Competition between excitation and bleaching of thermoluminescence

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Abstract. The bleaching of thermoluminescence (TL) yield to a residual value by light is explained, at least in some cases, to be due to an equilibrium between excitation and de-excitation by the illuminating light. Kinetic differential equations are given governing the process for the simple case of a single trapping state for electrons and a single variety of hole recombination centre. The equations are solved numerically for chosen sets of the relevant parameters starting either from empty traps and centres or from highly populated ones. In agreement with experimental results, the numerical computation predicts that after a long enough illumination the process of filling of the traps converges to the same equilibrium value as that produced by bleaching. It is also found that the equilibrium value is independent of the light intensity, though, of course, this equilibrium is approached faster with more intense light. The computed dependencies of the filling of trapping states as a function of illumination time are shown. The final equilibrium value for the filling of trapping states can also be evaluated analytically for any set of given parameters; these compare very favourably with the calculated results. The change of the results with the variation of the relevant parameters is discussed.

1. Introduction

Exposure to sunlight has been considered to be the cause for zeroing TL in sea sediments (Wintle and Huntley 1979). Huntley (1985) pointed out that some traps in minerals are emptied very quickly by sunlight; others require longer times and some traps may not be completely emptied by sunlight at all. Singhvi et al (1982) also reported that exposure to sunlight causes the bleaching of sediments to a residual value of TL rather than to zero even when the exposure is very long. Spooner et al (1988) have studied the bleaching of TL in quartz and found different behaviours for different wavelengths. Whereas 320 nm light was very efficient in bleaching the TL peaks, 370 nm light was less effective and 500 nm light was even less effective. Light of 500 nm wavelength brought about a decrease of the TL intensity to a residual value only after a very long exposure. Similar results have been reported by Shlukov and Shakhovetz (1987) on an apparently different kind of quartz. These authors explained their results in terms of an equilibrium between bleaching and excitation produced by the illuminating UV light

they used. In order to show that excitation is a factor in reaching this equilibrium these researchers de-activated their samples thermally and then illuminated them by the same UV light source. This resulted in the excitation of the same TL peaks. Thus Shlukov and Shakhovetz conclude that the equilibrium value is reached as a result of competing UV excitation and bleaching processes whether one starts from a highly excited sample or with an entirely unexcited one. Preliminary results of the same nature with apparently a different type of quartz and with the use of visible light have been found by Prescott and Fox (private communication).

To be noted in this connection is a much older work on TL in semiconducting diamonds by Halperin and Chen (1966). In this work, a TL peak at ~150 K was reported to be strongly excited by a band-to-band transition using 225 nm (5.5 eV) UV light. Longer-wavelength light was found to bleach this peak. When light with wavelength >400 nm was used, complete bleaching would result. However, when light in the wavelength range 400 nm > λ > 300 nm was used, bleaching could only be achieved down to a residual value even after a long exposure. When an unexcited sample was illuminated with light in this same wavelength range, the same build-up equilibrium value was reached after a long exposure. Here also, the effect was explained to be a result of competition between excitation and bleaching caused by light of given wavelength.

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Figure 1. Diagrammatic representation of the simple kinetic model for the excitation and bleaching of a TL phosphor under continuous light irradiation.

Also to be noted is a recent work by Jones *et al* (1988) studying the zero-setting (bleaching) of different samples of sand from sand dunes in Castelforziano, Italy. As expected, sand from the dunes give increasingly more TL the older the dune. Exposure to bleaching by a sunlamp produced lower residuals as a percentage of the initial TL intensity the older the dune from which the sample is taken. For 'active dune' samples, yielding the lowest values of TL, exposure to the same sunlight source resulted in an increase of the TL.

In the present work, we give a simple theoretical account of this kind of competition.

2. The model

In order to explain semiquantitatively the possibility of reaching equilibrium between excitation and bleaching using a certain wavelength, usually in the visible or UV, the simplest model for the process is selected. The phosphor material is assumed to possess a single type of electron trap (e-trap) site and a single type of recombination center (r-centre).

