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Physical Parameters of Glow Peaks 4, 5 and 6 in TLD-100 (LiF:Mg)*,**

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In order to determine more precise values of the trap depth and the frequency factor of the so called peak 6 in magnesium doped LiF, produced by Harshaw Chemical Co., which is commercially known as TLD-100, an appropriate pre – as well as post-annealing treatment was used to isolate the peak 6 from the peak 5. Further post-annealing for different intervals of time at 109,129,140, and 145°C has shown a decay curve that can be fitted with continuous trap model, but not with the original Randall-Wilkins model. It was found $E_6 = 1.38$ eV, $S_6 = 8.0 \times 10^{11}$ sec^{-1}, $\sigma_6 = 0.06$ eV and $T_6 = 272$°C. The trial to fit the observed glow curve, comprising peaks 4 and 5, using E – and S – values determined from decay data of each peak when isolated, and using also experimental values of peaks 4 and 5 temperature, T_4 and T_5, did not reproduce the observed glow curve. By representing the experimental glow curve, around T_5, by a 6-terms polynomial function and by identifying its coefficients with corresponding coefficients in a power expansion, around T_5, of the expression $I(T) = I_4(T) + I_5(T)$, where $I_i(T)$ is the Randall-Wilkins formula for peak i, more accurate values of activation energy E, frequency factors, T_4, T_5, and the ratio $n(E_4, 0)/n(E_5, 0)$ were determined; $n(E_i, 0)$ is the density of filled traps of kind i.

A fim de determinar valores mais precisos da profundidade das armadilhas e fator de freqüência do assim chamado pico 6 no LiF ativado com magnésio, preparado por Harshaw Chemical Co., que é comercialmente conhecido com o nome de TLD-100, um tratamento pré e pós-recozimento apropriado foi usado para isolar o pico 6 do pico 5. Pós-recozimentos em 109°, 129°, 140° e 145°C dão origem a curvas de decaimento que podem ser ajustadas com o modelo contínuo, porém, não com o de Randall-Wilkins. Foram obtidos $E_6 = 1{,}38$ eV e $S_6 = 8{,}0 \times 10^{11}$ $^{-1}$. A tentativa de ajustar a curva de emissão contendo os dois picos 4 e 5, usando os valores de E e S determinados das curvas de decaimento de cada um dos picos isolados, e usando as temperaturas dos picos 4 e 5, T_4 e T_5, obtidos experimentalmente, não reproduz a curva de emissão observada. Ajustando a curva experimental a uma função polinomial com 6 termos, em torno de T_5, e identificando seus coeficientes com os coeficientes correspondentes na série de potência em tomo de T_5, da expressão $I(T) = I_4(T) + I_5(T)$, onde $I_i(T)$ é a fórmula de Randall-Wilkins para o pico i, foram determinados a energia de ativação, fator de freqüência, T_4, T_5 e a razão $n(E_4, 0)/n(E_5, 0)$; $n(E_i, 0)$ é a densidade de armadilhas preenchidas do tipo i.

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1. Introduction

TLD-100 is the dosimetric LiF doped with 300 ppm of Mg and grown by Harshaw Chemical Co., Cleveland, Ohio, USA. It has a characteristic

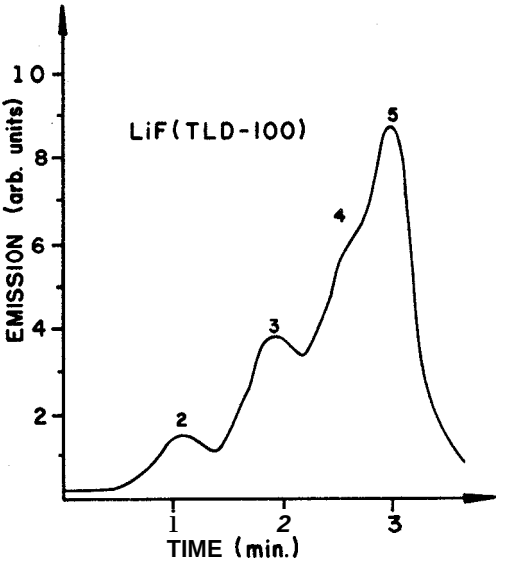

Fig. 1— Typical glow-curve of TLD-100 after annealing 1 hr at 400°C and γ-irradiating to 800 R of ^{137}Cs. Heating-rate: 60°C/min.

