A model for dose-rate dependence of thermoluminescence intensity

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Abstract. In the applications of thermoluminescence (TL) in dosimetry and archaeological dating, it is usually assumed that the measured TL depends on the total dose applied and it is independent of the dose rate. Thus, calibration of a TL specimen is usually performed at a significantly higher dose rate than that of the dose to be determined. A few experimental accounts in the literature report on dose-rate dependences of TL intensity for a given total dose. One theoretical work published gave a numerical solution of the simultaneous differential equations governing the filling of traps and centres at different dose rates. In the present work, the numerical solution is extended so that it includes the other important stage of TL, namely the heating phase. It is shown that with a rather simple model of one trapping state and two kinds of recombination centres, dose-rate effects may occur. An appropriate choice of the relevant parameters indeed yields one emission, which increases with increasing dose rate, whereas another emission decreases with the dose rate with a constant total dose, in agreement with an experimental result in quartz quoted in the literature.

1. Introduction

Thermoluminescence (TL), the emission of light during heating from solids previously irradiated by different sources, is routinely utilized for dosimetry. Another important application of TL is the dating of ancient archaeological pottery samples as well as of geological samples. In all these cases, the response of the sample to a given dose is to be determined in the laboratory for calibration and in most cases the laboratory dose is administered at a higher dose rate than the original one. The question may arise whether the total dose should be the determining factor concerning the resulting TL intensity. It should be noted that rather complex processes are taking place in the traffic of charge carriers between trapping states and luminescent recombination centres, both during the excitation by irradiation phase and during the heating of the sample. Therefore, there is no reason to believe that the dependence of the TL is always only on the total dose. Even if one thinks of only situations with constant dose excitation of a given sample, the total TL emitted may not be the same if the given dose is imparted at a low dose rate and long time, or at a high dose rate for a short period of time. The existence of several trapping states and recombination centres makes the processes more complicated, which increases the chance that dose-rate effects will occur. Thus, the dose rate and the length of irradiation should be considered, in principle, as two separate parameters.

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Before going into some experimental results reported in the literature concerning dose-rate effects, we should mention a rather trivial effect of dose-rate dependence which may occur but which is not a 'genuine' dose-rate effect. If a sample is irradiated at a temperature rather close to that of the expected TL peak, the thermal decay of the peak takes place simultaneously with the build-up. As a result of this dynamical competition, it is clear that more TL will be emitted with high dose rates and short irradiation times than with low dose rates imparted at longer times. Thus, for example, the dose-rate effect reported by Facey (1966) is merely a result of such thermal decay during excitation. In the present work we will not consider this situation.

A number of researchers studied experimentally the dose-rate effects in different materials and under different excitation conditions. In many of these studies, no dose-rate effects were observed in a very broad range of dose rates (see, e.g., Huntley *et al* 1988, 1993). However, whereas many of these studies resulted in no dose-rate effects, in some other cases such effects were found.

The general feeling by several researchers dealing with archaeological dating that no dose-rate effects are to be expected stems from the early works by Karzmark *et al* (1964) and Tochilin and Goldstein (1966), who observed a dose-rate independent TL response from LiF for dose rates varying from 5 to 1.7×10^8 Gy s^{-1}. Cameron *et al* (1968) and Aitken (1974) used in their books these works as an indication that dose-rate effects are unimportant and that one can always use fast laboratory calibration for the evaluation of doses which have been administered at much lower rates. Of course, the above-mentioned works as well as others not showing dose-rate effects do not prove that dose-rate effects

are impossible in other materials or even in the same materials but in different dose-rate ranges. This is important, in particular in the study of archaeological samples in which the natural dose rate to which the sample is exposed in antiquity may be as low as 10^{-3} Gy/years ($\sim 3 \times 10^{-11}$ Gy s^{-1}) whereas the laboratory dose rate, applied for calibration, may be as high as several Gy s^{-1}. Groom *et al* (1978) reported a decrease of TL by up to a factor of five while the dose rate increased in powdered samples of Brazilian quartz irradiated by ^{60}Co γ-rays ranging from 1.4×10^{-3} to 3.3 Gy s^{-1}. A smaller effect of the same sort was reported by Hsu and Weng (1980). An opposite effect of higher TL for larger dose rate was reported by Kvasnička (1979, 1983) who found the effect in Brazilian and milky quartz excited by ^{60}Co γ-rays, using dose rates from 2×10^{-5} to 2×10^{-2} Gy s^{-1}. The apparent discrepancy between the two sets of results may be due to the different ranges of dose utilized.

