J. Phys. D: Appl. Phys. **28** (1995) 408–414. Printed in the UK

Explanation of the superlinear behaviour of thermoluminescence by considering the residual holes in the recombination centres before irradiation

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Received 16 August 1994, in final form 1 November 1994

Abstract. A model is proposed to explain the superlinear growth of thermoluminescence, based on a consideration of competition both in excitation and during heating between occupation of traps and luminescence centres. Before excitation, it is assumed that a population of electrons n_0 remains in the competing traps while the same number of holes is left in the luminescence centres. On this basis, an implicit expression is obtained for the area under a glow curve, from which several thermoluminescence response curves for different sets of parameters can be obtained. The results show that the area under a glow curve at low doses has a linear dose-dependence for a large n_0 and has a quadratic dose-dependence for a small value of n_0. In the case of early saturation of the competing traps, the dose-dependence is more than quadratic.

1. Introduction

In cases in which superlinearity occurs in the dose-dependence of thermoluminescence (TL), the effect usually appears in two different ways. Some samples show superlinearity at low dose levels, followed by a linear growth, while other samples start with a linear response and then become superlinear. Various explanations of the superlinear growth of TL have been reported. Aitken *et al* (1968) have introduced a competition model to explain the superlinear growth. Chen and Bowman (1978) further studied the model and showed that superlinearity arises from the nonlinear response of electron trapping. Their analysis requires that the competing traps saturate earlier than the TL traps. Kristianpoller *et al* (1974) explained superlinearity by means of electron competition during read-out. They showed that, under certain conditions, the TL intensity is proportional to the concentrations both of the trapped electrons and of holes after irradiation. The superlinearity arises from the product of the concentrations of the two carriers, and the analysis yields superlinearity for low doses. Some papers have reported a more than quadratic superlinearity. Halperin and Chen (1966) suggested a multi-stage transition model to explain the strong superlinear growth in semiconducting diamonds. They argued that a three-stage transition would give a cubic dependence on the dose. Kristianpoller *et al* (1974) also obtained a strong superlinear growth for some ranges of the parameters. Chen *et al* (1988) applied a similar model to explain a strong superlinear dose-dependence of the 110 °C peak in synthetic quartz. Two subsequent papers by McKeever (1990) and Horowitz (1990) point out that, in the important specific case of LiF:Mg, Ti, although the dose-dependence is linear–superlinear, the model of competition during excitation cannot explain the dose-dependence, and one has to resort to excitation during heating. This conclusion is made by using information on the optical absorption of the material, which was found to be linear with the dose and to be associated with the filling of the traps. It should be noted, however, that these conclusions are specific to LiF:Mg, Ti and therefore do not exclude a significant contribution of competition during excitation to the observed superlinearity in different cases. Sunta *et al* (1994) considered superlinearity in terms of a model consisting of interactive and non-interactive electron traps. The superlinear growth is produced by the competition of interactive traps during heating while the

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initial linear part of the response curve is produced by the non-interactive traps, which are spatially associated with the luminescence centres.

In this paper, a model consisting of two electron traps and one recombination centre is considered. One of the traps corresponds to the TL formation and the other serves as an electron competitor. When an electron is excited to the conduction band by ionization, it may either be captured by an electron trap, or recombine with a hole in the luminescence centre. This is the case of competition during irradiation. A similar situation is also considered during heating. In the analysis, it is assumed that the TL traps are empty but a population of electrons n_0 is trapped in the competing traps before irradiation. Under this consideration, the TL response can be proved to depend on the initial concentration of holes remaining in the centres before irradiation. Some relations between TL and the excitation dose are obtained to verify the TL characteristics.

As a result, in the case of the competing traps being far from saturation, the area S under a glow curve for low doses will be proportional to the square of dose if $n_0 \approx 0$. In contrast to the former situation, S will be linearly dependent on the dose if there is a high concentration of holes retained in the centres.

2. Theory

The energy level diagram during irradiation as shown in figure 1(a) is a two-traps, one-centre model. It consists of a TL trap Tr and a competing trap C, from which an electron cannot be thermally released. Before irradiation, we assume that the TL traps are empty while the competing traps have been occupied by electrons of concentration n_0. The same number of holes is assumed to accumulate in the luminescence centres for neutrality. When an electron is released by ionizing irradiation, it wanders in the conduction band and relaxes through paths a, b or c. Path a is a process of recombination, path b gives rise to the TL formation, and path c leads to an accumulation of electrons in traps C. Figure 1(b) is a transition diagram during heating, in which trap C still serves as an electron competitor in this process.