When high-energy radiation is being used, the excitation process in this model is usually explained to be that due to exciting an electron from the valence to the conduction band in a band-to-band transition. The electrons in the conduction band may be trapped at the e-trap sites whereas the remaining holes in the valence band may be trapped at the r-centres. A subsequent heating would thermally raise the electrons from the trap into the conduction band from where they can recombine with trapped holes, yielding the TL.

In the present situation, when lower-energy light (unable to produce a band-to-band transition) is used, photons may still be able to elevate electrons from neutral r-centres into the conduction band leaving a trapped hole behind. This transition is expected to be much less probable than the excitation of electrons from the valence to the conduction band by high-energy radiation, but it is of great importance in the present context. The electrons thus raised can either be trapped in an e-trap or recombine with a hole at a r-centre. In a similar way, this light may release a trapped electron from an e-trap. Once in the conduction band, this electron can either be retrapped or recombine with a hole at an r-centre. The relative effectiveness of raising electrons from occupied e-traps and r-centres empty of holes should depend on the specific properties of the e-trap and r-centre involved, as well as on the wavelength of light used. Thus, it is conceivable that certain wavelengths will favour the excitation whereas others will preferentially produce de-excitation. The equilibrium values expected after a long exposure will depend on these factors. It is to be noted that, although reference so far has been to a situation in which a narrow wavelength range is used for bleaching or excitation, the model should be able
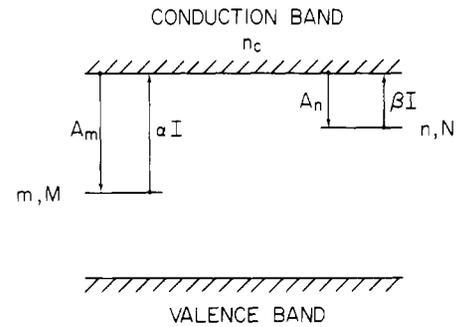
to cover the more general situation of a broad range of wavelengths as well (e.g. such as for a sun exposure). In this case the whole spectrum itself would be expected to have effective probability for raising electrons from e-traps and from r-centres.

A schematic diagram of the energy levels involved and the relevant designations for the various quantities is shown in figure 1. n, n_c and m (all in units of cm^{-3}) are the occupation numbers of electrons at e-traps, the number of electrons in the conduction band and the occupation number of holes at r-centres respectively. These are functions of time. Their initial values will be denoted by n_0, n_{c0} and m_0 (cm^{-3}) which may be all zero in an unexcited sample or non-zero value in an excited sample. N and M (cm^{-3}) are, respectively, the total numbers of e-trap sites and r-centre sites. A_m and A_n are the recombination and retrapping probabilities (cm^3 s^1). I is the intensity of light illuminating the sample in arbitrary units (which can be, for example, photons/s cm^2). α and β are the efficiencies of raising electrons from r-centres and e-traps respectively, their dimensions are such that αI and βI have dimensions of s^{-1}. The kinetic equations governing the process are

$$\frac{dm}{dt} = \alpha I(M - m) - A_m m n_c \qquad (1)$$

$$\frac{dn}{dt} = -\beta I n + A_n(N - n)n_c \qquad (2)$$

and

$$\frac{dn_c}{dt} = \frac{dm}{dt} - \frac{dn}{dt}. \qquad (3)$$

Before describing the numerical procedure and results, some simple analytical conclusions should be noted. In the framework of this simple model including only a single trapping state and a single kind of recombination centre,

$$m = n + n_c. \qquad (4)$$

Furthermore, as long as the light intensity used is not extremely large, n_c is substantially smaller than n and therefore $m = n$. This turns out to be the case for all the results of the computations described below.

Clearly equilibrium can be described by having the net rate of change of the occupation numbers equal to zero, i.e.

$$\frac{dm}{dt} = \frac{dn}{dt} = \frac{dn_c}{dt} = 0. \tag{5}$$

These equilibrium conditions associated with equations (1) and (2) yield

$$\alpha(M - m)I = A_m mn_c \tag{6}$$

and

$$\beta In = A_n(N - n)n_c. \tag{7}$$

Combining these two equations for $n_{eq} = m_{eq}$, the equilibrium values, we get

$$n_{eq}^2(\beta A_m - \alpha A_n) + n_{eq}\alpha A_n(M + N) - \alpha A_n MN = 0. \tag{8}$$

