IOP PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS

J. Phys. D: Appl. Phys. **42** (2009) 155409 (8pp) doi:10.1088/0022-3727/42/15/155409

On the theoretical basis for the duplicitous thermoluminescence peak

J L Lawless[1,4], **R Chen**[2] **and V Pagonis**[3]

[1] Redwood Scientific Incorporated, Pacifica, CA 94044-4300, USA
[2] Raymond and Beverly Sackler School of Physics and Astronomy, Tel-Aviv University, Tel-Aviv 69978, Israel
[3] Physics Department, McDaniel College, Westminster, MD 21157, USA

E-mail: lawless@alumni.princeton.edu (J Lawless)

Received 15 January 2009, in final form 7 June 2009
Published 13 July 2009
Online at stacks.iop.org/JPhysD/42/155409

Abstract
The simultaneous release of electrons and holes by what seems to be a single trap has been observed experimentally. We previously performed numerical simulations on a phenomenological model which showed similar behaviour. Here, we provide an analytical solution to this model. This model explains trends in radioluminescence, thermoluminescence and thermally stimulated conductivity of a material with one electron trap, one hole trap and one radiative recombination centre, in which thermal excitation of the electron trap occurs before that of the hole trap. It is shown that TL emission due to *electron* recombination at centres can be controlled by a *hole* trap and the electron recombination will have a peak shape associated with the hole trap's parameters. When this happens, the peaks in free electron concentration, free hole concentration and TL all occur nearly simultaneously. The analytical model allows this to be explained along with scaling laws and initial rise behaviour. Under the conditions illustrated by this model, the usual methods used to distinguish between electron traps and hole traps will give incorrect results.

1. Introduction

After exposure to ionizing radiation, insulators and semiconductors often exhibit thermoluminescence. Measurement of this luminescence can be used to infer the dose which makes this phenomenon useful for dosimetry and for dating of rocks and antiquities (Aitken 1985, McKeever 1985, Chen and McKeever 1997). The luminescence is generally believed to be due to the radiative recombination of holes or electrons after their thermal release from traps. For several decades, substantial effort has been devoted to distinguishing electron traps from hole traps and identifying the other properties of each trap. We investigate herein a situation where a trap of one type may masquerade as a trap of the other type. In a previous paper (Chen *et al* 2008), we studied this effect using numerical methods. Herein, we provide an analytical solution.

The simplest model which exhibits this effect has one electron trap, one hole trap and one recombination centre from which radiation is emitted when an electron recombines at the centre. Under some circumstances, this model shows two peaks in the TL glow curve. The first peak is due to thermal stimulation of electrons from the electron trap. These recombine with holes in the centre until those holes are depleted. At this point, the TL emission due to electron recombination is stopped and, due to lack of holes in the centre, electrons emitted from the electron trap are re-trapped. This continues until free holes start to be created from thermal stimulation of the hole trap. This replenishes holes in the centre and allows electron recombination to continue. This results in a second TL peak. We show that, even though the emission is due to electron recombination and thus its spectral emission appears the same as for other electron traps, the second TL peak has the initial rise and peak shape associated with the hole trap, not the electron trap. The thermally stimulated conductivity (TSC) curves will also be shown to be anomalous. Consequently, the usual method for distinguishing electron traps from hole traps may fail in this circumstance. The analytical results allow this duplicitous behaviour to be explained and trends quantified.

Three assumptions are used to simplify the model. First, we assume that, during heating, the electron trap experiences

[4] Author to whom any correspondence should be addressed.

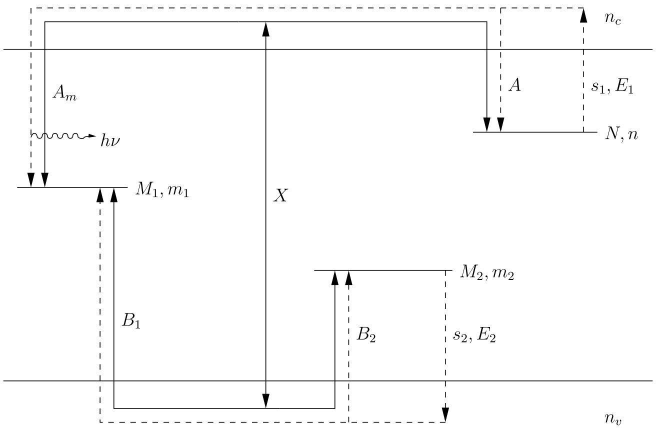

Figure 1. The energy level diagram of one electron and one hole trapping states, along with one kind of recombination centre. Solid lines indicate transitions occurring during excitation. Transitions taking place during read-out are shown by dashed lines.

significant thermal excitation well before the hole trap. This enables the duplicitous peak behaviour that is of interest in this paper. Second, we assume that the occupancy of all levels is well below saturation. Saturation is not of interest in this paper and assuming levels well below saturation allows the equations to be simplified significantly. Lastly, we assume that irradiation and the subsequent heating occur slowly enough that the quasi-steady assumption may be made for free electrons and free holes. The quasi-steady assumption seems to correspond to the usual experimental situation (Sunta *et al* 2001, 2002) and it also simplifies the equations allowing us to focus on the issues of interest here.

The analytical theory is developed in the next section. This development is divided into three parts: (1) irradiation, (2) the first TL peak and (3) the second TL peak. This is followed by a section showing results which illustrate the interesting features of this model. Lastly, conclusions are drawn.

