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## **Analysis of Thermoluminescence Data Dominated by Second-Order Kinetics**

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In the analysis of the thermoluminescence glow curves, and in particular when applied to TL dosimetry and TL dating of archaeological and geological samples, a first order behaviour of the peaks involved is usually implicitly assumed. In this work the TL response for second order kinetics is described and shown that the usual analysis, in which a linear growth of TL with excitation dose is assumed, is correct to a good approximation provided that the curves are first shifted in temperature so that their peaks coincide. This is true for a single isolated peak and for a series of overlapping peaks.

Dans l'analyse des courbes de thermoluminescence (TL), particulièrement quand elle est appliquée à TL dosimétrie et la datation TL d'échantillons archéologiques et géologiques, on suppose régulièrement, quelquesfois implicitement, une conduite de premier ordre des pics TL. Nous considérons ici les autres possibilités de l'ordre de la cinétique et nous donnons, par exemple, une analyse détaillée des pics TL de deuxième ordre. Nous suggérons que pour établir la propriété de deuxième ordre d'un pic, il faut examiner quelques caractéristiques des résultats expérimentaux. Il faut considérer: a. la symétrie du pic, b. le changement de sa position quand on excite l'échantillon avec des doses différentes, et c. la dépendance non-linéaire de la dose des régions différentes du pic. Nous considérons aussi le „plateau-test“ qui a été utilisé pour établir la stabilité thermique des pics de TL. Cet examen doit être modifié dans les cas où le deuxième ordre se trouvera dominant. La modification suggérée est l'étude du changement de position des pics lorsque les maxima coïncident, et l'examen du „plateau“ dans les pics ainsi transformés. Cette méthode est examinée pour un pic unique synthétique (calculée par ordinateur) de deuxième ordre, et pour une combinaison de quatre pics synthétiques de deuxième ordre.

### **1. Introduction**

The thermoluminescence (TL) of minerals is widely used for the determination of past radiation doses. In archaeology and, to a limited extent, in geology, such doses when combined with dose rates (which are separately evaluated) are used to determine the age of past events in the technique of thermoluminescence dating. Details of the methods used are found in books by Aitken [1] and Fleming [2]. It is generally assumed implicitly that the mineral grains extracted from a specimen (pottery, brick, etc.) exhibit first order kinetics. The possibility of second order or other kinetics is seldom mentioned, and apparently seldom observed.

First order kinetics is characterized by a TL glow curve (light intensity versus temperature) which increases uniformly linearly with radiation dose. In such a case the determination of a past radiation dose is straightforward even if the TL results from a complex distribution of electron (or hole) traps. In the case of second order kinetics the glow curve resulting from a single trap shows a markedly different behaviour for which as yet no simple method of analysis exists. In this work we find that an ad hoc method in which the glow curves were shifted so that their peaks aligned, described in Berger and Huntley [3], has significant justification.

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The motivation for this work arose in the course of studies aimed at the development of a TL dating method for sediments (Berger and Huntley [3], Wintle and Huntley [4]) which has been hampered by second order kinetics behaviour shown by some samples. In this context, the work of Levy [10, 19] should be mentioned, in which second order kinetics TL peaks were reported in albite ( $\text{NaAl Si}_3\text{O}_8$ ) [19, 26] as well as in feldspars and ocean sediments [10]. Putative second order and other non-first order peaks have also been reported in quartz and feldspar [23] and in quartz in some more recent works [24, 25].

Finally, we note that although a few authors studying well defined crystalline solids have suggested that their samples exhibited second order behaviour, the evidence presented is inadequate. We present here a set of criteria which we hope will allow more satisfactory identification.

## 2. Second Order Peaks — Basic Considerations

The relatively simple case of a single TL peak resulting from a single trap and a single recombination centre is mathematically represented by a set of three simultaneous differential equations in the three unknown functions:  $n(t)$  — the concentration of electrons in traps at time  $t$ ,  $m(t)$  — the concentration of holes in centres and  $n_c(t)$  — the concentration of free electrons in the conduction band (see Section 2.1 in [5]). Adding a simplifying assumption (e.g. Halperin and Braner [6]), that no substantial concentration of electrons builds up in the conduction band, the following expression emerges

$$I = -\frac{dm}{dt} = sn \exp\left(-\frac{E}{kT}\right) \frac{A_m m}{[A_m m + A_n(N - n)]}, \quad (1)$$

