. If equation (18) is not satisfied, then  $\frac{n_v}{n_c}$  will increase with dose and the excitation-driven non-monotonic effect will not occur. This discussion applies to the case of  $m_2 \ll m_1$  with the initial condition  $m_2 = 0$ .

Equation (18) can be provided with an intuitive interpretation. Equation (18) requires that  $A_{m_1}/A_n < 1$ . Referring back to the conservation of free electrons, equation (4), this

means that, as  $n$  increases, and remembering  $n \approx m_1$ , the drop in the free electron capture coefficient by the trap,  $A_n(N - n)$ , is stronger than the increase in electron capture coefficient by the centre,  $A_{m_1}m_1$ . Thus, as the dose increases, the free electron density,  $n_c$ , increases as indicated by equation (13). Equation (18) further requires that  $N/M_1 < 1$ . This means that, with increasing dose, the electron trap,  $n$ , approaches saturation faster than the recombination centre,  $m_1$ . This means that  $n_c$  increases with dose faster than  $n_v$  increases. The result is a declining ratio  $\frac{n_v}{n_c}$ , which means that the small centre  $m_2$  is depopulated due to a relative increase in electron capture over hole capture.

The model above is for the excitation stage. Because this model assumed slow excitation ( $X$  small), the free carrier concentrations,  $n_c$  and  $n_v$ , remain small throughout the excitation stage (see equations (12) and (13)). A consequence of this is that the analytical model has no need to consider a relaxation stage. In contrast, our numerical solutions are capable of solving problems with rapid excitation (large  $X$ ), which leave significant populations of free carriers at the end of excitation, necessitating a relaxation stage. To verify the analytical model and the computer codes, numerical solutions were performed for slow excitation, and the numerical and analytical results were found to be in good agreement.

The above considerations showed that the excitation-driven non-monotonic effect occurs when the non-radiative centre is stronger than the radiative centre. This indicates that this type of non-monotonic dose dependence only occurs in TL materials with low radiative efficiency. Many TL materials are quite inefficient in absolute terms, as can be seen in a review paper by Bos [45]. Here, efficiencies of 0.03%–0.04% are reported for LiF:Mg, Ti (TLD-100), 0.44% for CaF<sub>2</sub>:Tm, 0.84% for Al<sub>2</sub>O<sub>3</sub>:C and values in the same range for other dosimetric materials. It can be expected that in natural materials like quartz, the absolute efficiencies are even lower.

In sum, we have examined the conditions required to see a non-monotonic effect in the radiative centre population,  $m_2$ , in a two-centre system. If the radiative centre is the dominant centre, i.e.  $m_2 \gg m_1$ , there can be no significant non-monotonic effect. In the opposite case,  $m_2 \ll m_1$  as detailed above, a necessary requirement to see the non-monotonic effect is equation (18). This reflects the conditions needed for electron capture by  $m_2$  to dominate over hole capture, resulting in a net decrease in  $m_2$  with increasing dose. In other words, the behaviour of the radiative centre  $m_2$  is due to competition between free electron capture by  $m_2$  and free hole capture by  $m_2$ .  $m_2$  can decrease with increasing dose if the ratio  $\frac{n_v}{n_c}$  decreases so that electron capture becomes stronger relative to hole capture. Equation (18) agrees with the numerical solution for two centres and one trap presented later.

As an additional note, several of the experimental results showed that, as the dose increased, a maximum intensity was observed followed by a decline and then a levelling off of intensity. This is consistent with equations (16) and (8), which show that as saturation is approached,  $n \rightarrow N$ , the ratio  $\frac{n_v}{n_c}$  approaches a constant and therefore  $m_2$  should asymptotically approach a constant  $m_{2QS}$ .