While the actual mechanism of the TL formation is complicated when competitions during excitation and heating are to be accounted for, a semi-intuitive interpretation of the result for low doses can be given. Kristianpoller *et al* (1974) showed that, if the competitors are far from saturation, then the amount of TL at low dose levels will be proportional to the product of the number of electrons in traps Tr and the number of holes in centres. If the numbers of both carriers are proportional to the excitation dose D, then the TL will be approximately proportional to $D(D_0 + D)$, where D_0 is a constant related to the number of holes retained in the centres before irradiation. For an archaeological sample, these holes are mainly created by a heavy geological dose and its concentration can be changed through annealing. In the case of a well-annealed sample, most

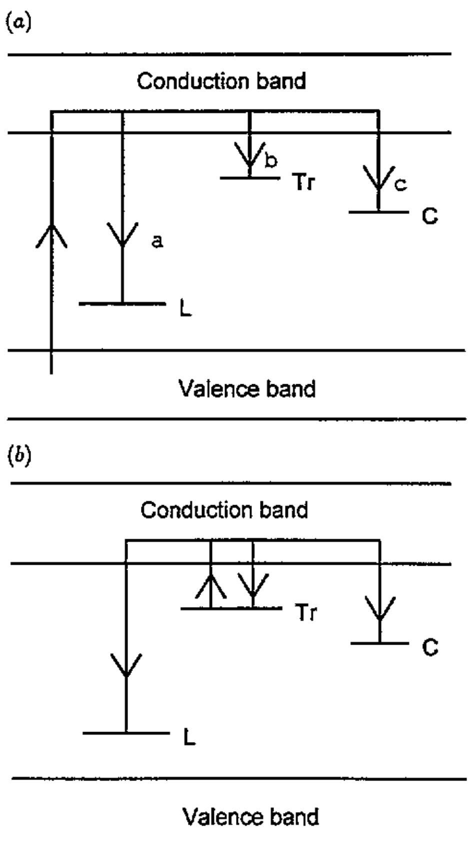

Figure 1. (a) An energy level diagram for the model during irradiation. Tr is the thermoluminescence formation trap, C is the competing trap and L is the recombination centre. Path a is a process of recombination, path b gives rise to the thermoluminescence formation and path c leads to an accumulation of electrons in C. (b) The transition diagram during heating. An electron released from trap Tr may either be captured by the competitor C, retrapped by Tr again or recombine with a hole in L to emit light.

of the holes retained in the centres are neutralized by electrons released from deep traps, resulting in $D_0 \approx 0$, then TL $\propto D^2$. For an insufficiently annealed sample, most of the holes retained in the centres are still there after firing. Thus $D_0 \gg D$ and consequently we have TL $\propto D$. Some calculations are performed in the following sections in order to study the glow curves for higher doses.

2.1. Population of thermoluminescence traps by irradiation

Aitken *et al* (1968) have introduced a model of two traps and one centre which describes the system by the following set of equations:

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = A_1 n_c (N_1 - n_1) \tag{1}$$

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = A_2 n_c (N_2 - n_2) \tag{2}$$

$$\frac{\mathrm{d}n_c}{\mathrm{d}t} = \alpha \frac{\mathrm{d}D}{\mathrm{d}t} - \frac{\mathrm{d}n_1}{\mathrm{d}t} - \frac{\mathrm{d}n_2}{\mathrm{d}t} - A_m n_c m \tag{3}$$

$$m = n_1 + n_2 + n_c \tag{4}$$

where n_1, n_2 and n_c are the concentrations of electrons in traps Tr, C and the conduction band respectively. N_1 and N_2 are the concentrations of electron traps Tr and C respectively. m is the concentration of holes in the luminescence centres. A_1, A_2 and A_m are the transition probabilities into Tr, C and the centres respectively. The term $\alpha\, dD/dt$, in which α is a constant, denotes the rate of creation of electron–hole pairs.

Aitken *et al* (1968) solved the system of equations by assuming that $n_1 = 0$ and $n_2 = 0$ at $t = 0$.

In the present model, the initial values for the system are taken as $n_1 = 0$ and $n_2 = n_0$ at $t = 0$. This means that the traps C are populated by electrons and a residual concentration of holes n_0 is present in the centres before irradiation.