where  $I$  is the TL intensity (in arbitrary units),  $s$  — the frequency factor ( $\text{s}^{-1}$ ),  $E$  — the activation energy (eV),  $k$  — the Boltzmann factor ( $\text{eVK}^{-1}$ ),  $T$  — the absolute temperature (K),  $N$  — the concentration of traps ( $\text{m}^{-3}$ ) (out of which  $n$  have electrons at a given moment), and  $A_m$  and  $A_n$  are the recombination and retrapping probabilities respectively ( $\text{m}^3\text{s}^{-1}$ ). Assuming dominating recombination, i.e.  $A_m m \gg A_n(N - n)$  one obtains the first order case

$$I = -\frac{dn}{dt} = s \exp\left(-\frac{E}{kT}\right) n \quad (2)$$

first suggested by Randall and Wilkins [7] and extensively investigated later on. The solution of this equation for a linear heating function  $T = T_0 + \beta t$  yields an asymmetric curve having a "symmetry factor"  $\mu_g \approx 0.42$  where  $\mu_g = \delta/\omega$ , and where  $\delta = T_2 - T_m$ ,  $\omega = T_2 - T_1$  and  $T_m$  is the temperature at the maximum;  $T_1$  and  $T_2$  are the low and high half-maximum-intensity temperatures [8].

Garlick and Gibson [9] were the first to investigate the case of non-negligible retrapping. Assuming equal recombination and retrapping probabilities  $A_m = A_n$  as well as equal concentrations of electrons and holes in traps and centres respectively,  $n = m$ , they obtained

$$I = -\frac{dn}{dt} = \left(\frac{s}{N}\right) \exp\left(-\frac{E}{kT}\right) n^2. \quad (3)$$

A similar equation which may be more likely to occur results from "dominating retrapping", namely  $A_n(N - n) \gg A_m m$ , along with the assumptions that the trap is far from saturation,  $n \ll N$ , and, again  $n = m$ . Considering (1) with these assumptions, one gets

$$I = -\frac{dn}{dt} = \left(\frac{sA_m}{NA_n}\right) \exp\left(-\frac{E}{kT}\right) n^2. \quad (4)$$

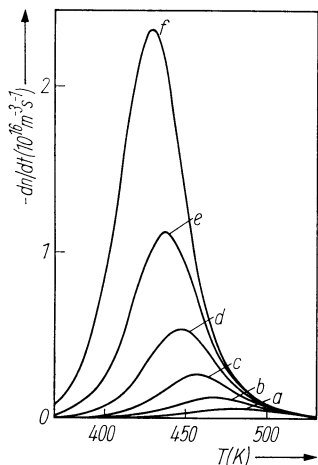


Fig. 1. A set of ideal second order glow curves with different initial trap fillings, (6). The parameters used were  $E = 1.1$  eV,  $s' = 10^{-6}$   $\text{m}^3\text{s}^{-1}$ ,  $\beta = 1$   $\text{Ks}^{-1}$ , (a)  $n_0 = 2 \times 10^{16}$ , (b)  $4 \times 10^{16}$ , (c)  $8 \times 10^{16}$ , (d)  $1.6 \times 10^{17}$ , (e)  $3.2 \times 10^{17}$ , (f)  $6.4 \times 10^{17}$   $\text{m}^{-3}$

Equations (3) and (4) can be written as

$$I = -\frac{dn}{dt} = s'n^2 \exp\left(-\frac{E}{kT}\right) \quad (5)$$

where  $s'$  is a constant having dimensions of  $\text{m}^3\text{s}^{-1}$ , which is  $s/N$  in the former case and  $sA_m/NA_n$  in the latter. The solution of (5) for a constant heating rate is

$$I = n_0^2 s' \exp\left(-\frac{E}{kT}\right) \left[1 + \left(\frac{n_0 s'}{\beta}\right) \int_{T_0}^T \exp\left(-\frac{E}{kT'}\right) dT'\right]^{-2}, \quad (6)$$

where  $n_0$  is the initial value of  $n$  at  $T_0$ . A set of curves of  $I(T)$  for varying  $n_0$  is shown in Fig. 1. Similar sets have been previously published [9, 10]. Such curves are nearly symmetric with  $\mu_g \approx 0.52$ .

We emphasize that by no means does one have to assume that a given TL peak is necessarily of first or second order. On the contrary, the sets of assumptions made above leading to the first or second orders were quite particular, and many kinds of intermediate cases are possible. The main reason for an in-depth study of second order kinetics is to point out features which may be common to non-first-order kinetics cases.