glow curve consisting mainly of 5 glow peaks' (Fig. 1). Each one has its maximum at a given temperature for a given heating rate to produce the glow curve. Several other peaks at higher temperatures[2] have also been reported. They will not be considered here, except for the one very close to the fifth peak. This peak, called peak 6, was first found by pre-irradiation annealing at 120 to 145°C for time longer than 3 hours'. It can also be isolated from peak 5 by post-annealing at about 130°C for more than 3 hours. To this date, there is only one determination of the activation energy E_6 and frequency factor S_6 of peak 6 by Zimmerman *et al*[1]. These values are $E_6 \sim 2.1$ eV and $S_6 \sim 10^{22}$ sec^{-1}, which appears much larger than one expects. Even for peaks 4 and 5, there are considerable variations between the E— and S-values determined by different workers, as can be seen in Table I.

In the present work, we tried to obtain reasonable values of E_6 and S_6, as well as, values of E_4, S_4, E_5, and S_5 to be compared with values listed in Table I. For the obtainment of isothermal decay data, we used different techniques to isolate each one of the peaks.

Peaks	E(eV)	S(sec^{-1})	Authors
4	1.19 ± 0.5	$(1.0 - 15) \times 10^{11}$	Zimmerman et *al*[1].
5	1.25 ± 0.6	$(0.5 - 14) \times 10^{11}$	
5	2.4	5×10^{23}	Gorbics et *al*[3]
4	1.15 ± 0.06	$(1.2 \pm 0.06) \times 10^{12}$	Grant et *al*[4].
5	1.36 ± 0.07	$(2.2 \pm 0.11) \times 10^{15}$	
5	$E(T_{low}) = 13$	10^{12}	Moran and Podgorsak[5]
	$E(T_{high}) = 0.8$		

Table 1 - Observ.: Moran and Podgorsak used heatmg rate = 35°C/min. Gorbics *et al.* obtained above values ot E and S from the dependence between peak temperature and heatmg rate.

2. Experimental Methods

TLD-100 powder, from Harshaw Chemical Co., and Harshaw TL Detector Model 2 000 A coupled to an Automatic Integrating Picoammeter Model 2 000 B, were useú in this experiment. The usual heat treatment of 400°C for 1 hour and 80°C for 24 hours was given to the samples. A ^{137}Cs gamma-source was employed for irradiation. Each experimental point in the graphs is an average of about 10 readings.

3. Results

a. Pre-and Post-Irradiation Annealing for Observation of Peak 6 for Isolation of Peaks 4 and 5

Zimmerman et *al.*[1] showed that 3 to 5 hours annealing, at temperature in the range of 125°C to 145°C, enables peak 6 to be seen distinctly. Another way to isolate peak 6 from peak 5 is to perform post-irradiation annealing, at temperatures around 120°C to 165°C. Figure 2 shows glow curves after 0, 2, 4, 6, 8, 10, 20 and 30 hours post-annealing, at 127°C. After 2 hours, the peak 4 decays almost completely and the peak 5 predominates.

After 7 to 8 hours heating, the peak 6 becomes observable together with the peak 5. After 30 hours, the peak 5 decays almost completely, leaving peak 6. The glow curve, in Fig. 3, shows peak 6 after the decay of peak 5. A peak at still higher temperature, namely at about 320°C, can also be seen.

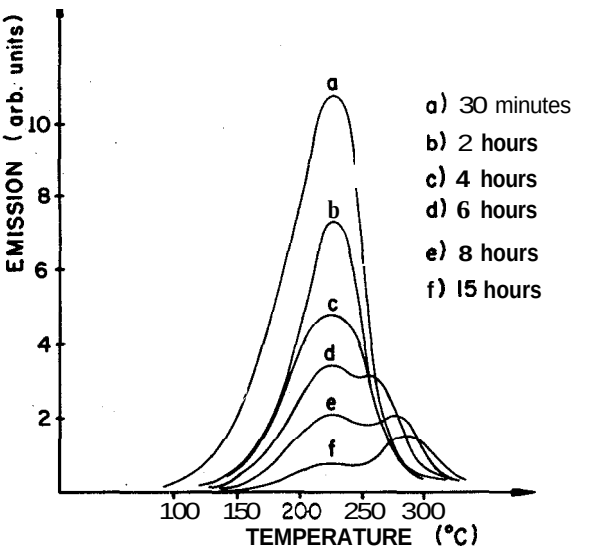

Fig. 2— *Post-annealing* effects *at* 127°C *on peaks 4,* 5 *and 6, after a. 0 hrs, b. 2 hrs, c. 4 hrs,* d. *6 hrs,* e. 8 *hrs,* **f.** 10 *hrs, g. 20 hrs, h. 30 hrs.*

