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On the quasi-equilibrium assumptions in the theory of thermoluminescence (TL)

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ABSTRACT

The phenomenon of thermoluminescence (TL) is governed by a set of simultaneous differential equations. When one studies the properties of a single peak, resulting from the thermal release of electrons from a trap into the conduction band, followed by radiative recombination with holes in centers, the set consists of three non-linear equations. Even in this simple case, the equations cannot be solved analytically. In order to get approximate solutions, the conventional way has been to make the "quasi-equilibrium" assumptions, namely that $|dn_c/dt|$ is significantly smaller than $|dn/dt|$ and $|dm/dt|$, where n and m are the occupancies of traps and centers, respectively, n_c is the concentration of electrons in the conduction band, and $n_c \ll n$; $n_c \ll m$. We show, using simulations as well as analytical arguments that the former condition often does not occur; however, its consequences are valid. The reason is that the conventional quasi-equilibrium assertion must be replaced by a different condition. As for the smallness of the concentration of free electrons, we show that it may not be fulfilled at the high-temperature end of a single glow peak or in the highest-temperature peak in a series. In some cases, this condition results in a broad high-temperature tail of the TL peak, as previously observed experimentally in several materials.

1. Introduction

The well-known model for explaining a single thermoluminescence (TL) peak consists of an electron trapping state, the conduction band and a hole center. The process of TL consists of the transition of electrons released thermally from the electron trap into the conduction band from which they may either recombine with holes in the center or retrap, namely, fall back into the trap.

Halperin and Braner [1] wrote the set of three simultaneous differential equations governing the TL process for the one trap, one center case (see Fig. 1), and for electrons going through the conduction band before performing recombination:

$$I = -\frac{dm}{dt} = A_m m n_c, \tag{1}$$

$$-\frac{dn}{dt} = sn\exp(-E/kT) - A_n(N-n)n_c, \tag{2}$$

$$\frac{dn_c}{dt} = sn\exp(-E/kT) - n_c[A_m m + A_n(N-n)]. \tag{3}$$

The meaning of the parameters is given in the caption of Fig. 1. Solving these equations along with the heating function $T(t)$ should yield the shape of the TL peak $I(T)$. In most cases, the heating function used is linear, namely, $T = T_0 + \beta t$, where T (K) is the variable temperature, T_0 (K) is the initial temperature, t (s) is time and β (K s^{-1}) is the constant heating rate. k (eV K^{-1}) is the Boltzmann constant.

This set of nonlinear differential equations cannot be solved analytically, and in order to get simpler expressions, Halperin and Braner have now assumed that $dn_c/dt = 0$, which is, more or less, the quasi-equilibrium assumption. Using this in Eq. (3) yields

$$n_c = \frac{sn\exp(-E/kT)}{A_m m + A_n(N-n)}, \tag{4}$$

and substituting this expression in Eq. (1) yields

$$I = -\frac{dm}{dt} = sn\exp(-E/kT)\frac{A_m m}{A_m m + A_n(N-n)}. \tag{5}$$

Obviously, the condition $dn_c/dt = 0$ cannot be fulfilled strictly since the concentration of electrons in the conduction band varies during heating, and later the quasi-equilibrium condition has been stated as

$$\left|\frac{dn_c}{dt}\right| \ll \left|\frac{dm}{dt}\right|, \ \left|\frac{dn}{dt}\right|. \tag{6}$$

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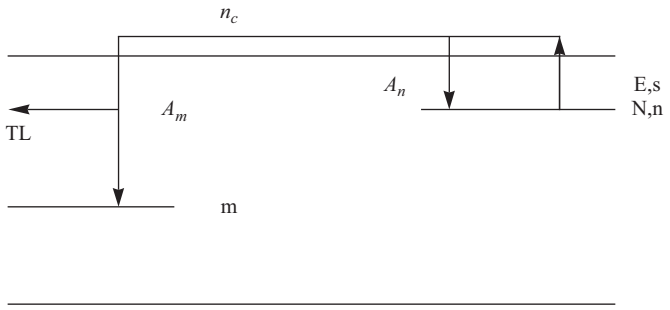

Fig. 1. Energy level diagram of the model explaining a single TL peak. N (cm^{-3}) is the total concentration of trapping states and n (cm^{-3}) its instantaneous occupancy. m (cm^{-3}) is the instantaneous concentration of holes in centers and n_c (cm^{-3}) the instantaneous concentration of electrons in the conduction band. A_m (cm^3s^{-1}) and A_n (cm^3s^{-1}) are the recombination- and retrapping-probability coefficients. E (eV) is the activation energy and s (s^{-1}) is the frequency factor. "TL" denotes the emitted thermoluminescence.