Characteristics of these second order curves which distinguish them from first order ones are:

- (i) A decrease in the temperature of the peak,  $T_m$ , with increasing  $n_0$ .
- (ii) A slightly superlinear increase of the peak intensity,  $I_m$ , with  $n_0$ .
- (iii) A quadratic increase in intensity with  $n_0$  at a given temperature well below the peak.
- (iv) an asymptotic approach to a constant intensity with increasing  $n_0$  at a given temperature well above the peak.

The increase in TL with  $n_0$  at a fixed temperature is shown in Fig. 2; this shows both (iii) and (iv) as the peak moves from above to below this temperature.

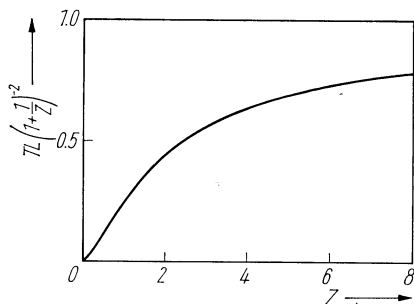


Fig. 2. Second order growth curve, (7) with  $Z = n_0/C$ . Note that approach to a constant TL at large  $n_0$  is not due to saturation (traps all filled) and that this curve is very different from that in the first order case when non-linearity due to saturation may occur

### 3. Detailed Considerations

Let us consider the dependence of  $I$  on  $n_0$  for a given value of  $T$  from (6). The integral on the right-hand side starts off from 0 at  $T = T_0$  and grows rapidly so that at a high enough temperature (well above the peak) we have  $(n_0 s' / \beta) \int_{T_0}^T \exp(-E/kT') dT' \gg 1$ . Thus if  $T$  is well below the maximum,  $I \sim n_0^2$  whereas if  $T$  is well above the maximum,  $I$  is independent of  $n_0$ . At a fixed  $T$ , (6) can be simplified to

$$I = A \left( 1 + \frac{C}{n_0} \right)^{-2}, \quad (7)$$

where  $A$  and  $C$  are constants defined by (6) and (7). This is the curve shown in Fig. 2.

For dosimetry applications, the best measure is the area under the whole glow curve, because this is proportional to  $n_0$ . (Physically this arises because each trapped electron yields a photon in the model.) However, since in many cases TL peaks are accompanied by adjacent overlapping peaks, the behaviour of which may be different from the main peak, one quite often takes the intensity at the peak,  $I_m = I(T_m)$ , as a measure of the accumulated dose. Let us thus consider  $I = f(n_0, T)$  with fixed  $s'$ ,  $E$ , and  $\beta$ . The expression for the differential at  $T = T_m$  is

$$dI_m = \left( \frac{\partial f}{\partial n_0} \right) dn_0 \quad (8)$$

because  $(\partial f / \partial T)_{T_m} = 0$  here. Using (6) and (8) we obtain

$$\frac{dI_m}{I_m} = \left[ \frac{\beta E \exp(E/kT_m)}{(n_0 k T_m^2 s')} \right] \frac{dn_0}{n_0} \quad (9)$$

or which we can write a solution

$$I_m \sim n_0^\gamma,$$

where

$$\gamma = \frac{\beta E \exp(E/kT_m)}{(n_0 k T_m^2 s')} \quad (10)$$

because  $\gamma$  is very nearly constant. One can test the near constancy of  $\gamma$  by choosing a set of parameters and solving numerically the condition for  $T_m$  (see e.g. [8]) and substituting in (10).

An alternative approach is to use the asymptotic series approximation (e.g. see [12]) for the integral in (6)

$$F(T, E) = \int_0^T \exp\left(-\frac{E}{kT'}\right) dT' = \left(\frac{kT^2}{E}\right) \sum_{i=0}^{\infty} \left(\frac{kT}{E}\right)^i (-1)^i i! = \left(\frac{kT^2}{E}\right) \eta\left(\frac{E}{kT}\right), \quad (11)$$

where  $\eta(x)$  denotes the asymptotic series [8].