**3.1.4. Bounding the decline in  $m_2$ .** As we have discussed, there are two types of non-monotonic effect: one due to competition during excitation and one due to competition during heating. A distinctive feature is that the intensity levels off at high doses for the competition-during-excitation effect but generally not for the competition-during-heating effect. We will examine here how much of a decline can be expected for the competition-during-excitation effect. For small  $M_2$ , the behaviour of  $m_2$  is described by equation (7): we have previously found that  $m_{2QS}$  changes monotonically as time (or dose) increases and that the excitation-driven non-monotonic effect only occurs if  $m_{2QS}$  is decreasing. For the decreasing case, we can conclude:

- (1) The peak in  $m_2$  occurs at the time  $t$  when  $m_2 = m_{2QS}$ . Therefore, the maximum value of  $m_2$  is less than the initial (maximum) value of  $m_{2QS}$ .
- (2) If a maximum in  $m_2$  occurs, then, as per equation (7), after the maximum,  $m_2$  will always be greater than  $m_{2QS}$ . So, the minimum value of  $m_2$  after the peak will always be greater than the final (minimum) value of  $m_{2QS}$ . From the above two considerations, the maximum possible fractional drop in  $m_2$  is  $(m_{2QS})_{\text{final}}/(m_{2QS})_{\text{initial}}$ . Thus, we can bind the drop in  $m_2$  by

$$1 \geq \frac{(m_2)_{\text{min}}}{(m_2)_{\text{peak}}} \geq \frac{(m_{2QS})_{\text{final}}}{(m_{2QS})_{\text{initial}}}. \quad (19)$$

To quantify the drop in  $m_{2QS}$ , remember the definition of  $m_{2QS}$  in equation (8) and the previous result for  $\frac{u_v}{n_c}$  in equation (16). The initial value of  $m_{2QS}$  which, if  $m_{2QS}$  is declining, is also the maximum is found by setting  $n = 0$  in equation (16) and substituting into equation (8). The result is

$$(m_{2QS})_{\text{initial}} = \frac{M_2}{1 + \frac{A_{m_2} B_1 M_1}{A_n B_2 N}}. \quad (20)$$

To find the final value of  $m_{2QS}$ , we need the final value of  $n$ . Since our model requires that  $N < M_1$ ,  $n$  will approach  $N$  at high dose, and the final value of  $m_{2QS}$  is found to be

$$(m_{2QS})_{\text{final}} = \frac{M_2}{1 + \frac{A_{m_2} B_1 (M_1 - N)}{A_{m_1} B_2 N}}. \quad (21)$$

Substituting equations (20) and (21) into (19) gives us our bound on the drop in  $m_2$ :

$$\frac{(m_2)_{\text{min}}}{(m_2)_{\text{peak}}} \geq \left[ 1 + \left( 1 - \frac{A_{m_1}}{A_n} - \frac{N}{M_1} \right) \frac{A_n A_{m_2} B_1 M_1}{A_{m_1} A_{m_2} B_1 M_1 + A_n A_{m_1} B_2 N} \right]^{-1}, \quad (22)$$

or, equivalently,

$$\frac{(m_2)_{\text{min}}}{(m_2)_{\text{peak}}} \geq \left[ 1 + \frac{1 - \frac{A_{m_1}}{A_n} - \frac{N}{M_1}}{\frac{A_{m_1}}{A_n} + \frac{A_{m_1} B_2 N}{B_1 A_{m_2} M_1}} \right]^{-1}. \quad (23)$$

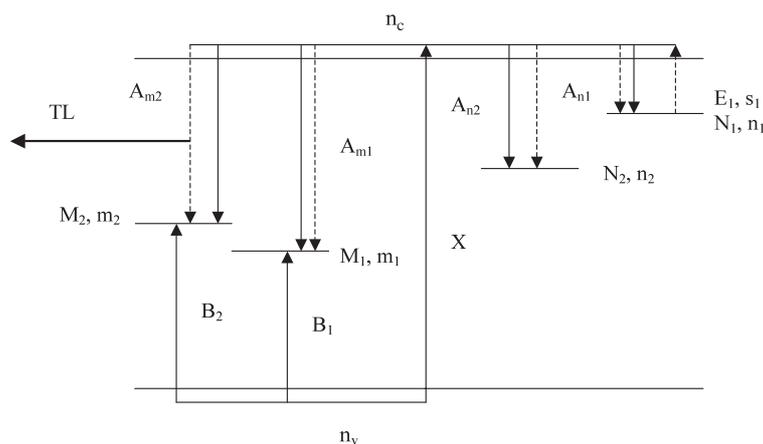
Note that the sign of the numerator of the fraction inside the square brackets is determined by equation (18). If equation (18) is satisfied, the numerator is positive and equation (23) will be between 0 and 1, as it should be if  $m_2$  is declining.

