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Full Length Article

Monte Carlo simulations of tunneling phenomena and nearest neighbor hopping mechanism in feldspars

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ABSTRACT

The study of luminescence signals from geological materials is of importance in dosimetric and dating applications. Monte Carlo simulations are often used to describe the charge creation, charge trapping and donor/acceptor recombination processes in luminescent and dosimetric materials. While such stochastic methods are in wide use in many applied areas of physics, there have been few studies of such phenomena on the origin and production of luminescence signals for feldspars, apatites and similar materials exhibiting loss of charge due to quantum tunneling phenomena. Previous Monte Carlo work on feldspars has been based on the assumption that the number density of donors and acceptors are equal at any time. These previous studies were able to get good agreement with experiment only when they assumed that the crystal consisted of small sub-volumes, and that charge carriers were only allowed to recombine within these nanocrystals. This paper provides a different version of this previously suggested model, in which the number density of acceptors far exceeds that of donors. The new version of the model describes the loss of charge due to ground state tunneling, as well as the charge creation by natural irradiation of samples. The results from the model compare well with previously derived approximate analytical equations for feldspars. In addition, the Monte Carlo simulations provide valuable insight into the various factors which affect the luminescence mechanism in these materials. The simulations can describe the loss of charge on a wide variety of time scales, from microseconds to thousands of years. The effect of crystal size, charge carrier density, natural irradiation dose rate and total number of charge carriers is studied in a quantitative manner. Finally we examine the possibility of extending the present version of the model to describe luminescence signals originating in the nearest neighbor hopping mechanism in feldspars. The results from the model are compared with experimental data from time-resolved infrared stimulated luminescence (TR-IRSL) in these materials.

1. Introduction

During the past decade significant progress has been made both experimentally and by modeling towards understanding the behavior of luminescence signals from feldspars and apatites. Quantum mechanical tunneling and the associated phenomenon of "anomalous fading" of these luminescence signals are now well established as the dominant mechanisms in these materials. Quantum mechanical tunneling is considered to take place either directly from the ground state of the trap, or by prior excitation into the excited state of the trapped electron [1–18].

Monte Carlo simulations are often used to describe the charge creation/trapping and donor/acceptor recombination processes in luminescent and/or dosimetric materials. Several types of simulations exist in the literature, based on either delocalized transitions involving the energy bands, or on transitions between localized states [19–26]. While such methods are used in many applied areas of physics, there have been few Monte Carlo studies of luminescence signals from feldspars.

There have been several efforts to develop models for luminescence signals in feldspars, based on a random distribution of donor-acceptor pairs. One of the basic assumptions of these models is that whenever an electron trap is occupied, the electron will always have the same nearest hole with which to recombine, i.e. the number density of trapped holes in the phosphor is assumed to be much larger than the concentration of trapped electrons. Larsen et al. [7] presented a numerical Monte Carlo model that simulated the processes of charge loss, charge creation and charge recombination in feldspar. In contrast to the assumptions made by previous analytical models, they assumed that the number density of electrons and holes are equal at all times. The focus of their study was to reproduce the experimentally observed

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values of the well-known g-factor describing anomalous fading effects. These authors were not able to get reliable results for bulk crystals, and obtained good agreement with experiment only when they assumed that the material consisted of small nano-crystals, and that charge carriers were allowed to recombine only within these smaller volumes.

In parallel to this Monte Carlo modeling effort, several recent papers have developed approximate analytical equations for both the dose response of feldspars in nature, as well as for the loss of charge in these materials over geological times, due to ground state tunneling phenomena [27]. These approximate analytical equations are discussed in Section 2 of this paper. It is then important to compare the results from these analytical equations with the Monte Carlo models, and to examine the strengths and weaknesses of these two parallel simulation methods.

The main purpose of the present paper is to provide a modified quantitative version of the model by Larsen et al. [7]. In the modified version presented in this paper, the number density of acceptors far exceeds that of donors, and it is shown that the model can be applied to both bulk samples and nano-sized crystals.

