

# Numerical curve fitting for calculating glow parameters

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**Abstract.** Numerical curve fitting of glow peaks, using a computer, is shown to be more objective and accurate than the existing graphical curve fitting method in evaluating trap activation energies. Besides using the numerical curve fitting method for glow peaks of first-order kinetics, the method is extended to the case of second-order thermoluminescence or thermally stimulated current peaks. The method was checked both for numerically generated peaks and experimental thermoluminescence curves of NaCl and ZnS : Er<sup>3+</sup> samples. The results are in good agreement with the given values of activation energies in the former case and values calculated by other means in the latter.

## 1. Introduction

Several methods for calculating trap activation energies of first- and second-order thermoluminescence (TL) and thermally stimulated current (TSC) curves are known. Many of them are based on the measurement of the maximum and the high and low half-intensity temperatures (Grossweiner 1953, Lushchik 1955, Halperin and Braner 1960, Nicholas and Woods 1964, Chen 1969). More reliable values can be found in many cases if more data are used. One of these methods is the initial rise method of Garlick and Gibson (1948).

Cowell and Woods (1967) suggested a graphical method of curve fitting for finding activation energies of first-order TSC curves. The method can be used for first-order TL curves (Randall and Wilkins 1945) as well. A first-order curve can be written as

$$I(T) = A \exp \left\{ \frac{-E}{kT} - \frac{\nu}{\beta} \int_{T_0}^T \exp \left( \frac{-E}{kT'} \right) dT' \right\} \quad (1)$$

where  $A$  is a constant,  $E$  the activation energy in eV,  $k$  the Boltzmann constant in eV degK<sup>-1</sup>,  $T$  the temperature in °K,  $T_0$  the initial temperature in °K,  $\nu$  the frequency factor of the trap in s<sup>-1</sup> and  $\beta$  the linear heating rate in degK s<sup>-1</sup>. An asymptotic series for evaluating the integral in equation (1) has been given by Haake (1957)

$$\int_{T_0}^T \exp \left( \frac{-E}{kT'} \right) dT' \cong T \exp \left( \frac{-E}{kT} \right) \sum_{n=1}^{\infty} \left( \frac{kT}{E} \right)^n (-1)^{n-1} n! \quad (2)$$

By using two terms of equation (2), a good approximation to equation (1) can be obtained from

$$I(T) \cong A \exp \{ -t - B \exp(-t) t^{-2} \} \quad (3)$$

where  $B$  is a constant given by  $B = \nu E / \beta k$ , and  $t = E/kT$ .  $B$  can be approximated by

$$B \cong B' \cong \exp(t_m) \frac{t_m^3}{t_m + 2} \quad (4)$$

where  $t_m = E/kT_m$ .  $T_m$  is the temperature in °K at maximum intensity  $I_m$ . By using  $B'$  instead of  $B$ , the free parameters become  $E$  and  $T_m$  instead of  $E$  and  $\nu$ . This leads to a

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convenient method of curve fitting, with only one variable parameter  $E$ , since  $T_m$  is known experimentally.

The procedure for this was as follows. Once the glow curve is measured, an estimate for  $E$  is obtained by using one of the known methods and a theoretical curve is plotted using equation (3) in conjunction with equation (4). The constant  $A$  is adjusted so that the intensity maxima of the experimental and theoretical curves coincide. The fitting of the rest of the curve is then checked. If the chosen value of  $E$  is too small, the theoretical curve will lie above the experimental curve (except for the maximum) and the reverse is true for too high a value for  $E$ . Using this as the criterion, a new value of  $E$  is chosen and the procedure is repeated until the desired fit is obtained.

In the present paper, the method of curve fitting is followed in a numerical way. By doing so, we have a more objective method for finding the best fit for the curve and, thus, the accuracy in the evaluation of the activation energy  $E$  is expected to be much better than in the graphical method. A similar method for second order peaks is also developed. Both methods are checked by 'synthetic' glow curves—peaks calculated by the use of the asymptotic series (Haake 1957) up to 15 terms. In addition, both methods are checked by using experimental peaks of sodium chloride for first-order peaks and zinc sulphide doped with erbium for second order. The results are in good agreement with those known from other methods.

## 2. First-order method

From the experimental curve, the intensities  $I_i$  corresponding to a certain number  $N$  of temperatures of  $T_i$  are taken. We usually chose  $T_i$  from a range of about  $0.9-1.1T_m$ , and used  $N=20$ . The curve is normalized by dividing each  $I_i$  by  $I_m$  to give the intensities  $I_i'$ . Using equations (3) and (4), the definition of  $t$ , and a 'guess' for  $E$  (the 'guess' may be the value obtained by using any other known method), a theoretical curve is calculated at the same temperatures taken from the experimental curve and a similar normalization is used. The sum  $S_1$  of the differences between corresponding intensities (hereafter called 'mean deviation' for convenience of reference) is then calculated from

$$S_1 = \sum_{i=1}^N \{I'(T_i) - I_i'\} / N \quad (5)$$

where  $I'(T_i)$  is the normalized intensity of the theoretical curve at temperature  $T_i$ . If  $S_1$  is positive,  $E$  is increased by 10%, and if  $S_1$  is negative,  $E$  is decreased by 10% of its original value. Again, a new theoretical curve is generated with the new value of  $E$  and the procedure is repeated until  $S_1$  changes sign. At this point, the percentage of variation of  $E$  is reduced to 5% in addition to the direction of correction of  $E$  (increments or decrements). From this point on, the percentage of correction of  $E$  is reduced to half its previous value in each step while the direction of correction is still dictated by the sign of  $S_1$ .

