Optically stimulated exoelectron emission processes in quartz: comparison of experiment and theory

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1. Introduction

The study of exoelectron emission yields useful information on the trapped charge populations in solids. This phenomenon results from the emission of electrons which absorb enough excitation energy to overcome the work function of the material; these electrons may originate directly from traps, or from the conduction band. Ankjærgaard et al. [1] used a flow-through Geiger-Müller pancake electron detector to simultaneously measure optically stimulated electrons (OSE) and optically stimulated luminescence (OSL) from a sedimentary quartz sample. These authors demonstrated that OSE signals from natural quartz grains are easily detectable and reproducible, although they are not as frequent as the OSL signals. Their experiments studied the thermal stability of the OSE and OSL signals, as well as their dependence on the stimulation temperature. The OSL and OSE dose response was also measured, and conclusions were drawn on the movement of electrons in a sample of sedimentary quartz (WIDG8), which has been the subject of several previous experimental studies (e.g. [2,3]). Ankjærgaard et al. [1] found that the OSE and OSL signals behave differently as a function of the preheat temperature (the temperature the sample is heated to after irradiation but prior to the stimulation). The OSE signal decreases steadily between 120 and 400 °C. At the same time, the OSL signal initially increases with the preheat temperature and subsequently decreases rapidly in this temperature range. The OSL results were consistent with previous measurements of this sample by Wintle and Murray [2], with the decrease in the OSL signal apparently due to thermal depletion of the 320 °C OSL trap. The behavior of the OSE signals was interpreted as being inconsistent with thermal detrapping of the electrons, because it is much slower and takes place over a much wider temperature range.

In a second experiment, Ankjærgaard et al. [1] studied the behavior of the OSE and OSL signals as a function of the
stimulation temperature. The OSL signal decreased between room temperature and 400 °C, in agreement with previous measurements which were explained on the basis of thermal quenching [3]. On the other hand, the OSE signal exhibited a peak-shape temperature dependence starting at ~100 °C, with a maximum at ~280 °C. This peak-shaped behavior was found for both the initial 0.5 s of the OSE signal, and for the total OSE signal integrated over 100 s. Ankjærgaard et al. [1] interpreted the initial increase of the OSE signal as due to the increased mean energy of electrons in the conduction band at higher temperatures. They also suggested that thermal erosion of the OSE trap becomes dominant at temperatures above ~280 °C.

This paper makes use of a previously published model for photostimulated exoelectron emission (PSEE) processes in solids to explain the experimental data of Ankjærgaard et al. [1]. The OSL experiment. As will be shown in a later section, in some of the OSE experiments of Ankjærgaard et al. [1] the recombination probability $A_R$ actually varies with the preheat temperature.

If $I_x$ is the number of electrons emitted per cm$^2$ per second from a layer at a depth between $x$ and $x+dx$, then the contribution to OSE from this layer will be given by

$$I_x = N_s dN_s/dx = N_s \Omega_T A_m dx,$$

where $\Omega_T$ is the probability of electron emission from the conduction band, which is a function of the distance $x$ between the electron and the surface. In this equation, $g_s$ is the probability for electrons in the conduction band to move from depth $x$ to the surface, and $D$ is the average transparency of the surface barrier for hot electrons. $\Omega_T$ is the probability of thermal electron emission from the conduction band.

The probability $\Omega_T$ of thermal electron emission from the conduction band is given by the Boltzmann factor

$$\Omega_T = \Omega_0 \exp\left(\frac{-\hbar \nu + \chi - h \nu}{kT}\right),$$

where $\Omega_0$ is a dimensionless coefficient, $\chi$ the work function (in eV), $h \nu$ = energy of the stimulating photons (in eV), $T$ the temperature (in K), $k$ = Boltzmann constant and $\hbar \nu$ is the depth of the optically sensitive trap (in eV). These energy levels are shown schematically in Fig. 1.

By solving Eqs. (1) and (2) using the quasi-equilibrium assumption $dn/dt = 0$, and by integrating over the layer $I$ of the sample, Oster and Haddad [4] obtained the following expression for the instantaneous OSE intensity

$$I = f(\lambda) \int_0^\infty \frac{\Omega_T}{A_R + \Omega_T} \exp(-E_s t),$$

where the function $f(\lambda)$ is given by

$$f(\lambda) = 1 - e^{(\lambda-1)^2}.$$
and where \( l \) is the entire excited layer and \( \lambda \) represents the effective depth of the emission layer (Oster et al., [6]). The quantity \( n_0 \) represents the initial electron concentration in the traps.