2. Theory

In this model, we consider three levels. The electron trap has a total concentration of N_1 and an occupancy of n_1. The recombination centre has a total concentration of M_1 and an instantaneous occupancy of m_1. We assume that this is a hole-type recombination centre, meaning that, after annealing but before irradiation, $m_1 = 0$. The hole trap has a total concentration of M_2 and an occupancy of m_2. The energy-level diagram for this model is shown in figure 1. We are analysing this because it is the simplest model that enables the demonstration of the 'duplicitous' peak, which results from the release of electrons and holes from trapping states, with recombination occurring in one centre. While this model is not expected to compare quantitatively with real, i.e. complicated, materials, it does allow us to explore how some unintuitive behaviours occur without excess complication.

2.1. Irradiation

During irradiation, electron–hole pairs are created. The free holes may be captured by the centre, M_1, or by the hole trap, M_2. The rate constants for capture for these two levels are B_1 and B_2, respectively. The free electrons can be captured by the electron trap, N, with rate constant A, or recombine at the centre, M_1 with rate constant A_m. The occupancies of these levels are governed by the following equations:

$$\frac{dn}{dt} = A(N-n)n_c, \tag{1}$$

$$\frac{dn_c}{dt} = X - A(N-n)n_c - A_m m_1 n_c, \tag{2}$$

$$\frac{dm_1}{dt} = B_1(M_1-m_1)n_v - A_m m_1 n_c, \tag{3}$$

$$\frac{dm_2}{dt} = B_2(M_2-m_2)n_v, \tag{4}$$

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

where n_c and n_v are the concentrations of free electrons and free holes, respectively. n, m_1, and m_2 are the instantaneous occupancies of the electron trap, the recombination centre and the hole trap, respectively. N, M_1 and M_2 are the respective total populations of these levels. X is the rate of electron–hole pair creation induced by the radiation. The various rate constants have meanings as identified in figure 1.

For initial conditions, we assume the traps and centre are empty at the beginning of irradiation: $n = m_1 = m_2 = n_v = n_c = 0$. Since, for this paper, we are not interested in saturation effects, we will assume $n \ll N$, $m_1 \ll M_1$ and $m_2 \ll M_2$. Thus, equation (1) through equation (5) can be simplified to

$$\frac{dn}{dt} = ANn_c, \tag{6}$$

$$\frac{dn_c}{dt} = X - ANn_c - A_m m_1 n_c, \tag{7}$$

$$\frac{dm_1}{dt} = B_1 M_1 n_v - A_m m_1 n_c, \tag{8}$$

$$\frac{dm_2}{dt} = B_2 M_2 n_v, \tag{9}$$

$$\frac{dn_v}{dt} = X - B_1 M_1 n_v - B_2 M_2 n_v. \tag{10}$$

Examination of equations (7) and (10) shows that the lifetimes, in seconds, of free electrons and free holes are $1/(AN+A_m m_1)$ and $1/(B_1M_1+B_2M_2)$, respectively. For usual ranges of cross-sections and trap populations, these lifetimes are very short, often measured in microseconds or nanoseconds (Lax 1960, Rose 1963, Sunta *et al* 2001, 2002). Consequently, we make the quasi-steady assumption for n_c and n_v so that equations (7) and (10) are replaced by

$$n_c = \frac{X}{AN + A_m m_1}, \tag{11}$$

$$n_v = \frac{X}{B_1M_1 + B_2M_2}. \tag{12}$$

It follows that the remaining conservation equations can be simplified to

$$\frac{dn}{dt} = \frac{AN}{AN + A_m m_1} X, \tag{13}$$

$$\frac{dm_1}{dt} = \frac{B_1 M_1}{B_1 M_1 + B_2 M_2} X - \frac{A_m m_1}{AN + A_m m_1} X, \tag{14}$$

$$\frac{dm_2}{dt} = \frac{B_2 M_2}{B_1 M_1 + B_2 M_2} X. \tag{15}$$

From equation (13), one can see that, initially, n grows linearly with dose: $n \approx Xt$. Initially, m_1 and m_2 also grow linearly with dose, although not as fast as n. As time progresses, an increasing number of free electrons may recombine at the centre, m_1 rather than be captured by trap N_1. This causes sublinear growth for both n_1 and m_1. Note that this sublinearity occurs even though both populations are, by assumption, well below saturation. This type of sublinearity was discussed previously (Lawless *et al* 2008).

Equation (15) can be integrated to find m_2 as a function of dose, Xt:

$$m_2 = \frac{B_2 M_2}{B_1 M_1 + B_2 M_2} Xt. \tag{16}$$

Equation (14) can also be integrated. After some math:

$$Xt = -\frac{AN}{A_m} \left(\frac{B_1 M_1 + B_2 M_2}{B_2 M_2} \right)^2 \log \left(1 - \frac{B_2 M_2}{B_1 M_1} \frac{A_m}{AN} m_1 \right) - \frac{B_1 M_1 + B_2 M_2}{B_2 M_2} m_1. \tag{17}$$

Given m_1, equation (17) provides an explicit value for the dose required to achieve that level of m_1. Alternatively, if the dose is known, one can solve equation (17) numerically to find m_1. The electron trap population can then be found from the above by conservation of charge:

$$n = m_1 + m_2. \tag{18}$$

If one monitors the emission intensity during irradiation, it is $I = A_m m_1 n_c$. Using equation (11), this becomes

$$I = \frac{A_m m_1}{AN + A_m m_1} X. \tag{19}$$

Equation (16) through equation (19) are the solution to the irradiation of a material with one electron trap, one recombination centre and one hole trap subject to the assumptions that n_v and n_c are quasi-steady and that all populations remain well below saturation.