This process can be stopped after a given number of steps, or when  $S_1$  becomes smaller than a given number, or when the last correction in  $E$  is smaller than a given value, for example, 0.1%. In this way the 'best' value of  $E$  can be obtained to the desired accuracy.

Apart from the 'mean deviation' of equation (5), the 'mean-square deviation' (this name is also used for convenience of reference)

$$S_2 = \sum_{i=1}^N \{I'(T_i) - I_i'\}^2 / N \quad (6)$$

is calculated and, by its very definition, it should be a good measure of the closeness of fit between the two curves. That is, the smaller the value of  $S_2$  the more reliable the calculated value of  $E$ . The final value of  $S_2$  could be used as a criterion for the closeness of the experimental peak to first-order kinetics, since a large value of  $S_2$  would mean that the peak is not strictly of first-order kinetics. Hence, the  $S_2$  criterion seems to be essential.

To check the method, a generated peak is used as the experimental data. Values of  $E$ ,  $\nu$  and  $T_i$  (twenty values are taken) are chosen and the corresponding intensities  $I_i$  are calcu-

lated using equations (1) and (2). For a 'synthetic' peak with  $E=0.4$  eV,  $\nu=10^{10}$  s $^{-1}$ , the calculated  $E$  value is 0.4 eV after 10 steps. The first three significant figures did not change after additional steps. The absolute value of  $S_1$  is down to  $1.0 \times 10^{-10}$  after 50 steps, whereas  $S_2$  converges to  $3.2 \times 10^{-8}$  (see table 1).

**Table 1.** Check of both methods using 'synthetic' peaks

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
A	1	0.4	$10^{10}$	0.2	175.0	1	0.4000	$3.22 \times 10^{-8}$
B	1	0.1	$10^5$	0.2	175.0	1	0.0996	$2.33 \times 10^{-7}$
C	1	0.4	$10^5$	0.2	78.5	1	0.3990	$4.92 \times 10^{-7}$
D	1	0.1	$10^9$	0.5	52.1	2	0.1490	$1.40 \times 10^{-2}$
E	1	0.1	$10^9$	0.5	52.1	2 <sup>a</sup>	0.1180	$1.80 \times 10^{-4}$
F	2	0.1	$10^{12}$	0.5	40.4	1	0.0844	$2.60 \times 10^{-2}$
G	2	0.1	$10^{12}$	0.5	40.4	1 <sup>b</sup>	0.0878	$8.00 \times 10^{-5}$
H	2	0.1	$10^{12}$	0.5	40.4	1 <sup>c</sup>	0.0940	$1.20 \times 10^{-5}$
I	2	0.1	$10^9$	0.5	52.0	2	0.1000	$8.00 \times 10^{-6}$

(1) order of generated curve; (2)  $E$  value of generated curve in eV; (3) frequency factor,  $\nu$  or  $\nu'n_0$ , in s $^{-1}$ ; (4)  $\beta$  in  $^\circ\text{K s}^{-1}$ ; (5) temperature at maximum intensity,  $T_m$ , in  $^\circ\text{K}$ ; (6) order of method used in computation for the numerical method; (7) value of  $E$  in eV obtained by the present numerical method; (8) value of  $S_2$ .

a, used only the first half of curve for computation.

b, used only the first quarter of the curve in computation.

c, same as b with the normalization at the first quarter point.

To simulate the case of using this method for peaks which are not strictly of first order, we took the extreme case of a second-order generated peak as an experimental curve. The second-order curve is generated using (Garlick and Gibson 1948)

$$I(T) = \nu'n_0^2 \exp\left(\frac{-E}{kT}\right) \left\{ 1 + \frac{\nu'n_0}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dT' \right\}^{-2} \quad (7)$$

where  $\nu'$  is a constant and  $n_0$  is the initial concentration of trapped carriers,  $\nu'n_0$  has the dimensions (time) $^{-1}$  (as  $\nu$  before) and may be of same order of magnitude as  $\nu$ . We chose  $\nu'n_0=10^{12}$  s $^{-1}$  and  $E=0.1$  eV, for the generated peak. The calculated  $E$  is 0.084 eV with  $S_2=0.026$ .