The specific goals of this paper are:

(a) To produce quantitative agreement of this Monte Carlo model with experimental data for both bulk and nano-sized crystals.
(b) To simulate the processes of charge loss by tunneling and charge creation by irradiation in nature, and to compare the results of the simulations with previously derived analytical equations. The simulations are compared with analytical expressions over a wide variety of time scales, from micro-seconds to thousands of years.
(c) To provide a quantitative study of the influence of various parameters in the model, such as the crystal size, charge carrier density, natural irradiation dose rate and total number of charge carriers.
(d) To investigate the possibility of extending the present model to describe nearest neighbor hopping processes in feldspars, and to quantitatively describe time-resolved relaxation signals in feldspars.

2. Monte Carlo simulations of charge loss due to tunneling

The model described in this section is a modified version of the Monte Carlo model by Larsen et al. [7]. In this paper we do not consider the effects of thermal detrapping, and the process of retrapping of charge carriers in empty traps is also assumed to be negligible. The results are organized as follows. Subsection 2.1 presents simulations of the loss of charge due to ground state tunneling, while the combined effect of natural irradiation and loss of charge due to tunneling is simulated in subsection 2.2. The dose response of samples to natural irradiations is considered in subsection 2.3, and finally thermally assisted hopping processes are discussed in section 2.4.

2.1. Monte Carlo simulation of charge loss due to ground state tunneling

Huntley [4] discussed the tunneling mechanism for a random distribution of donors and acceptors in feldspars, based on recombination taking place directly from the ground state of the system. The recombination of trapped charge is assumed to take place by quantum mechanical tunneling with a lifetime τ_{FADING} given by:

$$\tau_{FADING} = (1/s)\exp[\alpha\, r] \tag{1}$$

where α (m^{-1}) is the potential barrier penetration constant and s (s^{-1}) is the attempt-to-tunnel frequency. The instantaneous concentration of trapped electrons in the ground state depends on both the elapsed time t and on the separation distance r between donor and acceptor. One also defines a dimensionless distance parameter r', such that:

$$r' = (4\pi\rho/3)^{1/3} r, \tag{2}$$

where ρ (m^{-3}) represents the actual number density of acceptors per unit volume. In addition one defines a dimensionless parameter ρ' proportional to ρ by:

$$\rho' = (4\pi\rho/3)\alpha^{-3} \tag{3}$$

Larsen et al. [7] considered a phosphor as a three-dimensional box with volume V, containing an equal number of electron and hole traps. These defects are independently and randomly positioned in the volume of the box, and the number of donors and acceptors in this volume is denoted by n_{DONORS}, $n_{ACCEPTORS}$ correspondingly. Then the number density of acceptors can be calculated by:

$$\rho = \frac{n_{ACCEPTORS}}{V} = \frac{n_{ACCEPTORS}}{d^3} \tag{4}$$

where d is the dimension of the box. By combining (3) and (4), the dimensionless charge density ρ' can be calculated from:

$$\rho' = (4\pi/3)\frac{n_{ACCEPTORS}}{d^3}\alpha^{-3} \tag{5}$$

Fig. 1 shows a typical volume simulated in this paper, with the parameters $d=120$ nm, $n_{DONORS}=200$ and $n_{ACCEPTORS}=3000$. A basic difference between the simulations in this paper and the work by Larsen et al. [7], is that we are assuming a much larger concentration of acceptors than donors within the volume V. By using a typical barrier penetration constant $\alpha = 9\times10^9\ m^{-1}$ [4], the calculated dimensionless charge density from Eq. (5) is $\rho' = 10^{-5}$.

Fig. 1b shows the distribution of nearest neighbor distances at time $t=0$ for the system shown in Fig. 1a. The solid line in Fig. 1b is obtained from the following well-known analytical expression for the distribution of nearest neighbor distances ([4]):

$$P(r') = 3n_o(r')^2\exp\left[-(r')^3\right] \tag{6}$$

where n_o is the total initial number of donors in the system. Fig. 1b shows good agreement between the analytical expression (6) and the actual discrete distribution of distances of the system.