Also, an additional assumption has been made, namely,

$$n_c \ll n, \tag{7}$$

and since in this model $n+n_c=m$, obviously, this implies that $n\sim m$. Eq. (5) includes two functions, n and m, and additional information is required to solve it. If recombination dominates, namely, $A_m m \gg A_n(N-n)$, one gets the first-order kinetics equation whereas if retrapping dominates, $A_m m \ll A_n(N-n)$, and the trap is far from saturation, $n \ll N$, one gets second-order kinetics. Different kinds of intermediate cases are possible. As shown by Chen [2], first- and second-order TL peaks can be characterized by their symmetry factor μ_g, where $\mu_g=\delta/\omega$, $\delta=T_2-T_m$, $\omega=T_2-T_1$ and where T_m is the temperature at the maximum and T_1, and T_2, are the temperatures at the low and high points of half intensity, respectively. $\mu_g \approx 0.42$ indicates first order and $\mu_g \approx 0.52$ indicates second order.

It should be noted that Kelly et al. [3] pointed out that the quasi-equilibrium conditions as previously used are not convincing as they lack universal validity. Different aspects of the quasi-equilibrium assumption have been discussed by Lewandowski et al. [4,5] and by Sunta et al. [6–9]. Sunta et al. [8] studied the solution of the equations associated with a model with one recombination center, one active trap and one thermally disconnected deep trap (TDDT). They found that with certain sets of parameters, $|dn_c/dt| \sim |dn/dt|$. Shenker and Chen [10] and Opanowicz and Przybyszewki [11] described the results of numerical solutions of the set of Eqs. (1–3), and checked the occurrence of the condition (6). A similar work on the parallel condition in localized transitions has been reported by Bull [12].

In the present work we show examples of numerical solutions of Eqs. (1–3), where in addition to the temperature dependence of the emission intensity, we monitor the values of n, m, $|dn/dt|$, $|dm/dt|$ and $|dn_c/dt|$. It turns out that with a choice of plausible sets of parameters for the simulation, the condition (6) may not be fulfilled. Yet, when substituting the simulated values of n and m in Eq. (5) and comparing these results to the intensity from Eq. (1), as simulated by the solution of Eqs. (1–3), there is quite a good agreement between the two. We then propose a revised condition that replaces Eq. (6), which is fulfilled in the examples given and probably more generally. Instead of comparing the rate of change of the free electrons with the rate of change of trapped electrons and holes, it is compared to the rates of thermally adding electrons to the conduction band and depleting them by both retrapping and recombination.

Another interesting point has to do with the behavior of the declining part of a TL peak at the high-temperature end. In literature, there is evidence that at the high-temperature part of a single TL peak, or usually, when there are several peaks, at the high temperature part of the last peak in a series, a long tail is observed. The value of μ_g is significantly higher which is typical of an effective kinetics order higher than 2. Obviously, the study of Eq. (5) does not result in an order larger than 2, a case which is characterized by the peak being nearly symmetric. Experimental results of such a long tail have been given by several authors concerning several materials. Herman and Meyer [13] reported such long tail in willemite. Singh and Charlesby [14] described it in Thymine whereas Liu et al. [15] showed it in PET. Kristianpoller et al. [16] reported a long high-temperature tail in mica and Sakurai [17] found it in brown microline. More results of the same sort were given by Furetta et al. [18] in RbCl:OH^-, by Mathur et al. [19] in $CaSO_4$:Dy, by Denis et al. [20] in Eu^{2+} doped $Ba_{13-x}Al_{22-2x}Si_{10+2x}O_{66}$ (x∼0.6) and by Smet et al. [21] in $M_2Si_5N_8$:Eu (M=Ca, Sr, Ba). In the present study we find that at the high temperature range, the condition (7) may not be fulfilled, and rather we get that $n_c \sim m$ whereas n is significantly smaller. We show that this may result in the occurrence of a high-temperature tail similar to the reported experimental results.

