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ABSTRACT

The thermoluminescence (TL) of CaF_2:Mn has been studied using photon counting and digital recording. For doses of 10 rad or less the TL glow curves appear to consist of a single glow peak. However, there are indications - which are pronounced at larger doses - that one additional low intensity peak (area $\leq$ one percent) is superimposed on each side of the central peak. The intense peak is not described by 1st or 2nd order kinetics but is well described by the more general kinetics from which these kinetics are derived. These observations, and the results of additional kinetic analysis, demonstrate that retrapping is not negligible and may include all three peaks. In such systems, which are likely to include other dosimeter materials and minerals, peak height will not increase linearly with dose; an important factor for dosimetry and dating applications.

Archaeological, geological and dosimetry applications of thermoluminescence (TL) almost always depend on a curve of TL signal intensity as a

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function of dose, often called a sensitivity curve. Proper interpretation of such curves require a determination of the applicable TL kinetics. To understand TL kinetics, which has not been adequately studied in the minerals most often encountered in archaeological and geological applications or in the common dosimeter materials, it is obviously useful to study the simplist possible materials, i.e. to study TL emitters that produce, or appear to produce, glow curves that contain a single TL glow peak. The CaF_2:Mn dosimeter material described in this paper appears to give rise to a single glow peak when irradiated at room temperature. Such materials are very rare. The investigation of single peak emitters is important for basic TL studies and particularly so for applications. The present CaF_2:Mn studies were undertaken, in part, to test the single peak TL kinetics.

Almost all TL theory and the analysis of almost all TL data is based on the assumption that each glow peak can be regarded as a single peak that is independent of -- or does not interact in any way with -- other peaks in the same glow curve. However, glow curves containing more than one peak may be expected in general to interact with each other as the trafficking of charges between the trap sites proceeds at elevated temperatures. Such interactive kinetics has a profound effect on the intensity against dose or sensitivity characteristics of TL. The dependence of sensitivity curve behavior on the kinetics of the TL emitters is described, in some detail, in a seperate paper (Levy, 1984c).

The CaF_2:Mn glow curves described below were obtained from small samples, usually in the 5 to 10 mg range, seperated from pressed pellet dosimeter material (purchased from Harshaw). Glow curves were recorded with Littlemore apparatus additionally equipped with fast-electronics, photon-counting, and digital recording. All data were corrected for counting losses. Conse-

quently, glow curves consist of digital intensity vs. temperature data sets that are essential for computerized numerical analysis. The samples were irradiated with ^{60}Co gamma-rays and measured a few days after irradiation. Typical data sets are included in the figures.

One method often used for characterizing a single glow peak is based on the values of the full width (ω) (at half intensity) and the high temperature half width (δ) and low temperature half width (τ), see Fig. 1. Chen and Kirsh (1981) have introduced the shape parameter δ/ω which for first order kinetics should be equal to 0.42 and for second order should be 0.52. In between values are commonly observed. They give expressions for the activation energy E and the "preexponential factor" s when T_m the peak temperature is also given. It should be emphasized that this type of analysis does not fully take into account the exact shape of the glow curve, only the values of ω, δ, and τ . Fig. 1 shows the glow curve for CaF_2:Mn obtained with a 1.0 rad dose. The value of δ/ω= 0.42 would indicate that very close to first order kinetics is operating. The observed values of T_m, ω, δ, τ yield the values E = 0.95 eV and s = 1.87×10^7.

Fig. 2, however, shows that these values of E and s are illusory. A sliding average program was used to compute the value of E for 20°C intervals along the entire glow curve assuming first order kinetics. These values are plotted opposite the channel (temperature) at the center of each interval. Not unexpectedly, the formulas of Chen and Kirsh attempt to give the best average constant value of E in the temperature interval ω . Fig. 2, however, also shows per se, that an effort to fit first order kinetics to the glow curve fails since a constant value for E does not result. Attention is drawn to the considerably higher value of E ≈ 1.34 eV obtained from the initial rise portion of the glow curve.

A general simple model for TL-kinetics is shown in Fig. 3 both in diagramatic and equation form. The isolated single glow peak is assumed to be associated with only the electron trap sites N. The temperatures reached in obtaining the glow curve are assumed to be too low to significantly drain electrons from the deeper trap identified with sites M. A complete discussion of the implications of this general one-trap (GOT) kinetic model appears in the companion paper by Levy (1984c).