From equations (1) and (2), we have

$$\left(1 - \frac{n_1}{N_1}\right)^{A_2/A_1} = \frac{N_2 - n_2}{N_2 - n_0}. \qquad (5)$$

By substituting n_2 from (5) into (4) and assuming $n_c \ll m$, one gets the following expression for the concentration of holes:

$$m = n_1 + N_2 - (N_2 - n_0)\left(1 - \frac{n_1}{N_1}\right)^{A_2/A_1}. \qquad (6)$$

Under quasi-equilibrium conditions, we have

$$\left|\frac{dn_c}{dt}\right| \ll \left|\frac{dm}{dt}\right|.$$

By substitution, we now get the solution of equations (1)–(4) as

$$\alpha D = n_1\left(1 - \frac{A_m}{A_1}\right) + (N_2 - n_0)\left(1 - \frac{A_m}{A_2}\right) \times \left[1 - \left(1 - \frac{n_1}{N_1}\right)^{A_2/A_1}\right] - \frac{A_m}{A_1}(N_1 + N_2)\log\left(1 - \frac{n_1}{N_1}\right). \qquad (7)$$

From this expression, the superlinear dependence of n_1 on D at a certain dose range can be deduced.

2.2. Thermoluminescence emission during read-out

Kristianpoller *et al* (1974) considered the read-out process in terms of a set of differential equations. Under the conditions of very small retrapping in Tr and traps C being far from saturation, they found that the area under a glow curve for low doses is proportional both to the concentration of holes in centres and to the concentration of electrons in Tr. It therefore shows a quadratic dose-dependence for the area under a glow curve.

We consider the read-out process in the same way. By assuming $|dm/dt| \gg |dn_c/dt|$, one gets the following differential equations:

$$\frac{dn_1}{dt} = -sn_1\exp\left(-\frac{E}{kT}\right) + A_1 n_c(N_1 - n_1) \qquad (8)$$

$$\frac{dn_2}{dt} = A_2 n_c(N_2 - n_2) \qquad (9)$$

$$\frac{dm}{dt} = -A_m n_c m \qquad (10)$$

$$\frac{dm}{dt} = \frac{dn_1}{dt} + \frac{dn_2}{dt} \qquad (11)$$

where s is the frequency factor, E is the activation energy, k is the Boltzmann constant and T is the temperature. Solving equations (9) and (10), we have

$$(N_2 - n_2) = (N_2 - n_{20})\left(\frac{m}{m_0}\right)^{A_2/A_m} \qquad (12)$$

where n_{20} is the concentration of electrons in traps C and m_0 is the concentration of holes in the luminescence centres before heating.

Substituting equations (9), (10) and (12) into (11) gives

$$\left[1 + \frac{A_2}{A_m}\frac{(N_2 - n_{20})}{m}\left(\frac{m}{m_0}\right)^{A_2/A_m}\right]\frac{dm}{dt} = \frac{dn_1}{dt}. \qquad (13)$$

Integrating both sides of (13) yields

$$(m - m_0) + (N_2 - n_{20})\left[\left(\frac{m}{m_0}\right)^{A_2/A_m} - 1\right] = n_1 - n_{10}. \qquad (14)$$

For $t = \infty$, we have $m = m_\infty$ and $n_1 = 0$. Hence

$$(m_0 - m_\infty) + (N_2 - n_{20})\left[1 - \left(\frac{m_\infty}{m_0}\right)^{A_2/A_m}\right] = n_{10}. \qquad (15)$$

If $S = m_0 - m_\infty$ is the area under the glow peak, then an implicit expression for S is

$$S + (N_2 - n_{20})\left[1 - \left(1 - \frac{S}{m_0}\right)^{A_2/A_m}\right] = n_{10}. \qquad (16)$$

It should be noted from the calculation that, no matter whether there are electrons retrapped in (8) or not, the expression (16) for S is valid. The parameter A_1, therefore, does not appear in the expression for the area.