An interesting question is how much of a decline in  $m_2$  is possible. Examination of equation (23) shows that conditions for which  $A_{m_1}/A_n$  and  $(N/M_1)$  and  $(A_{m_1}/B_1)(B_2/A_{m_2})$  are all much smaller than 1 will lead to large declines. If all three are small, then equation (23) can be approximated by

$$\frac{(m_2)_{\text{min}}}{(m_2)_{\text{peak}}} \geq \max \left( \frac{A_{m_1}}{A_n}, \frac{A_{m_1} B_2 N}{B_1 A_{m_2} M_1} \right). \quad (24)$$

The reader may find equation (24) to be an aid in understanding the bounds on large declines. For quantitative work, equation (23) is both more accurate and more general.

Note the rate constants for  $m_2$  enter into equation (23) only through the ratio  $B_2/A_{m_2}$ . This is because  $m_{2QS}$  depends only on this ratio, and equation (23) was derived from  $m_{2QS}$ . The magnitudes of  $B_2$  and  $A_{m_2}$  do affect the timescale  $\tau_2$ . Keeping their ratio fixed, larger values of  $B_2$  and  $A_{m_2}$  lead to shorter times  $\tau_2$ . If  $\tau_2$  is short, then  $m_2$  more closely follows  $m_{2QS}$  and equation (23) approaches an equality. Again holding the ratio constant, small values of  $B_2$  and  $A_{m_2}$  lead to long  $\tau_2$ , and for long enough  $\tau_2$ ,  $m_2$  will not decline at all.



**Figure 1.** The energy level scheme of two trapping levels and two kinds of recombination centres. Transitions occurring during excitation are given by solid lines, and transitions taking place during the heating by dashed lines.

3.1.5. *More on competition during excitation.* Obviously, if more trapping states and recombination centres are involved, this kind of non-monotonic behaviour, namely, that the competition during excitation dominates the process, may take place as well and the TL signal may follow the dose dependence of the radiative centre. In order to understand better the essence of the effect, we are interested in the most reduced model. The question may arise whether the model with two centres and one trapping state is indeed the most compact one in this sense. One can consider the situation of one trapping state and one kind of recombination centre where, say, the centre  $M_1$  does not exist and, therefore, we do not consider equation (1). Equation (2) has, like before, a positive and a negative term, but we suggest that  $\frac{dm_2}{dr}$  must always be positive. The reason is that in equation (3),  $\frac{dn_2}{dr}$  is always positive, and since with the use of the quasi-equilibrium assumption,  $\frac{dn_2}{dr} \approx \frac{dm_2}{dr}$ , the latter must be positive as well.

The same is true for a situation with two (or more) trapping states and one kind of recombination centre; this is the situation shown in figure 1 when one of the recombination centres,  $M_1$ , is ignored. Instead of equation (3) we should write

$$\frac{dn_1}{dt} = A_{n1}(N_1 - n_1)n_c, \tag{3a}$$

$$\frac{dn_2}{dt} = A_{n2}(N_2 - n_2)n_c. \tag{3b}$$

Here too, the right-hand side of equation (2) has a positive and a negative term, but since at the end of irradiation and relaxation  $m_2 = n_1 + n_2$  and since both  $n_1$  and  $n_2$  are necessarily monotonically increasing functions of the dose, so is  $m_2$ . The situation may be different if any of the trapping states is shallow enough to lose electrons thermally into the conduction band during excitation, which results in the right-hand side of equation (3) having an extra negative term. This, however, is a situation that one tries to avoid in the experiments by keeping the excitation temperature low enough, and, therefore, it appears that the only viable possibility for having a non-monotonic dose dependence of the TL due to competition during excitation is when one has at least one trapping state and two kinds of competing recombination centres.