In order to isolate peak 4, we used the optical bleaching method[6]: 310 nm UV light bleaches peak 5, little affecting peak 4. The result is shown in Fig. 4. For a bleaching time longer than 3 to 4 hours, the height of peak 5 becomes smaller than that of peak 4.

b. Post-Annealing Decay Curves

Starting with these isolated peaks, isothennal decay data were obtained. For peak 4, post-annealing was carried out at 103, 109, and 120°C for different intervals of time; at 127, 137, 140 and 165°C for peak 5, and at 129, 140 and 145°C for peak 6. The decay curves are shown in Fig. 5, 6, and 7.

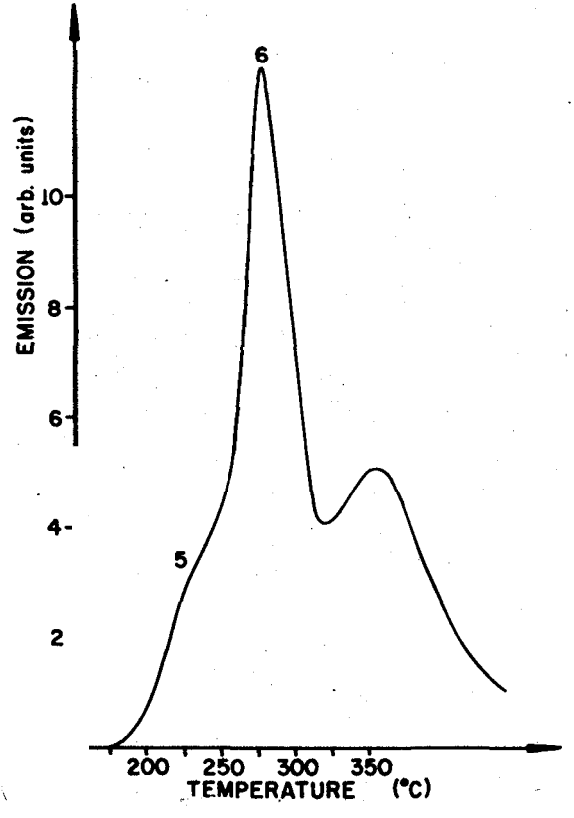

Fig. 3 — Peak *6* isolated by post-annealing at 130°C/(20 hours).

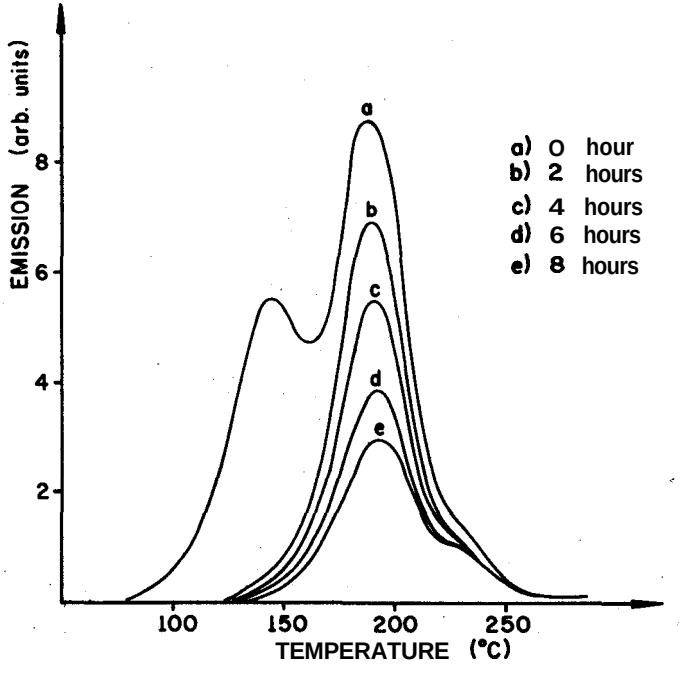

Fig. 4 — Peak 4 isolated after post-annealing 103°C and optical bleaching ultraviolet 310 nm light for 90 minutes: a. 0 hrs at 103°C, b. 2 hrs, 103°C, c. 4 hrs, 103°C, d. 6 hrs, 103°C, e. 8 hrs, 103°C.

c. Supralinearity, Peak Position of Peak 6

Several samples of TLD-100 were irradiated to cesium gamma-rays, varying its exposures from 100 to 7 x 10^4R. Subsequently, they were annealed at 130°C for 20 hours and then its TL was read out to obtain TL response vs. exposure. The result shows that the peak 6 is more supralinear than the peak 5, which is in agreement with Sunta et *al.*[2], i.e., higher the peak ternperature T_p, more supralinear is the behaviour of this peak (Fig. 8).