The solution of this quadratic equation should yield the equilibrium value n_{eq} to which the total area under the TL glow curve should be proportional. If $\beta A_m = \alpha A_n$ which, in a sense, means that the recombination and trapping have the same efficiency, equation (8) reduces to a simple first-order equation in n_{eq}, the solution of which is

$$n_{eq} = MN/(M + N). \tag{9}$$

If $\beta A_m \neq \alpha A_n$, the obvious solution of equation (8) is

$$n_{eq} = \{-\alpha A_n(M + N) \pm [\alpha^2 A_n^2(M + N)^2 \\ + 4\alpha A_n MN(\beta A_m - \alpha A_n)]^{1/2}\}/[2(\beta A_m - \alpha A_n)]. \tag{10}$$

It can be easily shown that the expression under the square root is always positive. It is also obvious that the two possible solutions have opposite signs, and that only the positive one may have physical significance. Thus, when $\beta A_m > \alpha A_n$ one should choose the plus sign, and when $\beta A_m < \alpha A_n$, the minus sign should be chosen.

3. Numerical solution

The three simultaneous differential equations (1)–(3) were numerically solved using a Runge–Kutta sixth-order predictor-corrector program. For each set of chosen parameters the program was run once starting from entirely empty e-traps and r-centres, and again starting with e-traps and r-centres completely filled or saturated. It is to be noted that within the framework of the single e-trap and single r-centre model, the maximum occupancy of e-traps and r-centres is $m_0 = n_0 = \min(M, N)$. The results of a number of runs are shown in the following figures. In each case, the final equilibrium result was compared with n_{eq} derived from equation (8) with the same parameters. These results always agreed to better than 0.1%.

It is important to realise that a certain number of free electrons, n_c, remain in the conduction band at
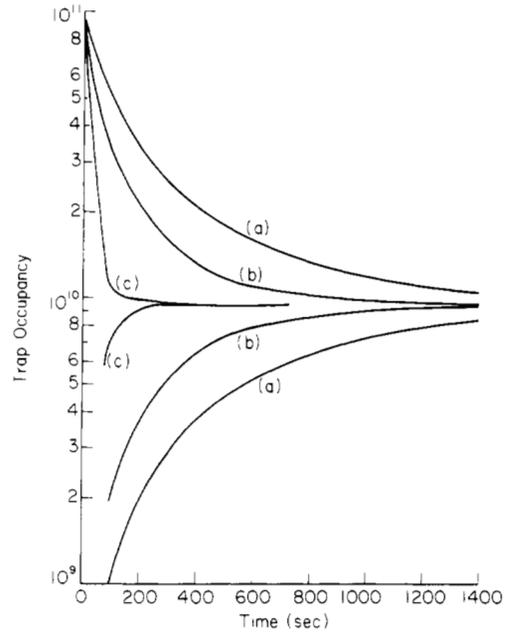

Figure 2. Excitation and bleaching curves with parameters $\alpha = 10^{-15}$, $\beta = 10^{-12}$, $A_m = A_n = 10^{-9}$ cm^3 s^{-1}, $N = 10^{12}$ cm^{-3} and $M = 10^{11}$ cm^{-3}. In curves (a) $I = 10^{10}$, in (b) $I = 2 \times 10^{10}$ and in (c) $I = 10^{11}$. The value of $n_{eq}/n_0 \simeq 0.10$.

the end of the illumination period even if equilibrium has been reached. When the light is turned off, these decay partly into the holes at r-centres and partly into the e-traps, thus decreasing m and increasing n. In order to simulate this situation, the program is allowed to continue for a certain period of time with $I = 0$ at the end of each period of illumination until n_c practically vanishes. We thus end up with $n = m$ to which the subsequent total TL should be proportional.

Figure 2 depicts the results of the computation for the following parameters: $\alpha = 10^{-15}$, $\beta = 10^{-12}$, $A_m = A_n = 10^{-9}$ cm^3 s^{-1}, $N = 10^{12}$ cm^{-3}, $M = 10^{11}$ cm^{-3}. As mentioned above, the units for αI and βI are s^{-1}. In curves (a) $I = 10^{10}$, in (b) $I = 2 \times 10^{10}$, and in (c) $I = 10^{11}$. The approach to the same equilibrium value is clearly evident and, obviously, the approach to this asymptote is faster with larger values of I. The value of n_{eq} found from equation (10) is 9.469×10^9 for these given parameters, in excellent agreement with the numerical results. Note that for $I = 10^{10}$, the growth to one half of the equilibrium value takes ~530 s whereas the decay to one half the original value minus n_{eq} takes ~120 s. With $I = 2 \times 10^{10}$, the corresponding numbers are ~260 s and ~40 s respectively.