Perhaps the most interesting results on dose-rate effects have been reported by Valladas and Ferreira (1980). They distinguish between three components in the emission of TL in quartz, namely, UV, blue and green. Giving the same dose of excitation at two dose rates, which are three orders of magnitude apart, they found different behaviours for the three components. The UV component was nearly twice as large with the high dose rate than with the low dose rate. With the green component, the low dose rate yielded about 10% less than the high one. However, with the blue component, the low dose rate yielded about 50% more TL than the high one. Valladas and Valladas (1982) gave some further details concerning TL results in detrital quartz following annealing at different temperatures, as well as variations of the response of the samples irradiated at the high dose rate (10 Gy min^{-1}) as a function of the temperature during irradiation.

Two recent works also mention dose-rate effects. Chawla *et al* (1998) sum up the previously known evidence on dose-rate effects in quartz and discuss their implication on TL dating. Urbina *et al* (1998) discuss the dose-rate effects of TL in calcites but their results are more complex since they include a combination of γ and β irradiations.

Theoretical work by McKeever *et al* (1980) and Chen *et al* (1981) demonstrated that using rather simple models of trapping states and recombination centres one can obtain a dose-rate dependency of trap filling. Furthermore, Chen *et al* (1981, 1982) also showed that, as far as the centre filling is concerned, when two centres exist in the same material, it is possible for the population of one of them to increase and that of the other to decrease with the dose rate for a given total dose. However, the phenomenon of TL includes also the heating stage, which follows the excitation stage of filling traps and centres and the relaxation stage. Therefore, in order to follow the TL behaviour at different dose rates, one should follow the whole cycle of trap and centre filling during excitation and trap emptying during heating. In the present work, we follow numerically the solution of the sets of simultaneous differential equations governing the processes in these stages, thus demonstrating possible dose-rate behaviours. The model we use here is of one trapping state and two kinds of recombination centres.

2. The model

A basic task in this work is to demonstrate that the dose-rate effect seen in experiments is consistent with the basic models of trapping, detrapping and recombination using reasonable values for the physical parameters. Following the results by Valladas and Ferreira (1980), which showed opposite directions of dose-rate dependence of different spectral components of the TL emission, we included in the model two kinds of recombination centres and one trapping state. The model utilized is shown in figure 1. M_1 and M_2 are the two recombination centres, with M_1 and M_2 the concentrations (e.g. in m^{-3}) of these two kinds of centres. m_1 and m_2 (in m^{-3}) are the instantaneous concentrations of holes in these centres, respectively. The irradiation is assumed to produce electrons and holes at a rate of x (m^{-3} s^{-1})† in the conduction and valence bands, respectively. The instantaneous concentration of electrons in the conduction band is denoted by n_c (m^{-3}) and that of holes in the valence band by n_v (m^{-3}). B_1 and B_2 (m^3 s^{-1}) are the probabilities of capturing holes in M_1 and M_2, respectively, whereas A_{m1} and A_{m2} (m^3 s^{-1}) are, respectively, the two recombination probabilities of free electrons with captured holes. It is to be noted that although the nearly constant magnitudes A_{m1} and A_{m2} are usually termed 'recombination probabilities', in fact, their multiplication by a concentration yields a magnitude that is probability per second (e.g. $A_{m1}m_1$). The same is true for the hole trapping probabilities B_1 and B_2 as well as for the retrapping probability A_n. These magnitudes (the A's and B's) can be defined as the product of the cross section for trapping/recombination and the thermal velocity of the free carriers, for example $A_n = \sigma_n \cdot v$ where σ_n is the cross section for retrapping (in m^2) and v (m s^{-1}) is the thermal velocity of free electrons in the conduction band. These recombinations take place both during the excitation stage and during the heating of the sample. Both transitions into M_1 and M_2 are considered to be radiative, but with different wavelengths, so that it is assumed that each emission can be measured separately. This relates mainly to the work by Valladas and Ferreira (1980), and to the 'UV' and 'Blue' emissions they saw from quartz. Of course, under different conditions, only one of these emissions may be measured since the other one is either radiationless or radiative, but not measurable due to a mismatch with the sensitivity spectrum of the photomultiplier. N (m^{-3}) denotes here the total concentration of electron trapping states which is a constant and n (m^{-3}) the instantaneous concentration of filled traps which is a variable. E (eV) and s (s^{-1}) are the activation energy and frequency factor of the electron trap, respectively, k is the Boltzmann constant (eV K^{-1}) and A_n (m^3 s^{-1}) is the trapping (retrapping during heating) probability of electrons from the conduction band. All these magnitudes play a part in the excitation stage. This is followed by a relaxation stage that will be discussed below. During this stage as well as during the heating stage, it is obvious that no electron–hole production takes place, which means that during these stages,