### 1.2. Photo-thermostimulated emission

In the case of transition (1) shown in Fig. 1, the trapped electrons can be excited optically to the conduction band, and subsequently will be emitted from the surface via a thermally assisted process. In this case, the energy of the photon is such that

\[
\epsilon_0 < h\nu < \epsilon_0 + \chi
\]

and one obtains the following simplified expression for the OSE signal (Oster and Haddad, [4], their Eq. (9)):

\[
l = B \exp \left\{ -\left( \epsilon_0 + \chi - h\nu \right) \right\} \frac{\exp(-E_l)}{kT} = I_0 \exp(-E_l t), \tag{9}
\]

where

\[
I_0 = f(\lambda)Dn_0E_l \frac{\Omega}{\lambda l}
\]

and \( n_0 \) represents the initial concentration of trapped electrons at time \( t = 0 \). By taking the natural logarithm of Eq. (9), one obtains the expression

\[
\ln I_0 = \ln B - \frac{\epsilon_0 + \chi}{kT} + \frac{h\nu}{kT}.
\]

From Eq. (9) it is clear that the initial emission intensity \( I_o \) depends on the temperature \( T \) and also on the frequency of the stimulating light \( \nu \). The total intensity \( I \) depends on \( I_0 \) and decreases exponentially with time. The rate of exponential decay of the OSE signal from Eq. (9) is equal to \( I_0 \). This is the same as the time decay rate of the OSL signal, in agreement with the experimental findings of Ankjærgaard et al. [1].

It must be noted that the initial concentration of trapped electrons \( n_0 \) will be a function of the stimulation temperature and/or the preheat temperature of the sample.

### 2. Comparison of the model and experimental data

#### 2.1. Dependence of the OSE signal on the stimulation temperature

The dependence of OSE signal on stimulation temperature was recorded using a single aliquot of sedimentary quartz (WIDG8). The aliquot was given a beta dose of 44 Gy from a \(^{90}\)Sr/Y source and preheated to 260 °C for 10 s before blue (470 nm) LED stimulation at some temperature. This was followed by a test dose measurement where the same aliquot was given a dose of 18 Gy, preheated to 260 °C and blue light stimulated at 125 °C. This cycle was repeated for different stimulation temperatures. The OSE and OSL signals were recorded simultaneously; the electrons were emitted into a counting gas (99% argon and 1% isobutane) and detected by a Geiger-Müller counter, the photons measured through an U-340 glass filter using a PM-tube.

Note that the experimental uncertainties in the data shown in Figs. 3, 5, 7–9 are based only on counting statistical errors (the square-root of the total number of counts per channel). They are smaller than the size of the symbols used in these figures, and are thus not visible.

The experimental dependence of the OSE signal \( I(T) \) on the stimulation temperature is shown in Fig. 2a. According to Eq. (11), a graph of \( \ln I \) against \( 1/kT \) should yield a straight line at low temperatures \( T \), with a negative slope of \( W = h\nu - \epsilon_0 - \chi \). Fig. 2b shows that the initial rise part of this graph is indeed linear, with a negative slope of \( W = -(0.29 \pm 0.02) \) eV for the total OSE data.

To the best of our knowledge, there are no previously published values for the work function \( \chi \) of quartz samples in the literature. This value of \( \chi \) is now used to obtain a quantitative fit to the experimental data of OSE dependence on stimulation temperature shown in Fig. 2a. Ankjærgaard et al. [1] interpreted the descending part of the data in Fig. 2a as due to thermal depletion of the main OSL traps at \( \sim 320 \) °C. For a first-order kinetic process, the thermal depletion of a single thermoluminescence (TL) or OSL trap is given by

\[
\ln(\text{OSE}_{\text{total}}) = \ln(\text{OSE}_{\text{initial}}) - W (1 - e^{-t/T})
\]

where \( \text{OSE}_{\text{initial}} \) is the entire excited layer and \( \lambda \) represents the effective depth of the emission layer (Oster et al., [6]). The quantity \( n_0 \) will be a function of the stimulation temperature and/or the preheat temperature of the sample.
by the well-known first-order expression

\[ n = n_0 \exp(-\lambda t) = n_0 \exp(-E_i/kT)t, \]  

