Dose dependence of thermoluminescence peaks

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Abstract. The dependence on the excitation dose of the maximum thermoluminescence intensity as well as of the peak temperature are investigated theoretically. It is shown that certain irregularities of the dose dependences can be explained by assuming the existence of a trapping level, the transition into which competes with the retrapping and recombination of the free carriers. By numerical solution of the appropriate equations, it is demonstrated that the maximum thermoluminescence intensity may depend super-linearly on the excitation dose. The power of the dose dependence was found to be 2 under certain circumstances at low doses, and reached even higher values before saturation of the competing level. The maximum temperature sometimes behaved in an unusual way; namely, it increased with increasing dose. The relation between the area under a glow peak and its maximum intensity is also studied; it is shown that the latter can usually serve as a measure for the former. This finding is of practical importance, especially in thermoluminescent dosimetry, since the evaluation of the maximum intensity is obviously more convenient than that of the area.

1. Introduction

The dependence of the thermoluminescence (TL) intensity on the dose of excitation is of primary importance from the theoretical point of view as well as from the aspect of applications, such as thermoluminescent dosimetry (TLD). Another point of importance is the dependence of the temperature at the maximum of a glow peak on the excitation dose. Let us consider first the simplest case; namely, the first-order equation (Randall and Wilkins 1945)

$$I = - \mathrm{d}n/\mathrm{d}t = sn \exp \left(- E/kT \right) \tag{1.1}$$

where I is the TL intensity, n (cm^{-3}) is the concentration of trapped carriers, t (s) is the time, s (s^{-1}) is the frequency factor, E (eV) is the activation energy, k (eV K^{-1}) is Boltzmann's constant, and T(K) is the absolute temperature. The solution of equation (1.1) with a linear heating rate $T = T_0 + \beta t$ gives $I = I(T)$. The maximum condition for this equation is $\beta E/kT_m^2 = s \exp \left(- E/kT_m \right)$, where T_m is the temperature at the maximum. It is readily seen that in this simple first-order case T_m is independent of the initial concentration of trapped carriers n_0, and is therefore independent of the excitation dose. From the detailed shape of $I(T)$ it can be seen that the maximum intensity of the glow peak is proportional to n_0, and so is the area under the glow curve.

Garlick and Gibson (1948) considered the possibility of a second-order kinetics TL peak. They showed that the temperature T_m of the second-order peak decreases with the increase of the initial concentration n_0. More-complicated equations to account for a

TL peak were later developed by Halperin and Braner (1960), who took into account the existence of a single trap and a single recombination centre. They assumed that thermally released carriers can either recombine with carriers of opposite sign in a recombination centre or fall back into the trap (retrapping). Under these circumstances, the area under a peak is proportional to the initial concentration of electrons in traps (n_0) or the concentration of holes in recombination centres (m_0), whichever is the smaller. In a more recent paper, Rodine and Land (1971) suggested the existence of an additional trap, which competes with the recombination centres and the empty traps for the thermally released electrons, in order to explain a quadratic dose dependence. They showed qualitatively that the TL intensity could depend on both n_0 and m_0 if the probability for trapping into this competing trap was large enough compared with the probability of recombination; thus the maximum intensity could depend on the square of the excitation dose.

Alternative explanations for superlinear effects in TL have been given previously. Cameron *et al* (1968) described the superlinear excitation of TL dosimeters under excitation by γ-radiation. If one writes for a certain range $I_m \propto D^p$, the value of p gives the 'degree' of superlinearity. In the cases discussed by Cameron *et al*, p exceeded unity only slightly, and the explanation given assumed the creation of new traps in addition to the filling of the existing ones. Much higher values of p were found in the excitation by UV light of TL in semiconducting diamonds (Halperin and Chen 1966) and in ZnS (Savikhin 1972). The effect was explained to be due to a multistage transition of excited electrons from the valence to the conduction band. Another mechanism for explaining a superlinear excitation of TL has previously been given by Israeli *et al* (1972). This mechanism assumed competition processes during the excitation and creation of defects rather than during their thermal annealing. This mechanism was found to fit well the experimental results for the TL of alkali halides. However, it could not explain the different cases of superlinear dose dependences which were accompanied by unusual shifts of T_m with dose, as observed in other crystals.

