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SUPERLINEARITY IN THERMOLUMINESCENCE REVISITED

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Abstract — The dependence of thermoluminescence (TL) on the excitation dose was found in some cases to be superlinear. In particular, the peak at 110°C in an unannealed synthetic quartz showed quadratic and super-quadratic behaviour. This strong superlinearity was explained by the possibility that electrons released during the heating phase may recombine with trapped holes yielding TL, get retrapped or get trapped in a competing state. The strong superlinearity was shown in a previous theoretical study to occur, using approximations such as small retrapping and small rate of change of free electrons concentration. In another theoretical work, superlinearity of the filling of traps was found by assuming a competition during the excitation phase. In the present work the solution of the excitation equations has been carried out first. The relaxation of excited carriers at a constant temperature was then simulated, and using the results as initial values for the competition during heating stage, the solution of the equations has been run. The final results of superlinearity thus obtained are discussed.

INTRODUCTION

A superlinear dependence on the dose has been reported for certain thermoluminescence (TL) peaks in some materials. For example, Cameron *et al*[1] reported some superlinear behaviour in the dependence of TL in LiF on the gamma radiation dose. The main feature of these results was that at low doses the dependence was linear, turned superlinear at higher doses ($d^2S/dD^2>0$ where S is the TL intensity and D the dose; see Chen and Bowman[2]), before turning sub-linear while approaching saturation. As explained by some authors (e.g. Suntharalingam and Cameron[3]), this behaviour is characteristic of a competition during the excitation of the sample. According to this model, competing traps, not related directly to TL are being filled along with the TL ones. When these competitors approach saturation, more electrons are made available to the traps, and the filling of the relevant traps becomes faster.

Later investigators[4,5] showed that, at least in LiF:Mg,Ti, this explanation does not hold. McKeever[4] who studied the gamma excited TL in these samples showed that the linear-superlinear growth of the optical absorption bands associated with TL peak 5 in this material precludes any model which involves mechanisms active during the absorption stage. McKeever argues that in this case, a competition during heating model is more appropriate, assuming a spatial association between the traps and recombination sites. Horowitz[5], dealing with peaks 5, 7, 8 and 9 in the same material, excited by alpha particles, shows that in this case, the track interaction model (TIM) describes the linear-superlinear dose dependence.

A much stronger superlinearity was discovered by Halperin and Chen[6] who excited semiconducting diamonds at LNT by UV light with photon energies lower than the band gap, and found quadratic and even a third power dependence on the dose at certain wavelength ranges, starting at low doses.

Rodine and Land[7] suggested that the superlinear behaviour may be due to competition during the heating phase which may result in a quadratic dependence on the dose. As opposed to the above mentioned works[4,5], this kind of competition during heating is related to transitions through the conduction band rather than the localised transitions described above. Kristianpoller *et al*[8] gave this model a mathematical formulation, and using some plausible approximations showed that the total TL may depend on the initial fillings of both the relevant trap and centre. If each of these separately depends linearly on the dose, the TL should be quadratic with the dose.

Chen *et al*[9] have discovered more recently a strong superlinearity in the well known 110°C peak in unannealed synthetic quartz excited by β irradiation. In this case, a strong superlinearity with the dose was found as of the very lowest doses. Re-evaluating the previously mentioned work by Kristianpoller *et al*[8], Chen *et al*[9] showed that super-quadratic behaviour may be associated with the same model of competition during heating. Further evidence, along the same lines, was given by Yang and McKeever[10].

THE MODEL

As pointed out above, two kinds of competition-related superlinearity were previously

considered. Figure 1 depicts the schematic energy level diagram considered in connection with the competition during excitation. The excitation irradiation with intensity f raises electrons at a rate αf, α being a proportionality factor, from the valence to the conduction band. The holes get trapped in the recombination centre M whereas the electrons may be trapped either in N_1 or N_2, two electron trapping states. In this model[2], the authors disregard the possible recombination of conduction band (n_c) electrons with trapped holes during the excitation, and indeed including this possibility should not interfere drastically with the conclusions (see Reference 11 and below). Suppose that N_1 is the trap responsible for the TL peak in question and assume that A_2, the trapping probability into N_2 is substantially larger than A_1, the trapping probability into N_1. The latter will start getting filled during the excitation at a linear but slow rate since most of the flow of electrons will be into N_2. At a certain point, N_2 will approach saturation which will make more electrons available to N_1 and it will grow faster with the dose. When N_2 is entirely saturated, the rate of filling of N_1 is expected to be fast but linear. The intermediate range of transition from the low rate linear to the high rate linear is a region of a superlinear increase of n_1, the filling of N_1. According to this model, $n_1<m$ where m is the