However, a better fit may be expected if only points below the maximum temperature ( $T_m$ ) are taken, since the main difference between a first-order peak and a second-order peak, according to Nicholas and Woods (1964) and others, is in the region above the maximum. This is confirmed since we obtained a value of 0.088 eV for  $E$ , with  $S_2=1.6 \times 10^{-3}$ , when we considered points only up to the first quarter of the curve ( $0.9-0.94T_m$ ) with the normalization still at  $T_m$ . The value improved further when the normalization was changed to points below  $T_m$  (for example, the first quarter point) and points below the normalization temperature were taken for  $T_i$ . The lower the normalization temperature the better the final  $E$  value is expected to be. This, in principle, is similar to the initial rise method of Garlick and Gibson (1948) and may be efficient in high intensity peaks but cannot be relied upon (because of experimental reasons) when all the information has to be taken from the initial rise range of a low intensity peak (see also Chen and Haber 1968). A slight improvement is seen when more than two terms in the series are used in approximating for the integrals (thus having more terms in equation (3)). All the results obtained with the 'synthetic' peaks are shown in the table.

### 3. Second-order method

To deal with peaks of second order, or close to second order, we have developed a method similar to the one above. Again, the first task is to have  $E$  and  $T_m$  as independent variables

rather than  $E$  and  $\nu'$ , so that  $T_m$  can be found from experiment and  $E$  can be varied to get the best fit between the experimental and theoretical curves.

The condition for the maximum is obtained from equation (7) by differentiating with respect to  $T$  and equating the derivative to zero. This leads to

$$\nu'n_0 = \beta \left\{ \frac{2kT_m^2}{E} \exp\left(\frac{-E}{kT_m}\right) - \int_{T_0}^{T_m} \exp\left(\frac{-E}{kT}\right) dT \right\}^{-1}. \quad (8)$$

Again, the integral on the right-hand side may be approximated by using equation (2). From equation (7) we can find the maximum intensity which leads to the evaluation of normalized intensity  $I'(T_i)$  at temperature  $T_i$

$$I'(T_i) = \frac{\exp(-E/kT_i) \left( 1 + (\nu'n_0/\beta) \int_{T_0}^{T_m} \exp(-E/kT) dT \right)^2}{\exp(-E/kT_m) \left( 1 + (\nu'n_0/\beta) \int_{T_0}^{T_m} \exp(-E/kT) dT \right)} \quad (9)$$

which, when used with equation (8), will have  $E$  and  $T_m$  as independent parameters, since  $\beta$  is known.

The procedure for curve fitting is similar to the case of the first-order method from this point on. Intensities  $I_i$  at temperatures  $T_i$  are taken from the experimental curve, which is normalized using the maximum intensity  $I_m$  at the temperature  $T_m$ . The intensities  $I'(T_i)$  of the normalized theoretical curve are compared with the aid of equations (8) and (9), since  $T_m$  and  $\beta$  are known from experiment. A 'guess' for  $E$  is made, as before, using other methods of evaluation of  $E$ . The same criteria for the variation of  $E$  are constructed with the aid of  $S_1$  and  $S_2$ , which are calculated as before, until the desired fit is obtained.

As before, the final value of  $S_2$  could be used as an indication of the deviation of the experimental curve from second-order kinetics.

#### 4. Results and discussion

The results obtained with the 'synthetic' peaks are given in table 1 and have already been discussed in detail in §2 of this paper. It is seen that the results from the generated peaks are very good if the proper order kinetics is used in the computation.

Experimental TL peaks in x-ray excited NaCl samples, reported to be of first order (Halperin *et al.* 1960 a), and in ultra-violet excited ZnS : 1% ErF<sub>3</sub>, 5% NH<sub>4</sub>F, reported to be of second order (Halperin *et al.* 1967), were analysed by means of the present technique. In both cases, both the first- and second-order methods were tried, yielding smaller  $S_2$  values with the first-order method in the former and with the second-order one in the latter. The activation energies found by the present method for the NaCl peaks were within 15% of those found by other known methods. It is possible that the values found here (0.51, 0.88, 1.14 and 1.15 eV for peaks at 207, 268, 360 and 524 °K respectively) are better than the previously reported ones, since much more information of the peak is included. The variations between the present and previous activation energies in the ZnS samples are larger, probably because the peaks are not 'clean' (Halperin *et al.* 1967).

In conclusion, we feel that this method of computing  $E$  is more objective and accurate than the graphical curve fitting method. The smallness of  $S_2$  seems to be a good criterion with which to obtain a value for  $E$ , and it will also help us in determining the order of the kinetics. The order of kinetics with which we get a smaller  $S_2$  is the closer one. It seems reasonable to assume that  $S_2$  should be in the range of or less than  $10^{-2}$  in order to obtain a good fit. The only disadvantage is that it is sometimes necessary to put into the program a 'guess' value for  $E$ , not too far from the actual one. This problem exists only when the kinetics is not definitely known or when the peak is not 'cleaned'. In such a case it may happen that, if the first approximation is too far from the real activation energy, the process may converge to a wrong value of  $E$ , giving also a very high value of  $S_2$ . However, in the

'synthetic' peaks, which represent perfectly clean peaks, very good results were found, even when the first approximation was three times as high as the final one. It is to be noted that the use of more than two terms in the approximation for the integral in equation (2) did not cause any inconvenience, since the calculations were done by the computer.

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