Processes of sensitization of thermoluminescence in insulators

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Abstract. The increase in sensitivity of quartz caused by β or γ irradiation followed by high-temperature activation has been studied further. The model previously suggested, including a reservoir through which holes get into the recombination centre, thus increasing the sensitivity to a given test dose, is now given a concrete mathematical form. Sets of simultaneous differential equations for the various stages of irradiation and heating are written and numerically solved sequentially in order to simulate the physical processes taking place during the experiments. The dependence of the sensitivity on the excitation dose is followed, in particular for the high-dose range in which the sensitivity approaches saturation. A distinction between reservoir and centre saturation is made. The assumption of an exponential approach to saturation is tested, showing that, indeed, even in this complicated situation the exponential approximation is valid. As shown in previous works, using the exponential approximation in cases in which the sensitivity dependence is beyond the linear range helps in evaluating the archaeological doses in the dating of pottery by irradiation of the quartz grains in it. Also the effect of radiation quenching and the attempts to correct for quenching in order to improve the determination of the extrapolated natural dose which leads to the age determination are considered. The effect of the existence of a competing electron trap which appears to be a necessary condition for the occurrence of these effects is also discussed.

1. Introduction

The sensitization of various thermoluminescence (TL) materials by β or γ irradiation followed by annealing at high temperature is a well known phenomenon [1–5]. Briefly described, the sensitivity of a given sample is its TL emission in response to a given *test dose*. The sensitivity of the sample can be changed in such a way that, during a subsequent heating, the response of the same TL peak in the same sample is different, normally larger. The main reason, discussed here, for such a change of the sensitivity is the application of a relatively large dose to the sample, followed by relatively high-temperature annealing. It should be mentioned that the following discussion pertains mainly to the $110\,°C$ peak in natural quartz and the results considered are utilized for the pre-dose dating technique. A typical example of the sequence of actions performed and measurements made with a sample of quartz is as follows [5].

(i) The initial sensitivity S_0 to a small *test dose* ($\simeq 0.01$ Gy) is measured by heating the sample to about $150\,°C$ following the administration of the test dose.

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(ii) The 'high' dose N (of the order of magnitude of 1 Gy), which simulates the natural dose in archaeological samples, is applied followed by annealing at about $500\,°C$; the sample is then cooled back to room temperature (RT).

(iii) Another test dose of the same size is applied and the sample is heated at the same heating rate as in step (i) to $150\,°C$. The occurrence of the pre-dose sensitization effect is expressed by the response to the second test dose, S_N being larger than the response S_0 to the first due to the large irradiation followed by annealing.

Three important points are to be mentioned in this respect.

(i) This description explains only the basic fact that there is an increase in the intensity. The full sequence required to evaluate the total dose previously applied (typically in antiquity in quartz from pottery samples) in the *pre-dose technique* has to take into consideration the fact that the sample has received an unknown dose which is to be determined for the sake of age evaluation. Here, calibration has to be performed following the previous excitation with the unknown dose. Thus, the sample, with sensitivity S_N, is given a known β dose of β Gy followed by annealing to $500\,°C$, yielding a higher sensitivity of $S_{N+\beta}$. A comparison between the differences $S_N - S_0$ and $S_{N+\beta} - S_N$ can now be made, thus providing an evaluation of the unknown dose N. The important question of whether these changes of sensitivity are linear with the dose is one
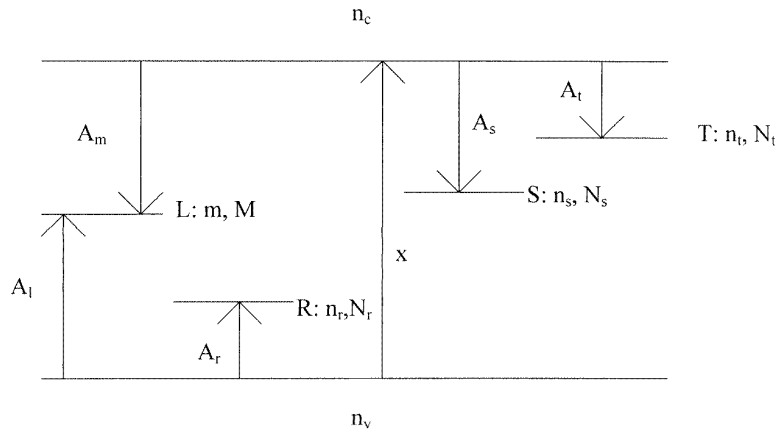
Figure 1. An energy level diagram including the electron trapping state, T, the competitor, S, the hole reservoir, R, and the luminescence centre L. n_c and n_v are the free electron and hole concentrations, respectively, and x is the rate of production of free electrons and holes. The transitions shown are those taking place during the excitation stage.

of the key issues concerning the derived pre-dose technique and will be considered below. The full sequence required for this dose evaluation has been given before [5].