The position in degrees C of the peak 6 is a function of time intervals of pre – as well as post – annealing. In both cases, there is a maximum shift of about 10°C for a pre-annealing at a temperature in the range of 125 to 145°C and, for a post-annealing at a temperature in the range of 120 to 165°C, used in this work.

d. Correlation of Peak 6 to Some Absorption Band

As a further property of peak 6, we searched for some absorption band connected to that peak. TL measurements and optical absorption were carried out on single crystal of LiF : Mg with a similar characteristic of TLD-100. For the optical absorption, Zeiss spectrophotometer model DMR 21, with double beam, in the range of 2 500 to 190 nm wave length was used.

No specific absorption band correlated to peak 6, in this wave length range, was found.

4. Randall-Wilkins Model and Determination of Trap Depth E and Frequency Factor S

From the decay curves of Figs. 5, 6, and 7, we can compute trap depths and frequency factors of peaks 4, 5, and 6.

Denoting by p the escaping probability of electrons from traps of a given hind, $n(t)$ the number of electrons in the traps at instant t, and $\beta(t) = dT/dt$ the heating rate, we can write in accordance with the Randall-Wilkins mode1[7],

$$p = S \exp(-E/kT), \tag{1}$$

where k is the Boltzmann constant and

$$\frac{dn}{dt} = -np \tag{2}$$

or

$$\frac{dn}{dt} = -np/\beta(t). \tag{2a}$$

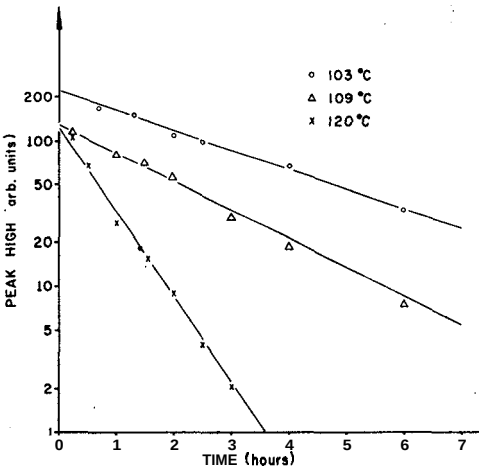

Fig. 5 — Exponential decay of peak 4. Post-annealings at 103 C, 109 C, 120°C.

The glow curve due to a group of traps, each with a definite E – value, is then described by the equation

$$I(t) = n(E, 0)\, S \exp\left[\frac{E}{kT} - \int_{T_0}^{T} \frac{S}{\beta(T')} \exp\left(\frac{-E}{kT'}\right) dT'\right], \tag{3}$$

where T_0 can be taken as the room temperature. If t_a denotes the length of post-annealing time, at temperature T_a, the glow curve is given by

$$I(T, t_a) = n(E, 0)\, S \exp\left[-\frac{E}{kT} - t_a\, S \exp\left(-\frac{E}{kT_a}\right) - \int_{T_0}^{T} \frac{S}{\beta(T')} \exp\left(-\frac{E}{kT'}\right) dT'\right]. \tag{4}$$

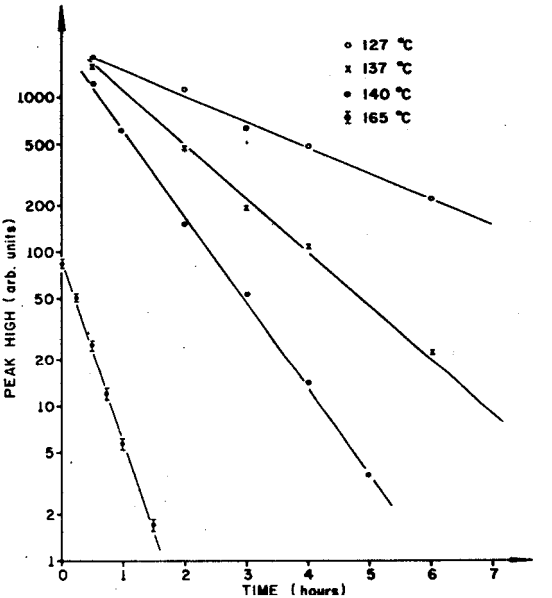

Fig. 6 — Exponential decay of peak 5. Post-annealings at 127°C, 137°C, 140-C and 165-C.