As discussed in detail in Larsen et al. [7], during the simulation each of the electrons in the volume is examined, and the distances of this electron from all holes are calculated. The minimum distance r_{MIN} to the nearest neighbor is found, and the Monte Carlo algorithm generates $i=1\ldots n_{DONORS}$ possible random fading times t^i_{FADING} given by:

$$t^i_{FADING} = -s^{-1}\exp(\alpha\, r_{MIN})\ln(1-P_i) \quad i = 1\ldots n_{DONORS} \tag{7}$$

where P_i is a random number between 0 and 1, representing the probability of recombination for each surviving electron. These possible times t^i_{FADING} depend on the tunneling frequency s, on the barrier penetration parameter α, and on the instantaneous distribution of distances r_{MIN} in the system. Close-by pairs are more likely to recombine first, and further away pairs are likely to recombine later. Only the event corresponding to the shortest of all the possible times in Eq. (7) happens, i.e. the donor-acceptor pair corresponding to this shortest time is allowed to recombine. After this pair is removed from the system in the simulation, the distances between each donor and each acceptor are re-evaluated, and the minimum t^i_{FADING} time is used to update the total time elapsed from the beginning of the simulation. This process is repeated until there are no more donors left in the system.

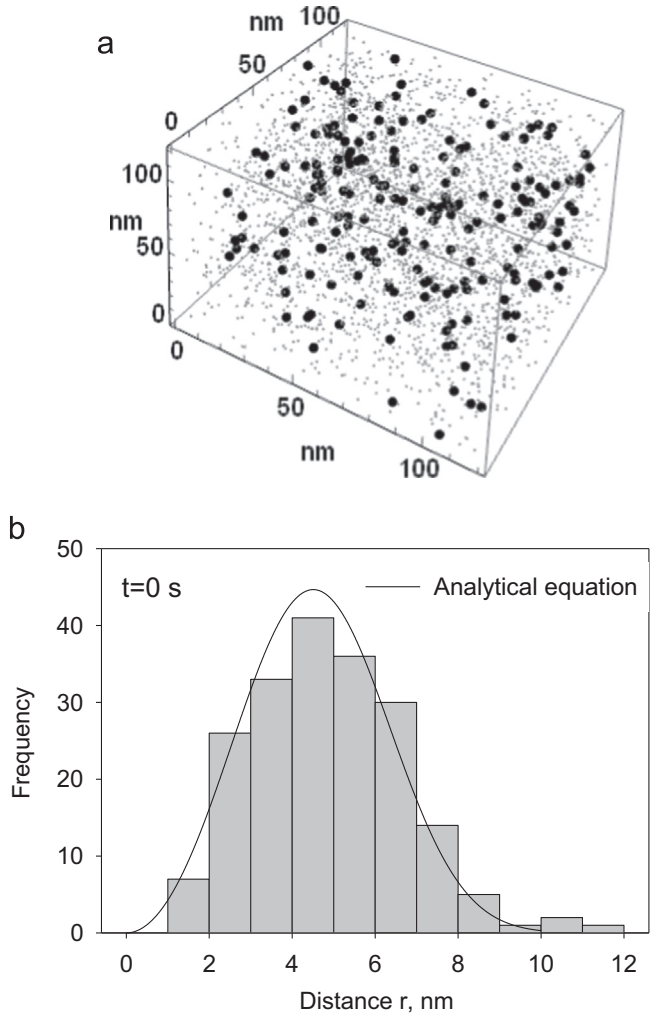

Fig. 1. (a) A typical simulated phosphor volume with side $d=120$ nm, $n_{DONORS}=200$ (black dots) , $n_{ACCEPTORS}=3000$ (small gray dots) and tunneling constant $\alpha=9\times10^{9}$ m^{-1}. The calculated dimensionless charge density of this system is $\rho'=10^{-5}$. (b) The distribution of nearest neighbor distances at time $t=0$ for the system shown in (a). The solid line represents the well-known analytical equation (6).