2.2. Readout

The governing equations for thermoluminescence with one electron trap, one hole trap and one recombination centre are

$$\frac{dn}{dt} = A(N - n)n_c - s_1 e^{-E_1/kT} n, \tag{20}$$

$$\frac{dn_c}{dt} = s_1 e^{-E_1/kT} n - A(N - n)n_c - A_m m_1 n_c, \tag{21}$$

$$\frac{dm_1}{dt} = B_1(M_1 - m_1)n_v - A_m m_1 n_c, \tag{22}$$

$$\frac{dm_2}{dt} = B_2(M_2 - m_2)n_v - s_2 e^{-E_2/kT} m_2, \tag{23}$$

$$\frac{dn_v}{dt} = s_2 e^{-E_2/kT} m_2 - B_1(M_1 - m_1)n_v - B_2(M_2 - m_2)n_v, \tag{24}$$

where s_1 and s_2 are the pre-exponential factors and E_1 and E_2 are the activation energies for thermal excitation of the electron trap and hole trap, respectively. We assume that recombination between a free electron and the centre produces TL emission so that the TL intensity is given by

$$I = A_m m_1 n_c. \tag{25}$$

Since, for this paper, we are not interested in the saturation effects associated with high doses, we will assume $n \ll N$, $m_1 \ll M_1$ and $m_2 \ll M_2$. Thus

$$\frac{dn}{dt} = ANn_c - s_1 e^{-E_1/kT} n, \tag{26}$$

$$\frac{dn_c}{dt} = s_1 e^{-E_1/kT} n - ANn_c - A_m m_1 n_c, \tag{27}$$

$$\frac{dm_1}{dt} = B_1 M_1 n_v - A_m m_1 n_c, \tag{28}$$

$$\frac{dm_2}{dt} = B_2 M_2 n_v - s_2 e^{-E_2/kT} m_2, \tag{29}$$

$$\frac{dn_v}{dt} = s_2 e^{-E_2/kT} m_2 - B_1 M_1 n_v - B_2 M_2 n_v. \tag{30}$$

We will assume that the free electron lifetime, $1/(AN + A_m m_1)$, is much shorter than the time scale on which n_c changes, $n_c/(dn_c/dt)$. Similarly, for free holes we assume that the free hole lifetime, $1/(B_1 M_1 + B_2 M_2)$, is much shorter than the time scale on which n_v changes, $n_v/(dn_v/dt)$. Further, we assume that n_v and n_c are both small compared with other populations. This allows us to make the quasi-steady assumption for free electrons and free holes. Experiments indicate that these lifetimes are short (Lax 1960, Rose 1963), and consequently the quasi-steady assumption is usually valid (Sunta *et al* 2001, 2002). In this case equations (27) and (30) simplify to

$$n_c = \frac{s_1 e^{-E_1/kT} n}{AN + A_m m_1}, \tag{31}$$

$$n_v = \frac{s_2 e^{-E_2/kT} m_2}{B_1 M_1 + B_2 M_2}. \tag{32}$$

It follows that the remaining conservation equations simplify to

$$\frac{dn}{dt} = -\frac{A_m m_1}{AN + A_m m_1} s_1 e^{-E_1/kT} n, \tag{33}$$

$$\frac{dm_1}{dt} = \frac{B_1 M_1}{B_1 M_1 + B_2 M_2} s_2 e^{-E_2/kT} m_2 - \frac{A_m m_1}{AN + A_m m_1} s_1 e^{-E_1/kT} n, \tag{34}$$

$$\frac{dm_2}{dt} = -\frac{B_1 M_1}{B_1 M_1 + B_2 M_2} s_2 e^{-E_2/kT} m_2. \tag{35}$$

As a consequence of making the quasi-steady approximation in equation (27), the net rate at which electrons leave the electron trap, $-\mathrm{d}n/\mathrm{d}t$ as per equation (26), is equal to the recombination rate at the centre, $A_m m_1 n_c$, which, via equation (25), is equal to TL intensity, I. This leads to the useful relation:

$$I = -\frac{\mathrm{d}n}{\mathrm{d}t}. \tag{36}$$

Equation (35) can be immediately integrated to yield

$$m_2 = m_{2,0}\exp\left(-s_2'\int_0^t \mathrm{e}^{-E_2/kT(t')}\,\mathrm{d}t'\right), \tag{37}$$

where s_2' is a convenient abbreviation defined by

$$s_2' = \frac{B_1 M_1}{B_1 M_1 + B_2 M_2} s_2. \tag{38}$$

For the common case of a linear heating profile, $T(t) = T_0 + \beta t$, the above can be integrated analytically to find

$$m_2 = m_{2,0}\exp\left(-\frac{E_2 s_2'}{k\beta}(\Gamma(-1, E_2/kT) - \Gamma(-1, E_2/kT_0))\right), \tag{39}$$

where T_0 is the initial temperature and $\Gamma(-1, E_2/kT)$ is the incomplete gamma function as defined by Abramowitz and Stegun (1970). The analytical forms of the integral for other temperature profiles are reviewed by Lawless and Lo (2001).