† The dose rate and total dose are given here in units of m^{-3} s^{-1} and m^{-3} respectively. These are, in fact, the rate of electron–hole pair production and the total number of electron–hole pairs produced. For transition to the units of Gy s^{-1} and Gy, see below. Of course, any other suitable units can be used.
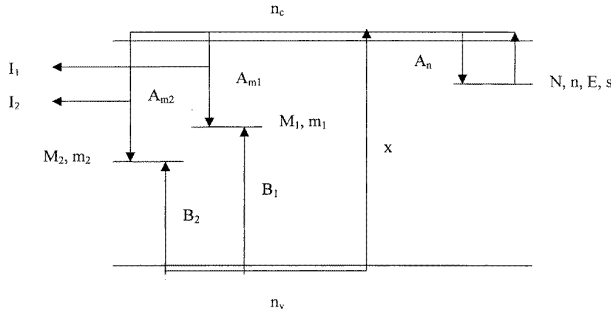
Figure 1. The energy level scheme of a solid with one trapping state and two recombination centres. The transitions taking place both during the excitation and the heating of the sample are shown. The meaning of the different parameters and the values chosen for them are given in the text.

$x = 0$. Also, M_1 and M_2 are assumed to be rather far from the valence band, thus no holes are 'raised' (energy-wise) into the valence band and therefore $n_v = 0$; thus B_1 and B_2 are irrelevant during this stage. As opposed to this, electrons from N may be thermally released into the conduction band and then either retrap or recombine with holes in M_1 and M_2.

The set of coupled differential equations governing the process during the excitation stage is

$$dn_v/dt = x - B_1(M_1 - m_1)n_v - B_2(M_2 - m_2)n_v \quad (1)$$

$$dm_1/dt = -A_{m1}m_1 n_c + B_1(M_1 - m_1)n_v \quad (2)$$

$$dm_2/dt = -A_{m2}m_2 n_c + B_2(M_2 - m_2)n_v \quad (3)$$

$$dn/dt = A_n(N - n)n_c \quad (4)$$

$$dn_c/dt = dm_1/dt + dm_2/dt + dn_v/dt - dn/dt. \quad (5)$$

For a given set of trapping parameters, these equations were numerically solved using the *ode23* solver in the MatLab package, for a time of excitation t_D. Thus, the dose of excitation is $D = xt_D$. Concerning the dimensions of D, see the footnote above. Since at the termination of the excitation we end up with $n_c \neq 0$ and $n_v \neq 0$, in order to follow the experimental conditions the solution procedure is continued for a further period of relaxation time with $x = 0$ until the values of n_c and n_v become negligible.

