

Numerical curve fitting of general order kinetics glow peaks

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Abstract. A method of extracting information about trapping levels in crystals by numerical curve fitting, known for first- and second-order kinetics curves, has now been extended to general-order kinetics glow peaks. This generalized method, suitable for use by digital computer, enables the evaluation of the activation energy as well as the kinetics order. The method has been used on thermoluminescence peaks of SrF₂ : Tb crystals. The results are compared with activation energies and kinetics orders found by other methods.

1. Introduction

A graphical method has been given by Cowell and Woods (1967) for evaluating the activation energy E of first-order (Randall and Wilkins 1945) thermoluminescence or thermally stimulated current (TSC) glow curves. A numerical method (Mohan and Chen 1970) similar to the graphical method was shown to be more objective, and to yield a more accurate value of E , the activation energy. Mohan and Chen have also extended the method to the case of second-order glow peaks (Garlick and Gibson 1948).

The kinetics of certain glow peaks are neither of first nor of second order, but rather are of 'general order' (Partridge and May 1965, Muntoni *et al.* 1968, Capelletti and de Benedetti 1968, Chen 1969 a, Taylor 1970). This is the case, for example, when two electrons are contained in a single trap (May and Partridge 1964); under these circumstances, one has $l=1.5$. The equation governing the process in this more general case is

$$I = -\frac{dn}{dt} = s'n^l \exp\left(-\frac{E}{kT}\right) \quad (1)$$

where I represents the glow intensity, n the concentration of trapped carriers (cm^{-3}), t the time (s), s' a constant ($\text{s}^{-1} \text{cm}^{3(l-1)}$), l a positive number (usually between 0.5 and 3) representing the kinetics order, E the activation energy (eV), k Boltzmann constant (eV K^{-1}) and T is the absolute temperature (K). Special cases of this equation are the first-order kinetics, for $l=1$ and the second-order, for $l=2$. The solution of this equation for $l \neq 1$ was shown to be (Chen 1969 a)

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

where n_0 (cm^{-3}) is the initial concentration of trapped carriers and β (K s^{-1}) the (linear) heating rate. Equation (2) gives the expression for the second-order kinetics directly by substituting $l=2$. The expression for the glow curve of first-order kinetics (Randall and Wilkins 1945) results from equation (2) as the limit for $l \rightarrow 1$. Since E/kT usually has values of 10 or more, the value of

$$\int_{T_0}^T \exp\left(-\frac{E}{kT'}\right) dT'$$

can be found to a high accuracy by the suitable asymptotic series (Chen 1969 b).

In the present paper we extend the numerical method of glow curve fitting to the case of general-order kinetics. Doing so, we are able to extract more accurately the activation energy and to find the kinetics order l . The method has been investigated by applying it to (a) 'synthetic' peaks generated numerically according to equation (2) and (b) experimental thermoluminescence curves taken from an x-ray irradiated SrF₂:Tb sample.

2. The method

Let us use the notation (Chen 1969 a), $s = s'n_0^{l-1}$. The expression (2) can be normalized by dividing $I(T)$ by I_m , the maximum intensity, found by substituting T_m for T in equation (2). We now have

$$I'(T) = \left(\frac{\exp(E/kT_m - E/kT) \left\{ 1 + (s/\beta) (l-1) \int_{T_0}^{T_m} \exp(-E/kT) dt \right\}^{l/(l-1)}}{1 + (s/\beta) (l-1) \int_{T_0}^T \exp(-E/kT') dT'} \right) \quad (3)$$

where $I'(T)$ is the thus defined normalized glow.

Using the condition for the maximum, it has been shown (Chen 1969 a) that

$$s = \beta E \left\{ lkT_m^2 \exp\left(-\frac{E}{kT_m}\right) - (l-1) E \int_{T_0}^{T_m} \exp\left(-\frac{E}{kT}\right) dT \right\}^{-1} \quad (4)$$