From this it is immediately seen that

$$\int_{T_0}^{T_m} \exp\left(-\frac{E}{kT}\right) dT = F(T_m, E) - F(T_0, E) \quad (12)$$

however, since  $F(T, E)$  is a rapidly increasing function of  $T$ , the integral in (12) is very accurately represented by  $F(T_m, E)$  provided that  $T_0$  is not very close to  $T_m$  (which is in practice usually the case). Denoting  $kT_m/E$  by  $X_m$ , we obtain the peak

condition

$$\frac{1}{n_0} = \left( \frac{kT_m^2 s'}{\beta E} \right) \exp \left( -\frac{E}{kT_m} \right) (1 + 2X_m - 6X_m^2 + 24X_m^3 - \dots) \quad (13)$$

and therefore in (10)

$$\gamma \approx 1 + 2X_m - 6X_m^2 + 24X_m^3 - \dots = 2 - \eta(X_m). \quad (14)$$

In most cases that are likely to be considered,  $X_m < 0.1$  (in the examples in Table 1,  $0.03 < X_m < 0.08$ ), thus we see immediately that for second order peaks the maximum intensity  $I_m$  varies slightly superlinearly with the initial filling of traps  $n_0$  since  $\gamma$  in (14) is slightly larger than unity. The best accuracy in evaluating  $\gamma$  is by taking the terms down to the smallest one in absolute value and adding one half of the next, i.e.

$$\gamma = 1 + \sum_{i=1}^K (i+1)! (-1)^{i+1} X_m^i + \frac{1}{2} (K+2)! (-1)^{K+2} X_m^{K+1}, \quad (15)$$

where  $K$  is the integer part of  $1/X_m$ . The procedure for evaluating and checking its approximate constancy is to choose a set of parameters, solve (13) numerically to get  $T_m$ , find  $X_m = kT_m/E$  and insert into (15).

Three points are to be considered here. First, looking at (6) and (10) one can immediately see that the relevant parameter to be varied is  $s'n_0/\beta$  rather than  $s'$ ,  $n_0$  or  $\beta$  separately. Changing  $s'$  and  $n_0$  (for given  $E$  and  $\beta$ ) in such a way that the product  $s'n_0$  remains the same would leave  $T_m$  unchanged. In this sense,  $s'n_0$  is a "frequency factor" having units of  $s^{-1}$  similarly to the  $s$  parameter in the first order case (equation (2)), but unlike the first order case, this parameter is dependent on the initial filling  $n_0$ .

The second point has to do with the range of values of  $s'n_0$  that are physically relevant. As discussed above, the value of  $s'$  is given either by  $s/N$  or by  $(sA_m/NA_n)$  when retrapping dominates, i.e.  $A_n$  is large as compared to  $A_m$ . Since  $n_0 \leq N$  in all cases ( $n_0 = N$  when the traps are filled to saturation),  $n_0 s'$  should be lower than the frequency factor  $s$ . Since  $s$  is known (e.g. [8]) to be up to  $10^{13} s^{-1}$ ,  $s'n_0$  should be smaller. In Table 1, some results of  $T_m$ ,  $X_m$  and  $\gamma$  are given for  $s'n_0 = 10^4, 10^8, 10^{12} s^{-1}$  and

Table 1

Table values of peak temperature,  $T_m$ ,  $X_m = kT_m/E$ , and peak growth exponent,  $\gamma$ , for several values of  $s'n_0$  and  $E$  in second order kinetics. A heating rate  $\beta = 1 \text{ K s}^{-1}$  was assumed. For other heating rates the table can be used if the first column is relabelled  $s'n_0/\beta$  in units of  $\text{K}^{-1}$

$s'n_0$ ( $s^{-1}$ )	$E$ (eV)	$T_m$ (K)	$X_m$	$\gamma$
$10^4$	0.5	450.4	0.0776	1.1273
$10^4$	1.0	860.7	0.0742	1.1226
$10^4$	1.5	1258.3	0.0723	1.1200
$10^4$	2.0	1647.9	0.0710	1.1182
$10^8$	0.5	275.4	0.0475	1.0836
$10^8$	1.0	534.7	0.0461	1.0814
$10^8$	1.5	788.6	0.0453	1.0801
$10^8$	2.0	1039.1	0.0448	1.0793
$10^{12}$	0.5	196.1	0.0338	1.0615
$10^{12}$	1.0	383.9	0.0331	1.0604
$10^{12}$	1.5	568.7	0.0327	1.0597
$10^{12}$	2.0	751.6	0.0324	1.0592

$E = 0.5, 1.0, 1.5, 2.0$  eV. It is readily seen that the value of  $\gamma$  is hardly dependent on the activation energy and does depend more appreciably on the parameter  $s'n_0$ .