From experimental curves of Log $I(T, t)$ vs. t, and Eq. (4), we can obtain S exp $(-E/kT_a)$ for different values of T_a, and from this, S and E. The semi-logarithmic plot of Eq. *(4)* is a straight line; this fact characterizes Randall-Wilkins assumption that E is a well defined value. There are several instances, like for peak 6 in Fig. 7, where this hypothesis is not obeyed. Morato and Watanabe[8] assumed that E has a continuous distribution around a given value E_0 and half-width $\boldsymbol{a}$. Assuming a Gaussian distribution, glow curve and isothermal decay for a post-annealing at T_a, for a time t_a, can be described by the equation

$$I(T,\ t_a) = \frac{n(E,\ 0)\ S}{\sqrt{2\pi}\ \sigma} \int_{E_1}^{E_2} \exp\left[-\frac{(E-E_0)^2}{2\sigma^2} - t_a\ S \exp\left(-\frac{E}{kT_a}\right) - \frac{E}{kT} - \int_{T_0}^{T} \frac{S}{\beta(T')} \exp\left(-\frac{E}{kT'}\right) dT' \right] dE.$$

By a best fit of experimental points in Fig. 5 and 6 and using Eq. (4), we obtained the values of E and S listed in Table II.

Peak n."	E(eV)	$S(sec^{-1})$
4	**1.10** $\pm$ 0.05	(1 – 10) x 10^{10}
5	1.24f0.04	(1 – 10) × 10^{11}
6	1.56 $\pm$ 0.12	(1 – 10) × 10^{12}

Table II

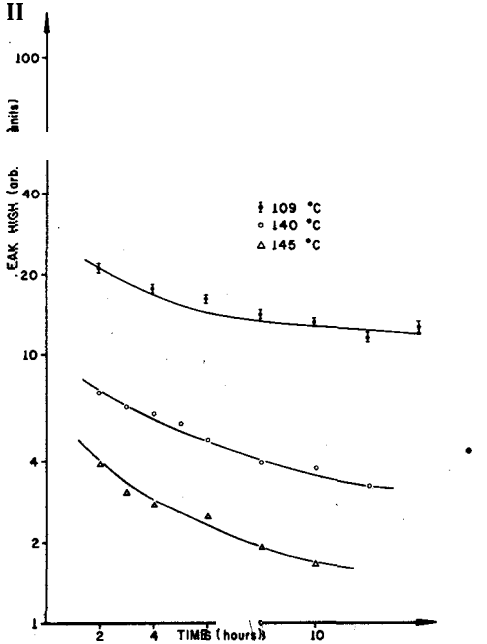

Fig. 7 — Decay of peak 6. Post-annealings at: 129°C and 140°C.

In this calculation for peak 6, the slope of the curves in Fig. 7, for large t_a end, was considered. Since it is obvious that these curves do not obey rigorously Eq. (4), we used Eq. (5). As starting values of parameters, we used those listed in Table II. In Fig. 7, solid lines are the theoretical ones with the following values of the parameters:

$$E_6 = 1.38 \pm 0.07 \text{ eV},$$
$$S_6 = (8.0 \pm 0.10) \times 10^{11} \text{ sec}^{-1},$$
$$\sigma_6 = 0.06 \text{ eV},$$
$$T_6 = 272°\text{C (peak temperature)}. \qquad (6)$$

Connected to the non-exponential decay behaviour of the peak 6, it is found experimentally that there is a shift in peak temperature as the isothermal annealing proceeds. In Fig. 9, the solid line is the theoretical shift as predicted by the continuous model, while the crosses are the experimental points.

5. Theoretical Best Fit to Actual Glow Curve

Having obtained the above parameters, we tried to fit the actual experimental glow curve (peak 4 + peak 5), taking the ratio of the heights of these two peaks as adjustable parameters. We always obtained a broad single peak without the observed peak 4 shoulder. This was proved to be due to the small value of $\Delta T = T_5 - T_4$, where T_5 and T_4 are the peak 4 and peak 5 temperatures determined from the experimental heating curve. Actually, besides the usual experimental error, there is an intrinsic difficulty in determining the real experimental peak ternperature. For this deter-