The next stage is to solve the relevant set of simultaneous differential equations during the heating phase, when the final values for the functions n, m_1, m_2, n_c and n_v calculated in the excitation+relaxation stages are used as initial values for the next stage. The set of simultaneous differential equations governing the process at the heating phase is given by

$$-dm_1/dt = A_{m1}m_1 n_c \quad (6)$$

$$-dm_2/dt = A_{m2}m_2 n_c \quad (7)$$

$$dn/dt = -sn\exp(-E/kT) + A(N - n)n_c \quad (8)$$

$$dn_c/dt = dm_1/dt + dm_2/dt - dn/dt. \quad (9)$$

The same MatLab *ode23* solver was used to solve this set of equations, this time with the temperature changing linearly with a constant heating rate β, namely

$$T = T_0 + \beta t \quad (10)$$

where T_0 is the initial temperature at the beginning of heating. Both recombinations into m_1 and m_2 are considered to be radiative, but separable. Thus, the intensity in photons per m^3 per s of one spectral component of TL is proportional to the rate of change of m_1, i.e.

$$I_1(T) = -dm_1/dt \quad (11)$$

and the second spectral component is assumed to be proportional to the rate of change of m_2, namely,

$$I_2(T) = -dm_2/dt. \quad (12)$$

The right-hand side of equations (11) and (12) could have included a constant with dimensions that would have changed the $m^{-3}\,s^{-1}$ dimension on the right-hand side to light intensity dimensions on the left-hand side. Without loss of generality, however, we choose the constant to be unity, which, in fact, defines new units for the light intensity.

3. Numerical results

Sets of plausible parameters were looked for which could demonstrate the desired behaviour of having one spectral component increasing with the dose rate and another decreasing, when the sample in hand undergoes the same heating following excitation. Also, the range of temperatures in which the peaks occur should be the same as that reported by Valladas and Ferreira (1980), namely, 325–375 °C (600–650 K). Using parameters in the same range as chosen by Chen *et al* (1981) (though not exactly the same), and after some trial and error, the following set of parameters was found to yield quite convincing results: $E = 1.38$ eV; $s = 10^{10}\,s^{-1}$; $A_{m1} = 10^{-18}\,m^3\,s^{-1}$; $A_{m2} = 10^{-19}\,m^3\,s^{-1}$; $B_1 = 10^{-19}\,m^3\,s^{-1}$; $B_2 = 1.5 \times 10^{-21}\,m^3\,s^{-1}$; $N = 10^{20}\,m^{-3}$; $M_1 = 10^{20}\,m^{-3}$; $M_2 = 10^{21}\,m^{-3}$; $A_n = 3 \times 10^{-20}\,m^3\,s^{-1}$.

Figure 2 depicts the result of the solution of the equations in the sequence of excitation–relaxation–heating with the set of chosen parameters and with $x = 10^{18}\,m^{-3}\,s^{-1}$ and $t_D = 10^3$ s. The dotted curve indicates the intensity as a function of temperature of $I_1(T)$, whereas the full curve shows $I_2(T)$. Note that the shape of the peaks shows the effect of competition in the range of overlap; $I_1(T)$ is narrow at its fall-off part whereas $I_2(T)$ is narrow in the low-temperature half.