### 3.2. Competition during heating

We have concentrated in the previous subsections on cases in which the dependence of the occupancy of the radiative centre following excitation and prior to the read-out stage during heating was non-monotonic, and suggested that the TL dependence may follow, more or less, the same pattern. As shown by Chen *et al* [2], the non-monotonic dose behaviour can also be observed in situations where all the relevant occupancy functions  $n_1$ ,  $n_2$ ,  $m_1$  and  $m_2$  are increasing functions of the dose. The general idea is that if in the relevant dose range the occupancy of the non-radiative centre increases with the dose faster than that of the radiative one, the measured TL signal may be reaching a maximum and then decrease due to competition during heating. We will discuss later the question of whether all four levels shown in figure 1 are necessary to yield the non-monotonic dose dependence of TL. Let us write, however, the simultaneous differential equations governing the flow of carriers during heating:

$$\frac{dn_1}{dt} = -s_1 n_1 \exp(-E_1/kT) + A_{n1}(N_1 - n_1)n_c, \quad (25)$$

$$\frac{dn_2}{dt} = A_{n2}(N_2 - n_2)n_c, \quad (26)$$

$$\frac{dm_1}{dt} = -A_{m1}m_1n_c, \quad (27)$$

$$\frac{dm_2}{dt} = -A_{m2}m_2n_c, \quad (28)$$

$$\frac{dn_1}{dt} + \frac{dn_2}{dt} + \frac{dn_c}{dt} = \frac{dm_1}{dt} + \frac{dm_2}{dt}. \quad (29)$$

In principle, the right-hand side of equation (26) should include the term  $-s_2 n_2 \exp(-E_2/kT)$ , but it is assumed that the trap is deep enough not to be able to release electrons in the relevant temperature range. We have to specify the heating function which we conventionally choose to be linear, namely,  $T = T_0 + \beta t$ , where  $\beta$  is the constant heating rate. The TL intensity is associated with the recombination into  $m_2$ , therefore the intensity  $I(T)$  is

$$I(T) = A_{m2}m_2n_c. \quad (30)$$

The set of equations (25)–(29) obviously includes all the competing processes occurring during heating. The magnitude  $n_c$  couples all these equations, and since it appears to be rather difficult to predict analytically its time dependence (or temperature dependence), it is very hard to give an intuitive explanation to the dose dependence associated with the competition during heating. In the next section, we give some examples of simulations of the non-monotonic dose dependence dominated by competition during heating. As opposed to the non-monotonic behaviour discussed in the previous subsection, dominated by competition during excitation, here the occupancy of the luminescence centre at the end of irradiation is a monotonically increasing function of the dose. The non-monotonic dose dependence of TL is ascribed here to the increasing competition of the non-radiative centre  $m_1$  during heating, which must be associated with  $m_1$  being a much faster increasing function of the dose than  $m_2$ , the radiative centre. As shown below, we record in the simulation the TL maximum intensity as well as the values of  $m_2$  and  $m_2/m_1$ , all as a function of the excitation dose. Generally speaking, we found two kinds of behaviour that lead to non-monotonicity related to the competition during the heating stage. We found sets of parameters that yielded an increasing  $m_2$  with dose and a curve of  $m_2/m_1$ , which had a peak shape, with the function of TL versus dose reaching a maximum at about the same simulated dose. We also found cases where  $m_2(D)$  was again an increasing function whereas  $m_2/m_1$  was a decreasing function of the dose. The maximum TL