(ii) In some cases, annealing alone or irradiation alone can result in an increase in the sensitivity. The simplest example is that of a superlinear dependence of the TL on the dose, in which the administration of a first amount of dose makes the sample more sensitive to further irradiation [6].

(iii) As reported by several authors [7, 8], an effect of quenching of the sensitivity by the irradiation is often observed. This merits some further explanation. When, for example, after activating at 500 °C the naturally pre-dosed sample which now has a sensitivity S_N, we administer an additional dose of, say, $\beta = 2$ Gy and heat to >110 °C (but not too high, to prevent high-temperature activation), the sensitivity measured before re-heating to 500 °C is $S_N^\downarrow$ with $S_N^\downarrow < S_N$. A qualitative explanation of this effect will be discussed below when the model is described. Also, the numerical results which follow show the effect clearly.

The first theory explaining the pre-dose effect has been given by Zimmerman [2, 3]. The basic energy level scheme given by her includes one electron trapping state T and two hole states R (the reservoir) and L (the luminescence centre). During the excitation by β or γ rays, electrons are raised from the valence to the conduction band and can be trapped in the trapping states T (see figure 1). The holes go preferably to the reservoir R; however, there is a non-negligible probability of the holes going to L so that thermally freed electrons can recombine with them during the heating, which results in the emission of TL of the unsensitized material. The annealing, typically to 500 °C following the application of a high dose, empties all the electrons from T, yielding a rather high TL peak at about 110 °C (which may but need not be recorded). Its more important effect is to release thermally the holes in the reservoir R, which will subsequently be trapped in the luminescence centre L. According to Zimmerman, this increase in the concentration of holes in the luminescence centre is the reason for the higher response to a subsequent test dose. In a later work, Chen [9] argued that, in the

framework of the model with T, R and L levels, the observations that the finally measured TL is proportional to the filling of L and, at the same time, that there is a linear dependence on the test dose, namely on the concentration of trapped electrons in T, are contradictory. Following previous concepts published by Kristianpoller *et al* [10] for explaining superlinearity, which indeed occurs in the 110 °C peak in the unannealed quartz (Chen *et al* [11]), Chen [9] solved the above-mentioned contradiction by assuming an extra electron level which competes for electrons during the heating stage. The full energy level diagram is shown in figure 1.

In the present work, we follow the model described, with two electron and two hole trapping states, by writing the relevant simultaneous differential equations and solving them numerically for certain choices of sets of trapping parameters. The sets of equations are to be presented and solved for the different stages of 'short' irradiation (with the test dose) and heating (readout), 'long', high-dose irradiation followed by annealing and another 'short' irradiation and heating. Obviously, the sample parameters are kept constant along such a sequence; thus, if a certain choice of one or more parameters is required for explaining a certain feature, the same values of the parameters are to be kept along the sequence and only the final results would show whether the feature in question really behaves as expected when all the stages of the experiment are being followed. Obviously, the situation is rather complicated due to the large number of parameters involved. However, what one can demonstrate is that a certain feature is commensurate with an appropriate choice of the parameters. Examples will be given below.

It is to be noted that an alternative model for sensitization has been considered in the literature. McKeever [12] suggested the possibility that the procedure of high-dose irradiation followed by heating may remove competitors which thus can increase the sensitivity to a subsequent test dose. It should be mentioned that results found in the present work will include this element since the model includes such competitors and the solution takes

into consideration transitions into them both during the excitation and the heating stages.

One other important point is to be considered. The basic pre-dose method assumed that, in the relevant dose range, the dependence of the sensitivity on the dose is linear. This need not be the case in particular when a number of additional calibration doses are given to the sample following the 'natural' dose which is to be determined. Chen [9] suggested a way to extend the applicability of the method to determine the dose (and thereby the age) by assuming that the sensitivity depends on the dose exponentially, namely,

$$S = S_\infty(1 - e^{-D/B}) \qquad (1)$$

where S_∞ is the saturation value of S, D is the dose and B is a constant with the dimensions of a dose. A further account taking into consideration the exponential dose dependence was given by Bailiff and Haskell [13]. In a recent work by Leung *et al* [14], a regression method has been developed for the evaluation of a paleodose using the pre-dose technique, making use of the assumption that the approach to saturation is exponential. All this has been done under the assumption that it is the luminescence centre which goes exponentially with the dose whereas the reservoir is being filled linearly. It has been obvious to these authors that, when the reservoir is being filled non-linearly, the results regarding the dose thus evaluated are questionable. Using the numerical solutions in the present work, we can follow these possibilities within the framework of a comprehensive model.