2. Numerical simulation and analytical considerations.

In order to check the assumptions and results, we have chosen a set of parameters, shown below in the caption of Fig. 2. We have solved the set of equations numerically to yield the TL intensity ($-dm/dt$), and in parallel, used the computed values of m and n to evaluate the approximation given by Eq. (5). The results are shown in Fig. 2. Except for a small percent of difference in the absolute intensity, the two curves look very similar. We have checked now the time derivatives of the concentrations; the results are shown in Fig. 3. Obviously, the TL intensity is equal to $-dm/dt$. Surprisingly, $|dn_c/dt|$ is significantly larger than $|dm/dt|$ and only a little smaller than $|dn/dt|$ which means that the condition in Eq. (6) is not fulfilled. How is it that the common approximation, which is apparently confirmed in Fig. 2, is valid in this case?

Let us consider more closely Eq. (3). While saying that $dn_c/dt \approx 0$ we do not really mean that $dn_c/dt=0$, but rather, we may mean that $dm/dt \approx dn/dt$. Using Eqs. (1) and (2) this

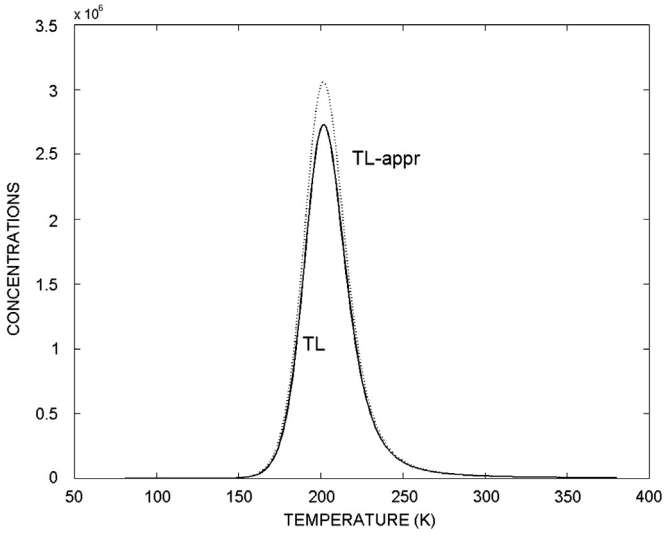

Fig. 2. TL curve simulated by numerical solutions of Eqs. (1–3). "TL" denotes the simulated results from Eq. (1) whereas "TL appr" is found by Eq. (5). The parameters chosen are $n_0=m_0=10^8\ cm^{-3}$; $N=10^9\ cm^{-3}$; $E=0.4$ eV; $s=10^{11}\ s^{-1}$; $A_m=10^{-8}\ cm^3s^{-1}$; and $A_n=10^{-7}\ cm^3s^{-1}$. The heating rate is $\beta=1\ K\ s^{-1}$.