(13)

where \( n \) is the concentration of electrons at time \( t \) (in cm\(^{-3}\)), \( n_0 \) the initial concentration at time \( t = 0 \), \( \lambda = s \exp(-E_i/kT) \) represents the decay constant at temperature \( T \) (in s\(^{-1}\)), \( E_i \) the energy of the trap below the conduction band (in eV), and \( s \) the frequency factor of the trap (in s\(^{-1}\)). The time \( t \) is the duration of heating of the sample at the temperature \( T \) and \( k \) is the Boltzmann constant.

The decrease in the concentration of electrons due to the increased temperature \( T \) is, therefore, given by the depletion factor \( D(T) \) expressed by

\[ D(T) = n/n_0 = \exp(-s \exp(-E_i/kT)t_\beta). \]  

(14)

This depletion factor \( D(T) \) is shown in Fig. 3a. The values of the constants in this expression are taken as \( E_i = 1.75 \text{ eV} \) for the 320 °C OSL trap, \( s = 5 \times 10^{13} \text{ s}^{-1} \) and \( t_\beta = 10 \text{ s} \) is the preheat time used in experiments of Ankjærgaard et al. [1]. The thermal assistance factor \( \exp(-W/kT) \) is also shown in Fig. 3a; the product of the effective depletion factor \( D_{\text{eff}}(T) \) and of the decreasing function \( D(T) \) yields a broad peak shape with a maximum at \( -580 \text{ K} (\sim 307 \text{ °C}) \). This broad peak shape is shown superimposed on the experimental data in Fig. 3b. Inspection of Fig. 3b shows a general qualitative agreement of theory and experiment, but the overall calculated temperature dependence of the OSE signal is narrower than indicated in the experimental data. This suggests a possible thermal broadening of the observed temperature dependence of the OSE data, possibly due to interactions with the lattice vibrations.

This thermal broadening can be expressed by using a normalized random Gaussian distribution of the energy \( E \) given by

\[ g(E) = \exp\left(-\frac{(E - E_1)^2}{2\sigma^2}\right), \]  

(15)

where \( E_1 = 1.75 \text{ eV} \) and \( \sigma \) represents the standard deviation or width parameter of the Gaussian distribution. The effect of this energy distribution will be to produce an effective depletion factor \( D_{\text{eff}}(T) \), which can be calculated by integrating the expression \( D(T) \) in Eq. (14) over all possible energies \( E \)

\[ D_{\text{eff}}(T) = \int_{-\infty}^{+\infty} g(E)D(T)\,dE. \]  

(16)

By substituting the value of \( D(T) \) from Eq. (14), this becomes

\[ D_{\text{eff}}(T) = \int_{-\infty}^{+\infty} g(E)\exp(-s \exp(-E/kT)t_\beta)\,dE. \]  

(17)

This integral can be calculated numerically rather easily to yield a graph of the effective depletion factor \( D_{\text{eff}}(T) \) as a function of the stimulation temperature \( T \), as shown in Fig. 4, for several values of the Gaussian width parameter \( \sigma \). As may be expected on physical grounds, increasing of the Gaussian width parameter \( \sigma \) leads to an overall thermal broadening of the depletion factor \( D_{\text{eff}}(T) \). Fig. 5a shows the optimal \( g(E) \) distribution with \( E_1 = 1.75 \text{ eV} \) and \( \sigma = 0.14 \text{ eV} \); this \( g(E) \) distribution gives a good quantitative fit to the experimental data, as shown in Fig. 5b.