3. Results

Expression (16) gives an approximate expression for S if $S \ll m_0$:

$$S \approx \frac{A_m n_{10} m_0}{A_m m_0 + A_2(N_2 - n_{20})}. \qquad (17)$$

For low doses and dominating trapping into C, that is $A_2(N_2 - n_{20}) \gg A_m m_0$, equation (17) shows that S is proportional to the product of n_{10} and m_0. If n_{10} and m_0 are both linearly dependent on the radiation dose D, S will be more or less proportional to D^2. If, on the

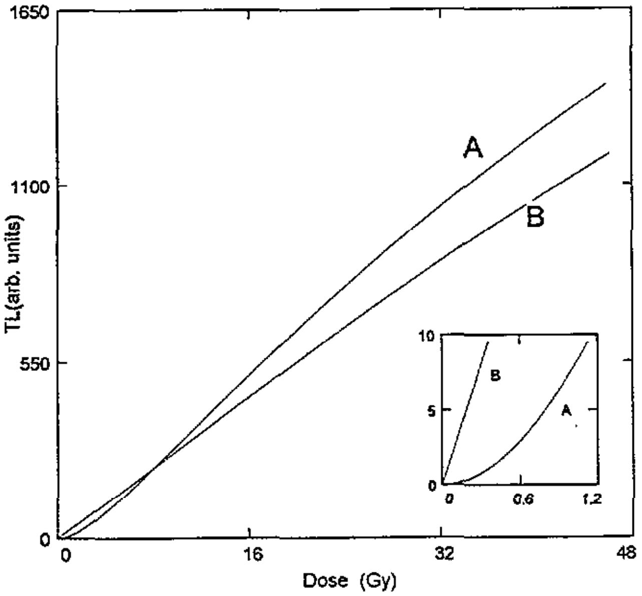

Figure 2. The thermoluminescence response curves show the dose-dependence of the area under the glow peak. The parameters used are $A_1 = A_2 = 0.1A_m$, $N_1 = 10^{13}$ cm^{-3}, $N_2 = 10^{14}$ cm^{-3} and $\alpha = 10^{12}$ cm^{-3} Gy^{-1}. The concentrations of the residual holes in the centres for curves A and B are $n_0 = 0$ and 10^{13} cm^{-3} respectively. The thermoluminescence sensitivity increases with n_0 for low doses but decreases above a certain dose.

other hand, the competing trap is close to saturation, then equation (17) implies that $S \approx n_{10}$, or S will be linearly dependent on D.

More generally, expression (16) can be numerically solved for various sets of parameters. On the other hand, we can use equation (7) to find the electron concentration n_1 in the traps Tr at the end of irradiation. This value is set equal to n_{10} in equation (16) as the initial values for the read-out process. A relation between S and D is thus obtained through this variable n_{10}.

For the situation without early saturation in C, figures 2–8 represent the TL responses described by equations (7) and (16) with the following parameters:

$$A_1 = A_2 = 0.1A_m$$
$$A_1 = A_2 = A_m$$
$$A_1 = A_2 = 10A_m$$
$$A_1 = 0.1A_2 = A_m$$
$$A_1 = 10A_2 = A_m$$
$$0.1A_1 = A_2 = A_m$$
$$10A_1 = A_2 = A_m$$

for figures 2–8 respectively.

Curves A and B in each figure are calculated with the same set of parameters, except that $n_0 = 0$ and 10^{13} cm^{-3} for curves A and B respectively. It is found that all the figures show the same characteristics for low doses: curves A start with superlinear growth and curves B exhibit a linear response. Considering the relation $S \propto D^p$, we have $p \approx 2$ for curve A and $p \approx 1$ for curve B. In general, a situation of $n_0 = 0$ results in superlinear growth for low doses, followed by