Equations (31), (32) and (37) (or equation (39)) provide the analytical solutions for n_c, n_v, and m_2 during readout. To complete the analytical model of thermoluminescence, we need to find expressions for n and m_1. To do this, we need to consider thermal excitation of the first trap, n, separately from thermal excitation of the second trap, m_2. This is done in the following subsections.

2.2.1. Region I: first peak. By assumption, the kinetic parameters (s_1, E_1, s_2 and E_2) are such that thermal excitation of the electron trap, n, occurs before that of the hole trap, m_2. In this subsection, we consider thermal excitation of the electron trap, n. To solve for n, we begin by rearranging equation (33) to find

$$\frac{AN + A_m m_1}{A_m m_1}\frac{\mathrm{d}n}{n} = -s_1 \mathrm{e}^{-E_1/kT}\,\mathrm{d}t. \tag{40}$$

But, conservation of charge requires $n = m_1 + m_2$ and, since, by assumption, negligible thermal excitation of the hole trap occurs during the first peak, $m_2 \approx m_{2,0} =$ constant, then $\mathrm{d}n \approx \mathrm{d}m_1$ and equation (40) simplifies to

$$\frac{AN + A_m m_1}{A_m m_1}\frac{dm_1}{m_1 + m_{2,0}} = -s_1 \mathrm{e}^{-E_1/kT}\,\mathrm{d}t. \tag{41}$$

Since $m_1 < n \ll N$, it might be tempting to drop $A_m m_1$ from the term $(AN + A_m m_1)$. However, it is possible to choose parameters such that $A_m \gg A$ in which case the term $A_m m_1$ could be important even though $m_1 \ll N$. Thus, to include that case, we keep the term as is.

Equation (41) can be readily integrated to yield

$$\frac{AN}{A_m m_{2,0}}\ln\left(\frac{m_1}{m_{1,0}}\frac{m_{1,0} + m_{2,0}}{m_1 + m_{2,0}}\right) + \ln\left(\frac{m_1 + m_{2,0}}{m_{1,0} + m_{2,0}}\right) = -\int_0^t s_1 \mathrm{e}^{-E_1/kT(t')}\,\mathrm{d}t'. \tag{42}$$

The right-hand-side of the above can be integrated analytically for various temperature versus time profiles. For the usual linear profile, the right-hand-side becomes an incomplete gamma function:

$$\frac{AN}{A_m m_{2,0}}\ln\left(\frac{m_1}{m_{1,0}}\frac{m_{1,0} + m_{2,0}}{m_1 + m_{2,0}}\right) + \ln\left(\frac{m_1 + m_{2,0}}{m_{1,0} + m_{2,0}}\right) = -s_1\left[\Gamma(-1, E_1/kT) - \Gamma(-1, E_1/kT_0)\right]. \tag{43}$$

Further, if $AN/(A_m m_{2,0})$ is either large or small, then we can find an explicit solution for m_1 as a function of T but we will not pursue that here.

The TL intensity, equation (25), is $I = A_m m_1 n_c$. Substituting in the quasi-steady concentration of n_c, equation (31), the TL intensity during readout is given by

$$I(t) = \frac{A_m m_1}{AN + A_m m_1} s_1 \mathrm{e}^{-E_1/kT}(m_1 + m_{2,0}). \tag{44}$$

Equation (44) completes the solution for region I. Equation (42) or, as appropriate, equation (43) provide the solution for m_1 in region I. n can then be found from $n = m_1 + m_2$. Combined with equations (31), (32) and (37), we have the complete solution for region I. This solution is valid as long as m_2 has not started to empty during the heating stage, that is, as long as $m_2 \approx m_{2,0}$.

The TL emission in this region, as given by equation (44), drops precipitously as the centre population, m_1 becomes depleted. The TL emission does not rise again until thermal stimulation of m_2 becomes significant but that is the subject of the next subsection.

2.2.2. Region II: second peak. At the end of region I, recombination with electrons had depleted the population of the centre. We now develop a model valid when the centre population, m_1, is small. We assume

$$m_1 \ll m_2. \tag{45}$$

Consequently, by conservation of charge, $n \approx m_2$. Consistent with equation (45), we further assume

$$\left|\frac{\mathrm{d}m_1}{\mathrm{d}t}\right| \ll \left|\frac{\mathrm{d}m_2}{\mathrm{d}t}\right|. \tag{46}$$

From equations (29), (30) and the quasi-steady assumption for free holes, n_v, we know that the net rate at which m_2 loses holes is equal to the net rate at which the centre captures holes: $-\mathrm{d}m_2/\mathrm{d}t = B_1 M_1 n_v$. Combining this with equation (46) yields

$$\left|\frac{\mathrm{d}m_1}{\mathrm{d}t}\right| \ll B_1 M_1 n_v. \tag{47}$$

Consequently, $\mathrm{d}m_1/\mathrm{d}t$ may be neglected in equation (28) and equation (28) simplifies to a balance between the rate of hole capture by the centre, $B_1 M_1 n_v$, and the rate of electron recombination, $A_m m_1 n_c$:

$$B_1 M_1 n_v = A_m m_1 n_c. \quad (48)$$

There is only one value of m_1 that satisfies this balance and it is

$$m_1 = \frac{B_1 M_1}{A_m} \frac{n_v}{n_c}. \quad (49)$$

The behaviour of equation (49) is intuitively reasonable: it says that larger values of n_v, which mean faster hole capture by the centre, result in a larger centre population, m_1, while larger values of n_c, which mean faster electron recombination with the centre, result in smaller values of m_1.