The third point to be considered is that on one hand the value of  $\gamma$  is the power of dependence of  $I_m$  on  $n_0$ , namely it expresses the variation of  $I_m$  with  $n_0$ . On the other hand, for a given value of the constant  $s'$ ,  $\gamma$  depends on  $n_0$  as seen in Table 1. Note however, that  $\gamma$  can be considered to be practically a constant when  $n_0$  is varied by say, an order of magnitude which is in many cases the range of variation of the excitation dose in experiments, whereas the appreciable variation of  $\gamma$  with  $s'n_0$  shown in Table 1 is related to changes of factors of  $10^4$  in  $n_0$ .

#### 4. Application of the Plateau Test to Single Second Order Peaks

Because of the nonlinear growth curve, and the shift in temperature (Fig. 2), it is evident that application of the plateau test [1] as used in first-order cases is quite inappropriate. Berger and Huntley [3] found that shifting a set of experimental curves along the temperature axis in such a way that the peaks were aligned and then applying the plateau test, gave encouraging results. This procedure lacked proper theoretical justification and we explore this now. The problem is not amenable to algebraic analysis so instead we use theoretical curves generated from (6) and using parameters which give curves similar to those we usually observe in sediments.

The parameters we use are  $E = 1.1$  eV,  $s' = 10^{-6} \text{ m}^3\text{s}^{-1}$ ,  $\beta = 1 \text{ Ks}^{-1}$  and  $n_0$  between  $10^{16}$  and  $10^{17} \text{ m}^{-3}$ . Fig. 3 shows curves for three values of  $n_0$ , shifted to have their maxima coincide. Curve d shows the ratio of the values for b and a. The variation of this ratio with temperature is rather small, about 10% in a range where the intensities of a and b change by a factor of  $\approx 6$ . The approximately constant ratio, curve d, is to be compared to the exactly constant ratio for first order TL peaks.

An alternative way of discussing the matter is to examine the growth curves at a fixed temperature (after shifting). Fig. 4 shows four of these; that at the peak is curve b in which the slight superlinearity ( $\gamma \approx 1.07$ ) is seen. The dependence of the intensity on  $n_0$ , 30 K below and above  $T_m$  are shown in curves a and c respectively. The dependence of  $n_0$  is practically linear in both. The behaviour at 60 K above  $T_m$  is shown in curve d. This is repeated in curve d' on a (X10) scale where it is seen to be slightly sublinear. It is to be noted that both the superlinearity and sublinearity depicted mainly in curves b and d' respectively are rather minor because once the peaks are shifted to have maximum temperatures coincide, they have rather similar shapes as seen in Fig. 3.

In cases intermediate between first and second order it seems likely that linear growth curves will result if the TL curves are first shifted to align their maxima. We make this suggestion because it is true in both extremes, there being linearity in first order (no shift required) and near linearity in second order.

In this context, the work by Balarin [12] should be mentioned. Balarin solved the extension of (5) in which  $n^2$  is replaced by  $n^b$  where  $b$  is a general kinetic order, not necessarily 1 or 2 (see also (16) below). He further normalized the resulting curves with

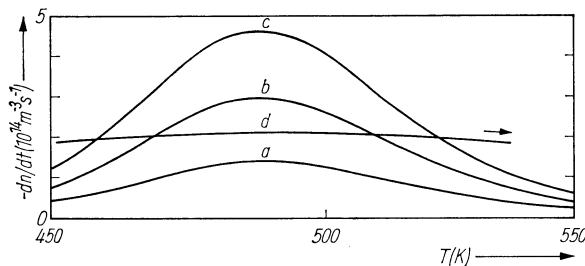


Fig. 3. Three calculated second order curves with  $E = 1.1$  eV,  $s' = 10^{-6} \text{ m}^3\text{s}^{-1}$  and  $\beta = 1 \text{ Ks}^{-1}$ . Curve (a) is for  $n_0 = 10^{16} \text{ m}^{-3}$ , (b) for  $n_0 = 2 \times 10^{16} \text{ m}^{-3}$ , and (c) for  $n_0 = 3 \times 10^{16} \text{ m}^{-3}$ . Curve b is shifted by 12 K upwards and c by 18 K so that the maxima coincide. Curve d represents the approximate plateau, namely, the ratio of values of (shifted) b to a

