CALCULATION OF GLOW CURVES' ACTIVATION ENERGIES
BY NUMERICAL INITIAL RISE METHOD *

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A numerical method for the calculation of activation energies by the "initial rise" portion of glow curves is given. The method is shown to apply most conveniently by the use of a computer. Some thermoluminiscence results measured in ZnS (activated with ErF_3 and NH_4F) powder samples. are analyzed by the use of this method.

The graphical method of finding the activation energy of a trap by using the "initial rise" range of thermoluminescence (TL) or thermally stimulated current (TSC) glow curves is well known [1-5]. The method is based on measuring the glow intensities at temperatures sufficiently lower than the maximum of the peak. In this limited region it has been shown that the glow intensity I can be written as

$$I = Ae^{-E/kT} \qquad (1)$$

where A is a constant, E the activation energy, T the absolute temperature and k the Boltzmann constant. By plotting $\ln I$ as a function of $(1/T)$ a straight line is expected to be found. The slope of this line, $-E/k$, can be used for immediate calculation of the activation energy. Apart from some exceptions [6,7] this method is considered to be the most general way of finding the energies corresponding to measured glow curves. This is so since this method does not depend on the order of the process (first, second or some intermediate order).

The criterion for the "initial rise" limit is the decline of the curve of $\ln I = f(1/T)$ from the straight line found for the first points. In some cases the initial rise intensity was shown to be slightly different with A somewhat depending on temperature, $A = A'T^a$ where A' and a are constants, $-2 \leqslant a \leqslant 2$ [4,8]. In this case, the $\ln I$ versus $1/T$ curve should deviate from the desired straight line and the closest straight line should

give a slightly different slope. Thus an error is expected in the activation energy.

Although I is usually recorded continuously as a function of T, the plots of $\ln I$ versus $1/T$ are done point by point. Deviations of the straight line occur because of inaccuracies in the intensity and temperature readings and thus the task of plotting the best straight line is usually difficult. The possible inaccuracies in plotting the straight line may bring about large errors in the measured slope and the activation energy thereof. Gobrecht and Hofmann [5] suggested the possibility of applying directly on an X-Y recorder $\ln I$ (on the y axis) and $1/T$ (on the x axis). The slopes of the observed curves give directly $-E/k$. Gobrecht and Hofmann used this method for calculating the "spectrum" of traps by several cycles of heating and cooling after one irradiation.

The present paper is meant to enable a more objective way of calculating the activation energy (or spectrum of activation energies) when the more complicated equipment used by Gobrecht and Hofmann is not available, i.e. when only the intensities and temperatures are directly read.

This is done by finding the slope of the best (in the sense of "least squares") straight line numerically, by the use of a computer. This method seems to be very useful now, when "time sharing" computer terminals are available in many laboratories. The accuracy of this method seems to be better than that of the previous graphical one (including the version of Gobrecht and Hofmann).

The values to be fitted onto a straight line are $y_i = \ln I_i$ versus $x_i = 1/T_i$. The values of a and b in

$$y = ax + b \qquad (2)$$

which would give the least square deviations are known to be [9]

$$a = (\bar{x}\bar{y} - \overline{xy})/(\bar{x}^2 - \overline{x^2}), \qquad (3a)$$

$$b = (\bar{x}\,\overline{xy} - \overline{x^2}\,\bar{y})/(\bar{x}^2 - \overline{x^2}), \qquad (3b)$$

where

$$\bar{x} = \sum_{i=1}^{N} x_i/N, \qquad \bar{y} = \sum_{i=1}^{N} y_i/N,$$

$$\overline{x^2} = \sum_{i=1}^{N} x_i^2/N \quad \text{and} \quad \overline{xy} = \sum_{i=1}^{N} x_i y_i/N.$$

Once the slope a is thus found, the value of the activation energy is directly found by $E = -ka$. By the aid of the calculated b, the values of $y(x_i)$ are easily found from eq. (2) and thus the standard deviation

$$\sigma = \{\sum_{i=1}^{N} [y(x_i) - y_i]^2/(N-1)\}^{\frac{1}{2}} \qquad (4)$$

may be calculated immediately. It is expected that a reliable value of the activation energy will be found by not less than three or four points. As long as the "initial rise" approximation is a good one, the more points we take, the better is the calculated energy value expected to be. On the other hand, when we pass this region, the calculated value of activation energy decreases when more points are taken, and the standard deviation increases. Thus it was found useful to calculate the slopes and standard deviations for the first two points, then the first three points etc. and in this way to decide which is the best energy value.