For the interested readers, the procedure is translated here into several lines of algorithm pseudo-code as follows:

1. Initialization: $i=1$; $t_1=0$;
2. Lifetime randomization: $t_{fading,j}=-s^{-1}\exp(\alpha r_{min})\ln(1-P_j)$, $j=1.\ n_{donors}$
3. Time advance by shortest lifetime: $t_{i+1}=t_i+\min(t_{fading})$;
4. Recombination: delete n_j corresponding to $t_{fading,j}=\min(t_{fading})$; delete corresponding m.
5. Proceed to next step: $i=i+1$; Return to step 2 unless all electrons recombined.

The simulation is coded in the commercial software package *Mathematica*. The distances of each donor from all acceptors is calculated by using the native *Mathematica* command *EuclideanDistance*, and the positions of donors/acceptors are stored in appropriate numerical arrays called *lists* in *Mathematica*. Typical running times in *Mathematica* are 5–6 min for a simulation consisting of 500 electrons and 3000 acceptors. The use of native commands in *Mathematica* as well as the use of compiled functions provide very significant time savings during execution of the simulations. If desired, the relevant Mathematica code is available by request from the corresponding author.

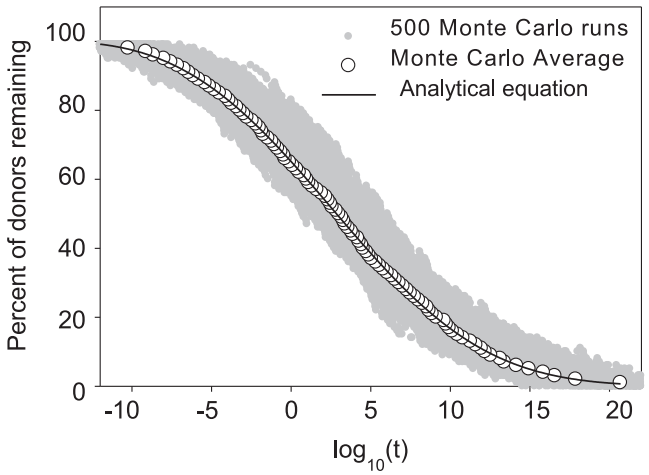

Fig. 2. Simulation of ground state tunneling using a random distribution of donors and acceptors similar to Fig. 1, with parameters $\rho'=10^{-5}$, $s=3\times10^{15}$ s^{-1}, $n_{DONORS}=100$, $n_{ACCEPTORS}=1222$, $\alpha=4\times10^{9}$ m^{-1} and $d=200$ nm. The gray area indicates the results from 500 simulations of the same system, and the solid circle indicates the average of the 500 runs. The standard errors of the 500 runs is about equal to the drawing size of individual circles. The solid line represents the analytical equation (8).

In the Monte Carlo runs we simulate and average the results from 500 such random cubes of the same size, with typical results shown in Fig. 2. The parameters used for the simulation in Fig. 2 are $\rho'=10^{-5}$, $s=3\times10^{15}$ s^{-1}, $n_{DONORS}=100$ and $n_{ACCEPTORS}=1222$, the potential barrier penetration constant $\alpha=4\times10^{9}$ m^{-1} and the size of the cube $d=200$ nm.

The solid line in Fig. 2 represents the following analytical solution for the loss of charge due to ground state tunneling [27]:

$$n(t)=n_0\exp\left[-\rho'\ln(1.8st)^3\right], \quad (8)$$

Very good agreement is obtained between the approximate analytical Eq. (8) and the results of the Monte Carlo simulation. One of the goals of this paper is to test the analytical equations in the literature for a wide range of experimentally observed density values ρ'. For feldspars typical values for ground state tunneling are $\rho'=10^{-6}-6\times10^{-6}$ [4], while experimental work on luminescence signals from feldspars and apatites has shown the existence of both "fast" tunneling components with values in the range $\rho'=10^{-2}-10^{-3}$, and "slower" tunneling components with $\rho'=10^{-4}-10^{-6}$ (see for example Ref. [15] for a detailed analysis of TL and OSL signals from several feldspars, and Ref. [18] for a case study of CW-IRSL signals from a variety of samples).