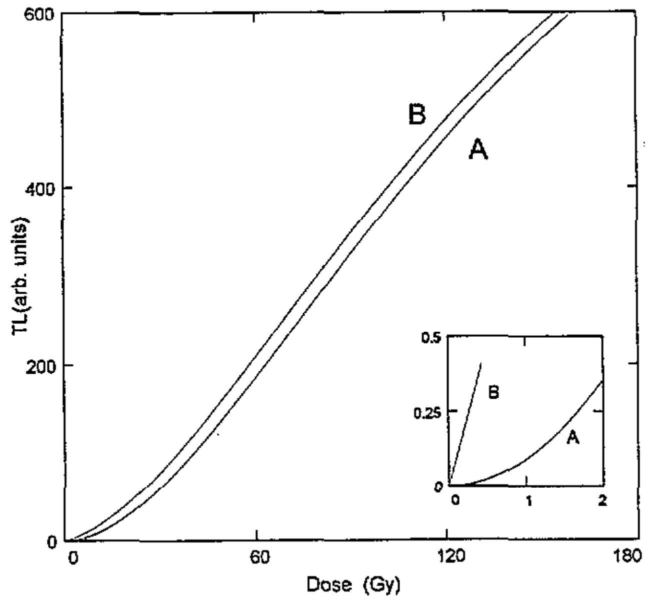

Figure 3. The thermoluminescence curves show the dose-dependence of the area under the glow peak. The parameters used are $A_1 = A_2 = A_m$, $N_1 = 10^{13}$ cm^{-3}, $N_2 = 10^{14}$ cm^{-3} and $\alpha = 10^{12}$ cm^{-3} Gy^{-1}. The concentrations of the residual holes in the centres for curves A and B are $n_0 = 0$ and 10^{13} cm^{-3} respectively. The thermoluminescence sensitivity increases with n_0 for all doses.

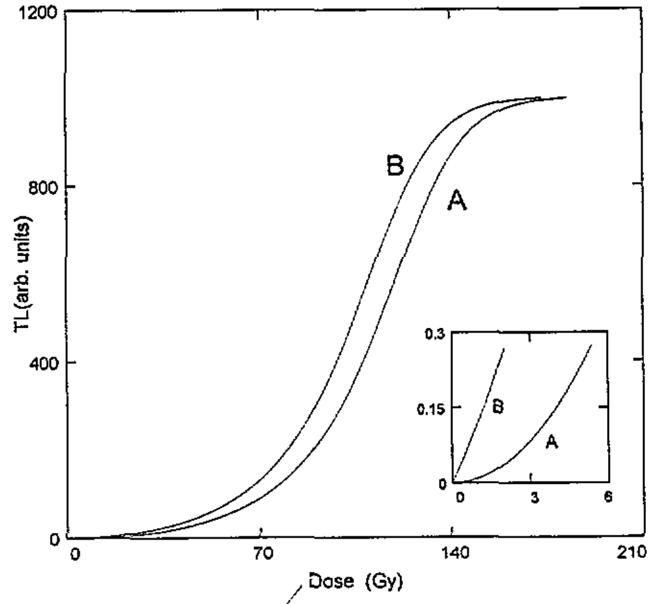

Figure 4. The thermoluminescence response curves show the dose-dependence of the area under the glow peak. The parameters used are $A_1 = A_2 = 10A_m$, $N_1 = 10^{13}$ cm^{-3}, $N_2 = 10^{14}$ cm^{-3} and $\alpha = 10^{12}$ cm^{-3} Gy^{-1}. The concentrations of the residual holes in the centres for curves A and B, are $n_0 = 0$ and 10^{13} cm^{-3} respectively. The thermoluminescence sensitivity increases with n_0 for all doses.

a linear region, indicating a superlinear–linear–saturation behaviour. For a larger value of n_0, the curve starts with a linear growth and becomes superlinear at certain doses, followed by a linear growth again, indicating a linear–superlinear–linear–saturation characteristic.

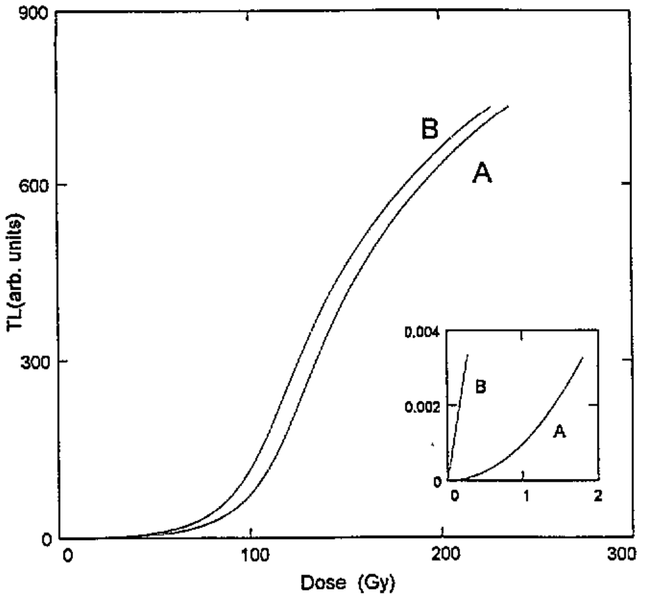

Figure 5. The thermoluminescence response curves show the dose-dependence of the area under the glow peak. The parameters used are $A_1 = 0.1A_2 = A_m$, $N_1 = 10^{13}$ cm^{-3}, $N_2 = 10^{14}$ cm^{-3} and $\alpha = 10^{12}$ cm^{-3} Gy^{-1}. The concentrations of the residual holes in the centres for curves A and B are $n_0 = 0$ and 10^{13} cm^{-3} respectively. The thermoluminescence sensitivity increases with n_0 for all doses.