In the present work, these phenomena are considered. The dependences on radiation dose of the maximum TL temperature and intensity as well as of the area under the glow peak are investigated. The model, which takes into account the possibility of competition during the thermal annealing process, is treated quantitatively. The circumstances under which a quadratic dose dependence ($p=2$) occurs, as well as the special conditions leading to higher values of p, are discussed. In the course of this work, the area under a glow peak S is compared with its maximum intensity I_m. This is of practical importance, since in the literature some workers report the dose dependence of S, whereas others consider the dose dependence of I_m.

2. Mathematical analysis

For the mathematical treatment, three levels are considered in the forbidden band (shown schematically in figure 1).

(I) The trap from which electrons are thermally released. $N_1(\text{cm}^{-3})$ denotes the total concentration of these traps and $n_1(\text{cm}^{-3})$ the concentration of electrons trapped therein.

(II) The competing traps where electrons are thermally stable. $N_2(\text{cm}^{-3})$ denotes their total concentration out of which $n_2(\text{cm}^{-3})$ are occupied.

(III) The recombination centres. $m(\text{cm}^{-3})$ denotes the concentration of holes in these centres. $n_c(\text{cm}^{-3})$ is the concentration of free electrons in the conduction band.
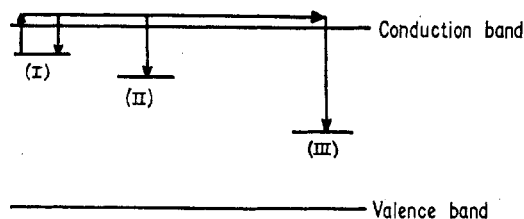

Figure 1. Energy level diagram, including an electron trap (I), a competing trap (II) and a recombination centre (III).

The rate equations governing the process (assuming that electrons cannot be thermally released from traps of type (II), at the temperature range of interest) are

$$\mathrm{d}n_1/\mathrm{d}t = -\gamma n_1 + A_1 n_c (N_1 - n_1) \tag{2.1}$$

$$\mathrm{d}n_2/\mathrm{d}t = A_2 (N_2 - n_2)\, n_c \tag{2.2}$$

$$I = -\mathrm{d}m/\mathrm{d}t = A_m m n_c \tag{2.3}$$

$$\mathrm{d}m/\mathrm{d}t = \mathrm{d}n_1/\mathrm{d}t + \mathrm{d}n_2/\mathrm{d}t + \mathrm{d}n_c/\mathrm{d}t \tag{2.4}$$

where $\gamma = s \exp(-E/kT)$, E (eV) is the activation energy for the release of electrons from traps of type (I), s (s^{-1}) is the frequency factor, T(K) is the temperature, k (eV K^{-1}) is Boltzmann's constant, A_1(s^{-1} cm^3) is the probability of retrapping into (I), A_2 (s^{-1} cm^3) is the probability of trapping into (II), A_m (s^{-1} cm^3) is the recombination probability, t(s) is the time, and I is the TL intensity. It should be noted that equation (2.4) is written in a differential form, which means that charge neutrality between the above-mentioned levels is not assumed. It is, however, assumed that additional traps exist at which charge carriers of both signs may be trapped. These traps are taken to be inactive at the temperature range of the studied glow peak.

From (2.2) and (2.3) one gets

$$n_c = \frac{1}{A_2} \frac{\mathrm{d}}{\mathrm{d}t} \left[\ln\,(N_2 - n_2) \right] = -\frac{1}{A_m} \frac{\mathrm{d}}{\mathrm{d}t}\,(\ln m) \tag{2.5}$$

which can be integrated to yield

$$N_2 - n_2 = (N_2 - n_{2_0})\,(m/m_0)^{A_2/A_m} \tag{2.6}$$

where m_0 and n_{2_0} denote the initial values of m and n_2.