2. The rate equations and their solutions

The first step in following numerically the above-mentioned model is writing down the equations governing the processes of excitation presented in figure 1. The set of simultaneous differential equations (rate equations) is

$$dn_t/dt = A_t n_c (N_t - n_t) \qquad (2)$$

$$dn_s/dt = A_s n_c (N_s - n_s) \qquad (3)$$

$$dn_c/dt = x - A_t n_c (N_t - n_t) - A_s n_c (N_s - n_s) - A_m m n_c \qquad (4)$$

$$dn_v/dt = x - A_l n_v (M - m) - A_r n_v (N_r - n_r) \qquad (5)$$

$$dm/dt = A_l n_v (M - m) - A_m m n_c \qquad (6)$$

$$dn_r/dt = A_r n_v (N_r - n_r). \qquad (7)$$

Here, n_t (cm^{-3}) and N_t (cm^{-3}) are the concentrations of trapped electrons and trapping states, respectively, in the 'main' T traps, n_s (cm^{-3}) and N_s (cm^{-3}) are the concentrations of trapped electrons and trapping states of the competitor, respectively, n_r (cm^{-3}) and N_r (cm^{-3}) are the concentrations of holes in the reservoir and the trapping states in the reservoir, respectively, m (cm^{-3}) and M (cm^{-3}) are the concentrations of the holes and states in the luminescence centres, respectively, n_c (cm^{-3}) and n_v (cm^{-3}) are the concentrations of free electrons and holes, respectively, A_t (cm^3 s^{-1}) and A_s (cm^3 s^{-1}) are the probabilities of trapping in T and S, respectively, A_r

(cm^3 s^{-1}) and A_l (cm^3 s^{-1}) are the probabilities of hole trapping in R and L, respectively, and A_m (cm^3 s^{-1}) is the probability of free electrons recombining with trapped holes in the luminescence centres. x (cm^{-3} s^{-1}) is the intensity of the excitation irradiation which produces pairs of free electrons and holes.

The set of equations has been solved by using the built-in ode23 Matlab package solver. In order to get reliable results, a very low value of the accuracy factor of tol = 10^{-9} has been chosen throughout. The price to pay has been that each chosen period of time has been divided into a large number of intervals, which increased the computation times. Once this set of equations is solved for an irradiation time of t seconds, the applied dose is calculated as $D = xt$. In order to simulate the experimental situation, a period of relaxation is to be taken into consideration. During this time, the remaining electrons and holes in the conduction band and valence band, respectively, are either trapped or undergo recombination, thus the next stage of heating starts with practically no carriers in the bands. This is done by further solving the same set of equations by setting $x = 0$ and following the solution until negligible concentrations of carriers remain in the conduction and valence bands. Of course, the program described so far which follows the process of excitation, can be used both for the test dose and for high-dose simulations.

A second part of the program developed is that which simulates the heating process. In addition to the magnitudes described above with respect to figure 1, E_t and s_t, the activation energy (eV) and frequency factor (s^{-1}) of the electron trapping state, as well as E_r and s_r, the activation energy and frequency factor, respectively, of the reservoir are shown in figure 2. It should be noted that, in low-temperature heating, up to about 150 °C, the main interest is the intensity at the maximum of the peak. We therefore let the program identify the maximum temperature and the intensity there, but let the run continue until about 150 °C in order to simulate properly the experimental conditions and the possible effect on the subsequent stages of the experiment. As explained by Aitken [7], the quenching effect seen following 'high' excitation followed by only low-temperature annealing (such as 150 °C) has to do with the recombination with holes in the recombination centre, which causes the final concentration m following the application of the next test dose to be smaller than expected.