In order to check the method, some numerically generated TL peaks have been taken, one of them will be described here in some detail. According to Garlick and Gibson [1] a second order TL peak is given by

$$I(T) = s' n_0^2 e^{-E/kT}/\left[1 + (s' n_0/\beta)\int_{T_0}^{T} e^{-E/kT'} dT'\right]^2 \qquad (5)$$

where n_0 is the initial concentration of trapped carriers, β the heating rate and s' a constant having dimensions of $cm^3 sec^{-1}$ (in some cases s' depends on temperature as $s' = s'' T^a$ where s'' and a are constants, $-2 \leqslant a \leqslant 2$). The integral on the right can be calculated numerically (see Haake [6]). Table 1 shows, for given values of the parameters ($n_0 = 10^{10} cm^{-3}$, $s' = 1 cm^3 sec^{-1}$, $E = 0.4$ eV, $\beta = 0.5°K sec^{-1}$), the calculated values of the intensities for given tempera-

Table 1
Temperatures and intensities of the first half of a second order numerically generated peak, and calculated activation energies and standard deviations by the present method

T (°K)	I (arb. units)	E (eV)	σ
142	6.3		
144	10.0	0.407	0.12×10^{-10}
146	15.5	0.401	0.0037
148	23.8	0.399	0.0045
150	36.1	0.398	0.0045
152	54	0.398	0.0047
154	80	0.398	0.0047
156	116	0.396	0.0069
158	168	0.395	0.0078
160	238	0.394	0.0102
162	334	0.393	0.0131
164	458	0.391	0.0183
166	615	0.388	0.0262
168	806	0.385	0.0371
170	1027	0.381	0.0517

tures. The temperatures given are up to 170°K whereas the maximum temperature for this case is 180°K. The intensity at 170°K is 1027 units compared to the calculated maximum intensity of 1906 units.

The third column in table 1 represents the values of activation energy calculated by the present method. The fourth column gives the standard deviation values. The results of the activation energies for the first points fit very well with the known value of $E = 0.4$ eV. The values of the standard deviations should be used as an aid for choosing the best activation energy. The value of σ for the first two points is very small since we just did the equivalent of drawing a straight line between two points. The next σ value is still relatively small, and for four additional points E and σ are changing only slightly. At 156°K, σ starts to increase rapidly and E declines, which shows that we are over the real "initial rise" range.

It seems that the best value to choose is the one calculated by seven points. The activation energy is 0.398 eV which deviates from the known value only by 0.5%. We should mention here that this value is found by going only up to 5% of the maximum intensity. If we go up to 50% of the maximum intensity (see last row in table 1), the activation energy is in error by 5% in spite of the

fact that this is really the best straight line! (See also Haake [6].) It is to be noted that since the function dealt with is logarithmic (y_i = lnI_i), the same E and σ values are found if all of the intensity data are multiplied by a constant. Thus the values of σ give some general criterion for the closeness to the exponential functions. The results can be compared not only when additional points are taken into account but also for comparison between various glow peaks.

Similar calculations have been done for first order peaks [10] generated numerically. The results were generally similar to the second order case with about the same agreement between the given and calculated E's. For cases where A in eq. (1) is temperature dependent, $A = A'T^\alpha$, the method was also workable in the following way. Suppose that the value of a is known (Halperin and Braner [11] show, for example, that when carriers are excited into a band, $a = 2$), then we can write in the initial rise range

$$\ln(I/T^\alpha) = \ln A' - E/kT \qquad (1')$$

by which E can be calculated as before. Our general program included the dependence on T^α where a has to be given with the input data. (For the previous case we took $a = 0$.) A checking of this possibility (for $a \neq 0$) has been done by a suitably calculated peak, the results were again found to be as good as in table 1. Although these checkings were done only for the simple first or second order cases, it should be remembered that the initial rise method is applicable for more complicated cases as well.