With the usual assumption (see eg Halperin and Braner 1960)

$$|\mathrm{d}n_c/\mathrm{d}t| \ll |\mathrm{d}m/\mathrm{d}t| \tag{2.7}$$

equation (2.4) can be rewritten as

$$\mathrm{d}m/\mathrm{d}t \simeq \mathrm{d}n_1/\mathrm{d}t + \mathrm{d}n_2/\mathrm{d}t. \tag{2.8}$$

By substituting (2.1), (2.2) and (2.3) into (2.8), one gets an explicit expression for n_c:

$$n_c = \gamma n_1 / [A_1(N_1 - n_1) + A_2(N_2 - n_2) + A_m m]. \tag{2.9}$$

By insertion of (2.9) into (2.3) we have

$$I = -\mathrm{d}m/\mathrm{d}t = A_\mathrm{m}\gamma n_1 m/[A_1(N_1-n_1)+A_2(N_2-n_2)+A_\mathrm{m}m]. \tag{2.10}$$

The three terms appearing in the denominator represent the probabilities (s^{-1}) for retrapping at (I), for trapping at (II) and for recombination at (III) respectively. Integration of (2.8) yields

$$m-m_0 = n_1 - n_{1_0} + n_2 - n_{2_0} \tag{2.8'}$$

where n_{1_0} is the initial value of n_1. By substituting (2.6) and (2.8') in (2.10), one gets the following differential equation for m:

$$I = -\frac{\mathrm{d}m}{\mathrm{d}t}$$

$$= \gamma A_\mathrm{m}m\frac{(n_{1_0}+n_{2_0}-m_0-N_2)+m+(N_2-n_{2_0})\,(m/m_0)^{A_2/A_\mathrm{m}}}{A_1(N_1+N_2-n_{1_0}-n_{2_0}+m_0)+(A_\mathrm{m}-A_1)m+(A_2-A_1)(N_2-n_{2_0})(m/m_0)^{A_2/A_\mathrm{m}}}. \tag{2.11}$$

This equation can be numerically solved for various sets of given parameters, as described in the following paragraph.

It can be seen that equation (2.11) includes the quadratic dose dependence of TL intensity (Rodine and Land 1971) as a special case. If we assume that the trapping in traps of type (II) is much faster than both recombination in (III) and retrapping into (I), namely

$$A_2(N_2-n_2) \gg A_1(N_1-n_1)+A_\mathrm{m}m$$

then equation (2.10) becomes

$$I = -\mathrm{d}m/\mathrm{d}t = A_\mathrm{m}\gamma n_1 m/[A_2(N_2-n_2)]. \tag{2.12}$$

If we assume, in addition, that the retrapping into (I) is very small compared with the rate of release of carriers from (I), namely

$$\gamma n_1 \gg A_1 n_\mathrm{c}(N_1-n_1)$$

equation (2.1) transforms to

$$\mathrm{d}n_1/\mathrm{d}t = -\gamma n_1. \tag{2.13}$$

The solution of this equation is given by

$$n_1 = n_{1_0}\exp\left(-\int_0^t \gamma\,\mathrm{d}t'\right). \tag{2.14}$$

Substituting (2.6) and (2.14) into (2.12) gives

$$I = -\mathrm{d}m/\mathrm{d}t = A_\mathrm{m}\gamma n_{1_0}\exp\left(-\int_0^t \gamma\,\mathrm{d}t'\right)m/[A_2(N_2-n_{2_0})\,(m/m_0)^{A_2/A_\mathrm{m}}]. \tag{2.15}$$

Integration of (2.15) gives

$$\int_0^t \gamma n_{1_0}\exp\left(-\int_0^{t'}\gamma\,\mathrm{d}t''\right)\mathrm{d}t' = (N_2-n_{2_0})\,[1-(m/m_0)^{A_2/A_\mathrm{m}}]. \tag{2.16}$$

Since

$$\int_0^\infty \gamma\exp\left(-\int_0^t\gamma\,\mathrm{d}t'\right)\mathrm{d}t = 1 \tag{2.17}$$

equation (2.16) transforms into

$$n_{1_0} = (N_2-n_{2_0})\,[1-(m_\infty/m_0)^{A_2/A_\mathrm{m}}] \tag{2.18}$$

for the case when $t=\infty$, where m_∞ is m at $t=\infty$.