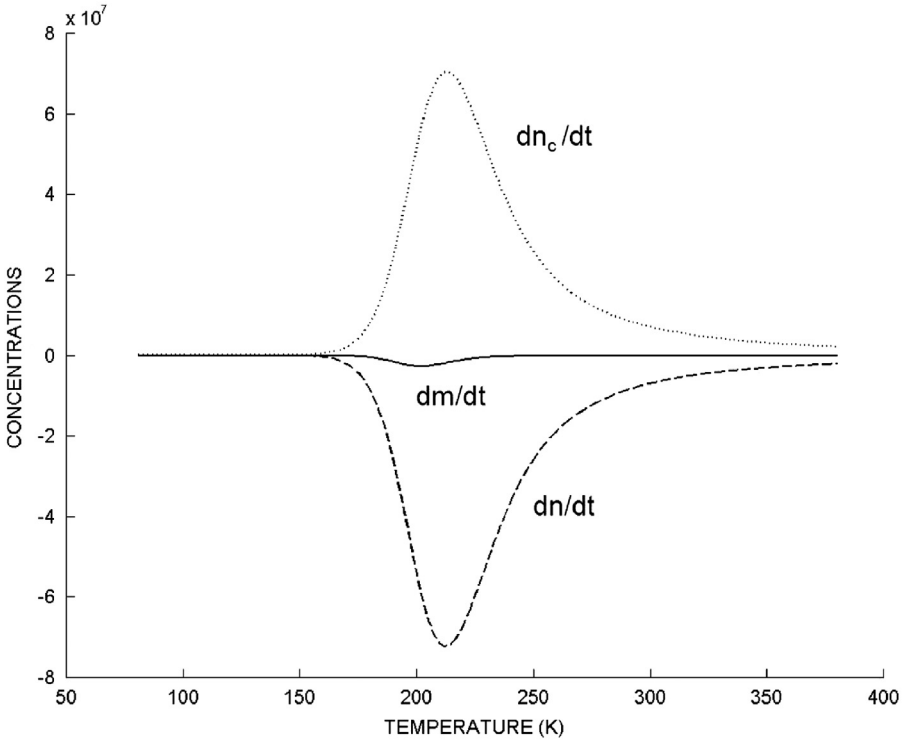

Fig. 3. With the same parameters as in Fig. 2, the simulated derivatives dn/dt, dm/dt and dn_c/dt are shown as functions of temperature.

would mean:

$$-A_m m n_c \approx A_n(N-n)n_c - sn\exp(-E/kT). \tag{8}$$

However, in order to get the expression in Eq. (4), we use the condition

$$sn\exp(-E/kT) \approx n_c[A_m m + A_n(N-n)]. \tag{9}$$

It is possible that the two sides of Eq. (8) are rather small quantities and therefore the difference between them, which, according to Eq. (3) is dn_c/dt, is not smaller than each of the two sides of the equation, which are dm/dt and dn/dt, respectively. It appears that the comparison to be made about the approximate validity of Eqs. (4) and (5) has to do with the terms

$$\text{term1} = sn\exp(-E/kT), \tag{10}$$

and

$$\text{term2} = n_c[A_n(N-n) + A_m m]. \tag{11}$$

In particular, we have to examine the magnitudes of term1 and term2 as compared to dn_c/dt which, according to Eq. (3), can be written as

$$\text{term1} - \text{term2} = \frac{dn_c}{dt}. \tag{12}$$

Fig. 4 shows that, indeed, at least in this particular case, term1 and term2 are nearly equal, and the difference dn_c/dt is small relative to these terms, which justifies the approximate validity of Eqs. (4) and (5). The physical meaning of these two terms is quite obvious; term1 represents the rate at which electrons are added thermally into the conduction band whereas term2 is the rate at which they are depleted from the conduction band in the two channels of retrapping and recombination.

It therefore seems that the assumption $|dn_c/dt| \approx 0$ should be understood in a slightly different way than before. The smallness of $|dn_c/dt|$ as compared to $|dm/dt|$ and $|dn/dt|$ seems not to be valid and the validity of the approximate expressions (4) and (5) depends on the smallness of $|dn_c/dt|$ as compared to term1 and term2, which approximately takes place. These two terms are, respectively, the rates of addition and subtraction of electrons from the conduction band. The difference between the numerically simulated and approximate curves in Fig. 2 seems to be associated with the fact that $|dn_c/dt|$ is small (though not negligibly small) as compared to term1 and term2. Although this has been shown for a specific set of parameters, it seems that it is quite general.

An alternative possibility of getting a TL peak is when the trapped electrons are stimulated thermally into a localized excited state from which radiative recombination into an adjacent recombination center is possible. As explained by Chen [22] and Bull [12], the set of governing equations for this situation is

$$I(T) = -\frac{dm}{dt} = pn_e, \tag{13}$$

$$-\frac{dn}{dt} = sn\exp(-E/kT) - sn_e, \tag{14}$$

$$m = n + n_e, \tag{15}$$

where $n_e(\text{cm}^{-3})$ is the instantaneous concentration of electrons in the excited state and $p(\text{s}^{-1})$ is the recombination probability of an excited electron. From Eq. (15), we can write for the derivatives

$$\frac{dn_e}{dt} = \frac{dm}{dt} - \frac{dn}{dt}. \tag{16}$$

By inserting Eqs. (13) and (14) into Eq. (16) one gets

$$\frac{dn_e}{dt} = sn\exp(-E/kT) - (p+s)n_e. \tag{17}$$

In order to proceed with the approximation, one assumes in analogy to the previous case that $|dn_e/dt| \approx 0$. Again, in analogy with the case of transition of electrons through the conduction band, it should not be understood as suggested before [12] that