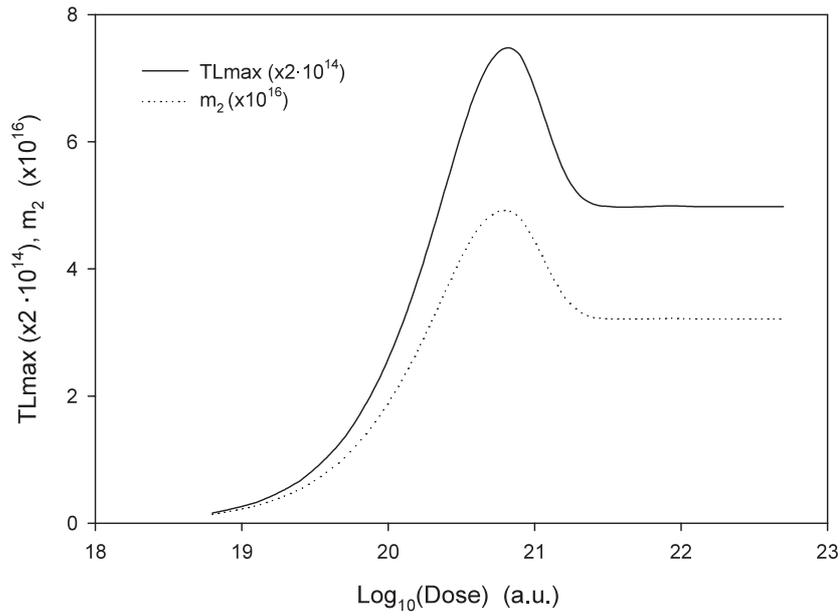
as a function of the dose displayed a peak shape, which resulted from the combined effect of the increase of  $m_2$  and the decrease of  $m_2/m_1$ , which in other words means that  $m_1$  is increasing with the dose significantly faster than  $m_2$ . An important point to mention is that, as opposed to the non-monotonic dose dependence dominated by competition during excitation, we could not find appropriate sets of parameters that yielded non-monotonic dose dependence due to competition during heating in three-level systems (two traps and one centre or two centres and one trap).

In fact, for the case of one trap and two centres, this can be explained as follows. Assume, as is conventional, that all levels are empty before excitation, namely,  $n = m_1 = m_2 = 0$ . After excitation and relaxation, the levels will have nonzero populations subject to the requirement of conservation of charge,  $n = m_1 = m_2$ . After heating, the trap is emptied, i.e.,  $n = 0$ , and due to conservation of charge, both centres will also be empty again. Thus,  $m_1$  electrons will have non-radiatively recombined while  $m_2$  electrons will have radiatively recombined. The integrated intensity is thus  $m_2$ , where  $m_2$  refers here to the population of  $m_2$  following radiation and relaxation and before heating. The conclusion is that, for one-trap systems with all levels initially empty, the intensity is determined entirely by the excitation process, and no competition-during-heating effect is possible. We do not have a similar proof for the case of two trapping states and one kind of recombination centre. Therefore, at present, we cannot prove or refute the assertion that, for the occurrence of non-monotonic behaviour, the minimum requirement is a system with two traps and two kinds of recombination centres, although our present results indicate that this is the case. The question of whether this kind of non-monotonic dose dependence is possible in a three-level system appears to be of only theoretical significance for two reasons. One is that most of the systems used for TL measurements include several trapping states and recombination centres. The other reason is that, as explained above, non-monotonic dose dependence can be seen in a three-level system (one trap and two centres) due to competition during excitation.

#### 4. Numerical results

In order to get the numerical results, sets of trapping parameters have been chosen, and the relevant sets of equations solved numerically. The Matlab `odes23` solver has been used as well as the Mathematica solver; the results reached by these parallel models were in excellent agreement. For the case of one trap and two centres, equations (1)–(5) were first solved for a certain value of the dose-rate  $X$  and for a certain length of the excitation time  $t_D$ , which together determine the dose  $D = Xt_D$ . (As explained above,  $X$  and  $D$  are not really the dose-rate and the dose, but are proportional to these quantities.) The solution of the same set of equations, but with  $X = 0$ , is continued for a further period of relaxation time. Finally, the coupled equations for the heating stage, (25) and (27)–(29) were solved, and along with equation (30) gave the TL intensity as a function of time and, through the heating function, of temperature. In the case of two trapping states, equation (3) is replaced by equations (3a) and (3b) in the first stages of excitation and relaxation. For the read-out stage, equations (25)–(29) are solved, and again, equation (30) gives the TL intensity.