From this we get

$$m_\infty = m_0[1 - n_{1_0}/(N_2 - n_{2_0})]^{A_m/A_2}. \tag{2.19}$$

Assuming further that traps of type (II) are far from saturation ($n_{2_0} \ll N_2$) and that $n_{1_0} \ll N_2$, we have

$$m_\infty \simeq m_0[1 - (A_m/A_2)(n_{1_0}/N_2)]. \tag{2.20}$$

The area S under a glow peak equals

$$\int_0^\infty I \, dt = \int_0^\infty (-dm/dt) \, dt = m_0 - m_\infty.$$

Equation (2.20) leads therefore to

$$S = m_0 - m_\infty \simeq [A_m/(A_2 N_2)] \, m_0 n_{1_0}. \tag{2.21}$$

If m_0 as well as n_{1_0} is proportional to the excitation dose D, which is generally correct for low doses, S will be proportional to D^2.

3. Numerical method and results

Equation (2.11) has been numerically solved for certain sets of parameters. For the solutions the fourth-order Runge–Kutta method (McCracken and Dorn 1964) was applied. The lengths of the integration intervals were varied in order to keep the relative error smaller than 10^{-4}. The highest value of $-dm/dt$ was taken as I_m, whereas the integration of I was continued down to $I = 10^{-3} I_m$. The value of m at this point was taken as m_∞, and thus the area under the curve, $S = m_0 - m_\infty$, was evaluated. The accuracy of this numerical method was checked by applying it to the first-order equation $I = -dm/dt = \gamma m$, and by comparing the numerical results to its known analytical solution; they were found to be in very good agreement.

The values of some parameters—namely, $E = 0.3$ eV, $s = 10^{12}$ s^{-1}, the initial temperature $T_0 = 80$ K, and the linear heating rate $\beta = 1$ K s^{-1}—were chosen to be the same for all calculations. For each run a different set of values was taken for the parameters A_m, A_1, A_2, N_1 and N_2. The initial concentrations m_0, n_{1_0} and n_{2_0} were taken as explicit functions of the excitation dose; the simplest case of linear dose dependences was first assumed. This is certainly true at relatively low doses, whereas one has to be cautious about the results when saturation of one of the levels is approached.

Figures 2–5 show for various cases the dependences of the maximum intensity I_m, the area under the glow curve S, and the temperature at the maximum T_m on the excitation dose.

Table 1. Parameters for the curves in figures 2–5

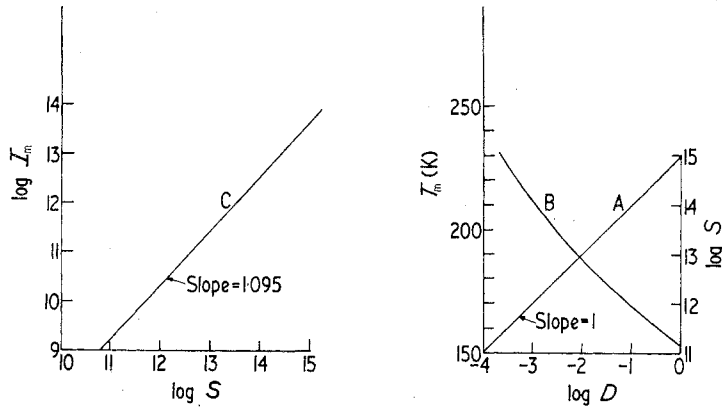| Figure	N_1(cm^{-3})	N_2(cm^{-3})	n_{1_0}(cm^{-3})	n_{2_0}(cm^{-3})	m_0(cm^{-3})	A_1/A_m	A_2/A_m
2	10^{16}	0	$10^{15}D$	0	$10^{15}D$	100	1
3	10^{16}	10^{17}	$10^{14}D$	$10^{16}D$	$10^{14}D$	1	1
4	10^{16}	10^{16}	$10^{14}D$	$10^{16}D$	$10^{14}D$	1	1
5	10^{17}	10^{16}	$10^{16}D$	$10^{16}(1-e^{-50D})$	$10^{16}D$	1	1

Figure 2. The area S (curve A) and the maximum temperature T_m (curve B) as functions of the dose D under conditions leading to second-order kinetics. Curve C gives the maximum intensity I_m against S on a log–log scale. Parameters are as given in table 1.