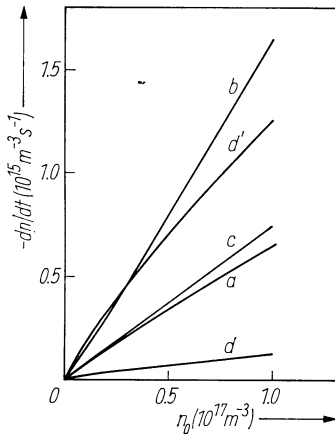


Fig. 4. The dependence of different parts of shifted second order calculated peaks on the initial filling. The peaks are all shifted to have their maxima at 453.2 K. The dependence 30 K below the maxima (a), at the maximum (b), 30 K above the maximum (c) and 60 K above the maximum (d) are shown. (d') gives the same data as (d) on a scale ( $\times 10$ ). The parameters chosen were  $E = 1.1$  eV,  $s' = 10^{-6}$  m<sup>3</sup>s<sup>-1</sup> and  $\beta = 1$  Ks<sup>-1</sup>.  $n_0$  varied between  $1.47 \times 10^{16}$  and  $10 \times 10^{16}$  m<sup>-3</sup>

respect to their maxima. It is possible that results similar to that depicted by curve d in Fig. 3 can be more analytically deduced from his results for  $b = 2$ . This is not entirely straightforward, however, since the element of shifting the peak is not so simple. We therefore feel that at present, the empirical-numerical conclusion suffices.

### 5. Application to a Distribution of Peaks

In real cases which appear to be of second order kinetics ([2, 3, 10]) the observed curve may and usually does consist of combinations of peaks rather than a single peak. In order to simulate this situation, we have taken a combination of four second order peaks, the sum of which agrees reasonably well with an experimental curve. It is shown as curve a of Fig. 5. The calculation was repeated with all the initial concentrations multiplied by 6.8 and the curve shifted 30 K to make the peaks coincide. In order to compare the shapes of the curves, we have normalized the results by dividing the intensity values by the same factor of 6.8; this is shown as curve b. Although the two curves do not coincide, the difference is within 10% from 40 K below to 100 K above the peak. The growth curves in this case looked very much like those of Fig. 4.

We thus conclude that the plateau test using shifted curves should be useful when second order kinetics is present, and probably also in cases intermediate between first and second order.

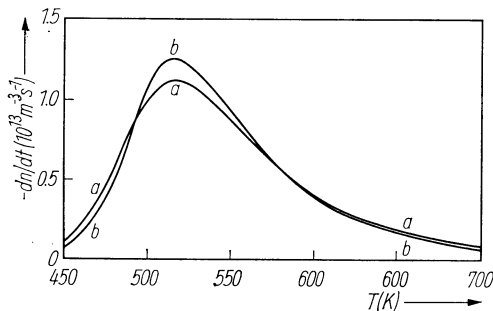


Fig. 5. Calculated combinations of four independent second order curves. The parameters chosen for curve (a) were:  $E_1 = 1.1$  eV,  $s'_1 = 5 \times 10^{-6}$  m<sup>3</sup>s<sup>-1</sup>,  $n_0 = 7 \times 10^{14}$  m<sup>-3</sup>;  $E_2 = 1.175$  eV,  $s'_2 = 5 \times 10^{-6}$  m<sup>3</sup>s<sup>-1</sup>,  $n_{02} = 4 \times 10^{14}$  m<sup>-3</sup>;  $E_3 = 1.25$  eV,  $s'_3 = 5 \times 10^{-6}$  m<sup>3</sup>s<sup>-1</sup>,  $n_{03} = 1.5 \times 10^{14}$  m<sup>-3</sup>;  $E_4 = 1.35$  eV,  $s'_4 = 5 \times 10^{-6}$  m<sup>3</sup>s<sup>-1</sup>,  $n_{04} = 0.8 \times 10^{14}$  m<sup>-3</sup>. In curve (b) all the values or  $n_{0i}$  were increased by a factor of 6.8. In order to see clearly the variation in the shape, b is normalized by dividing the final results by the same factor of 6.8. Also curve b is shifted by 30 K upwards in temperature

## 6. Criteria Indicating Second Order Kinetics

Some of the features of second order kinetics curves have been discussed above. If one has a clean single second order peak, each of these features can serve to classify the peak as second order. In practice, however, the situation may be complicated by two aspects briefly mentioned above.