The rate equations governing the process taking place during heating are related to the transitions shown in figure 2 and are as follows:

$$dn_t/dt = A_t n_c (N_t - n_t) - s_t \exp[-E_t/(kT)]n_t \qquad (8)$$

$$dn_s/dt = A_s n_c (N_s - n_s) \qquad (9)$$

$$dn_c/dt = s_t n_t \exp[-E_t/(kT)] - A_t n_c (N_t - n_t) \\ - A_m n_c m - A_s n_c (N_s - n_s) \qquad (10)$$

$$dn_v/dt = n_r s_t \exp[-E_r/(kT)] \\ - A_r n_v (N_r - n_r) - A_l n_v (M - m) \qquad (11)$$

$$dm/dt = A_l (M - m) n_v - A_m n_c m \qquad (12)$$

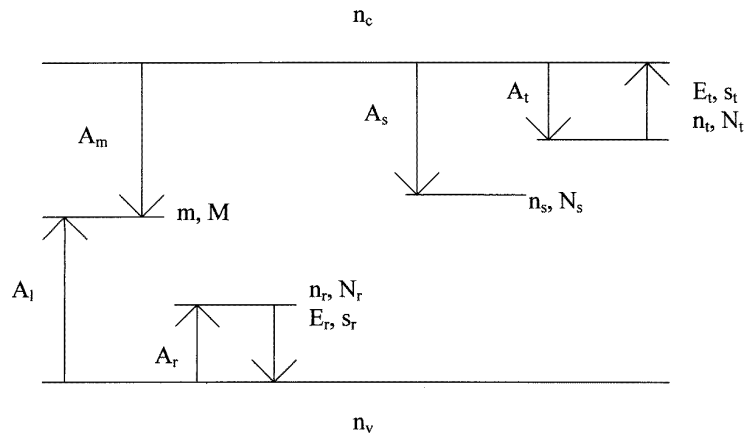$$dn_r/dt = A_r n_v (N_r - n_r) - n_r s_r \exp[-E_r/(kT)]. \qquad (13)$$

Figure 2. Transitions taking place during the heating stage in the same energy scheme as that shown in figure 1. Both the thermal excitations from the electron trapping state T and those from the reservoir R are shown, although they have different roles in different stages (see the text).

The intensity of the emitted TL is assumed, as mentioned above, to be the result of recombination of free electrons with trapped holes in the M centres; thus it is given by

$$I(T) = A_m m n_c. \tag{14}$$

It is to be noted that the implied heating function $T = T(t)$, a monotonically increasing function, is to be taken into account. In the rather conventional case, a linear heating function is utilized, namely, $T(t) = T_0 + \beta t$, where β is the (constant) heating rate and T_0 is the initial temperature. The parameters appearing in equations (8)–(14) are the same as those in equations (2)–(7) since we are dealing with the same physical system. Four additional parameters are considered here which were not included for the excitation stage since the excitation is performed at a relatively low temperature. These are E_t and E_r, the activation energies of trapping states and the reservoir and s_t and s_r, the respective frequency factors.

It is important to note that, although, in principle, all these levels are involved during the heating stage, be it the 'small' heating to about 150 °C or the 'large' one to about 500 °C, in the former, the temperature is not sufficiently high to release trapped holes from the reservoir into the valence band. Thus the equations governing the change of n_r and n_v can be ignored, whereas the only change in the concentration of the trapped holes in centres m is via recombinations from the conduction band electrons. This has been taken into account in the subprogram dealing with the heating to about 150 °C during which the measured TL, before and after sensitization, is being measured.

The part of the program dealing with the heating deserves some special attention. Again, the Matlab ode23 solver has been utilized in the programs dealing with the 'short' and 'long' heatings with the low value of tol = 10^{-9} for the accuracy factor. It is to be noted that all the solvers utilized in Matlab are for constant values of the parameters. Here, however, the exponents appearing in equations (8), (11) and (13) are temperature dependent and, therefore, during the heating are rather strongly time dependent. The approximation we have used to overcome this difficulty has

been to fix the temperature for 0.1 s, solve the equations using significantly smaller sub-intervals determined by the program to yield the required accuracy and continue to the next time interval of 0.1 s, raising the temperature by 0.5 K. Of course, this implies a heating rate of 5 K s^{-1}, which is rather typical to measurements of this sort with archaeological and geological quartz grains.

All the parts of the simulated procedure were integrated by a framework program termed predose.m. This program governs only the order of calling the programs of test-dose excitation and heating, high-dose excitation and annealing and a second test-dose excitation and read out by heating. In cases we wished to simulate a sequence of several high-dose irradiations followed by high-temperature annealings and test-dose responses to monitor the sensitivity, a small change has been made in the framework program such as to allow this repeated cycle of events.