The values of the parameters chosen for these cases are summarized in table 1. As far as the computation is concerned, only the relative magnitudes of the values of A are of importance, since only the ratios of two of them appear in equation (2.11). Figure 2 represents a case where the probability for retrapping is dominant:

$$A_1(N_1 - n_1) \gg A_2(N_2 - n_2) \quad \text{and} \quad A_1(N_1 - n_1) \gg A_m m.$$

Since the initial values n_{1_0} and m_0 were taken equal, and since a thermally released electron can, under the given conditions, be annihilated by recombination only, the values of m remain equal to those of n_1 during the heating. As long as trap (I) is far from saturation $(n_1 \ll N_1)$, equation (2.10) reduces in this case to

$$I = -\mathrm{d}m/\mathrm{d}t = (A_m/A_1 N_1)\, \gamma m^2.$$

Curve A on the right-hand side of figure 2 depicts, on a log–log scale, the dependence of the area S on the dose. The curve is a straight line with a slope of unity, ie S depends linearly on D. In curve B the maximum temperature T_m is plotted against $\log D$.
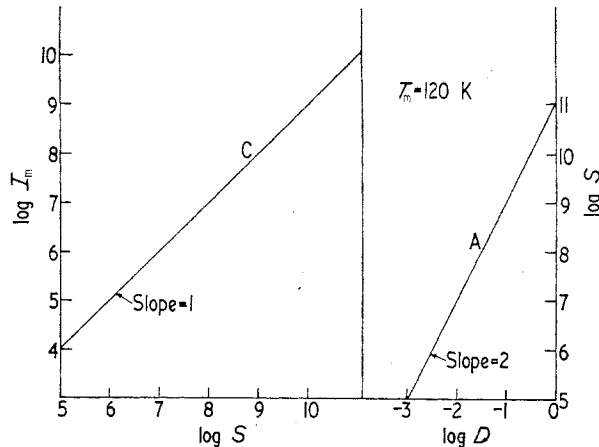

Figure 3. Plots of $\log S$ against $\log D$ (curve A) and $\log I_m$ against $\log S$ (curve C) for a 'Rodine–Land' case (see text). Curve B is obsolete, since $T_m = 120$ K is constant. Parameters are as given in table 1.

Increasing the dose by four orders of magnitude causes T_m to decrease from about 230 to 150 K. Curve C is given in order to check the possibility of representing the area S by I_m. In the present case the dependence of I_m on D or S is slightly superlinear, the slope on the log–log scale being 1·095.

Figure 3 represents a typical 'Rodine–Land' case. A_m, A_1 and A_2 were chosen to be equal, but the number of empty competing trapping centres $N_2 - n_2$ was large enough to make transitions into them much more probable than to the empty trapping centres $N_1 - n_1$ or to the recombination centres m. In this case m_0 and n_{1_0} were taken to be equal and to vary linearly with the excitation dose. Thus, even at the highest dose ($D = 1$), $N_2 - n_{2_0}$ was larger than m_0 or $N_1 - n_{1_0}$, and therefore the Rodine–Land condition prevailed. Here, the maximum temperature $T_m = 120$ K did not change with dose. The slope of the curve of log S against log D equals 2, as expected from equation (2.21). On the left-hand side, log I_m is plotted against log S to yield a straight line with a slope of unity, which again shows the linear relation between the maximum intensity and the area under the TL curve.
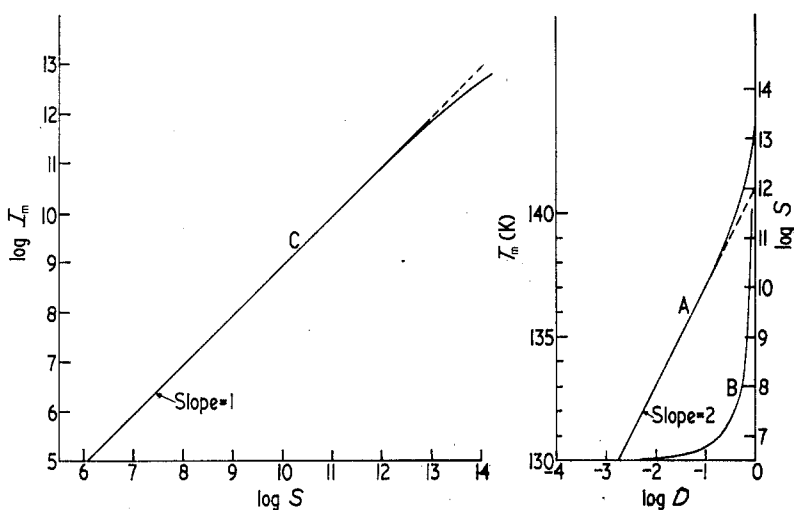