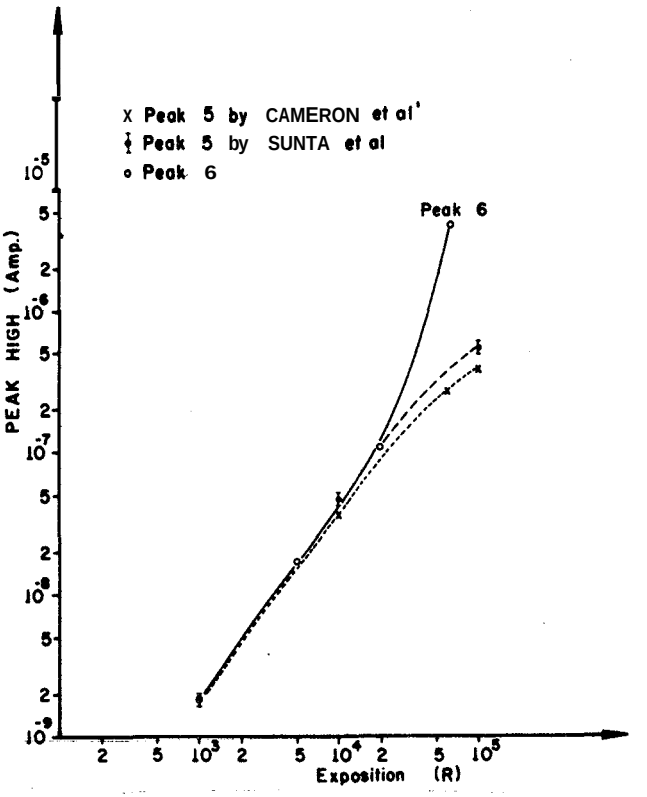

Fig. 8 — TL response of TLD-100 vs. gamma-rays exposure.

mination, if we solder the tip of thermocouple to the heating planchet, we obtain a heating curve distinct from a simple contact to the surface of the planchet. Gorbics et *al.*[2] immersed the tip of the thermocouple in the hot pressed TL powder under measurement mixed with gold powder to have a better thermal contact. Probably, this is the most correct way to determine the phosphor temperature during heating procedure. Of course, keeping the thermocouple immersed in the phosphor powder without mixing gold powder, a different ternperature reading is obtained.

It is evident that the actual temperature of TL phosphor is always lower than the planchet temperature. In most of the cases, the peak temperature is taken from the planchet heating curve.

A second factor that contributes to the error in the ΔT value is the fact that the peak 4 always appears as a shoulder of peak 5, being therefore difficult to define the exact position of its peak.

Hence, starting from values listed in Table II for peaks 4 and 5 and keeping T_5 and T_4 as variable parameters, we tried a direct fit of the experimental glow curve to

$$I(T) = I_4(T) + I_5(T), \tag{7}$$

where I_4 and I_5 are the Randall-Wilkins formulae for peaks 4 and 5, respectively. Two methods were employed for this calculation.

A. Power Series Expansion Around T_5

This method consists of

i) Finding coefficients A_i in the power series

$$I(T) = \Sigma_i\ A_i(T - T_5)^i, \tag{8}$$

that reproduce the observed glow curve around T_5;

ii) Expanding Eq. (7) in a power series similar to (8) and equating the corresponding coefficients;

iii) Extracting the values of the pararneters from the identification of these coefficients.

In practice, Eq. (8) is truncated, keeping k terms and then proceeding with a least squares fitting[9] to minimize

$$Y = \sum_{i=0}^{m} W_i\ [F'(X_i) - F(X_i)]^2, \tag{9}$$

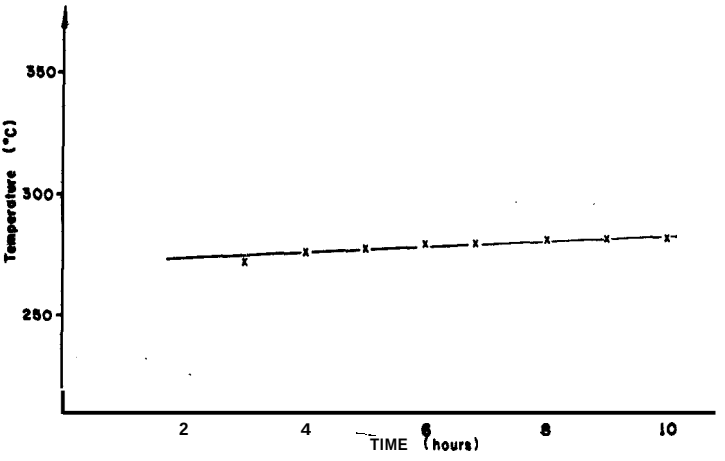

Fig. 9 — Peak 6 temperature shift for post-annealing at 137°C. Solid line — theory; (x), experiments.

where

$$X_i = T_i - T_5,$$

$F'(X_i)$ = experimental value of $I(T)$ at X_i,

$$F(X_i) = \sum_{i=0}^{k} A_j X_i^j, \tag{10}$$

$$W_i = \sigma_i^{-2},$$

σ_i = mean square deviation associated with X_i.