3. Details of the model and numerical results

The general considerations made in the past concerning the pre-dose effect usually took effects occurring during the excitation and during the heating of the sample into consideration separately. In this sense, the present treatment is more comprehensive, performing all the stages of the procedure, namely, low- and high-dose excitations as well as low- and high-temperature annealings, on the same sample which in our case is represented by the same set of trapping parameters. The experimental results to be explained by the model are as follows.

(i) The linear dependence of the signal on the size of the test dose.

(ii) The apparently exponential approach to saturation (see equation (1) above) of the sensitivity with repeated additive doses. At low doses, this can be approximated as a linear dependence.

(iii) The quenching effect on the sensitivity of exposure to a high dose followed by a low-temperature annealing at, say, about 150 °C. The correction for quenching suggested in the literature [7] of adding up the 'lost' sensitivity by

quenching to the measured one, thus extending the linear range of dependence, should be considered.

(iv) The UV reversal described by Zimmerman [2]. Once the irradiated and annealed sample is illuminated by UV light, the sensitivity decreases substantially. A repeated high-temperature annealing increases the sensitivity back to nearly the same level as the previous one following the first high-temperature annealing.

(v) One should distinguish between centre and reservoir saturations. As first discussed by Fleming [15] and further elaborated by Chen [9], the approach to saturation of the filling of the reservoir and that of the centre cannot be expected in general to be the same. The implication regarding the evaluated natural dose is that it can be considered reliable only if N, the natural dose, is equal to the incremental dose β (which may be administered a number of times). As explained by Chen [9], this requires performing a number of sets of measurements with various β and choosing as the best result the one with $N \approx \beta$.

The number of parameters to be chosen is very large, which may lead one to the conclusion that any behaviour can be explained. Indeed, different choices of parameters may bring about different behaviours; for example, the quenching mentioned above need not occur or even an inverse quenching may take place, namely, that the sensitivity increases with high dosing followed by low-temperature cleaning. This was seen experimentally with some quartz samples and could also be simulated by a certain choice of the parameters. The main point in this respect is, however, that it was easy to choose sets of parameters that result in a good simulation of *all* the above-mentioned phenomena just by keeping in mind some required relations between these parameters. The choice of sets of parameters and the numerical results associated with one such set follow.

The basic idea behind the concept of the reservoir is that, during the irradiation, the created holes go preferably into the reservoir R. In the example discussed here, referring to figures 1 and 2, we have chosen $A_r = 10^{-10}$ cm^3 s^{-1} and $A_l = 10^{-12}$ cm^3 s^{-1}. The E_r and s_r values are to be chosen such that heating to about 150 °C will not release any significant number of trapped holes whereas heating to 500 °C will do so. We have taken $E_r = 1.4$ eV and $s_r = 10^{13}$ s^{-1}. Thus, although the retrapping into R is stronger than the capture in M, most of the holes move into M during the high-temperature annealing. Moreover, this choice ensures that the UV reversal will occur since, once a hole is released (at RT) by UV from M into the valence band, it will preferably go back into R rather than to M. The N_r and M capacities have been chosen to be 10^{13} cm^{-3} and 10^{14} cm^{-3}, respectively. The values of E_t and s_t should be taken so that the peak will occur at about 110 °C ($\simeq$383 K). We have chosen here $E_t = 1.0$ eV and $s_t = 10^{13}$ s^{-1}. In order to have both a linear dependence of the signal on the test dose and a dependence of the measured sensitivity on the applied high dose, it has been argued by Chen [9] that a necessary condition is that the trapping into the competitor S should be faster than the recombination. We have taken here $A_s = 10^{-11}$ cm^3 s^{-1} and $A_m = 10^{-12}$ cm^3 s^{-1}. For the