Using the quasi-steady assumption for n_c (equation (31)) and n_v (equation (32)), equation (49) becomes

$$m_1 = \frac{AN + A_m m_1}{A_m} \frac{s_2'}{s_1} e^{-(E_2-E_1)/kT}, \quad (50)$$

where s_2' was defined by equation (38). However, as discussed above, the reason that m_1 was driven to a small value was that free electrons were made available for recombination at the centre at a rate much faster than that at which holes were replenishing the centre's population: $s_1 \exp(-E_1/kT) \gg s_2' \exp(-E_2/kT)$. Consequently, most of the freed electrons must be re-trapped by n_1 rather than recombine: $AN \gg A_m m_1$. In this case, we can further simplify region II equations for both n_c and m_1 to

$$n_c = \frac{s_1 e^{-E_1/kT}}{AN} m_2, \quad (51)$$

$$m_1 = \frac{AN}{A_m} \frac{s_2'}{s_1} e^{-(E_2-E_1)/kT}. \quad (52)$$

The TL intensity is $I = A_m m_1 n_c$. But from equation (48), this is the same as

$$I = B_1 M_1 n_v. \quad (53)$$

Since B_1 and M_1 are both constants, this shows that, in region II, the TL intensity is proportional to n_v. Substituting in the quasi-steady value for n_v, the TL intensity is given by

$$I = s_2' e^{-E_2/kT} m_2, \quad (54)$$

where m_2 is already known as a function of time from equation (37). We now have the complete solution for region II.

According to equation (37), the value of m_2 drops towards zero as heating progresses. Consequently, at some time during heating, equation (45) will cease to be valid. After that happens, the equations for region II can no longer be used. Note also that m_2, via equation (16), depends on dose but m_1, as given by equation (52), does not. Thus, for given set of rate constants, the approximations of region II are not useful if the dose is small enough that m_2 fails to satisfy equation (45). However, for a given dose, the approximations of this region become more accurate if recombination is stronger relative to recapture for the free electrons, i.e. as AN/A_m decreases, since this reduces the magnitude of m_1 in equation (52). Also, m_1 becomes smaller as the ratio $s_2' \exp(-E_2/kT)/s_1 \exp(-E_1/kT)$ decreases. This ratio decreases and thus the approximations of region II are more accurate as the two peaks become more widely separated in temperature.

Table 1. Summary of equations. Note that for linear heating profiles, equations (39) and (43) may be substituted for equations (37) and (42), respectively.

		Readout	
Quantity	Irradiation	Region I	Region II
m_2	Equation (16)	Equation (37)	Equation (37)
n_v	Equation (12)	Equation (32)	Equation (32)
m_1	Equation (17)	Equation (42)	Equation (52)
n	Equation (18)	Equation (18)	Equation (18)
n_c	Equation (11)	Equation (31)	Equation (31)
I	Equation (19)	Equation (44)	Equation (54)

2.2.3. Summary of equations. To summarize, we have developed solutions for the intensity and population during irradiation, thermal excitation of the first trap (region I) and the later excitation of the second trap (region II). The equations needed for each solution are presented in table 1.

For numerical calculations of irradiation, it is convenient to use m_1 as a parameter. Given m_1, one can use equation (17) to calculate the dose, Xt, explicitly. Then, knowing the dose, all the other parameters can be calculated explicitly using the equations as given in table 1.

3. Results and discussion

We will illustrate the behaviour of this model with sample calculations for two different sets of rate constants. Each set illustrates different features of the model but both display the duplicitous peak behaviour in which n_v, n_c and I all exhibit nearly simultaneous peaks.

We will start using the rate constants of our previous numerical solution (Chen *et al* 2008) which are as shown in table 2. The growth of level populations during irradiation is shown in figure 2. The hole trap population, m_2 grows linearly while the centre, m_1, and electron trap, n, are both growing slightly sublinearly. The free electron and free hole populations remain small throughout the irradiation process. At the end of 1000 s of irradiation, the population closest to saturation is n which reaches about 3×10^{10} cm^{-3} which is 3% of N. Our model is only valid as long as all populations remain well below saturation.

More interesting are the results during heating as shown in figure 3. From room temperature up to 405 K, the equations from region I are used. Above 408 K, the equations for region II are used. Observe that the thermoluminescence curve reaches its first peak at 370 K and a second peak at 481 K. Note that there are two peaks even though the TL emission is due solely to *electron* recombination and there is only one electron trap. What happens is that, during readout of the electron trap, the centre population becomes depleted: m_1 drops by four orders of magnitude from its initial population. The readout of the electron trap cannot be completed until the temperature is high enough that holes from the hole trap become available to replenish the centre population.

If the free electron concentration was measured, such as via TSC, it would show only one peak despite the TL curve showing two peaks. The peak in n_c also coincides closely with

Table 2. Rate constants used in calculations shown in figures 2 and 3. For irradiation, $X = 5 \times 10^7\,\mathrm{cm^{-3}\,s^{-1}}$ and $t = 1000\,\mathrm{s}$ and, for heating, $\beta = 1\,\mathrm{K\,s^{-1}}$.