In the present case, σ_i was varied between 2 and 5% and k = 5. We obtained

$$\begin{aligned} A_0 &= 1.0645 \times 10^{1}, & A_3 &= -0.2874 \times 10^{-2}, \\ A_1 &= 0.7613 \times 10^{-2}, & A_4 &= -0.1698 \times 10^{-4}, \\ A_2 &= -0.6195 \times 10^{-1}, & A_5 &= 0.2056 \times 10^{-5}. \end{aligned} \tag{11}$$

These values were equated to the corresponding coefficients in the expansion

$$I(T) = \sum_{i=0}^{k} (n!)^{-1} I^{(n)}(T_5) (T - T_5)^i. \tag{12}$$

There are several sets of solutions of the resulting set of equations for which E_4, S_4, T_4, E_5, S_5, and T_5 are unknowns. Decay curves were used to select the most reasonable set. We obtained

$$\begin{aligned} E_4 &= 1.07 \pm 0.03 \text{ eV}, & E_5 &= 1.29 \pm 0.04 \text{ eV}, \\ S_4 &= (3.0 \pm 0.1) \times 10^{10} \text{ sec}^{-1}, & S_5 &= (6.0 \pm 0.2) \times 10^{11} \text{ sec}^{-1}, \\ T_4 &= 197^\circ\text{C}, & T_5 &= 237^\circ\text{C}. \end{aligned} \tag{13}$$

Gorbics *et al.*[3] obtained $T_5 = 235^\circ$C using $\beta = 2.3^\circ$C/sec.

Figure 10 shows theoretical curves (solid lines). Dots are experimental points. First glow curve is for 0 hour post-annealing, the second one for 2 hours, while the third one for 4 hours post-annealing at 127°C.

B. Least Squares Best Fit for a Non-Linear Function of Several Variables[10]

In Eq. (7), let us consider as variables, the temperature T, TL response $I(T)$, post-annealing time t_a and the error o associated to $I(T)$, at temperature T; trap depth E, frequency factor S, and the ratio between initial number of filled peak 4 and peak 5 traps as adjustable parameters.

In the actual computation, we consider a discrete set of T values. If we denote, by T_i, the ith value of T, σ_i the mean square deviation at T_i, Y_i the experimental value of TL at T_i, $x_1 \ldots\ldots, x_n$ the n variables and E, $\ldots\ldots$ E,,, the m parameters of the problem in hand, we can construct the following difference

$$g_i = [I(T_i) - Y_i]/\sigma_i, \tag{14}$$

which is a non linear function of n variables and m parameters. The least squares best-fit consists in minimizing the sum

$$G = \sum_{i=1}^{r} g_i^2, \tag{15}$$

r being the number of discrete Tvalues appropriately chosen. σ_i was varied between 3 and 5%. For peak temperatures T_4 and T_5, we used the values found in the previous computation.

In Fig. 11, solid lines represent theory and dots have the same meaning as in Fig. 10. This result corresponds to the following set of parameters:

$$\begin{aligned} E_4 &= 1.05 \pm 0.03 \text{ eV}, & E_5 &= 1.29 \pm 0.04 \text{ eV}, \\ S_4 &= (1.00 \pm 0.05) \text{ sec}^{-1} \times 10^{10}, & S_5 &= (6.8 \pm 0.4) \times 10^{11} \text{ sec}^{-1} \\ n(E_4, 0)/n(E_5, 0) &= 0.38. \end{aligned} \tag{16}$$