The method was used for the analysis of TL glow curves found in ZnS activated with 1% ErF$_3$ and 5% NH$_4$F powder samples and excited by uv light. Various ZnS:Er^{3+} samples including the present kind were investigated by Halperin et al. [12]. Our samples gave usually two main peaks, one at ~140°K and the other at ~270°K. Halperin et al. found the activation energy of the latter to be 0.41 eV. By several subsequent heatings and coolings of our sample following one excitation, various initial rise curves were measured yielding various activation energies. These energies are shown in fig. 1 to increase with T_{avg}, the average temperature of the range used for finding the energy by our "numerical initial rise" method. A clear step is seen between 200°K and 260°K at which the activation energy is around 0.42 eV, with very good agreement with the value given by Halperin et al. for the peak at 270°K. The temperatures here are lower because this is the "initial rise" range rather than the maximum intensity temperature. The results given in this
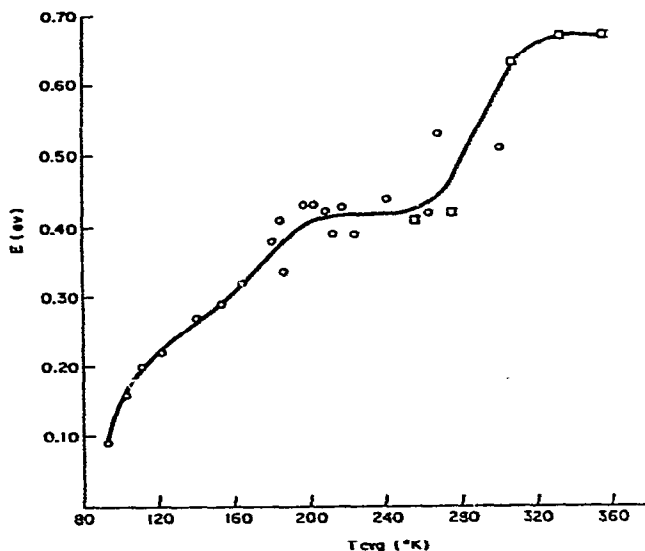

Fig. 1. Thermal activation energies as a function of temperature for the ZnS (ErF$_3$, NH$_4$F) powder sample. Squares and circles indicate results found in two separate sets of measurements.

figure may be compared with similar curves found for other Er doped ZnS samples found by the graphical initial rise method [12]. Some of these samples show stepwise behavior, similar to the two steps in fig. 1 (0.42 eV and 0.67 eV). Some other samples show a more continuous dependence of the activation energy on temperature which is more like the behavior of the present sample at temperature lower than 200°K.

REFERENCES

[1] G. F. J. Garlick and A. F. Gibson, Proc. Phys. Soc. (London) 60 (1948) 574.

[2] W. Hoogenstraaten, Philips Res. Rept. 13 (1958) 515.

[3] A. Halperin, A. A. Braner, A. Ben-Zvi and N. Kristianpoller, Phys. Rev. 117 (1960) 416.

[4] F. Aramu, P. Brovetto and A. Rucci, Phys. Letters 23 (1966) 308.

[5] H. Gobrecht and D. Hofmann, J. Phys. Chem. Solids 27 (1966) 509.

[6] J. Haake, J. Opt. Soc. Amer. 47 (1957) 649.

[7] P. Braunlich, J. Appl. Phys. 38 (1967) 2516.

[8] P. N. Keating, Proc. Phys. Soc. (London) 78 (1961) 1408.

[9] E. M. Pugh and G. H. Winslow, The Analysis of Physical Measurements (Addison-Wesley, 1960) p. 91.

[10] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) A184 (1945) 347, 365, 390.

[11] A. Halperin and A. A. Braner, Phys. Rev. 117 (1960) 408.

[12] A. Halperin, W. Y. Chu, G. A. Haber and J. J. Dropkin, International Conference on II - VI Semiconducting Compounds (Benjamin Press. New York, 1967) p. 68.