We digress here to give the range of dose rates and doses, in Gy s^{-1} and Gy, respectively, associated with the x values chosen. Let us consider LiF which has a specific gravity of 2.6 or a density of 2600 kg/m^3. According to Avila *et al* (1999), an average of 36 eV is required for heavy charged particles to produce one electron–hole pair, and ∼34 eV for γ-rays (this is about three times the band gap). Since 1 Gray equals 1 J kg^{-1} and 1 J equals 6×10^{18} eV, the number of pairs produced per kg when 1 Gy is applied is about 1.7×10^{17}. Therefore, the number of pairs produced in m^3 is 4.4×10^{20}. Thus, $x = 10^{18}\,m^{-3}\,s^{-1}$ is equivalent to 2.3×10^{-3} Gy s^{-1} and $x = 10^{22}\,m^{-3}\,s^{-1} = 23$ Gy s^{-1}. The transition shown in figure 4 around $10^{20}\,m^{-3}\,s^{-1}$ for the given set of parameters occurs at ∼0.23 Gy s^{-1}. This is within the range given by Groom *et al* (1978), mentioned above. The total dose of
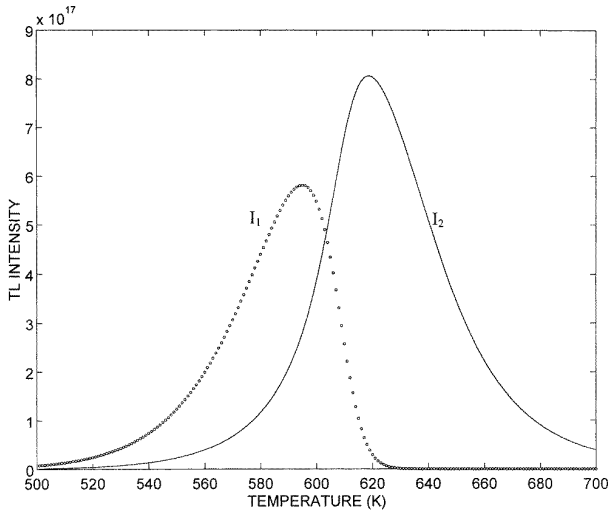
Figure 2. Two TL peaks as calculated with the model of two recombination centres and one trapping state. The set of parameters chosen is given in the text and the dose rate is 10^{18} m^{-3} s^{-1}. The dashed curve represents I_1, whereas the full curve represents I_2.
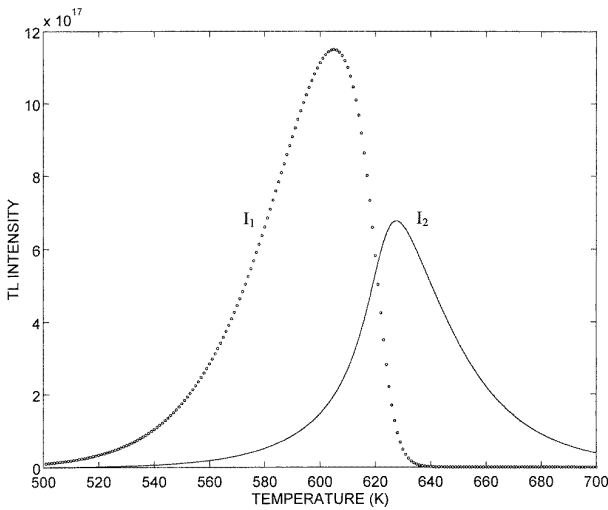

Figure 3. Same as in figure 2, but the dose rate is 10^{22} m^{-3} s^{-1}. The total dose is 10^{21} m^{-3}, the same as in figure 2.

10^{21} m^{-3} is, in fact, 2.3 Gy. The situation with quartz should be, more or less, similar to that with LiF.

Figure 3 shows the results of the same two peaks following an excitation with $x = 10^{22}$ m^{-3} s^{-1} for only $t_D = 0.1$ s. The total dose is the same in the two cases, with x increased to 10^{22} m^{-3} s^{-1} and t_D reduced to 0.1 s. It is readily seen that I_1 increases by a factor of nearly two whereas I_2 decreases by $\sim$20%.