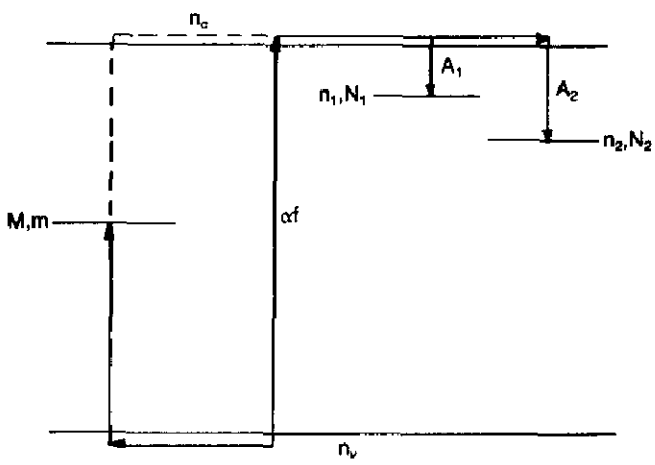

Figure 1. Schematic energy levels involved in the excitation of a sample with two trapping states and one recombination centre. f is the intensity of radiation, producing αf $m^{-3}.s^{-1}$ electron–hole pairs. n_c and n_v denote the concentrations of free electrons and holes in the conduction and valence bands respectively. N_1 and N_2 are the total concentrations of traps of the two kinds, with occupancies of n_1 and n_2 and transition probabilities of A_1 and A_2 respectively. M is the concentration of hole centres out of which m are occupied. A_n is the trapping probability of free holes in the centre whereas A_m is the trapping probability of free electrons with trapped holes.

filling of the hole trapping state, and since under normal conditions, the final TL is proportional to $\min(n_{10},m_0)$ where n_{10} and m_0 are the fillings of the relevant trapping and recombination states at the end of the excitation respectively. We should, therefore, expect the dose behaviour to follow the dependence of n_1 on the dose, thus being superlinear in the intermediate range.

The rate equations for this situation, as given by Chen *et al*[11] are

$$dn_1/dt = A_1 (N_1-n_1)n_c \quad (1)$$

$$dn_2/dt = A_2 (N_2-n_2) n_c \quad (2)$$

$$dm/dt = A_n n_v (M-m)-A_m m n_c \quad (3)$$

$$dn_v/dt = \alpha f-A_n n_v (M-m) \quad (4)$$

$$dn_c/dt = \alpha f-A_m m n_c-A_1 (N_1-n_1)n_c-A_2(N_2-n_2)n_c \quad (5)$$

As shown in References 2 and 11 by the use of numerical calculations, the filling of the trap N_1 is superlinear with the excitation dose, when sets of kinetic parameters compatible with the above mentioned qualitative considerations are chosen.

As pointed out by Kristianpoller *et al*[8], the dependence of the measured TL may not be on $\min(n_{10},m_0)$, but can, under circumstances of competition during the heating stage, be basically dependent on the product $n_{10}m_0$. In Figure 2, the directly related trapping state N_1 releases electrons during heating which may either recombine with holes in M or get trapped in the competing trap.