We choose to denote by $I(T)$ the experimental results given in a graph form, from which we use a certain number of points $I(T_i)$ for $i = 1, 2, \dots, N$. The values of T_0 , T_m , I_m and β are also known. We define the normalized experimental values as

$$I'(T_i) = I(T_i)/I_m \quad i = 1, 2, \dots, N. \quad (5)$$

Let us start with arbitrary values of E and l (for example, we started in most cases with $E = 0.3$ eV and $l = 1.5$). s can be computed by equation (4) using the present values of T_m , E , T_0 , and l . The normalized curve is computed by equation (3) and the 'mean deviation' S_1 and the 'root mean square deviation' S_2 are calculated as follows

$$S_1 = \frac{1}{N} \sum_{i=1}^N (I'(T_i) - I'(T_i)) \quad (6)$$

$$S_2 = \left\{ \frac{1}{N} \sum_{i=1}^N (I'(T_i) - I'(T_i))^2 \right\}^{1/2} \quad (7)$$

Since $I'(T_i)$ and $I'(T_i)$ are both normalized, $S_1 = S_2 = 0$ would mean a complete coincidence of the two curves. Our goal is, therefore, to find values of E and l that minimize S_1 and S_2 . For a given value of l , S_1 increases for decreasing values of E and vice versa. If S_1 is positive, we increase E by adding a certain constant, say 0.1 eV, to it. Now S_1 is recalculated and if it is still positive, we add the same amount to E . The process is repeated until S_1 changes sign. Now half of the previous amount is subtracted from E (0.05 in the present example) and this process is repeated, namely, the correction is halved in each step and its sign is determined by the sign of S_1 . Since S_1 is the sum of positive and negative differences, its absolute value can be reduced to any desired value by changing E , independent of the chosen value of l . Thus, we may carry out this process down to an arbitrarily small absolute value of S_1 or until the correction in E is small enough.

The dependence on l was checked by S_2 . We vary in steps the value of l in order to reduce S_2 and in each step E is recalculated such that S_1 gets arbitrarily small. We keep changing l in a certain direction as long as S_2 decreases. If it increases, we alter the direction

of change of l and reduce the amount of this increment. The process can be stopped when the changes in l are small enough. Owing to small computational errors (rounding off errors, for example), the value of S_2 does not reduce to zero even for a 'synthetic' peak computed by equation (2) and having definite values of E and l . S_2 is found to reduce to some positive minimum which, for the synthetic peak, is relatively small. For experimental peaks, however, one can expect a much larger minimum value of S_2 , partly because of experimental inaccuracies but mainly since the assumption that the peak can be described by equation (1) is in many cases only an approximation. It has been pointed out, however (Chen 1969 a), that this approximation is much better in most cases than just assuming first- or second-order kinetics, because of the introduction of the additional parameter l . Since we are always dealing with normalized curves, the smallness of the final S_2 can be used as a general measure for the validity of the assumption implied by equation (1).

It is to be noted that in addition to E and l we get as a by-product the value of $s = s'n_0^{l-1}$. The value of s to be taken is certainly the one corresponding to the final E and l .

3. Analysis of synthetic peaks

A few synthetic peaks have been computed and analysed. One of them will be described here in some detail. This synthetic peak has been calculated according to equation (2) with the given parameters $E=0.3$ eV, $l=1.5$, $s=10^{11}$ s⁻¹, $\beta=1$ K s⁻¹, $T_0=0$ K. The curve found in this way has its maximum at about 128 K. The results found by using this curve as input data for our program are given in table 1. In this case we preferred to start with $l \neq 1.5$ in order to be able to see the convergence toward the value $l=1.5$. Although the program changes automatically the values of l so as to minimize S_2 , few results with different values of l in the vicinity of the final value of 1.5, are also given. All the calculations were carried out until S_1 became as small as 10^{-7} . The very good agreement of the results found for the minimal S_1 , namely, $l=1.5$, $E=0.300$ eV and $s=10^{11}$ s⁻¹ shows the accuracy of the method for this ideal case. The program was very successfully applied to synthetic peaks having other values of l including second-order peaks ($l=2$). Because of the nature of equations (2) and (3) for $l=1$, the method was not usable for a peak which is strictly of first-order kinetics.