Figure 4 depicts the variation of the maximum intensity of I_1 and I_2 with the dose rate varying gradually within this range of four orders of magnitude at constant total dose. It is to be noted that most of the variation occurs within about two orders of magnitude in the dose rate, both in the increasing and decreasing glow peak. In order to understand the source of this variation of the two peaks with the dose rate, we also monitored the filling of the trap and the centre at the end of the excitation plus relaxation.
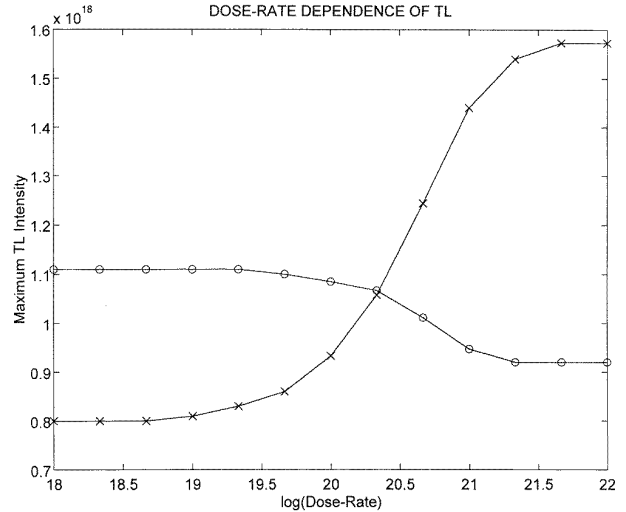

Figure 4. The dose-rate dependence of the maximum values of $I_1(T)$ (circles) and of $I_2(T)$ ($\times$), for the set of parameters stated above. The strong increase in the maximum of I_1 and the decrease in the maximum of I_2 are clearly seen, at a constant total dose.

The results with $x = 10^{18}$ m^{-3} s^{-1} and $t_D = 1000$ s were $m_1 = 2.67 \times 10^{19}$ m^{-3}, $m_2 = 4.61 \times 10^{19}$ m^{-3} and $n = 7.28 \times 10^{19}$ m^{-3}. With $x = 10^{22}$ m^{-3} s^{-1} and $t_D = 0.1$ s, we found $m_1 = 5.65 \times 10^{19}$ m^{-3}, $m_2 = 3.37 \times 10^{19}$ m^{-3} and $n = 9.02 \times 10^{19}$ m^{-3}. The $\sim$24% increase in the final n value can be explained by suggesting that fewer annihilations (through the recombination centres) take place in the shorter time (0.1 s). It is much more difficult to follow the different competing transitions so as to give an intuitive explanation to the dose-rate effect. The transition of electrons associated with A_{m1} competes with that associated with A_{m2} and both compete with the retrapping associated with A_n. Also the transition of holes associated with B_1 competes with that associated with B_2. Of course, the electron and hole transitions taking place during excitation are coupled since m_1 and m_2 participate in both kinds of transition.

The values of m_1 and m_2 at the end of the excitation plus relaxation and prior to the heating are qualitatively commensurate with the intensities of peak 1 and peak 2, respectively, shown in figures 2 and 3 with the low and high dose rates. This indicates the importance of the competition during the irradiation in the excitation stage. However, the fact that these concentrations are not really proportional to the calculated TL intensities shows the importance of competition during heating in determining the final results.

4. Conclusion

In the present work, we have discussed an energy level model for a thermoluminescent material that includes one trapping state and two kinds of recombination centre. We followed the stages of excitation, relaxation and heating. By solving the appropriate sets of coupled differential equations in sequence we showed that, for appropriate choices of the sets of trapping parameters, two TL peaks occur related to two recombination centres; thus they are expected to have different emission spectra. We then simulated the situation of applying a given dose at different dose rates and found that at certain choices

of the parameters, one peak may increase with the dose rate whereas the other decreases.

The results of the variations are not identical with those reported for the UV and blue components of quartz and, indeed, we do not claim that we have the real parameters involved in that sample. However, the behaviour resembles the experimental results qualitatively with even the small shift in the maximum temperature occurring in the same way with the variation of the dose rate. As for the 'green' emission reported by Valladas and Ferreira, we have not included it in the present theoretical account since its variation with the dose rate was rather small.