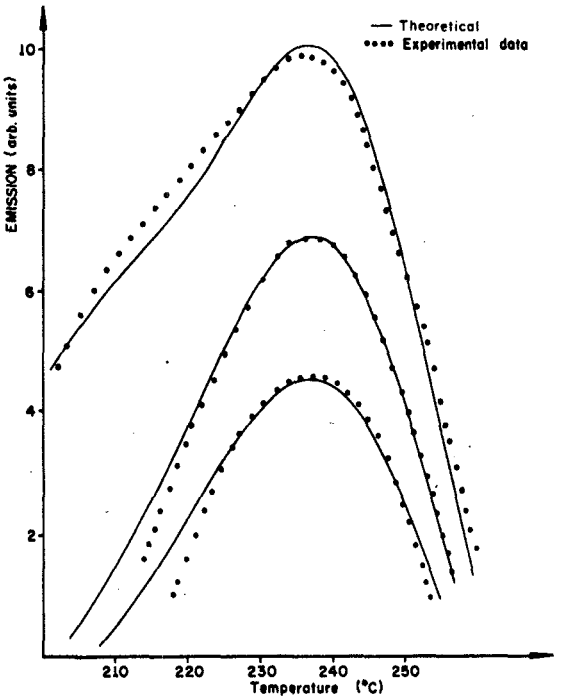

Fig. 10 — Best fit to actual glow curve of TLD-100, around peaks 4 and 5, by expanding Randall-Wilkins two peaks formulae into power series (6 terms are retained).

In both cases, A and B, the heating rate was taken constant and equal to 2.3°C/sec.

6. Conclusions

a. By singling out peak 5 as better as one can, by post-annealing at temperature between 125 and 135°C, and by isolating peak 4 by optical bleaching with 310 nm UV light, we obtained, from isothermal decay curves, the following trap depths and frequency factors for peaks 4 and 5:

$$E_4 = 1.10 \pm 0.05 \text{ eV}, \qquad S_4 = (1 - 10) \times 10^{10} \text{ sec}^{-1},$$
$$E_5 = 1.24 \pm 0.04 \text{ eV}, \qquad S_5 = (1 - 10) \times 10^{11} \text{ sec}^{-1}.$$

b. Pre-annealing, at temperature in the range 100 to 125°C or post-annealing at any temperature between 120 to 165°C, eliminate peak 5 leaving peak 6

alrnost isolated. The isothermal annealing shows that the decay curve is not exponential as expected by the Randall and Wilkins model. Furthermore, the peak position shifts as the annealing proceeds. The continuous trap model predicts both behaviors and the following values for the parameters:

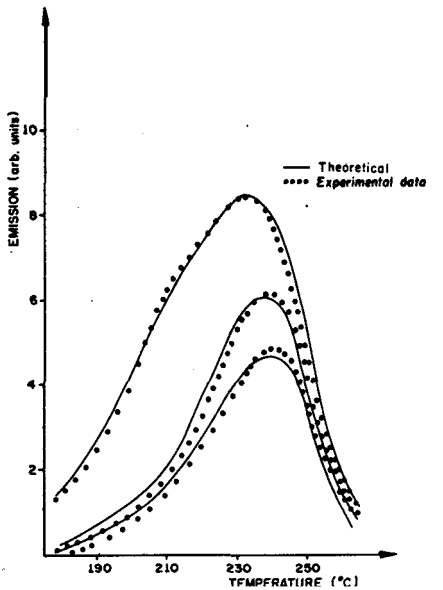

Fig. 11 — Peaks 4 and 5 simultaneous fit using Randall-Wilkins Model.

$$E_6 = 1.38 \pm 0.07 \text{ eV}, \qquad \sigma_6 = 0.06 \text{ eV},$$
$$S_6 = (8.0 \pm 0.1) \times 10^{11} \text{ sec}^{-1}, \qquad T_6 = 272°\text{C}.$$

c. Peak 6 is markedly more supralinear than peak 5 and this supralinearity starts at about 100 R; the saturation takes place in the vicinity of 10^5 R. Peak 6 height is, however, much smaller than that of peak 5.

In the range of 2500 nm to 190 nm, no specific absorption band correlated to peak 6 was found.

d. After failure to reproduce the observed glow curve comprising peaks 4 and 5, using the values of trap depth, frequency factor and peak temperature found in this work, the experimental curve was fitted with a polynomial function around T_5, the peak 5 temperature. Six terms were used

and the coefficients of the power series expansion of $I(T) = I_4(T) + I_5(T)$, where $I_i(T)$ is the Randall-Wilkins formula for peak *i*. The values of trap depth, frequency factor and peak temperature are:

$E_4 = 1.07 \pm 0.03$ eV, $E_5 = 1.29 \pm 0.04$ eV,
$S_4 = (3.0 \pm 0.1) \times 10^{10}$ sec^{-1}, $S_5 = (6.0 \pm 0.2) \times 10^{11}$ sec^{-1},
$T_4 = 197$°C, $T_5 = 237$°C.

The merit of this process is that, if we have a well defined heating rate, the peak temperature can be determined from the calculation. It gives, however, several sets of solutions. Isothermal decay data can be used to select the most reasonable one.

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