The rate equations governing the process during the heating phase are, as given by Kristianpoller *et al*[8]

$$dn_1/dt = -s \exp(-E/kT)\, n_1+A_1(N_1-n_1)n_c \quad (6)$$

$$dn_2/dt = A_2 (N_2-n_2)n_c \quad (7)$$

$$I = -dm/dt = A_m m n_c \quad (8)$$

$$dm/dt = dn_1/dt+dn_2/dt+dn_c/dt \quad (9)$$

where I is the TL emission intensity. Kristianpoller *et al*[8] showed that when N_2 is far from saturation, i.e. $(N_2-n_2 \sim N_2)$ and when m_0 and n_{10} are linearly dose dependent, the total TL is quadratically dependent on the dose. In fact, a more accurate expression was used by Chen *et al*[9] to explain the super-quadratic behaviour seen in the dose dependence of the 110°C peak in synthetic quartz, namely,

$$S=\{A_m/[(A_2(N_2-n_{20})]\}m_0 n_{10} \quad (10)$$

If, say, m_0, n_{10} and n_{20} depend linearly on the dose, then m_0n_{10} is responsible for a quadratic behaviour whereas the occurrence of N_2-n_{20} in the

denominator, causes the overall dependence to be super-quadratic. As part of their work, Kristianpoller *et al*[8] assumed an exponential dependence of n_{20} on the dose D, $n_{20} \propto N_2(1-\exp(-\beta D))$, where β is a constant, which yielded a strong superlinearity following a range of quadratic behaviour.

The main disadvantages of these two approaches are:

1. Each of the two approaches was taken separately, assuming that when competition occurs during excitation, no competition takes place during the heating phase and vice versa.
2. Approximations are made, e.g. the exponential behaviour of n_{20} on the dose which may describe the general kind of its dose dependence, but certainly does not precisely follow the process of filling.

This work starts with a relatively simple energy level scheme like that given in Figures 1 and 2, and numerically solves the relevant set of simultaneous differential equations in three stages simulating the actual physical process. This includes the excitation phase in which electrons are raised from the valence to the conduction band, and carriers are trapped in traps and centres. This is followed by a relaxation period in which electrons remaining in the conduction band at the end of irradiation get trapped or recombine with trapped holes. In the third stage, the temperature is raised, and the simultaneous differential equations are numerically solved to follow the process of thermal release of electrons from N_1 and their recombination with holes, thus yielding TL. As a measure of the emitted TL, we usually take the maximum intensity I_{max}.

NUMERICAL RESULTS

For the numerical solutions of the simultaneous kinetic equations, conventional algorithms were utilised (see e.g. Reference 11). For a given set of trapping parameters, Equations 1–5 were solved numerically for a certain length of time tex. This is followed by the relaxation period, in which one sets f=0 and solves the equations until the previously found values of n_c and n_v decay to negligible values. With the final values of m, n_1 and n_2, one now goes to the third phase and solves Equations 6–9 simultaneously with the previous filling of traps and centres as initial conditions. In this phase, the temperature is raised at a rate of 1 $K.s^{-1}$, and the TL curve is evaluated. Changing the dose D=ftex in the first stage, changes n_1, n_2, m and consequently I_{max} which are recorded as functions of the dose. A characteristic solution is depicted in Figure 3. The parameters chosen here were $N_1=10^{23}$ m^{-3}, $N_2=10^{21}$ m^{-3}, $M=1.01\times10^{23}$ m^{-3}, $A_1=A_m=A_n=10^{-21}$ $m^3.s^{-1}$, and $A_2=10^{-19}$ $m^3.s^{-1}$. The results are plotted on a log-log scale. As explained above, the trap N_2 acts both as a competitor during the excitation and the readout (heating). It is seen that in accordance with the qualitative considerations, the filling of n_1 starts linearly and gets superlinear at a dose where n_2 approaches saturation. m is seen to increase linearly all the way prior to its approach to full saturation. The dependence of I_{max} on the dose is of interest; at relatively low doses, it goes up quadratically with the dose. Even before the slight superlinearity of n occurs, I_{max} is seen to climb rather dramatically, which was explained above qualitatively as being related to the change in the value of (N_2-n_2) in the denominator of Equation 10. This behaviour resembles the strong superlinearity in Figure 5 of the paper by Kristianpoller *et al*[8], however, here as opposed to the previous work, the very strong super-linearity is found without making any of the simplifying assumptions leading to Equation 10. Also, the dependence of n_2 on the dose is assumed in the previous work to be exponential with the dose, whereas here it is calculated as an integral part of the computational procedure.