	Electron trap	Centre	Hole trap
Total concentration ($\mathrm{cm^{-3}}$)	$N = 10^{12}$	$M_1 = 10^{14}$	$M_2 = 10^{13}$
Electron capture rate constant ($\mathrm{cm^{-3}\,s^{-1}}$)	$A = 10^{-7}$	$A_m = 5 \times 10^{-6}$	—
Hole capture rate constant ($\mathrm{cm^{-3}\,s^{-1}}$)	—	$B_1 = 2 \times 10^{-8}$	$B_2 = 3 \times 10^{-8}$
Activation energy (eV)	$E_1 = 1$	—	$E_2 = 1.3$
Pre-exponential factor ($\mathrm{s^{-1}}$)	$s_1 = 5 \times 10^{12}$	—	$s_2 = 3 \times 10^{12}$

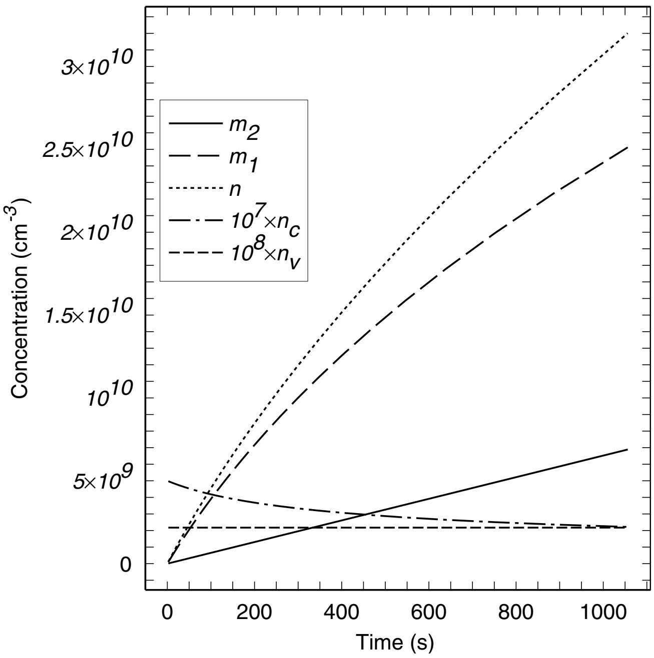

Figure 2. Analytical calculation of level populations as a function of irradiation time. These calculations were performed using the parameters of table 2.

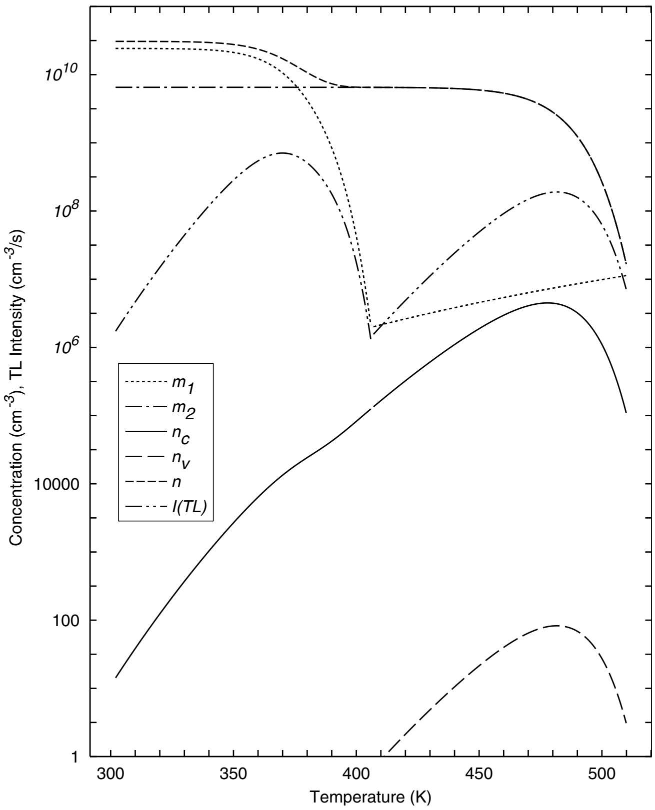

Figure 3. An analytical solution of the readout for the duplicitous peak is shown. The gap in the curves at 406 K is due to the switch from region I model to region II model. These calculations were performed using the parameters of table 2.

the peak for holes, n_v, and the second TL peak. The reason for this can be readily understood from the model of region II. From equation (53), we see that $I \propto n_v$. This means that region II TL peak and the peak in hole concentration, n_v, must coincide. Thus it is not surprising that the analysis of peak shape parameters in Chen *et al* (2008) found that I and n_v had the same peak shape accurate to all decimal places shown. The close similarity between n_v and n_c can be understood by looking at equation (48) which shows that $n_c \sim n_v/m_1$. In region II, as seen in figure 3, m_1 is a slowly rising function of temperature. As a consequence of $n_c \sim n_v/m_1$ and the fact that m_1 is slowly rising with temperature, it is clear that the peak of n_c will be at a lower temperature but near the peak of n_v. The reason that m_1 grows slowly in region II is also easily understood. From equation (50), it is seen that m_1 grows as $m_1 \sim \exp(-(E_2 - E_1)/kT)$. Since, from the parameters of table 2, $E_2 - E_1$ is positive, then m_1 grows in this region. Since $E_2 - E_1$ is only 0.3 eV, this growth rate is small compared with other variables.