In figure 2, an example of the dose dependence of TL and the occupancy of the radiative centre in a situation where competition during excitation causes the non-monotonic dose dependence is shown within the framework of a model with one trapping level and two kinds of recombination centres. The parameters chosen are:  $M_1 = 3 \times 10^{21} \text{ m}^{-3}$ ;  $M_2 = 1 \times 10^{18} \text{ m}^{-3}$ ;  $A_{m1} = 1 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ ;  $A_{m2} = 1 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$ ;  $A_n = 3 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ ;  $E = 1.0 \text{ eV}$ ;  $s = 1 \times 10^{12} \text{ s}^{-1}$ ;  $N = 1 \times 10^{21} \text{ m}^{-3}$ ;  $B_1 = 1.5 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ ;  $B_2 = 10^{-17} \text{ m}^3 \text{ s}^{-1}$ . The heating rate for all the simulated curves was  $\beta = 1 \text{ }^\circ\text{C s}^{-1}$ . The results show an increase of

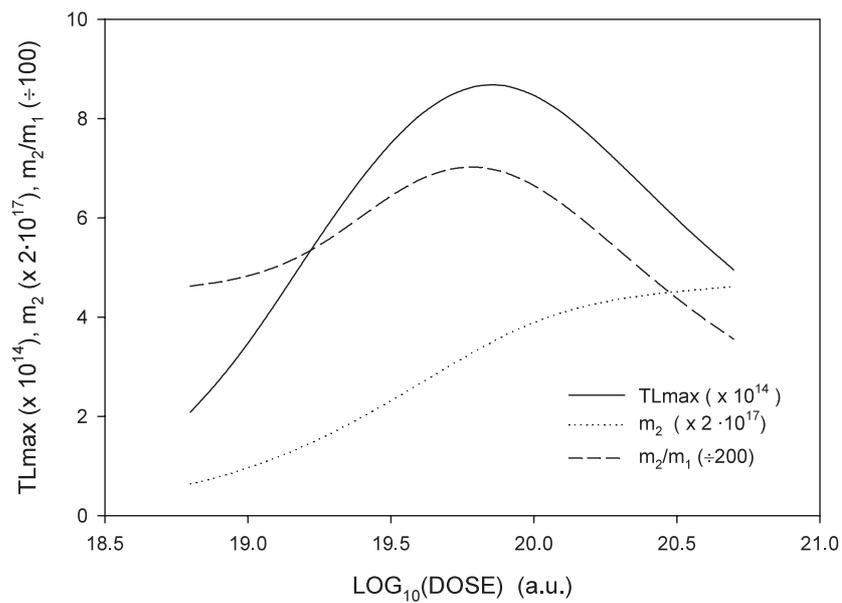


**Figure 2.** Simulated dose dependence of the maximum TL (solid curve), and the radiative centre,  $m_2$  (dotted curve), in a system with one trapping state and two kinds of recombination centres, when competition during excitation dominates. The relevant set of parameters is given in the text.