1. Even if the peak is single, it is not necessarily represented by either (2) or (5). Two kinds of intermediate cases have been discussed in the literature, the "general order" (e.g. [12, 13])

$$I = -\frac{dn}{dt} = s'n^b \exp\left(-\frac{E}{kT}\right) \quad (16)$$

with  $1 \leq b \leq 2$  the (effective) order of the kinetics, and the "mixed order" [14]

$$I = -\frac{dn}{dt} = s'n^2 \exp\left(-\frac{E}{kT}\right) + s'Cn \exp\left(-\frac{E}{kT}\right). \quad (17)$$

Both approaches are, however, empirical in nature and have physical justification only in specific cases, the general behaviour may be expected to be even more complicated. Some curves for different  $A_m/A_n$  ratios and different initial  $m/n$  ratios are published by Levy [10].

2. Some of the features of a curve consisting of, say, a main second order peak and accompanying satellites may not be those of a pure second order peak due to the effect of the additional ones. In addition, it is possible for a second-order characteristic to arise from a more complicated trap and recombination centre situation than that assumed. One should, therefore, demonstrate several properties of second order kinetics in order to establish that a peak is of second order.

For these reasons we present now a set of criteria which should be checked before claiming a particular peak follows second order kinetics.

*I. Peak shape:* In the (rare) case that one has a single peak, the shape of the peak provides sufficient information on the kinetics.  $\mu_g \approx 0.52$  is characteristic of second order and  $\mu_g \approx 0.42$  of first order; values between these are expected for intermediate orders [5, 11].

*II. Peak shift:* In second order peaks, or in fact, in most non-first order peaks, the maximum shifts to lower temperatures at higher initial trap fillings  $n_0$  or experimentally, at higher doses. This shift to lower temperature is however only an indication of second order kinetics. Since the shift may be due to a build-up of accompanying peaks, a quantitative test of the amount of shift as related to the parameters involved is desirable. One method of doing this is explained in IV below.

*III. Superlinearity:* As explained above, a second order peak is characterized by a slight superlinear dependence of the maximum intensity  $I_m$  on the initial filling  $n_0$ . If the latter is linear with the dose, which is usually expected when one is relatively far from saturation, a behaviour of the form  $I_m \sim D^\gamma$  is expected with  $\gamma$  being typically around 1.08.

*IV.  $I_m-T_m$  method:* Chen and Winer [15] suggested that when one has a TL curve of general order (e.g. (16)) with a known kinetics order  $b$ , one can plot

$$\ln \left[ I_m^{b-1} \left( \frac{T_m^2}{\beta} \right)^b \right]$$

as a function of  $1/T_m$  and get a straight line, with a slope of  $E/k$ . For a second order peak,  $b = 2$ , and a plot of  $\ln(I_m T_m^4)$  versus  $1/T_m$  should give a straight line (assuming a constant heating rate).



*V. Isothermal decay methods:* If a sample is held at a constant temperature, the number of trapped electrons  $n(t)$  decreases with time. This can be studied experimentally by measuring the light emitted during this time, the phosphorescence. Alternatively, if the heating is stopped at time  $t$ , the sample cooled, and a glow curve measured, the area of the last is proportional to  $n(t)$ . A series of such measurements for various values of  $t$  gives the shape of  $n(t)$  and is called the isothermal decay method. These time dependencies are different in first and second order and may be readily found by solving (2) and (5).

In the case of first order kinetics, a plot of  $\ln I$  versus  $t$  will yield a straight line with slope  $-s \exp(-E/kT)$ ; here  $I$  is the TL intensity of the phosphorescence curve of the TL peak area (or intensity) in the isothermal decay measurements. For second order phosphorescence, one must plot  $1/\sqrt{I}$  versus  $t$  to obtain a straight line with slope  $[s' \exp(-E/kT)]^{1/2}$ . In the second order isothermal decay case, a plot of  $1/n$  versus  $t$  will yield a straight line of slope  $s' \exp(-E/kT)$ ; here  $n$  is the trapped electron density at the end of the isothermal treatment and can be represented by the area of subsequent glow curve or, to a good approximation, by its maximum intensity. In each case, the variation of slope with holding temperature can be used to calculate the trap depth  $E$ . Two more isothermal phosphorescence methods which can provide information on the kinetics order will be briefly mentioned. May and Partridge [16] suggested a method in which one plots  $\lg(-dI/dt)$  as a function of  $\lg I$ . The expected results should form a straight line with a slope of  $(2 - 1/b)$  where  $b$  is the kinetics order (see (16)). For the special case of second order, the slope should be 1.5. Recently, Sinha and Mukherjee [17] utilized this method for glow in  $\text{CdF}_2:\text{Pr}$  crystals and found a straight line which yielded  $b = 1.6$ . Another method discussed by Visocekas [18] (see also [5] paragraph 6.6) is to plot  $y = tI$  versus  $x = \ln t$ . The result should be a TL-like curve which resembles a first order TL peak ( $\mu_g \approx 0.42$ ) in the first order case and a second order TL peak ( $\mu_g \approx 0.52$ ) in the second order case.