The dependence on the dose, which is here quadratic, followed by a steeper function, does not resemble accurately the experimental results of the 110°C peak in unannealed synthetic quartz which shows the very strong superlinearity right from the very lowest doses which produce measurable TL. This can be explained rather easily by asserting that the low dose quadratic behaviour occurs at the range in which TL is too low to be measurable. Moreover, these results do resemble curve D of Figure 4 of Reference 10 which depicts the dose

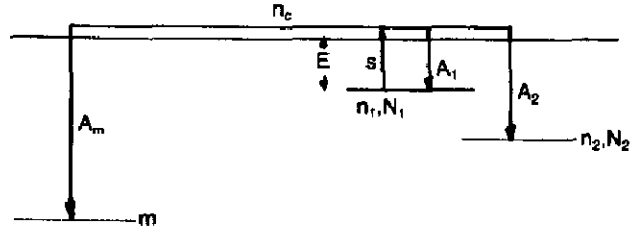

Figure 2. The same schematic energy levels as in Figure 1 but with the transitions occurring during the heating. The additional parameters here, E and s, are the activation energy (eV) and frequency factor (s^{-1}), respectively.

dependence of synthetic quartz annealed at the relatively low temperature of 250°C. At the higher doses range, the slope on the log-log scale in Figure 3, decreases and is nearly linear in the range where the competitor is fully saturated and therefore inactive. At higher doses, I_{max} levels off when saturation of n_1 and m takes place.

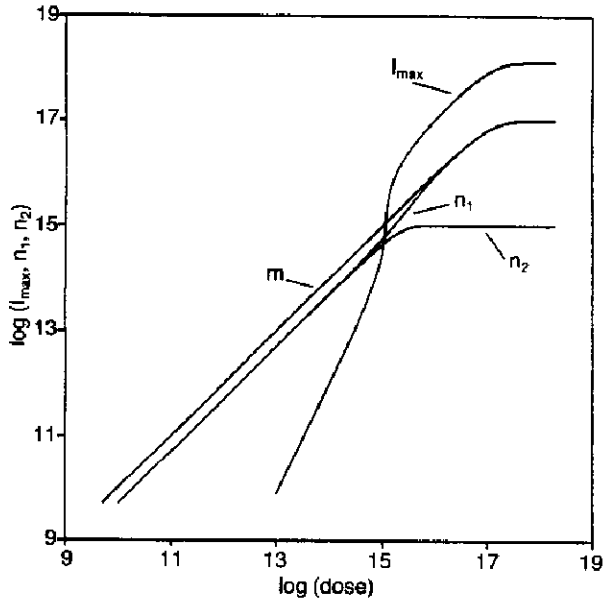

Figure 3. Representative results of the numerical calculations related to the energy levels in Figures 1 and 2 and with the parameters given in the text. n_1, n_2 and m are the values attained for given doses of irradiation following the first two stages of excitation and relaxation. I_{max} is the resulting maximum of TL calculated during the heating stage.

CONCLUSION

Two previous theoretical approaches to explain the superlinearity occurring in some cases in the dose dependence of TL, have been combined in this work. These are the competition during excitation, and competition during heating. The same trapping state, denoted here by N_2 is considered to be the competitor in both stages (which may or may not be the case in real situations). Under the representative choice of parameters made above, the fillings of the trap N_1 is indeed somewhat superlinear, but this seems to make a rather negligible contribution to the strong superlinearity which is mainly related to the competition during the heating phase. It is certainly possible that if a different choice of parameters is made, and in particular if more than one competitor is involved, the competition during excitation may be the governing process. It appears, however, that a weak superlinearity, characteristically preceded by a linear range, is related to a competition during excitation whereas a much stronger superlinearity is associated with competition during heating. When both processes take place, the latter is usually the predominant.

In addition to the combination of the two mechanisms in the present work, it should be reiterated that the results which can explain the very strong superlinearity in the 110°C TL peak in synthetic quartz, are found directly from the rate equations governing the process, with no additional simplifying assumptions made.

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