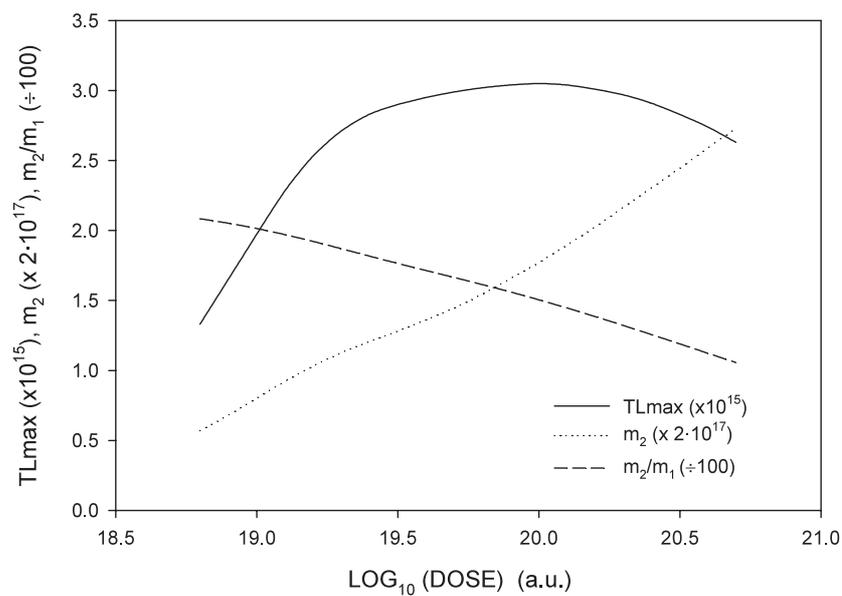
the TL maximum (solid curve) with the dose up to a maximum at a ‘dose’ of  $\sim 7 \times 10^{20} \text{ m}^{-3}$ , followed by a decrease of  $\sim 35\%$ , after which the maximum TL intensity levels off at higher doses. This behaviour is very similar to experimental results reported in some materials (see e.g. [7]). Similar behaviour is seen in the plot of  $m_2$ , the radiative centre occupancy at the end of the relaxation period as a function of the dose (dotted curve). It is noted that these parameters satisfy equation (18), which was shown to be a necessary condition for non-monotonic dependence of TL.

Two examples of non-monotonic dose dependence governed mainly by competition during heating are also shown. Here, the model involves two electron-trapping states and two kinds of recombination centres as shown in figure 1. The trapping parameters chosen for figure 3 are:  $M_1 = 3 \times 10^{21} \text{ m}^{-3}$ ;  $M_2 = 1 \times 10^{18} \text{ m}^{-3}$ ;  $A_{n1} = 3 \times 10^{-20} \text{ m}^3 \text{ s}^{-1}$ ;  $E_1 = 1.0 \text{ eV}$ ;  $A_{n2} = 3 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ ;  $E_2 = 1.8 \text{ eV}$ ;  $s_1 = 1 \times 10^{12} \text{ s}^{-1}$ ;  $s_2 = 1 \times 10^{10} \text{ s}^{-1}$ ;  $A_{m1} = 1 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ ;  $A_{m2} = 1 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$ ;  $B_1 = 1.5 \times 10^{-19} \text{ m}^3 \text{ s}^{-1}$ ;  $B_2 = 1 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ ;  $N_1 = 1 \times 10^{19} \text{ m}^{-3}$ ;  $N_2 = 1 \times 10^{21} \text{ m}^{-3}$ . The solid curve shows the dependence of the TL signal (defined as the maximum intensity) on the excitation dose. The curve reaches a maximum and decreases at higher doses. As opposed to the previous case, this does not reflect the behaviour of the occupancy of the radiative centre  $m_2$  shown by the dotted curve; this curve is seen to be an increasing function of the dose. However, as pointed out above, the non-radiative competitor,  $m_1$ , grows faster with the dose, and its effect seems to be the reason for the non-monotonic dose dependence of the TL signal. The dependence of the ratio  $m_2/m_1$  is depicted by the dashed curve, which reaches a maximum and declines at higher doses. The TL dose dependence curve has a non-monotonic peak shape, the maximum of which occurs at a somewhat higher dose than that of the  $m_2/m_1$  curve.

Yet another kind of non-monotonic dose dependence is shown in figure 4. Here, too, the model includes two trapping states and two kinds of recombination centres. The parameters



**Figure 3.** Simulated dose dependence of maximum TL (solid curve), the radiative centre concentration following irradiation and relaxation,  $m_2$ , and the ratio of radiative to non-radiative centres,  $m_2/m_1$ , when radiation during heating dominates. The relevant set of parameters is given in the text.