Figure 4. Same as figure 2, with parameters as given in table 1, leading to the increase of T_m with dose, and to $p > 2$ at high doses.

Figure 4 gives the results under circumstances similar to those of figure 3, but with one crucial difference; namely, that $N_2 = 10^{16}$ (instead of 10^{17}). The Rodine–Land condition is in this case correct only at low doses and ceases to hold when D approaches unity, in which case $N_2 - n_{2_0}$ substantially decreases, while $N_1 - n_{1_0}$ and m_0 surpass $N_2 - n_{2_0}$. Curve A gives, as before, log S against log D. It starts with a slope of 2, but increases faster at higher doses. Thus superlinearity with $p > 2$ becomes apparent. Curve B shows a different temperature behaviour than curve B in figure 2. Here T_m increases with increasing dose. Curve C shows that, even in this more-complicated case, I_m is proportional to S.

In the cases related to figures 2 and 3, the maximum dose considered was such that saturation was not approached in any of the energy levels. In the case of figure 4, trap (II) was filled up for the maximum dose treated ($D = 1$). The progress of filling was, however, linear all the way. It is more likely to assume a function which is linear at low

doses and tends gradually to saturation. As an example for such a behaviour, the function $n_{2_0} = N_2(1 - e^{-aD})$ was chosen in figure 5. As seen in curve A, the initial slope of the curve of log S against log D is 2; it increases at higher doses and finally decreases to unity when saturation of trap (II) is approached. The temperature dependence is rather unique under these circumstances (curve B). T_m increases with the dose in a similar manner to the previous case, but decreases again when $N_2 - n_{2_0}$ approaches zero for high doses. Such a dependence fits the experimental results shown in figure 4 of Rodine and Land's (1971) work on ThO_2. Curve C shows that, even under these extraordinary conditions, I_m is practically proportional to S.
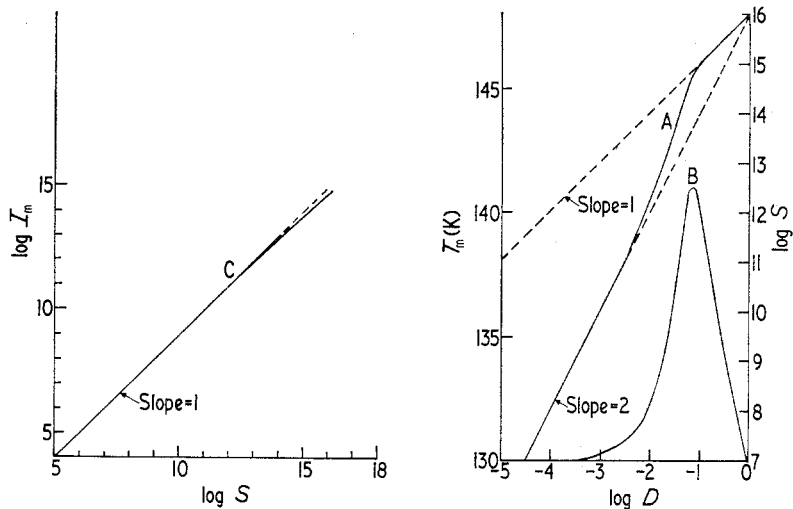

Figure 5. Same as figure 2, with parameters as given in table 1. T_m first increases and then decreases with D; $p = 2$ at low doses; $p > 2$ at higher doses; and then $p \to 1$.