retrapping probability A_t, the results were found to be rather insensitive to changes in this parameter and we have chosen $A_t = 10^{-12}$ cm^3 s^{-1}. The capacities of the trapping and competitor states have been taken as $N_t = 10^{13}$ cm^{-3} and $N_s = 10^{12}$ cm^{-3}, respectively. Finally, the initial values of the various functions should be set. At first sight, setting all of them to zero sounds reasonable. This indeed is the case insofar as n_c, n_v, n_t and n_r are concerned. If one assumes a prior heating to high temperature, the choice of $n_c(0) = n_v(0) = n_t(0) = n_r(0) = 0$ is obvious. However, S is considered to be disconnected at least insofar as heating to 500 °C (and perhaps more) is concerned. Up to this temperature, n_s is not depleted, which leaves $n_{s0} \neq 0$ for the next step. For the sake of neutrality, one has to assume that $m(0) = n_s(0)$ and these values may be non-zero. Another way to look at the possibility that $m(0) \neq 0$ is to consider that, during excitations and heatings, m changes via transitions from the valence band, as well as recombinations from the conduction band. At the end of such a process, one may remain with $m \neq 0$ which is $m_0 \neq 0$ for the next stage. The importance of choosing $m_0 \neq 0$ has to do with the linear dependence of the TL signal on the size of the test dose. As has been discussed before [10, 11], the occurrence of a strong competitor (S in the present case) may result in a superlinear dose dependence. Indeed, solving the sets of equations with the above parameters together with $m(0) = n_s(0) = 0$ yielded a quadratic test dose dependence. However, a choice of $n_s(0) = m(0) = 10^{10}$ cm^{-3} made the test-dose dependence linear and still provided all the other experimentally observed features of sensitization, quenching and UV reversal. We have also chosen the test dose to be 5×10^8 cm^{-3} and the increments of the 'large' dose 100 times larger, namely, 5×10^{10} cm^{-3}. Also, for the variation of the size of the first large dose, it has been changed from 50 to 500 times the test dose, as explained below.

It should be noted that taking ten times smaller 'high' incremental doses resulted in a nearly linear dependence. We have preferred, however, to look into the saturating range and have chosen the higher doses mentioned. In this respect, it is important to note that, although the approach to saturation looks natural in such a situation, the processes leading to the final results are rather complicated both in the real samples and in the presently simulated results. One can ask whether the exponential approach to saturation is a good approximation to the numerical results. Since, both in the experimental results for quartz and in the numerical values found here, S_0 is not negligibly small relative to the sensitized values of S, we preferred to write the approximated dose dependence of S as

$$S = S_0 + S_\infty (1 - e^{-D/B}) \qquad (15)$$

rather than equation (1). The sensitivities calculated above were fitted to this three-parameter expression, the parameters to be determined being S_0, S_∞ and B. Another indication that S_0 should be considered separately is the experimental fact pointed out by Bailiff [5] that the emission spectrum of the sensitized part of S is different than that of the original S_0.

The best fit for evaluating the three parameters is obtained by least squares as follows. The sum of squares of the difference between the function (15) of these three parameters and the 'experimental' values (here, the values calculated by the solution of the two sets of differential equations, sequentially) is minimized using the Matlab multi-variable minimization program 'fmins'. Once the best S_0, S_∞ and B are found, they are re-inserted into equation (15) and the best-fit curve is calculated. The 'experimental' points as well as the best fitted curve are plotted against the dose on the same graph.

Figure 3 shows the results ($\times$) obtained by the solution of the sets of equations in the sequence mentioned above and the given set of parameters. Here, each point is reached by starting every simulation from the initial values discussed above. Each point represents, therefore, a single 'high' dose and thus the non-linear behaviour observed may represent the approach to saturation either of the reservoir or of the luminescence centre. The curve fitted best to the exponential function (15), shown as the full line, is seen to be in very good agreement with the calculated points.

Figure 4 shows the results ($\bigcirc$) obtained again by the solution of the sets of equations. Here, each point is calculated with the initial values being the final concentrations of its predecessor. Thus, this calculation simulates the experiment with repeated 'high' doses and, therefore, is basically associated with the approach to saturation of the centre. Note that, here too, the exponential expression fits the numerical results very well. The upper curve ($\times$) shows the same results using corrections for the accumulated quenchings found in the simulation (see details below). With the higher values here, the initial part of this curve indeed is closer to a straight line. The whole curve still shows an approach to saturation and the best fitted exponential curve still gives a very good fit, though it is slightly inferior to that of the original points.

4. Discussion

In this work, the model with one active trapping state, one thermally disconnected competitor trap and two hole states, a radiationless reservoir and a radiative luminescence centre has been studied. The relevant sets of differential equations have been solved and the experimental procedures of either having different 'high' doses or using a sequence of high-dose increments have been simulated. Each of these curves is fitted to the expression (15), and the best fit looks very good in both cases. It should be noted that, when lower 'high' doses were utilized, the curve reached was much closer to linearity, as expected.

All the experimental features previously observed in the $110\,^\circ$C peak in quartz were found here as a result of these calculations, when the 'appropriate' set of parameters was chosen. Finding such a set of parameters turned out to be rather easy when the qualitative considerations mentioned in the literature concerning specific features were taken into consideration. These experimental features include the linear dependence of the signal on the size of the test dose, the approach to saturation, the UV reversal and the radiation-quenching effect.