Figure 3 shows the results of similar computations with $\alpha = 10^{-17}$ and $I = 2 \times 10^{12}$. Whereas in the previous case the equilibrium value was about 10% of the saturated value, here it is about 1%. The value of n_{eq} calculated from equation (10) is 9.945×10^8, again agreeing very well with the numerical results. Here the decay to half the maximum intensity takes ~20 s, whereas the increase to 50% of the equilibrium value takes ~280 s.
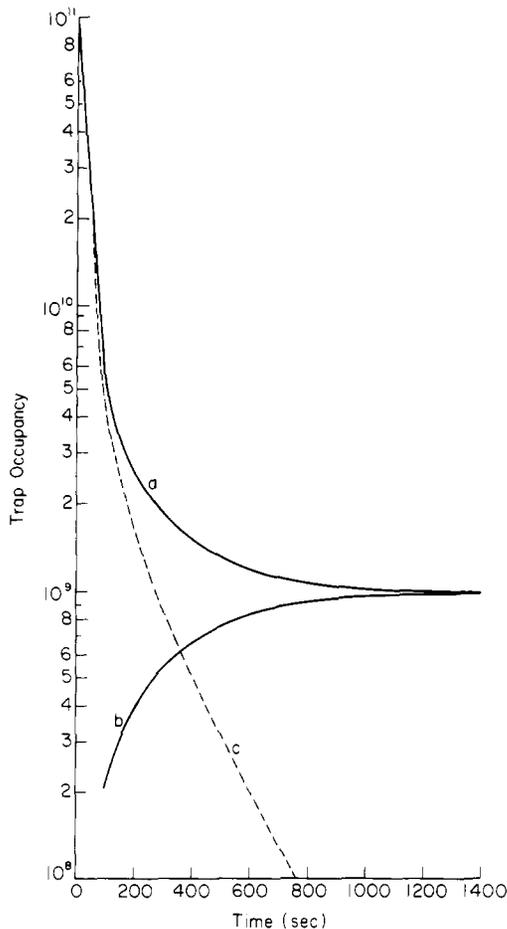
Figure 3. Excitation and bleaching curves with the same parameters as in figure 2 except $\alpha = 10^{-17}$. The value of I is 2×10^{12} for both bleaching (a) and excitation (b). The value of $n_{eq}/n_0 \simeq 0.01$. Curve (c) is for $n - n_{eq}$ for bleaching.

Figure 4. Excitation and bleaching curves as before but with $\alpha = 10^{-13}$. The value of I is 2×10^{12} for both bleaching (a) and excitation (b). The value of $n_{eq}/n_0 \simeq 0.60$. Curve (c) is for $n - n_{eq}$ for bleaching.

Figure 4 shows the results with $\alpha = 10^{-13}$ and $I = 2 \times 10^{10}$ with the other parameters remaining the same as before. The value of n_{eq} from equation (10) is 6.073×10^{10}, again in good agreement with the numerical results. The rise time to 50% of the final equilibrium value is ~ 190 s whereas the decay to half intensity is ~ 140 s.

The ratio of the rise time to one half of the equilibrium value n_{eq} to the decay time to half the value of $n_0 - n_{eq}$ varies from 1.4 when $n_{eq}/n_0 = 0.60$, to about 4.8 when $n_{eq}/n_0 = 0.10$, and to about 14 when $n_{eq}/n_0 = 0.01$. Thus the smaller the equilibrium value left after bleaching the longer the relative time it takes to rise to this equilibrium value starting with empty traps (and the same illuminating light intensity).

Curves c in figures 3 and 4 show the values of $n - n_{eq}$ as a function of time under bleaching conditions. When all early illumination times are included the results do not consist of a simple exponential decay curve. Thus bleaching is not simply of the form $n = n_0 e^{-\lambda t} + n_{eq}$.