The initial rises preceding the second peak are also interesting. The initial rise of free electrons in region II, see equation (51), is determined by E_1. Even though TL is due to recombination of these free electrons, $I = A_m m_1 n_c$, the initial rise of TL in region II does not scale as n_c does but rather is determined by E_2, as is seen from equation (54). The reason that this is possible is because, as noted above, m_1 has a rise determined by $E_2 - E_1$. The initial rise of free holes, n_v, is determined, via equation (32), by E_2. Since, in general, the TSC signal could be dominated either by free holes or free electrons, the initial rise of TSC could depend on either E_2 or E_1. For the example parameters of table 2, the results show that $n_v \ll n_c$, so the TSC signal is likely dominated by n_c and its initial rise would scale as E_1.

The shape of the second TL peak can be understood by combining equation (54) with equation (37) to find

$$I = s_2' \mathrm{e}^{-E_2/kT} m_2 \tag{55}$$

$$= s_2' \mathrm{e}^{-E_2/kT} m_{2,0} \exp\left(-s_2' \int_0^t \mathrm{e}^{-E_2/kT(t')}\,\mathrm{d}t'\right). \tag{56}$$

This shows that region II TL intensity has the shape of a first-order Randall–Wilkins peak with the activation energy of the hole trap, E_2, and an effective pre-exponential factor of s_2' as

Table 3. Rate constants used in the calculation of figures 4 and 5. For irradiation, $X = 5 \times 10^7$ and $t = 1000.0$ s and, for heating, a heating rate of $\beta = 1$ K s^{-1} was used.

	Electron trap	Centre	Hole trap
Total concentration (cm^{-3})	$N = 10^{14}$	$M_1 = 10^{14}$	$M_2 = 10^{14}$
Electron capture rate constant (cm^{-3} s^{-1})	$A = 10^{-9}$	$A_m = 5 \times 10^{-6}$	—
Hole capture rate constant (cm^{-3} s^{-1})	—	$B_1 = 2 \times 10^{-8}$	$B_2 = 3 \times 10^{-8}$
Activation energy (eV)	$E_1 = 1.1$	—	$E_2 = 0.89$
Pre-exponential factor (s^{-1})	$s_1 = 10^{14}$	—	$s_2 = 10^8$

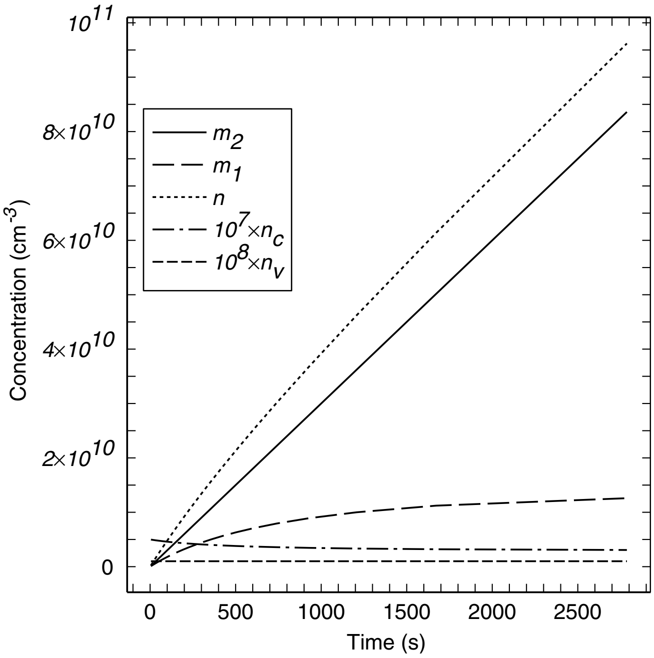

Figure 4. Analytical calculation of level populations as a function of irradiation time using the parameters as shown in table 3. Note that the centre population approaches an asymptotic value even though $m_1 \ll M_1$.

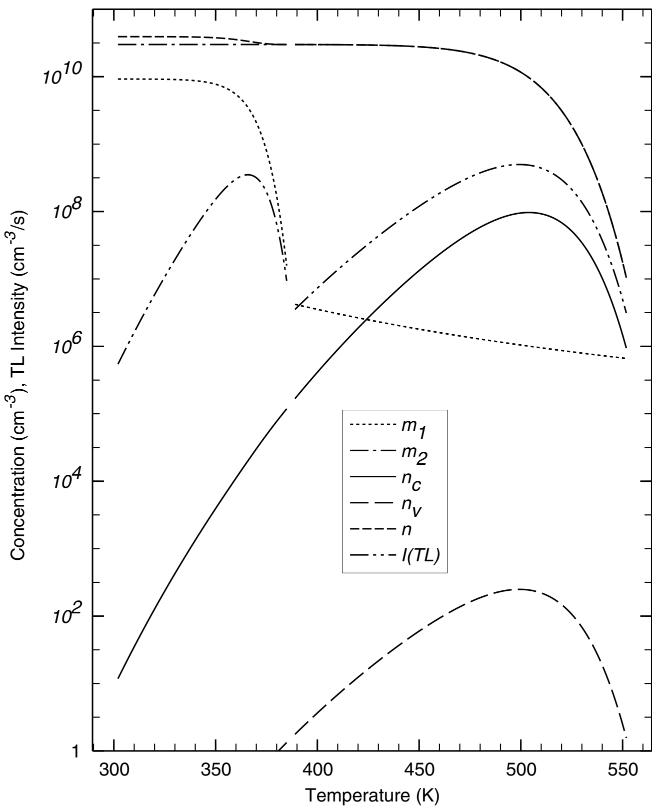

Figure 5. An analytical solution of the readout for the parameters of table 3 is shown. The gap in the curves at 406 K is due to the switch from region I model to region II model.

defined by equation (38). Peak shape analysis on the numerical simulation of the second peak (Chen *et al* 2008) shows a shape factor of $\mu_g = 0.417$ which is consistent with a first-order peak and this theory.