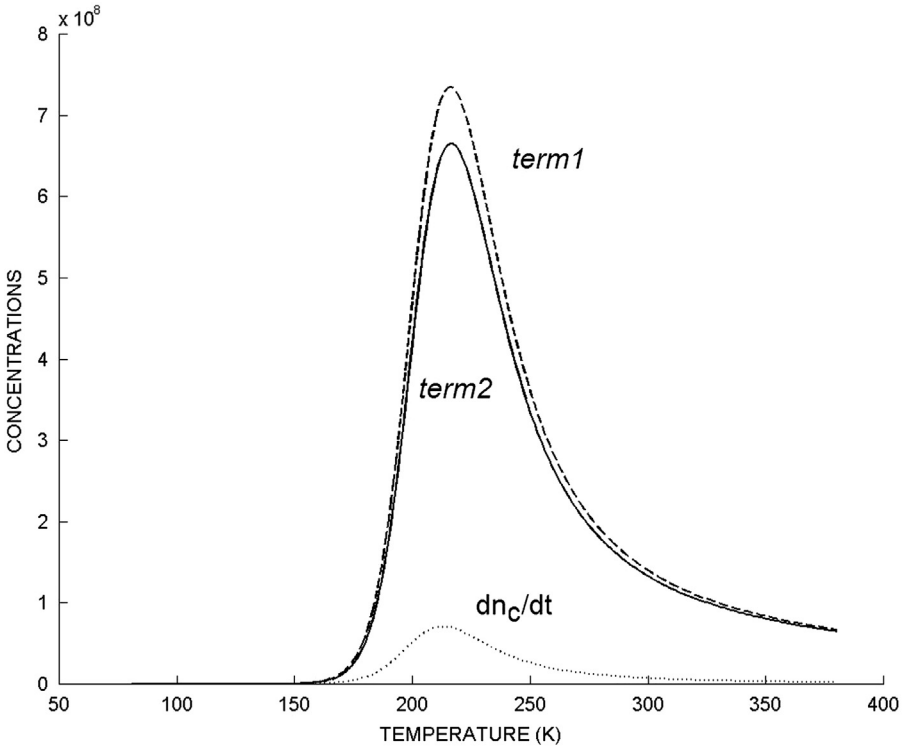

Fig. 4. With the same parameters as in Figs. 2 and 3, the simulated factors "term1" and "term2" along with dn_c/dt are shown as functions of temperature.

$|dn_e/dt| \ll |dn/dt|$, but rather

$$\left|\frac{dn_e}{dt}\right| \ll sn\exp(-E/kT); \quad (p+s)n_e. \tag{18}$$

Note that in comparison with the case of transition through the conduction band, $sn\exp(-E/kT)$ is the same as term1 in Eq. (10) whereas $(p+s)n_e$ replaces term2 in Eq. (11). By using the condition (18), Eq. (17) becomes

$$n_e \approx \frac{sn\exp(-E/kT)}{p+s}, \tag{19}$$

from which, the approximate equation for TL is reached:

$$I = -\frac{dm}{dt} = \frac{ps}{p+s} m\exp(-E/kT). \tag{20}$$

This is a first-order equation with an effective frequency factor of $ps/(p+s)$; the first-order feature holds for both high and low retrapping as long as condition (18) holds.

It should be noted that in a recent paper, Chen et al. [23] discussed a two-stage model of TL in which the first stage of excitation is localized and in the second stage, electrons are raised thermally into the conduction band before performing radiative recombination with holes in the centers. Here, the smallness of $|dn_e/dt|$ is compared to the value of the relevant magnitude which in this case is $p+s_2\exp(-E_2/kT)$ (see Eq. (6)). In analogy to the present cases, an approximate equation is reached for n_e, from which conclusions are drawn concerning the relevant two-stage TL peak.