It is noted that there are two possible ways of presenting the error bars in the Monte Carlo simulations, with the commonly used method requiring the "binning" of events within a chose time interval, e.g. binning of the events within each second. In this paper we use a slightly different method of evaluating the errors, by taking averages along the horizontal (time) axis, since the number of electrons is reduced by one in each step of the simulation. It is then much more natural and computationally easier to take averages and standard deviations along the horizontal (time) axis. From a physical point of view, this is equivalent to studying the spread over time, instead of the spread over the number of recombination events. The final result is the same, since as the number of Monte Carlo runs is increased, the corresponding errors become negligible in either approach.

Fig. 3 shows the results of repeating the simulation in Fig. 2, for different values of the dimensionless charge density in the range $\rho'=10^{-3}-10^{-5}$. The solid lines in Fig. 3 represent the analytical solution from Eq. (8), and they agree well with the Monte Carlo

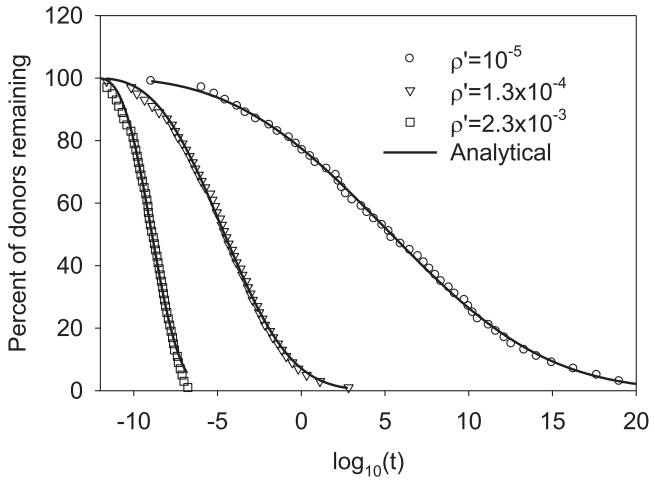

Fig. 3. Comparison of the Monte Carlo simulations in the experimentally observed range of $\rho' = 10^{-3} - 10^{-5}$. The solid lines represent the analytical solution from Eq. (8). Notice the logarithmic scale, showing good agreement in very wide time scales, from 10^{-10} s to thousands of years.

simulations. Based on the logarithmic time scale in Fig. 3, it is concluded that Eq. (8) represents accurately the loss of charge in a very wide range of time scales, from microseconds to thousands of years.

An important consideration during a Monte Carlo simulation is how the results may be affected by the size of the system (e.g. the dimensions of the cube). In addition, it is important to test that the results are independent of the actual total number of electrons used in the simulations (unbiased results). Fig. 4a shows the effect of using a variable number of electrons in the system simulated previously in Fig. 2, while keeping the charge density ρ' constant. In all shown simulated cases, the number of donors in the system is taken to be ~10% of the number of acceptors, in order to ensure that the distribution of distances between the acceptors stays almost constant during the duration of the simulation. Fig. 4b shows the results of simulating several such crystals of different sizes in the range $d = 200$–800 nm; no changes are observed in the graphs for crystals larger than $d \sim 400$ nm. It is concluded that the present model is likely to be applicable for both nanocrystals and for bulk samples.