## 7. Discussion

The properties of second order thermoluminescence curves have been further investigated in this paper. In particular the behaviours of the peak shape and maximum intensity while changing the initial filling of the traps have been studied. The main purpose of this research has been to expand the information one can extract from TL results in geological samples in cases where the second order property of the results can be established.

The method as applied to the "synthetic" curve depicted in Fig. 5 and to experimental ones of similar nature involves the shift of the whole glow curve by an amount determined basically by the shift of the main TL peak involved. This may be slightly altered if one has a series of separate second order peaks. If the shift is different for the various peaks, one can deal with each of the peaks separately and shift each of them by the correct amount so that the temperatures of the maxima coincide.

A word should be said about the feasibility of having a series of second order peaks from a given sample. Suppose that one has a single material with, say, a series of four traps and one centre which yield a series of four TL peaks which may be quite separate or may form a single composite glow peak. According to this picture, one should have

$$\sum_{i=0}^4 n_{0i} = m_0, \quad (18)$$

where  $m_0$  is the initial concentration of holes in centres and  $n_{0i}$  is the initial concentration of electrons in the  $i$ -th trap, where  $i = 1 \dots 4$ . As mentioned above, however, a necessary condition for a peak to be of second order is that  $m = n$  which cannot be exactly true for each peak separately if (18) holds. In fact, according to this line of thought, only for the last peak in such a series may one have  $n_0 = m_0$  (where  $m_0$  here is the remaining concentration at the end of the first three peaks), and thus a second order behaviour.

There still are, however, a number of possibilities of having a series of second order peaks. First of all, the sample in hand may not be a single material, in fact, in the archaeological and geological samples, the usual case is that many minerals are involved each of which may emit a non-first order TL peak. Another possibility is that several traps as well as several centres are involved and that traps and centres are exhausted more or less in pairs, so that within each pair one has  $n_0 \approx m_0$ . Also, it is possible that some of the peaks result from electron traps and hole centres and others from hole traps and electron centres, which make the two sets of peaks independent of each other, which in turn increases the likelihood of the occurrence of second order kinetics. Finally, even within the framework of a series of electron traps and one hole centre discussed above, one can think of a situation in which  $n_{01} \gg n_{02} \gg n_{03} \gg n_{04}$  which is, more or less, the case discussed with respect to Fig. 3 above. In this case  $n_{01}$  is related to the shallowest trap and the others are, in turn, deeper. If this is the case, we have  $m_{01} \approx n_{01}$  which may make the first peak approximately of second order. At the end of the first peak, one should have the remaining concentration of holes in centres  $m_{02}$  and this may be rather close to  $n_{02}$  and so on. Of course, this argument is not very strong when the peaks overlap, in which case second order kinetics would be only an approximation.

Due to the factors mentioned above, but mainly the interference of additional peaks, we would like to stress the need for utilizing as many criteria as possible for establishing the second order nature (or more generally — the non-first order one) of TL peaks. Some experimental results previously published (e.g. [17], [19 to 21]) utilized only one or two of these criteria for determining the second order property. We note that some of the considerations made here may be applied rather easily to other thermally stimulated processes (e.g. see [5], [11]) provided that the second order kinetics can be established. Finally, we would like to reiterate that first and second order kinetics are only limiting cases and many kinds of intermediate situations are possible. In this respect, we would like to mention a recent paper by Moharil [22], who defined general order kinetics by utilizing the ratio between recombination and retrapping probabilities  $A_n/A_m$ . His definition of "general order" is not the most general possible, however, since he assumed  $n = m$  which is not necessarily always the case [5, 6]. The method suggested here may possibly be refined in the future to take into account the exact process that takes place in various cases of non-first order kinetics.

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