### 2.2 Dependence of the OSE signal on the preheat temperature

In a second experiment, Ankjærgaard et al. [1] studied the dependence of the OSE signal on the preheat temperature by using a single aliquot of sample WIDG8. The aliquot was irradiated with a dose of 330 Gy, preheated to a given preheat temperature for 10 s, and optically stimulated at 125 °C using blue LEDs. This cycle was repeated for different preheat temperatures using the same aliquot, and the results of the experiment are shown in Fig. 6. Ankjærgaard et al. [1] found that the OSE signal decreases continuously with the preheat temperature between 130 and 400 °C. They suggested that there may be a discrepancy between this temperature dependence and the thermal depletion...
of the OSL traps in quartz, because the experimental curve decays much more gradually and over a larger temperature range than the expected thermal depletions of the OSL traps. This is shown clearly in Fig. 6, where the predicted depletion factor \( D(T) \) of the 320°C trap in quartz is also shown together with the experimentally measured OSE intensity.

By applying the model of Oster and Haddad [4], we will show that the apparent discrepancy in Fig. 6 between the experimental data and the depletion factor \( D(T) \) can be explained within the same photo-thermal mechanism discussed in the previous section.

We first combine Eqs. (9) and (10) to obtain the complete expression for the instantaneous OSE intensity:

\[
l = f(z)D(T)p \frac{\Omega_s}{A_p} \exp\left(-\frac{e_0 + \gamma - hv}{kT}\right) \exp(-zE_0).
\]  

(18)

Here \( T_{stim} \) is the temperature of the sample during the optical stimulation; during the experiment of Fig. 6, the stimulation temperature is fixed at \( T_{stim} = 125 \) °C. The only two quantities in Eq. (18) which are dependent on the preheat temperature \( T_p \) are the initial concentration of electrons in the trap \( n_o \) at the beginning of the optical stimulation, and the recombination probability \( A_p \). The initial concentration \( n_o \) will depend on the preheat temperature according to the thermal depletion factor \( D(T_p) \) as shown in Fig. 7a of this paper, together with the thermal depletion factor \( T_p \) required for the 320°C trap in quartz.

\[
D(T_p) = \exp(-s \exp(-E/kT_p))
\]

(14)

From Eq. (3), the recombination probability \( A_p \) is proportional to the concentration of holes in the recombinant center \( m(T_p) \), which in turn is a function of the preheat temperature \( T_p \). More specifically, it is possible during the preheat stage to thermally transfer holes from the Zimmerman hole reservoirs (levels 6 and 7) into the recombinant center; this thermal transfer of holes leads to an increase of the concentration of holes in the recombinant center \( m(T_p) \), and to corresponding increase of the OSL recombination probability \( A_p \); this increased competition will reduce the number of electrons contributing to the OSE signal. This thermal transfer phenomenon has been documented widely both by experiments and by simulations (see for example, Pagonis et al. [8] and references therein).

While it is not possible to measure directly the quantity \( m(T_p) \), one can measure by proxy the sensitivity \( S(T_p) \) of the sample to a small test dose, which is proportional to \( m(T_p) \). By substituting \( A_p \propto m(T_p) \propto S(T_p) \) into Eq. (18), we obtain

\[
l(T_p) \propto D(T_p) \frac{1}{S(T_p)}.
\]  

(19)

This equation indicates that the experimentally measured OSE intensity \( l(T_p) \) should be proportional to the ratio of the two factors \( D(T_p)/S(T_p) \). We now offer two possible ways of estimating the temperature-dependent sensitivity \( S(T_p) \), firstly by using experimental data and secondly by using simulation. Wintle and Murray [2] measured the sensitivity \( S(T_p) \) of WIDG8, the same sample used in the OSE experiments of Ankjærgaard et al. [1]. During the pulse-annealing experiments of Wintle and Murray [2], an aliquot of WIDG8 was irradiated with 56 Gy, then was preheated for 10 s at progressively higher temperatures from 160 to 500°C, each time measuring the OSL at 125°C using a short 0.1 s stimulation. The 110°C thermoluminescence peak was measured at each step by delivering a small test dose of 0.1 Gy. The sensitivity \( S(T_p) \) was measured by the response of the 110°C TL peak to the small test dose.

The experimental results of Wintle and Murray [2] are reproduced in Fig. 7a of this paper, together with the thermal depletion factor \( D(T_p)/S(T_p) \) shown in Fig. 7b, together with the normalized OSE data of Ankjærgaard et al. [1]. Fig. 7b shows that the two quantities are indeed proportional to each other in the temperature range for which the Wintle and Murray data are available.