3. Long tail at the High temperature side of a TL peak

In the simulations, it has been found that a single TL peak may have a long tail in the high-temperature side. Note that similar results are found in the highest-temperature peak in a series as described in the companion paper by Chen and Pagonis [24] (see also McKeever et al. [25]). An example of such a single peak is shown in Fig. 5. One should note that the parameters chosen for Figs. 2 and 5 are the same except that in the former, $A_m = 10^{-8}\,\mathrm{cm^3 s^{-1}}$ and $A_n = 10^{-7}\,\mathrm{cm^3 s^{-1}}$ and in the latter, $A_m = 10^{-10}\,\mathrm{cm^3 s^{-1}}$ and $A_n = 10^{-9}\,\mathrm{cm^3 s^{-1}}$. Thus, the ratio A_m/A_n is the same in both cases, but in the case of Fig. 5, the two probability coefficients are relatively low, which results in the mentioned accumulation of electrons in the conduction band. Also, the results of the simulations have shown that at the high temperature side, $m \approx n_c$ as depicted in Fig. 6. This may be the case, as will be shown in the results of simulations below when both A_m and A_n are rather small. At the high-temperature range, the rate of release of electrons from the trap gets very high and the recombination and retrapping probability coefficients are rather small, and therefore, electrons are accumulating in the conduction band.

Considering the fact that $m \approx n_c$ in this range, Eq. (1) will be

$$I = -\frac{dm}{dt} = A_m m^2, \tag{21}$$

and the solution is

$$\frac{1}{m} = \frac{1}{m_0} + \frac{A_m}{\beta} t. \tag{22}$$

It is obvious that this is a time dependent, not temperature dependent function. The point is that as of a certain temperature, although the Botlzmann function is increasing, the trap population is decreasing very fast, and the net effect is that the concentration m and the time dependence of TL intensity are practically independent of temperature. The TL intensity at this range will be

$$I = A_m m n_c = A_m m^2 = \frac{A_m m_0^2}{[1+m_0 A_m t]^2}. \tag{23}$$

The meaning of this equation is, for example, that if we are in a high enough temperature range, there is a decay of luminescence

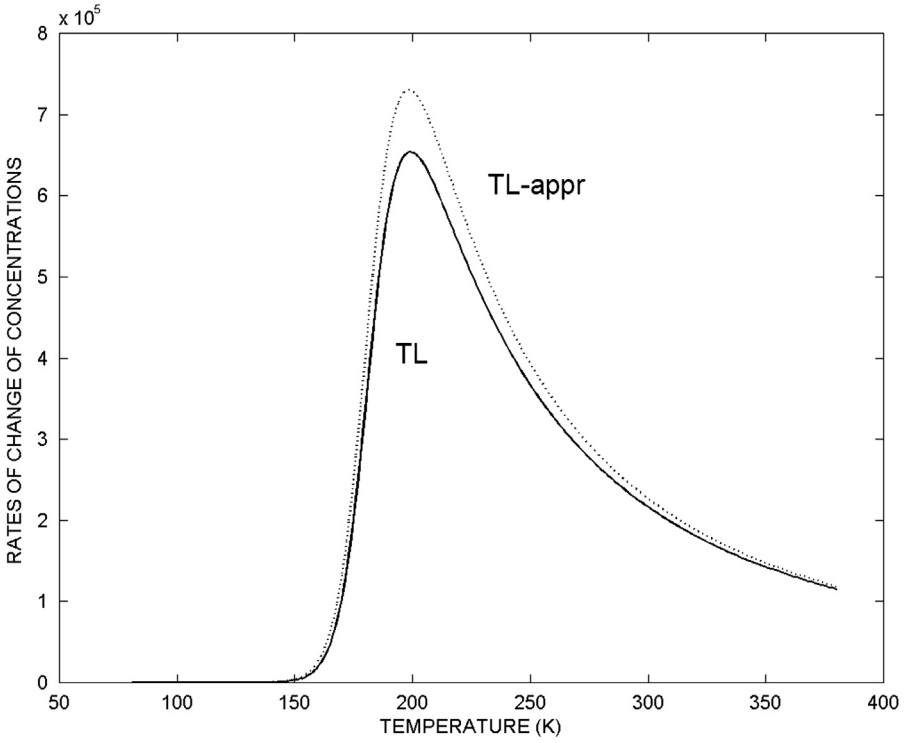

Fig. 5. Similar to Fig. 2, except that the retrapping and recombination probability coefficients are smaller by two orders of magnitude; $A_m = 10^{-10}\,\mathrm{cm^3 s^{-1}}$ and $A_n = 10^{-9}\,\mathrm{cm^3 s^{-1}}$.