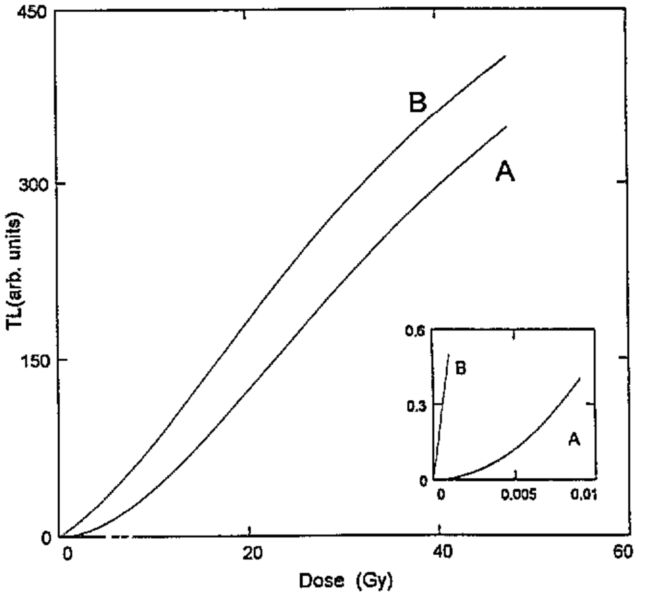

Figure 7. The thermoluminescence response curves show the dose-dependence of the area under the glow peak. The parameters used are $0.1A_1 = A_2 = A_m$, $N_1 = 10^{13}$ cm^{-3}, $N_2 = 10^{14}$ cm^{-3} and $\alpha = 10^{12}$ cm^{-3} Gy^{-1}. The concentrations of the residual holes in the centres for curves A and B are $n_0 = 0$ and 10^{13} cm^{-3} respectively. The thermoluminescence sensitivity increases with n_0 for all doses.

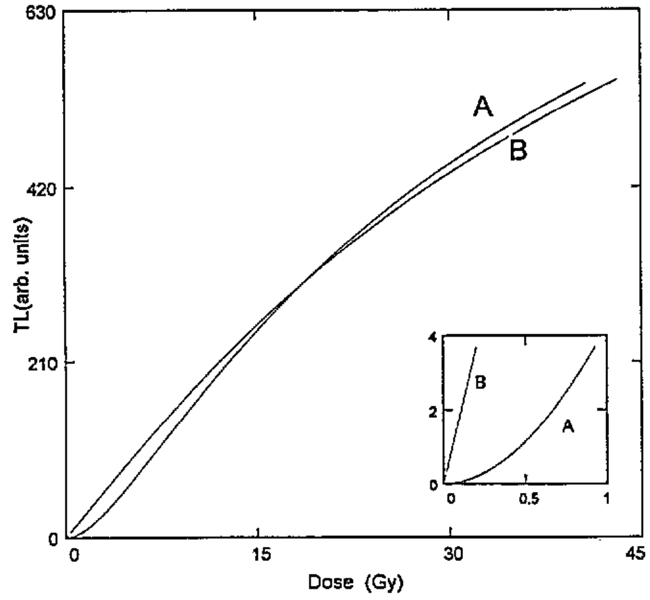

Figure 6. The thermoluminescence response curves show the dose-dependence of the area under the glow peak. The parameters used are $A_1 = 10A_2 = A_m$, $N_1 = 10^{13}$ cm^{-3}, $N_2 = 10^{14}$ cm^{-3} and $\alpha = 10^{12}$ cm^{-3} Gy^{-1}. The concentrations of the residual holes in the centres for curves A and B are $n_0 = 0$ and 10^{13} cm^{-3} respectively. The thermoluminescence sensitivity increases with n_0 for low doses but decreases above a certain dose.