The temperature-dependent sensitivity \( S(T_p) \) can also be estimated by simulation of the pulse-annealing experiment of Wintle and Murray [2]. Such a simulation was carried out recently by Pagonis et al. [8], who showed that it is possible to simulate the changes in sensitivity \( S(T_p) \) by using the comprehensive quartz model of Bailey [7]. The simulated sensitivity \( S(T_p) \) was shown in Fig. 6b and e of Pagonis et al. [8]. We have repeated the simulation...
by using the rather large beta dose of 330 Gy employed in the OSE experiments of Ankjærgaard et al. [1], and the results of the simulated $S(T_p)$ are shown in Fig. 8a. The ratio of the two simulated factors $D(T_p)/S(T_p)$ is shown in Fig. 8b together with the normalized OSE data. Fig. 8b shows again that the two graphed quantities are indeed proportional to each other, as expected from Eq. (15).

In conclusion, this section has shown that the experimentally measured OSE intensity $I(T_p)$ during the preheat experiment of Ankjærgaard et al. [1], can be explained satisfactorily by using the photo-thermostimulated process shown in Fig. 1. By using either simulation or previously published experimental data, it is found that there is no discrepancy between the results of the preheat experiment of Ankjærgaard et al. [1] and the thermal depletion rate of the 320 °C trap in quartz; the OSE signal decreases more rapidly than the OSL signal because of a change in competition between the two processes of luminescent recombination and electron ejection from the surface.

2.3. Dependence of the OSL signal on the preheat temperature

In a recent modeling study, Pagonis et al. [8] modeled the dependence of the OSL signal from quartz on the preheat temperature, using the comprehensive kinetic model by Bailey [7]. A description of the model of the parameters used and of the equations in the model was given in Pagonis et al. [8], and will not be repeated here. However, it is important to realize that this type of simulation involves optical and thermal stimulation of electrons and holes through both the conduction and the valence band, and is of a very different nature from the OSE processes shown in Fig. 1 of this paper.

We have simulated the experimental protocol of Ankjærgaard et al. [1] using the Bailey model [7]. In their protocol an aliquot of sample WIDG8 was irradiated with a dose of 330 Gy, preheated to a given preheated temperature for 10 s, and optically stimulated at 125 °C. This cycle was repeated for different preheat temperatures using the same aliquot, and the experimental data are shown in Fig. 9, together with the results of the model. The shape of the modeled data is very similar to that of the experimental data; the small differences can be easily accounted for by making small adjustments in the thermal kinetic parameters for the OSL traps in the model.

2.4. Dependence of the OSL signal on the stimulation temperature

We have also simulated the second experimental protocol of Ankjærgaard et al. [1] in which a variable stimulation temperature is used by using the Bailey [7] model. In this protocol, an aliquot was given a dose of 44 Gy and a preheat temperature of 260 °C was used, followed by blue light stimulation at a variable stimulation temperature. The same aliquot was then given a test dose of 18 Gy, preheated to 260 °C and stimulated at 125 °C. Finally, the aliquot was optically stimulated at 280 °C for 100 s. The experimental data of Ankjærgaard et al. [1] are shown
in Fig. 10, together with the results of the model. Apart from a factor of 2 difference for the value of the overall OSL intensities, the modeled data show the exact same behavior as the experimental data.

3. Conclusions

The model of Oster and Haddad [4] provides a quantitative description of the exoelectron emission measurements of Ankjærgaard et al. [1]. The experimental data are consistent with a value of $\chi \sim 1.2$ eV for the work function of quartz, and a thermal assistance energy of $W = (0.29 \pm 0.02)$ eV. Within this model, both the variable preheat and variable stimulation temperature dependences of the OSE signal were shown to involve the same photo-thermostimulated process associated with the main OSL trap at $\sim 320$ °C.

On the other hand, the corresponding OSL processes taking place in the same samples were explained using the comprehensive model of Bailey [7]. Within this model, the dependence of the OSL signal on the preheat and stimulation temperatures are explained on the basis of electron and hole transitions taking place through the conduction and valence bands. The two models used in this paper, namely the Oster and Haddad model for OSE and the Bailey model for OSL, are completely consistent with each other, and help elucidate the mechanisms involved in the charge movement in quartz samples.

References