The very good fit of the numerically evaluated points and the exponential approach to saturation merits a few more words. Obviously, in principle, there is an infinite number of ways for a function to approach saturation. The simulated points are computed by a rather complicated procedure and, therefore, no specific form of an approach to saturation can be expected. The fact that such a good fit is attained with a simple exponential function is somewhat surprising, but also encouraging. If a sample with an unknown dose N is to hand, incremental doses β can be given along the mentioned sequence and, using the exponential behaviour [9], N can be evaluated. As mentioned already, this is accurate only if $N \approx \beta$ due to the possibility of reservoir saturation.

The quenching effect mentioned above [7] was considered to be detrimental when one tries to determine the natural dose by extrapolation. It has been suggested [7] that a correction for quenching should be performed in order to account for the lost sensitivity. This was done by adding the loss of sensitivity to the measured one, say $S_{N+\beta}$, and, in the case of addition of several increments, the losses up to a stage k were summed up and the total correction added to $S_{N+k\beta}$. The corrected sensitivity S suggested [7] can be written as

$$S = S_{N+k\beta} + \sum_{i=0}^{k} (S_{N+i\beta} - S_{N+i\beta}^{\downarrow}) \qquad (16)$$

where $S_{N+i\beta}^{\downarrow}$ is the radiation-quenched sensitivity following i additional β increments and $S_{N+i\beta}$ is the sensitivity measured following the subsequent high-temperature annealing.

No justification for this linear summation has been given and, in fact, the rather complicated processes leading to this quenching cannot guarantee that such a correction has a great advantage. Empirically, however, the correction for quenching extended the initial linear range so that, when the original linear extrapolation was utilized, it appeared to be of help. The present results in figure 4 neither confirm nor refute the validity of this correction. Both curves fit quite convincingly exponential curves of the form given in equation (15), with different values of the three relevant parameters. Thus, if the extrapolation to the natural dose N is performed, the success with the two curves is expected to be more or less the same.

Complicated as the present model and, in particular, the sets of coupled differential equations to be solved may look, in fact, in most real-life samples, including quartz, the situation is even more involved. Insofar as the $110\,^\circ$C peak is concerned, the 325 and $375\,^\circ$C traps may be considered thermally disconnected for low-temperature heatings. However, most probably, deeper levels which do not empty at temperatures up to $500\,^\circ$C are to be assumed to act as the competitor S.

The details of the UV reversal have not been given here. We only briefly mention that a set of rate equations which follows the release of holes from recombination centres has been solved. With the given parameters for which the probability of capture in the reservoir is larger than that of capture in the centre, the transfer of holes from the latter into the former comes out naturally.
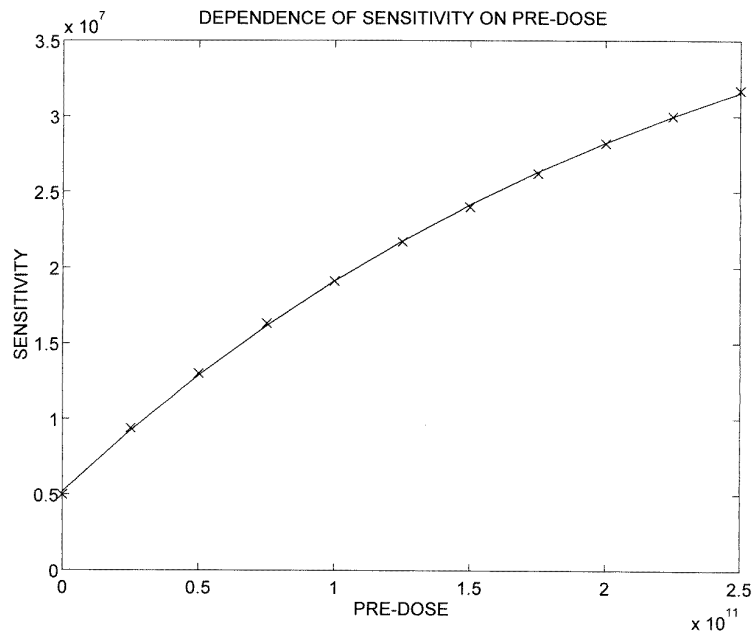
Figure 3. The simulated sensitivity calculated as a function of the 'high' dose, by solving sequentially the sets of equations for varying high doses, followed by high-temperature annealing, excitation by a test dose and heating above the maximum at about 110 °C. ($\times$), calculated points; full line, best fitted curve. The parameters are given in the text.
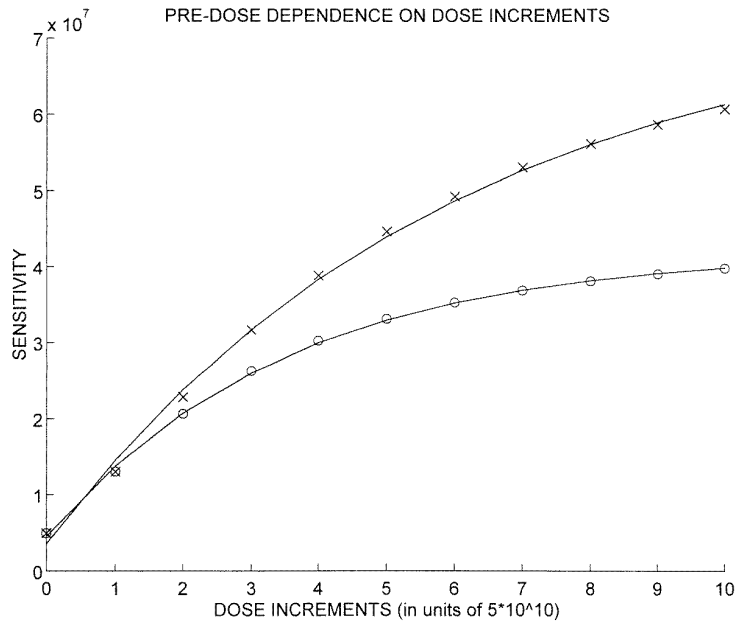