All the present experiments with CaF_2:Mn were for doses of less than 10^3 rad while N may be estimated to correspond to the saturation dose of $\approx 10^6$ rad, thus, in the retrapping term n in the factor (N - n) may be neglected compared to N. In this case, only the combination of parameters $N\sigma_t/\sigma_r$ enters, which for convenience we write simply as $N\sigma$ as in the preceding paper. The best fit tc the data for a 1.0 rad dose, based on the Brookhaven computer search program, is shown in Fig. 4 for both first order and second order kinetics. This fitting procedure utilizes a computerized best-fit program which continues to cycle until the mean square deviation is minimized. The second order fit is seen to be rather poor. Although the first order fit is reasonably acceptable over the higher intensity portion of the glow curve, considerable error is present in the low intensity "wings". Fig. 5 shows the fit achieved with the GOT kinetic model of Fig. 3 and Eq. (1) in the accompanying paper (Levy, 1984c), where $n_r = n + m$. The properties of this expression, which was originally introduced by Randall and Wilkins (1945) and Garlick and Gibson (1948), has been described in detail Levy (1982a, 1982b, 1983, 1984a, 1984b, and 1984c) and Hornyak, et al. (1984). The fit is seen to be excellent over most of the glow curve except for the persistent failure for fitting the initial rise portion of the curve below $I_m/10$. All of these above results hold for doses ranging from 0.01 to 10^3 rads, including the problem in the initial rise region.

Fig. 6 shows the results of the GOT kinetic model fit when the initial rise region below $I_m/10$ is ignored. Particular emphasis is called to the portion of the curve at temperatures above T_m where the retrapping factor plays a large role in determining the shape of the glow curve. Evidently, a reasonable fit to the data is possible over the peak region extending down to a level of $I \approx I_m \times 10^{-3}$ on the high temperature side. The resulting parameters of this fit E = 0.98 eV, $N\sigma = 2.1 \times 10^4$, and $s = 3.7 \times 10^7$ are similar to those of the whole glow curve fit of Fig. 5, E = 1.04 eV, $N\sigma = 4.7 \times 10^3$, and $s = 6.3 \times 10^7$. The larger value of $N\sigma$ associated with Fig. 6 is the result of including a small but significant value of $m = m_o \approx 0.01 \times n_o$ (m remains constant over the glow peak).

For the case of a linear heating rate, $T = T_o + \beta t$, the GOT kinetic equation may be written in the form

$$\ell n\left(\frac{\Delta n}{n}\right) = - E/kT + \ell n\left(\frac{s\Delta T}{\beta}\right) - \ell n\left[1 + \frac{\sigma N}{n + m}\right] \quad . \qquad (1)$$

Here the quantity Δn represents the number of luminescent pulses recorded in the temperature interval ΔT. The presentation of the same data previously shown in Fig. 6 is shown in Fig. 7 where $\ell n(\Delta n/n)$ is plotted as a function of 1/T. A strictly first order kinetics glow curve in this type of plot would be a straight line with a slope of -E/kT and a y-intercept of $\ell n(\frac{s\Delta T}{\beta})$ (in our case ΔT= 1.0 °C and β=1.25 °C/sec). The need for the retrapping correction, the third term on the right hand side of (1), is evident. Data for a dose of 35 mrads is also plotted. Note that in the linear portion of the two curves the two sets of (unnormalized) data approximately coincide. However, the lower dose curve breaks away earlier from linearity indicating the presence of a stronger retrapping correction. This is as it should be since n_o is some 30

times smaller for the lower dose. The initial rise value for the activation energy is E = 1.29 eV at the 1.0 rad dose level, which is again to be contrasted with the lower values that gives the best overall glow curve fits.

An experiment was conducted to see if long term fading in CaF_2:Mn could be simulated by preheating a freshly irradiated sample. A sample given a dose of 10 rad was set aside at room temperature for 9 months prior to running a glow curve. The resulting curve is rather symmetric and yields a shape factor $\delta/\omega = 0.47$. A separate sample was also given a dose of 10 rad and preheated to 265°C soon after irradiation. This sample was then heated to obtain the complete (second heating) glow curve. The typical asymmetric curve is obtained with $\delta/\omega = 0.42$. The two glow curves appear rather different in shape. Using the equations of Chen and Kirsh quite different activation energies result; E = 0.86 eV for the 9 month sample and E = 1.26 eV for the preheated freshly irradiated sample. This would suggest that there is no correspondence in the TL-kinetics for the two cases. However, Fig. 8 and 9 show the results in the $\ell n(\frac{\Delta n}{n})$ vs. 1/T type plot. The physical parameters obtained using the GOT model yields for the 9 month sample: E = 1.38 eV, $s = 1.4 \times 10^{11}$, $\sigma N = 7.2 \times 10^5$, and m = 0 while for the freshly irradiated sample preheated to 265°C: E = 1.40 eV, $s = 2.8 \times 10^{11}$, $\sigma N = 7.2 \times 10^5$, and $m = 4 \times 10^4$. Thus, the physical parameters now appear to suggest very similar TL-kinetics to be taking place. The glow curve shape differences are entirely due to the fact that $n_o = 1.9 \times 10^6$ for the 9 month sample and three times as large a value of $n_o = 5.7 \times 10^6$ for the preheated sample. The lower n_o yields a larger retrapping correction and produces a more symmetric glow curve for the 9 month sample.