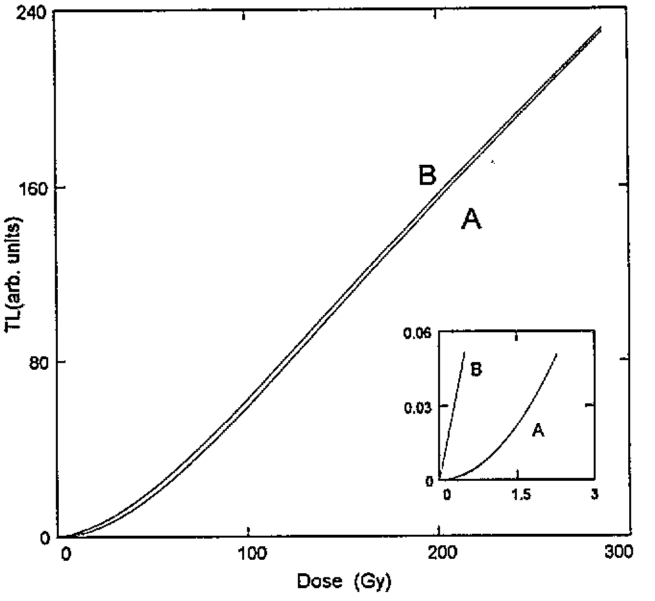

Figure 8. The thermoluminescence response curves show the dose-dependence of the area under the glow peak. The parameters used are $10A_1 = A_2 = A_m$, $N_1 = 10^{13}$ cm^{-3}, $N_2 = 10^{14}$ cm^{-3} and $\alpha = 10^{12}$ cm^{-3} Gy^{-1}. The concentrations of the residual holes in the centres for curves A and B are $n_0 = 0$ and 10^{13} cm^{-3} respectively. The thermoluminescence sensitivity increases with n_0 for all doses.

Considering the case of early saturation in the competitors C, curve A of $n_0 = 0$ in figure 9 has a very low sensitivity at low dose levels and is characterized by a sharp increase at a certain dose, followed by a linear response when saturation is reached. Curve B with $n_0 = 10^{10}$ cm^{-3} has a similar behaviour but the whole curve is shifted towards the left. The turning points (from the low-sensitivity region to the high-sensitivity region) in these curves are found to have a more than quadratic dose-dependence. They are due to the electrons' nonlinear trapping during excitation as explained by some investigators. The turning point of

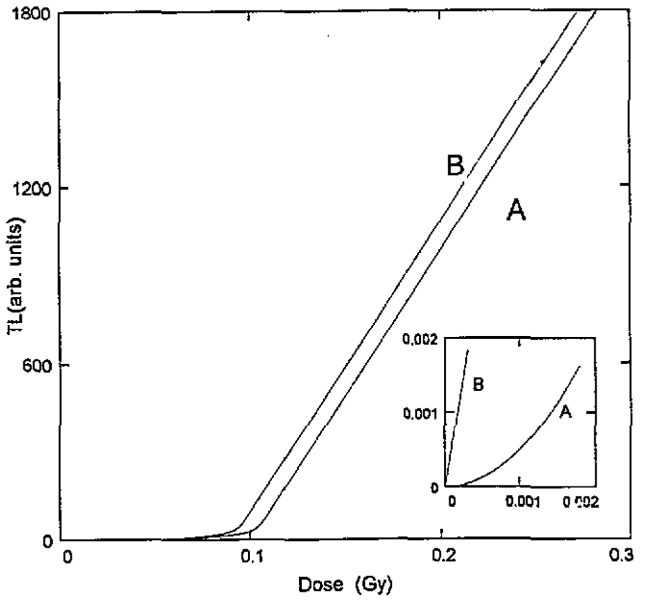

Figure 9. The thermoluminescence response curves for the case of early saturation in the competitors C. The parameters used are $A_1 = 0.01A_2 = A_m$, $N_1 = 10^{13}$ cm^{-3}, $N_2 = 10^{11}$ cm^{-3} and $\alpha = 10^{12}$ cm^{-3} Gy^{-1}. The concentrations of the residual holes in the centres for curves A and B are $n_0 = 0$ and 10^{10} cm^{-3} respectively. The thermoluminescence sensitivity increases with n_0 for all doses. These curves are found to have a more than quadratic dose-dependence at certain doses.

curve B appears at a lower dose region because the traps C are already occupied by some electrons and therefore are saturated earlier than in curve A. The inset of figure 9 represents the TL response for low doses. In the region far from the saturation of C, they do have a quadratic dose-dependence for $n_0 = 0$ and a linear response for a greater value of n_0.