Table 1. Calculated values of E , s and S_2 for some values of l from a synthetic glow peak

	E (eV)	s (s ⁻¹)	S_2
1.3	0.275	1.0×10^{10}	5.7×10^{-4}
1.4	0.288	3.2×10^{10}	1.0×10^{-4}
1.45	0.294	5.7×10^{10}	3.0×10^{-5}
1.475	0.297	7.6×10^{10}	7.3×10^{-6}
1.5	0.300	1.0×10^{11}	8.5×10^{-9}
1.525	0.303	1.3×10^{11}	7.8×10^{-6}
1.55	0.306	1.7×10^{11}	2.9×10^{-5}
1.6	0.312	2.9×10^{11}	1.0×10^{-4}
1.7	0.323	8.1×10^{11}	4.0×10^{-4}

Details of synthetic glow peak: $E=0.3$ eV, $l=1.5$,
 $s=10^{11}$ s⁻¹, $\beta=1$ K s⁻¹, $T_0=0$ K and $T_m=128$ K.

When a first-order synthetic peak was used as data, the method brought l quite close to unity but at a certain stage the improvement in S_2 stopped and thereupon l kept oscillating around the value of 1. The program was then improved in such a way that if this happened we switched to an alternative program constructed for first-order peaks (Mohan and Chen 1970).

We have also examined the influence of the chosen temperature range on the results. By taking results only around T_m , the decrease of S_2 at the 'correct' l is less pronounced. While taking broader temperature ranges, the region of temperatures below T_m was found

to yield less significant results than the range of higher temperatures. In the higher temperature range, the glow curve is highly sensitive to changes of l , therefore this range can be best used for extracting the correct value of l . On the other hand, if one is interested only in the best attainable value of E , the lower temperature range is better.

Table 2. Calculated values of E , s and S_2 for some values of l from a TL peak of SrF₂ : Tb at 145 K

l	E (eV)	s (s ⁻¹)	S_2
1.400	0.350	8.3×10^{10}	4.41×10^{-4}
1.500	0.363	2.5×10^{11}	2.91×10^{-4}
1.525	0.367	3.2×10^{11}	2.74×10^{-4}
1.573	0.373	5.3×10^{11}	2.62×10^{-4}
1.600	0.376	7.0×10^{11}	2.66×10^{-4}
1.650	0.382	1.1×10^{12}	2.90×10^{-4}
1.700	0.388	1.9×10^{12}	3.36×10^{-4}

4. Experimental results and discussion

The experimental set-up was similar to that described in previous work (Halperin and Chen 1966). Thermoluminescence glow curves were recorded after the Tb-doped SrF₂ samples were excited by x-rays. Our method was applied to a peak appearing at about 145 K. The computational procedure was again repeated until S_1 was reduced to about 10^{-7} . The results for E , s and S_2 are given for three values of l in table 2. The minimum value of S_2 is found at $l=1.573$, at this point we have $E=0.37$ eV. For comparison, the activation energy was calculated by three methods using the temperature at the maximum and the two temperatures at half intensity (Chen 1969 a). The results by these methods are $E_\tau=0.35$ eV, $E_\delta=0.36$ eV and $E_\omega=0.36$ eV, in very good agreement with our present result. The minimum in S_2 is certainly not so pronounced as in the case of the synthetic peak. As mentioned before, this seems to be due both to experimental inaccuracies and inaccuracies produced by the assumption that the behaviour is given by equation (2). Additional complication may result from the possibility that peaks are not clean, namely, that more than one glow peak contributes to the measured intensity at the same temperature. The comparison between the activation energy found by the present and the other methods is, however, very good. In order to check the value of l , we can use the measured value of $\mu_g' = \delta/\omega$ where $\delta = T_2 - T_m$, $\omega = T_2 - T_1$ and T_1 and T_2 are the lower and higher temperatures at half intensity, respectively. The value of μ_g' in our curve was found to be 0.486 which, according to figure 1 in the paper by Chen (1969 a) corresponds to $l=1.51$, again in a good agreement with the method described here.

The advantage of the present method is that it automatically gives the best values of E , l and s based on many points in the glow curve. Another advantage is that although different portions of the curve may have various sensitivities on each of the parameters, different ranges of the same peak can be used for finding the parameters. Thus, we can avoid 'dangerous' regions, namely, regions where neighbouring peaks may interfere. The comparison of values of E and l and the final S_2 calculated by using various portions of the glow curve as data, may be very instructive in many cases and can, in certain cases, reveal the existence of minor 'satellites'.

In conclusion, we can say that the method shown before to be more objective and accurate than the graphical curve fitting method for first- and second-order glow peaks, is now extended to general-order peaks. In addition to the calculation of the activation energy E and the frequency factor s we now get directly the value of the order of the kinetics l .

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