Of course, the same model demonstrates also the possibility, described in the literature, of having only one TL peak that increases or decreases with the dose rate. This is the case when one of the transitions described in the present work is either radiationless or radiative but not measurable with the existing detecting device.

In comparison with the previous work cited above, it is obvious that the present model is more comprehensive in the sense that both the excitation and heating stages are being considered, whereas in the previous work only the filling of traps and centres during excitation were considered. It is evident that the competition occurring during the heating phase plays an important role, although the comparison of the trap and centre filling with low and high dose rates indicates that with the present set of chosen parameters, the competition during excitation is of greater importance. Anyway, the simulation described here can be considered to be complete since both parts of the process are followed.

References

Aitken M J 1974 *Physics and Archaeology* 2nd edn (Madison, WI: Oxford University Press)

Avila O, Gamboa-de Buen I and Brandan M E 1999 Study of the energy deposition in LiF by heavy charged particle irradiation and its relation to the thermoluminescent efficiency of the material *J. Phys. D: Appl. Phys.* **32** 1175–81

Cameron J R, Suntaralingam N and Kenney G N 1968 *Thermoluminescent Dosimetry* (Madison, WI: University of Wisconsin Press)

Chawla S, Gundu Rao T K and Singhvi A K 1998 Quartz thermoluminescence dose and dose-rate effects and their implications *Rad. Meas.* **29** 53–63

Chen R, McKeever S W S and Durrani S A 1981 Solution of the kinetics equations governing trap filling. Consequences concerning dose dependence and dose-rate effects *Phys. Rev.* B **24** 4931–44

——1982 Dose-rate dependence of thermoluminescence: the possibility of different behaviours of different peaks *Eur. PACT J.* **6** 295–301

Facey R A 1966 Heating-rate effects in glow peak measurements for thermoluminescent dosimetry *Health Phys.* **12** 717–20

Groom P J, Durrani S A, Khazal K A R and McKeever S W S 1978 The dose-rate dependence of thermoluminescence and sensitivity in quartz *Eur. PACT J.* **2** 200–10

Hsu P C and Weng P S 1980 Reaffirmation on the low exposure rate dependence of the CaSO$_4$:Dy thermoluminescent dosimeter *Nucl. Instrum. Methods* **174** 73–6

Huntley D J, Godfrey-Smith D I, Thewalt M L W, Prescott J R and Hutton J J 1988 Some quartz thermoluminescence spectra relevant to thermoluminescence dating *Nucl. Tracks Rad. Meas.* **14** 27–33

Huntley D J, Hutton J T and Prescott J R 1993 The stranded beach-dune sequence of south-east Australia: A test of thermoluminescence dating, 0–800ka. *Quat. Sci. Rev.* **12** 1–20

Karzmark C J, White J and Fowler J F 1964 Lithium fluoride thermoluminescence dosimetry *Phys. Med. Biol.* **9** 273–80

Kvasnička J 1979 Dose-rate and flux density of cosmic muons estimate by TLD method *Health Phys.* **36** 521–4

——1983 TL response dependence on the dose-rate and its consequences *Int. Appl. Rad. Isot.* **38** 713–15

McKeever S W S, Chen R, Groom P J and Durrani S A 1980 Dose-rate dependence of thermoluminescence response *Nucl. Instrum. Methods* **175** 43–4

Tochilin E and Goldstein N 1966 Dose-rate and spectral measurements from pulsed x-ray generators *Health Phys.* **12** 1705–9

Urbina M, Millan A, Beneitz P and Calderón T 1998 Dose-rate effect in calcite *J. Lumin.* **79** 21–8

Valladas G and Ferreira J 1980 On the dose-rate dependence of the thermoluminescence response of quartz *Nucl. Instrum. Methods* **175** 216–8

Valladas G and Valladas H 1982 Influence du débit de dose sur la thermoluminescence du quartz (II) *Eur. PACT J.* **6** 281–91

Wintersgill M C and Townsend P D 1978 The non-linear response of thermoluminescence at different dose-rates *Radiat. Eff.* **38** 113–18