4. Discussion

In this paper, several types of TL response have been investigated. Some results are characterized by a linear response and followed by a superlinear region, while the opposite effect is observed in others. This behaviour can be explained by the presence of residual holes n_0 remaining in the luminescence centres before irradiation. As a result, a greater value of n_0 tends to improve the linearity for low doses, whereas a pronounced superlinear response will be observed for small n_0. The value of n_0 can be practically changed by using different annealing conditions. For an ancient ceramic, the quartz embedded has received a heavy geological dose before firing in a kiln, which introduces a high concentration of n_0 in the luminiscence centres. This n_0 can be reduced if the sample undergoes a suitable annealing. Its magnitude can be identified by the sensitivity of the characteristic glow peak of quartz at 110 °C when the sample is subjected to a small test dose. Chen *et al* (1988) reported a very strong superlinearity of the 110 °C peak in unfired synthetic quartz, which became linear with an increase in sensitivity after firing at high temperature. This change can be explained by the presence of n_0, which is negligibly small in unfired quartz and becomes relatively large after thermal annealing. The increase in TL sensitivity is evidence for an increase in n_0 after firing. Since the terms responsible for superlinearity during excitation and heating are (N_2-n_0) and (N_2-n_{20}) respectively (see for example equations (7) and (17)), a large value of n_0 means that n_2 becomes saturated. Consequently $(N_2 - n_0)$ and $(N_2 - n_{20})$ approach zero and the superlinearity disappears. It therefore turns out that the former case results in a superlinearity growth and the latter one gives a linear response.

Figures 2–8 indicate that sensitivity changes with n_0. The sensitivity can either increase or decrease, depending on the relation between A_1, A_2, A_m and the dose level. More often than not, TL sensitivity increases with n_0 for all doses. For the case of $10A_2 = A_m$ (figure 2 and 6), the TL sensitivity increases with n_0 only for low doses but decreases beyond a certain dose.

Superlinearity correction in the additive dose dating method (Fleming 1970) is the intercept obtained by extrapolating the linear region to the x axis, which is an important factor in getting an accurate palaeodose. Figures 2–9 show that the TL response curves change with n_0 and hence the superlinearity correction changes accordingly. For an archaeological sample, the superlinearity correction can only be obtained with samples from which the natural TL has been drained by the first glow. However, it is often reported that an increase in TL sensitivity is observed in quartz between the first and the second glows. The question then arises of whether there is a change in n_0 after a sample is thermally annealed. If n_0 is increased after annealing, then the TL response is closer to linearity at low doses in the second glow. The superlinearity correction obtained from the second glow will then deviate from the actual value. Thus further investigation on superlinearity correction is necessary for obtaining an accurate TL age by this dating method.

Another recent work that should be mentioned in this respect is that by Sunta *et al* (1994). The general dose-dependence behaviour given by these authors is similar to the present results, including linear–superlinear–saturation behaviour, as well as superlinearity as of the lowest doses, with other sets of parameters. The main difference between the two approaches is that Sunta *et al* (1994), similarly to Kristianpoller *et al* (1974), assume that the relevant traps and centres are being filled exponentially with the dose, according to $m = M[1 - \exp(-\varepsilon' D)]$. In the present work we take a step forward by dealing with the filling of the traps as results from the set of simultaneous differential equations governing this part of the process. This is, in general, a function that also approaches saturation, but not necessarily in an exponential manner.

References

Aitken M J, Thompson J and Fleming S J 1968 *Proc. 2nd Int. Congress on Luminosity and Dosimetry, Gatlinburg, TN*

(USA Atomic Energy Commission) p 364
Chen R and Bowman S G E 1978 *PACT* **2** 216–30
Chen R, Yang X H and McKeever S W S 1988 *J. Phys. D: Appl. Phys.* **21** 1452–7
Fleming S J 1970 *Archaeometry* **12** 133–47
Halperin A and Chen R 1966 *Phys. Rev.* **148** 839
Horowitz Y S 1990 *Radiat. Prot. Dosim.* **33** 75–81
Kristianpoller N, Chen R and Israeli M 1974 *J. Phys. D: Appl. Phys.* **7** 1063
McKeever S W S 1990 *Radiat. Prot. Dosim.* **33** 83–9
Sunta C M, Yoshimura E M and Okuno E 1994 *J. Phys. D: Appl. Phys.* **27** 852–60