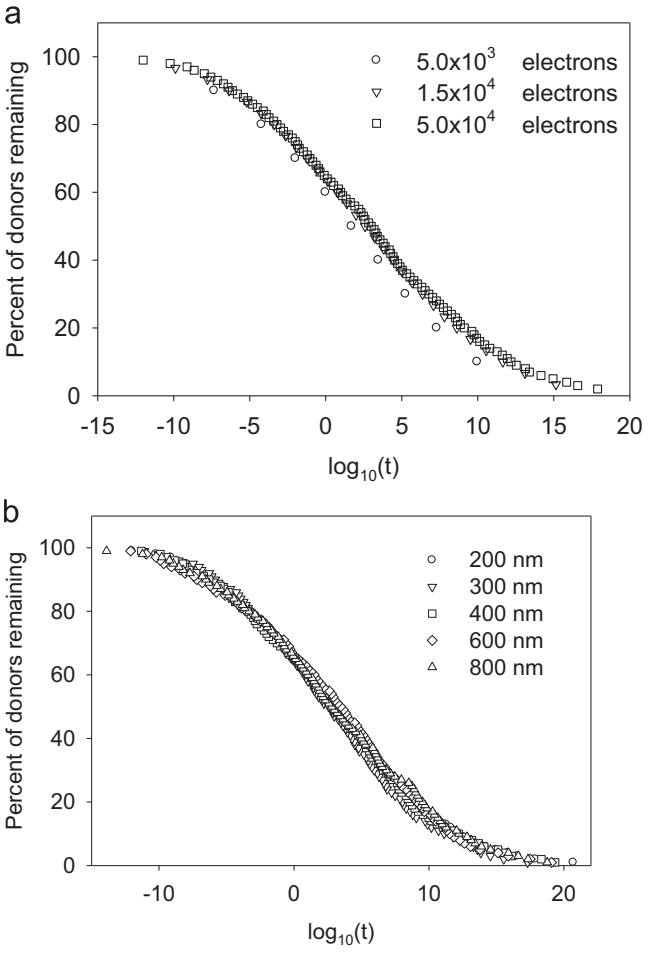

Fig. 4. (a) The effect of using a variable total number of electrons in the system. In all cases the number of donors in the system is taken to be ~10% of the number of acceptors, and the value of ρ' is kept constant. (b) Simulations of several cubes of different sizes, in the range $d = 200$–800 nm. No changes are observed after $d > 400$ nm.

2.2. *Monte Carlo simulations of natural irradiation in the presence of tunneling*

In this subsection we examine the dose response of a feldspar sample in nature, under conditions of simultaneous irradiation and loss of charge due to ground state tunneling. We again follow the algorithm and formulation of Ref. [7], in which the simulation generates several possible times for the tunneling processes according to Eq. (7). The irradiation process is treated non-stochastically in [7], by using the following expression for the time between two charge trapping events:

$$t_{TRAPPING} = \frac{D_o}{D_R} \frac{1}{N - n_{DONORS}}, \tag{9}$$

Where D_R is the natural irradiation rate (Gy/s), D_o is the characteristic dose (Gy), and N is the total number of donor traps. As discussed in [7], if all sampled recombination times from Eq. (7) are larger than the value of $t_{TRAPPING}$ calculated from Eq. (9), then the algorithm creates a new trapped electron-hole pair randomly in the volume of the crystal, and no recombination takes place in this time interval. On the other hand, if $t_{TRAPPING}$ is larger than the minimum recombination time from (9), then a donor-acceptor pair is removed from the volume, as in the previous section. Again as previously, the new distributions of distances are evaluated and stored, and the total time elapsed from the beginning of the simulation is updated. The whole simulation process is repeated until there are no more donors left in the system.

In terms of the algorithm and the pseudo-code listed in the previous section, it is necessary to replace line 3 with the following lines:

3a. If $t_{fading,j} < t_{trapping}$: remove electron-hole pair as previously
3b. If $t_{fading,j} > t_{trapping}$: create electron-hole pair randomly in volume
3c. Time advance by shortest lifetime: $t_{i+1} = t_i + \min(t_{fading}, t_{trapping})$

Fig. 5a shows an example of such a natural irradiation simulation using typical values for feldspars [4], namely $\rho' = 10^{-6}$, $s = 3 \times 10^{15}$ s^{-1}, $D_o = 300$ Gy, $\alpha = 9 \times 10^9$ m^{-1} and the natural irradiation rate $D_R = 1$ Gy/ka ($\sim 3 \times 10^{-11}$ Gy/s). The chosen value of D_o is rather arbitrary, and higher values have been reported in the literature [5]. Additional parameters in the simulation are $n_{ACCEPTORS} = 587$ and $d = 150$ nm. The shaded area in Fig. 5a represents the results of 500 Monte Carlo runs, and the standard errors of the average of these runs are about equal to the drawing size of the open circles in Fig. 5a. An additional time scale is shown at the top of the graph in Fig. 5a, in order to convert the irradiation time into thousands of years (ka).