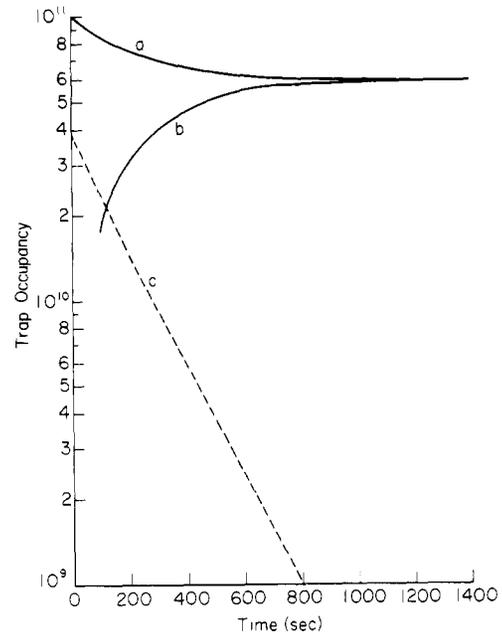In all cases examined the equilibrium value of n_c was two to three orders of magnitude smaller than m or n.

4. Discussion

Three simultaneous differential equations, simulating the simplest situation of excitation and de-excitation of e-traps and r-centres are presented. The equations are solved numerically starting from empty and full trapping states and the results show the approach to equilibrium values in both cases. For a given set of parameters, it is found that for long enough exposure the same equilibrium is reached independent of the initial filling and the exposure intensity. Simple analytical results of the equilibrium condition always yield practically the same value as the numerical solutions. It is to be remembered that the present account is limited to cases in which the light used is capable of exciting the TL peak in question while starting from empty e-traps and r-centres.

In some cases bleaching down to a residual equilibrium value has been reported, whereas no excitation could be found with light of the same wavelength range when starting from empty trap states. One possible explanation is that at least two components are present in the TL glow curve, one of which is entirely bleachable while the other one is not bleachable at all. Another partial explanation may be related to our present model findings that the relative 'half-lives' for excitation and de-excitation vary dramatically depending on the ratio of n_{eq}/n_0. When n_{eq}/n_0 is large these two half-lives are quite similar. However, when n_{eq}/n_0 is small the half-life for excitation may be many times longer than for de-excitation. For example when $n_{eq}/n_0 = 0.01$ it takes approximately 14 times longer to rise to half the equilibrium value compared with the

time it takes to bleach one half the way from the initial TL value to the equilibrium value. Thus in experimental situations, particularly those in which bleaching reveals equilibrium values of n_{eq}/n_0 that are small, sufficient time must be allowed for filling from low trap concentrations to permit a substantial near-equilibrium state to be reached.

As expected the equilibrium states reached are independent of the intensity I. This can be seen in equations (8)–(10) and confirmed by the numerical results. The magnitude of I does of course change the time required to reach near-equilibrium values (e.g. as seen in figure 2).

In the expressions for equilibrium (8) and (10) it is seen that α is always associated with A_n (the excitation branch) and β with A_m (the de-excitation branch). Thus, while trying different parameters, only variations of αA_n on one hand and βA_m on the other should be considered. In particular, if $\alpha A_n = \beta A_m$, there results $n_{eq} = MN/(M + N)$. If $M \approx N$ this results in $n_{eq} = N/2$. On the other hand, if there is a substantial difference between N and M, n_{eq} will be equal to the smaller of N or M.

References

Halperin A and Chen R 1966 *Phys. Rev.* **148** 839–45
Huntley D J 1985 *Phys. Chem. Miner.* **12** 122–7
Jones F H, Rendell H M and Townsend P D 1988 Synopses from a workshop on long and short limits in luminescence dating *Oxford Occasional Publication No 9*
Shlukov A I and Shakhovetz S A 1987 *Ancient TL* **5** (1) 11–5
Singhvi A K, Sharma Y P and Agrawal D P 1982 *Nature* **295** 313–15
Spooner N A, Prescott J R and Hutton J T 1988 *Q. Sci. Rev.* **7** 325–9
Wintle A G and Huntley D J 1979 *Nature* **279** 710–12