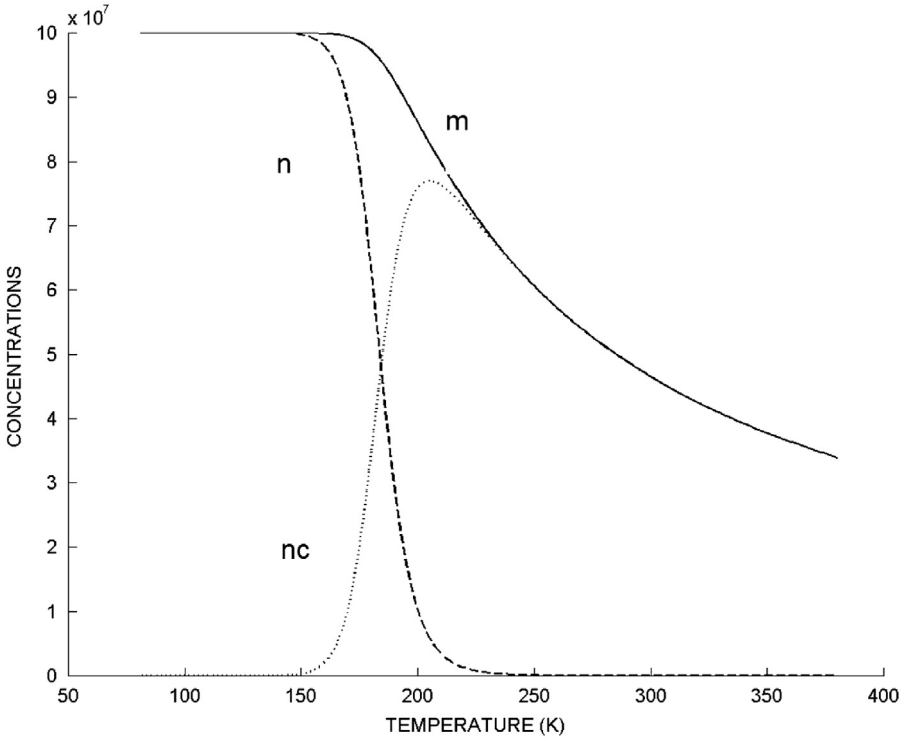

Fig. 6. With the same parameters as in Fig. 5, n, m, and n_c are shown as functions of temperature.

with time if we keep this high temperature constant. However, once we are in this range where the equation governing the process is (21), the decay curve given by Eq. (23) is independent of temperature. In a TL experiment, one keeps heating the sample using the same linear heating function as before, namely $T = T_0 + \beta t$. From this, one immediately gets $t = (T - T_0)/\beta$ and by inserting into Eq. (23), one gets

$$I(T) = \frac{A_m m_0^2}{\left[1 + m_0 A_m (T - T_0)/\beta\right]^2}, \tag{24}$$