**Figure 4.** Same as figure 3, with another set of trapping parameters, given in the text.

used here were:  $M_1 = 3 \times 10^{21} \text{ m}^{-3}$ ;  $M_2 = 1 \times 10^{18} \text{ m}^{-3}$ ;  $A_{n1} = 3 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ ;  $A_{n2} = 3 \times 10^{-20} \text{ m}^3 \text{ s}^{-1}$ ;  $E_1 = 1.0 \text{ eV}$ ;  $E_2 = 1.8 \text{ eV}$ ;  $s_1 = 1 \times 10^{12} \text{ s}^{-1}$ ;  $s_2 = 1 \times 10^{10} \text{ s}^{-1}$ ;  $A_{m1} = 1 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ ;  $A_{m2} = 1 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ ;  $B_1 = 1.5 \times 10^{-19} \text{ m}^3 \text{ s}^{-1}$ ;

$B_2 = 1 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ ;  $N_1 = 1 \times 10^{19} \text{ m}^{-3}$ ;  $N_2 = 1 \times 10^{21} \text{ m}^{-3}$ . In this case,  $m_2$  is a monotonically increasing function of the applied dose. The ratio of the occupancies of the radiative to non-radiative centres following excitation,  $m_2/m_1$ , is a continuously decreasing function. The TL signal exhibits a broad maximum, which appears to result from the combined effect of the increasing function of the concentration of the radiative centre,  $m_2$ , and the decreasing function  $m_2/m_1$ . In other words, the peak shape of the TL signal results here from the fact that, although the radiative centre population  $m_2$  increases with the dose, the non-radiative competing centre  $m_1$  decreases at a faster rate, and the combination of these behaviours results in the non-monotonic dose dependence.

As explained above, the contribution of the relaxation period to the final results is of importance only for large values of the dose-rate  $X$ . In order to check the size of the effect in the simulations shown in figures 2–4, we have checked the contribution of this period to the values of the relevant concentrations  $n_1$ ,  $n_2$ ,  $m_1$ , and  $m_2$ . With the given sets of parameters, the changes were of the order of 0.001%–0.1%, which can be considered negligible as far as the conclusions are concerned. Of course, with different sets of parameters, and, in particular, if  $X$  is very large, the effect of the relaxation time cannot be ignored.

## 5. Conclusion

In the present work, we have presented a model which can explain the quite common effect of non-monotonic dose dependence of TL. We show that ‘radiation damage’, mentioned in the literature as the reason for this effect, is not necessarily the governing process, and the effect may simply be the result of different kinds of competition between radiative and non-radiative centres, and sometimes between different kinds of trapping centres as well. This competition may take place during the excitation stage or during the read-out (heating) stage.

We distinguish between cases where the non-monotonic behaviour results mainly from competition during excitation and during heating. In the former case, which is characterized by the fact that the TL curve resembles the  $m_2$  dose dependence, we show analytically, using the well-established quasi-equilibrium assumption, that the possibility of non-monotonic dose dependence exists. We show that the minimum requirement for this kind of the effect to occur is a system with two kinds of recombination centre and one kind of trapping state. The analytical model found a necessary condition (equation (17)) for the excitation-stage non-monotonic effect to occur and then bound the drop in radiative centre population with equation (23). This is accompanied by a numerical simulation demonstrating the non-monotonic behaviour with such a three-level system. We also show analytically that the mirror image system of two trapping states and one kind of recombination centre cannot yield a non-monotonic dose dependence of TL. As for the heating-competition-dominated non-monotonic dose dependence, characterized by the TL reaching a peak when the  $m_2$  function is monotonically increasing, we can demonstrate the effect by numerical simulations and using the two-trap and two-centre model. We cannot show at present whether a reduced three-level system may result in this kind of non-monotonic dependence. We can only state that in our attempts so far we could not find a set of parameters that yield this behaviour within the three-level system.

Finally, it should be noted that although we ascribe the ‘competition-during-heating’ effect mainly to the relative growth of the radiative centres, we should remember that the overall situation is more complicated and, in fact, the growth of the occupancy of the trapping state(s) with the dose also has an effect on the final dose dependence curve. Also, despite the distinction between cases governed by competition during excitation and during heating, which helps in the intuitive understanding of the processes involved, one should remember that, in fact, both kinds of competition have an effect on the final results.

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