Figure 4. The simulated sensitivity as a function of the number of increments of the high dose ($\bigcirc$). The upper curve ($\times$) represents the sensitivity with correction for quenching as a function of the number of dose increments. In both cases, the full line is the best fitted experimental function. The relevant parameters are the same as those in figure 3.

Finally, although the present model has been quite successful in explaining the main phenomena associated with the pre-dose effect, it is not suggested here that this is the only possible explanation. In this respect, we should mention that Yang and McKeever [16] proposed the possibility that movement of hydrogen ions between defects during irradiation and annealing may be responsible for the pre-dose effect. In a later work, McKeever [17]

suggested that the UV reversal is associated with the release of electrons from deep traps which then recombine with trapped holes in $(H_3O_4)^0$ centres, thereby reducing the concentration of recombination centre. In our numerical experiments, the mere effect of sensitization could be seen even when the competitor S was entirely missing. As mentioned above, however, the whole set of trapping states was required in order to explain all the results of the 110 °C

peak in quartz and, as pointed out above, even under these circumstances only simulation with certain sets of parameters yielded all the experimental results.

References

[1] Cameron J R, Suntharalingam N and Kenney G N 1968 *Thermoluminescent Dosimetry* (Madison: University of Wisconsin Press)

[2] Zimmerman J 1971 *J. Phys. C: Solid State Phys.* **4** 3265–76

[3] Zimmerman J 1971 *J. Phys. C: Solid State Phys.* **4** 3277–91

[4] Piesch E, Burgkhardt B and Singh D 1977 *5th Int. Conf. on Luminescence and Dosismetry, São Paulo*

[5] Bailiff I K 1991 *Scientific Dating Methods* ed H Y Göksu et al (Doredrecht: Kluwer) 155–73

[6] Chen R and McKeever S W S 1997 *Thermoluminescence and its Applications* (Singapore: World Scientific)

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

[8] Leung P L, Stokes M J, Wang W D and Xia J 1996 *Nucl. Sci. Techn.* **7** 85–9

[9] Chen R 1979 *Europ. PACT J.* **3** 325–35

[10] Kristianpoller N, Chen R and Israeli M 1974 *J. Phys. D: Appl. Phys.* **7** 1063–72

[11] Chen R, Yang X H and McKeever S W S 1988 *J. Phys. D: Appl. Phys.* **21** 1452–7

[12] McKeever S W S 1990 *J. Appl. Phys.* **68** 724–31

[13] Bailiff I K and Haskell E H 1984 *Radiat. Prot. Dosim.* **6** 245–8

[14] Leung P L, Yang B and Stokes M 1997 *Ancient Thermolumin.* **15** 1–5

[15] Fleming S J 1973 *Archaeometry* **15** 13–30

[16] Yang X H and McKeever S W S 1988 *Nucl. Tracks Radiat. Meas.* **14** 75–9

[17] McKeever S W 1991 *Nucl. Tracks Radiat. Meas.* **18** 5–12