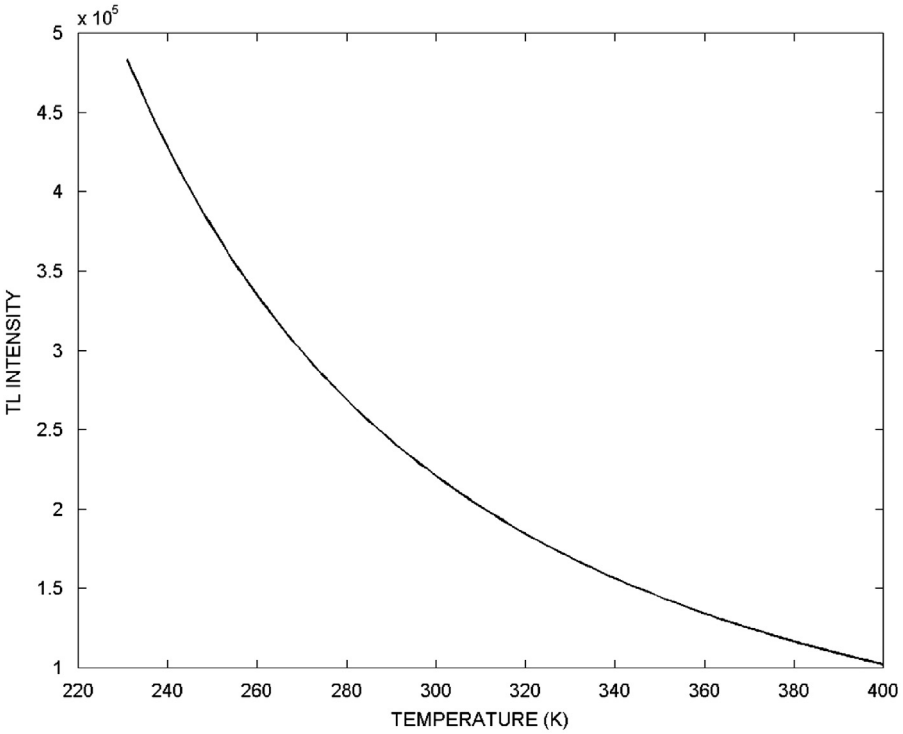

Fig. 7. High-temperature apparent temperature-dependent curve calculated by Eq. (24), with the same parameters as in Figs. 5 and 6. We used here $T_0=230$ K and $m_0=7\times10^7$ cm^{-3}, as explained in the text.

which describes the pseudo temperature dependence of the decay at the high-temperature side of the TL peak. An example of this function as compared to the numerical solution of the set of differential equations at the high-temperature range is given below. One should note that the rate of decay of this function depends on the magnitude of the heating rate β. Therefore, for the same set of parameters, the apparent value of the TL peak symmetry factor μ_g may change with β. Obviously, the simulated curve in Fig. 5 has an apparent value of μ_g significantly larger than that of a second-order TL peak. Note that Sunta et al. [8] have reported a simulated case where $\mu_g\sim0.6$ within the more complex TDDT model.

In order to check the validity of Eq. (24), and its relation to the high-temperature part of Fig. 5, we have monitored the dependence of n, m and n_c on temperature under the same parameters and conditions as in Fig. 5. The results are shown in Fig. 6. It is seen that the curves of m and n_c coincide at $\sim$230 K, and that the value of m at this temperature is $\sim7\times10^7$ cm^{-3}. We have now used these values as T_0 and m_0, respectively, in Eq. (24); the results are shown in Fig. 7. The apparent decline of the intensity with increasing temperature is the same as that shown in Fig. 5 from 230 K onwards.

4. Conclusion

In this work, we have dealt with the quasi-equilibrium assumptions and their consequences in the understanding of the kinetics of thermoluminescence (TL). Using numerical simulations along with analytical arguments we show that the condition (6) concerning the rates of change of the concentrations of trapped electrons and holes and free electrons, may not take place. However, it turns out that a better stated condition which compares the rate at which electrons are added into the conduction band and the rate at which they are depleted by retrapping and recombination is better fulfilled, and brings about the approximate Eq. (5). We also show that at least in some cases, at the high end of a single TL peak or the last peak in a series, the condition between the concentrations of free and trapped electrons, $n_c\ll n$ does not hold and, in fact, one may have a near equality between the free electrons and trapped holes, $n_c\sim m$, which means that the trap occupancy n is significantly smaller. This point has been previously made by Kelly et al. [3]. This is the case since at this temperature range electrons are very easily released into the conduction band. If the recombination and retrapping are rather small, electrons may be accumulating in the conduction band. Under these circumstances, the shape of the TL peak is not determined by A_n/A_m only and the absolute magnitudes of these coefficients are of importance. This explains the difference in shape between Figs. 2 and 5. In the case shown in Fig. 5, a very long tail at the high temperature side is seen, which resembles reports on TL in different materials. We show that in this range, the decline of TL intensity may be independent of temperature, and as a result, the apparent symmetric property of the TL curve may depend on the heating rate. In this situation, in the range where $n_c\sim m$, in the given example, we use the simulated results of m_0 at 230 K, the temperature at which the decline becomes temperature independent, from Fig. 6. Using Eq. (24), we get the declining curve which turns out to be practically the same as in the same range of temperatures simulated in Fig. 5. It should be noted that the condition $n_c\sim m$ which results in the occurrence of Eq. (24) and the explanation of the long high-temperature tail, depends on all the relevant parameters and in particular, the magnitudes of A_m and A_n. For high values of at least one of these two parameters, T_0 will be expected to be very high and m_0 very low, and therefore, the long-tail appearance will not be expected, whereas for low values of both probability coefficients, a long tail can be predicted.

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