By changing some parameters, we can observe some different features of this system. For the second case, we chose parameters as shown table 3. Using these parameters, the growth of the level populations during irradiation is shown, figure 4. In contrast with the previous case, the centre population, m_1, does not continue growing but instead approaches an asymptotic value of about 1.3×10^{10} cm^{-3}. On the plot, it looks like m_1 is saturating but it is important to note that $M_1 = 10^{14}$ cm^{-3} so that, for the observed saturation, $m_1 \ll M_1$.

For readout, the parameters of table 3 also show some interesting differences. The populations and TL intensity during readout are shown in figure 5 with region I model being used up to 385 K and region II model shown for temperatures between 390 and 550 K. Note that the second TL peak, the duplicitous one, is now much stronger than the first. This is because, as per equation (36), the integrated intensity, $\int I\,dt$, of the first (region I) peak is close to $n_0 - m_{2,0}$ and the integrated intensity of the second (region II) peak is close to $m_{2,0}$. Because of the rate constant changes that affect the irradiation phase, $m_{2,0}$ is, in this case, almost as large as n_0, so the second peak is relatively stronger. Separately, s_1, E_1, s_2 and E_2, were adjusted so that $E_1 > E_2$. Consequently, the centre population, m_1, which grew with temperature in the first case instead declines with temperature in this case. However, it can still be seen that the peaks in n_v, I and n_c are still at nearly the same temperature. Since m_1 is declining, however, the peak of n_c now appears slightly after the peak of TL emission, I.

We also performed numerical solutions of the full non-quasi-steady governing equations and the results agreed very closely with the analytical results that are presented in this section.

4. Conclusion

An analytical model of a three level TL system, covering both irradiation and readout, was developed. The three levels are an electron trap, a recombination centre and a hole trap. The analytical solution was obtained using three main simplifying assumptions: (a) the dose was low enough that all levels remain below saturation, (b) free electrons and holes are quasi-steady and (c) the TL readout of the electron trap begins well before thermal excitation of the hole trap is significant.

This model has the surprising feature, first shown numerically (Chen *et al* 2008), that the hole trap can be responsible for a TL peak that is observed at the same wavelength spectrum as a TL peak due to an electron trap. Further, both the free electrons and free holes reach a peak near this duplicitous TL peak giving the false impression that a single trap is responsible for emitting both holes and electrons.

The existence of this duplicitous TL peak is understood by considering the initial conditions before readout where the electron trap population is n_0, the centre population is $m_{1,0}$ and the hole trap population is $m_{2,0}$. By conservation of charge, $n_0 = m_{1,0} + m_{2,0}$. Thus, readout of the electron trap stops not when the electron trap population is depleted but when centre population, m_1, is depleted. When this occurs, conservation of charge tells us that the remaining concentration in the electron trap is $n = m_{2,0}$. That concentration remains in that trap until thermal excitation of the hole trap begins. At that time, the readout of the electron trap occurs at a rate determined by replenishment of holes in the recombination centre with holes from the hole trap. Thus the second peak is observed to have an initial rise and peak shape associated with the hole trap even though TL emission is due to electron recombination.

This model also shows anomalous behaviour for TSC. The first TL peak, for example, has no TSC peak associated with it. The second TL peak is associated with peaks in both free electrons and free holes. The initial rise in the TSC peak can depend on either the electron trap energy, E_1, or the hole trap energy, E_2, depending on whether the mobilities and other parameters are such that free electrons or free holes dominate the conductivity.

Various experimental observations which inspired the development of this phenomenological model were reviewed by Chen *et al* (2008).

References

Abramowitz M and Stegun I A (ed) 1970 *Handbook of Mathematical Functions* (Washington, DC: US Government Printing Office)

Aitken M J 1985 *Thermoluminescence Dating* (London: Academic)

Chen R and McKeever S W S 1997 *Theory of Thermoluminescence and Related Phenomena* (Singapore: World Scientific London)

Chen R, Pagonis V and Lawless J 2008 *Radiat. Meas.* **43** 162–66

Lawless J, Chen R and Pagonis V 2008 Paper presented at LED2008 *Rad. Meas.* at press

Lawless J and Lo D 2001 *J. Appl. Phys.* **89** 6145–52

Lax M 1960 *Phys. Rev.* **119** 1502–23

McKeever S W S 1985 *Thermoluminescence of Solids* (Cambridge: Cambridge University Press)

Rose A 1963 *Concepts in Photoconductivity and Allied Problems* (New York: Interscience)

Sunta C M, Ayta W E F, Chubaci J F D and Watanabe S 2001 *J. Phys. D: Appl. Phys.* **34** 3285–95

Sunta C M, Ayta W E F, Chubaci J F D and Watanabe S 2002 *Radiat. Prot. Dosim.* **100** 83–86