4. Discussion

In the present work, the dependences of the area under a glow peak and of the maximum temperature on the excitation dose have been quantitatively investigated assuming the existence of a competing electron trap. The relation between the area under the glow curve and the maximum intensity has also been studied.

In previous works, where the existence of the competing trap was not assumed, first- and second-order cases were treated mostly; it followed, obviously, that it was relatively easy to solve the corresponding equations. The present model includes these cases as special ones. The computed results and curves were therefore checked by taking for equation (2.11) initial conditions corresponding to these cases.

The first-order case is characterized, as mentioned, by a strictly linear dose dependence of both the area under a glow peak and its maximum intensity. In this simple case the temperature T_m is dose-independent.

The equation of a second-order TL peak is given by

$$I = -\mathrm{d}n/\mathrm{d}t = s' \exp\left(-E/kT\right) n^2 \tag{4.1}$$

where s' is a pre-exponential factor which replaces the frequency factor and has dimensions of $cm^3 \, s^{-1}$. The solution of (4.1) for a linear heating rate β is

$$I = n_0^2 s' \exp\left(-E/kT\right) \left[1 + (n_0 s'/\beta) \int_{T_0}^{T} \exp\left(-E/kT'\right) \mathrm{d}T'\right]^{-2} \tag{4.2}$$

and the equation for maximum (Chen 1969) is

$$(n_0 s'/\beta) \int_{T_0}^{T_m} \exp(-E/kT) \, dT + 1 = (2kT_m^2 \, n_0 s'/\beta E) \exp(-E/kT_m). \quad (4.3)$$

By inserting (4.3) into (4.2) one gets the expression for I_m:

$$I_m = (\beta E/kT_m^2)^2 \exp(E/kT_m)/s'. \quad (4.4)$$

We solved equations (4.3) and (4.4) numerically for various values of E and s', and found T_m and I_m as functions of n_0. Although the area S under the glow peak was directly proportional to n_0, we found that T_m always decreased monotonically with n_0, and I_m depended on the dose D as D^p, where p slightly exceeded unity (we assume here that $D \propto n_0$). The values found were $1 \cdot 05 \leqslant p \leqslant 1 \cdot 10$. The values of the parameters chosen for figure 2 lead to a case of second-order kinetics, as can be seen from equation (3.1). The curves shown in figure 2 behave as expected from the solutions of equations (4.3) and (4.4).

The introduction of an active competing trap can provide an explanation for the superlinear dose dependence of the TL intensity as well as for an increase of T_m with dose. As mentioned in relation to figure 5, the dependence of T_m on the radiation dose was found in certain cases to first increase and then decrease with dose. Such a behaviour has not previously been explained. The present model as formulated by equation (2.11) enables the explanation of this phenomenon by a choice of the appropriate parameters. In addition, the solution of the same equation (2.11) resulted in a quadratic dose dependence for cases where the competing trap dominated. The main feature of this situation is that the value of $p = 2$ starts at the lowest doses. This behaviour differs essentially from that previously found in NaCl, where the dependence was linear at low doses and became superlinear for higher doses before tending to saturation (Israeli *et al* 1972). Superlinearity in NaCl has been attributed to a competition process during irradiation rather than during the thermal release of the trapped carriers.

The occurrence of an even higher degree of superlinearity ($p > 2$) is also included among the possible solutions of equation (2.11), as shown in figures 4 and 5.

The use of the concept 'TL intensity' in the literature is sometimes confusing. In some works it stands for the area S under a glow curve, and in others for the luminescence intensity I_m at the maximum of the glow peak. The dose dependences of S and of I_m were therefore studied separately in the present work. The comparison between S and I_m showed, in all the cases investigated here, that the two were virtually proportional to one another. This fact is of practical value, since the measurement of the maximum intensity is much easier than that of the area under the glow peak, especially when adjacent peaks overlap. This proportionality is readily applicable for thermoluminescence dosimetry.

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