Fig. 8 and 9 also show initial rise activation energies ranging from E = 1.38 to 1.90 eV. These two curves are but two examples of the well known

application of the initial rise method applied to continued preheating to progressively higher temperatures. The activation energies that result continually increase with increased preheating temperature and span a wide range in values that are roughly 50 percent or more higher than the values found by fitting the "first glow" curves with the GOT kinetic equation. At this point the reason for these larger initial rise values of E than those that produce such good overall fits to the glow curves is not understood. Several possibilities are suggested:

a) the glow peak consists of a continuous distribution of activation energies spread about some mean energy E_o, or

b) several discrete overlapping glow peaks are involved that are strongly interactive.

The first of these possibilities is now under investigation and results will be published later. An investigation of the second possibility revealed that there are two low intensity glow peaks present on either side of the main glow peak, see Fig. 10. The glow curve area ascribable to these peaks are below one percent of the main peak. At dose exposures below 10^4 rad both peaks appear to increase linearly with dose. The more intense higher temperature peak at 405 °C begins to increase very rapidly as the main peak approaches saturation above 10^5 rad. Interaction between this peak and the main peak is quite evident since the shape of the main peak also becomes quite distorted at these high dose exposures. Investigation of the interactive behavior of the levels in continuing.

The shape of glow curves at different doses are commonly made use of in archaeological dating. The present results with a simple TL-system suggests that a knowledge of the TL-kinetics is necessary to give a proper interpretation of archaeological data particularly when low radiation doses are

involved. It is essential to demonstrate that TL intensity (area or peak height) is linear with irradiation dose up to at least archaeological doses. Theoretical ramifications are discussed in detail in the preceding companion paper by Levy (1984c)

FIGURE CAPTIONS

Fig. 1 Digitally recorded glow curve from CaF_2:Mn exposed to a 1.0 rad ^{60}Co γ-ray dose. A sample heating rate β = 1.25 °C/sec was used in this and all subsequent runs. The shape parameter δ/ω = 0.42 is suggestive of first order TL-kinetics. Only every fifth recorded point is plotted.

Fig. 2 A sliding average determination of the activation evergy E assuming first order TL-kinetics for the data of Fig. 1. True first order kinetics would have yielded a constant value throughout.

Fig. 3 A representation of the general one-trap (GOT) kinetic model showing the valence and conduction bands and assumed electron and hole trap sites. Only the n electrons in the shallower traps N are released during the TL measurement.

Fig. 4 Best computerized fits to CaF_2:Mn glow curve data at 1.0 rad exposure. Solid line is for first order TL-kinetics and dashed line is for seond order TL-kinetics.

Fig. 5 Same data as in Fig. 4 but fitted with the GOT kinetic model. The model parameters are given in the figure.

Fig. 6 CaF_2:Mn TL data obtained for an irradiation of 1.0 rad with ^{60}Co γ-rays. Solid curve is the best fit over the glow curve in the region above the initial rise to $I_m/10$ using the GOT kinetic model. The physical parameters that result are:
$E = 0.997$ eV, $s = 3.69 \times 10^7$, $\sigma N = 2.1 \times 10^4$, $m = 7 \times 10^3$ and
$n_o = 6.86 \times 10^5$.

Fig. 7 CaF_2:Mn glow curve data, for samples exposed to 1.0 and 0.035 rad plotted in the form $\ln(\frac{\Delta n}{n})$ vs. 1/T. The 1.0 rad dose data is the same as shown in Fig. 6. Note the near equal values of the E and s parameters for the two doses as evidenced by the near congruence of the two (unnormalized) data sets in the linear portion of the curves.

Fig 8 CaF_2:Mn given a 10 rad dose of ^{60}Co γ-rays and stored at room temperature for 9 months prior to taking the glow curve. Best fit parameters using the GOT kinetic model are: $E = 1.38$ eV, $s = 1.41 \times 10^{11}$, $\sigma N = 7.2 \times 10^5$, $m = 0$, and $n_o = 1.89 \times 10^6$.

Fig. 9 CaF_2:Mn given a 10 rad dose of ^{60}Co γ-rays with subsequent preheating to 265°C (yielding an initial rise activation energy $E = 1.39$ eV) followed by running a complete second heating glow curve. The best complete glow curve fit is with the physical parameters: $E = 1.40$ eV, $s = 2.81 \times 10^{11}$, $\sigma N = 7.2 \times 10^5$, $m = 4 \times 10^4$, and $n_o = 5.74 \times 10^6$. The initial rise value for the activation energy is $E = 1.90$ eV.

Fig. 10 CaF_2:Mn glow curve rate meter data for a 10^3 rad exposure. The main peak rate was allowed to saturate the system in order to more clearly show the two low intensity sacellite peaks on either side of the main peak.

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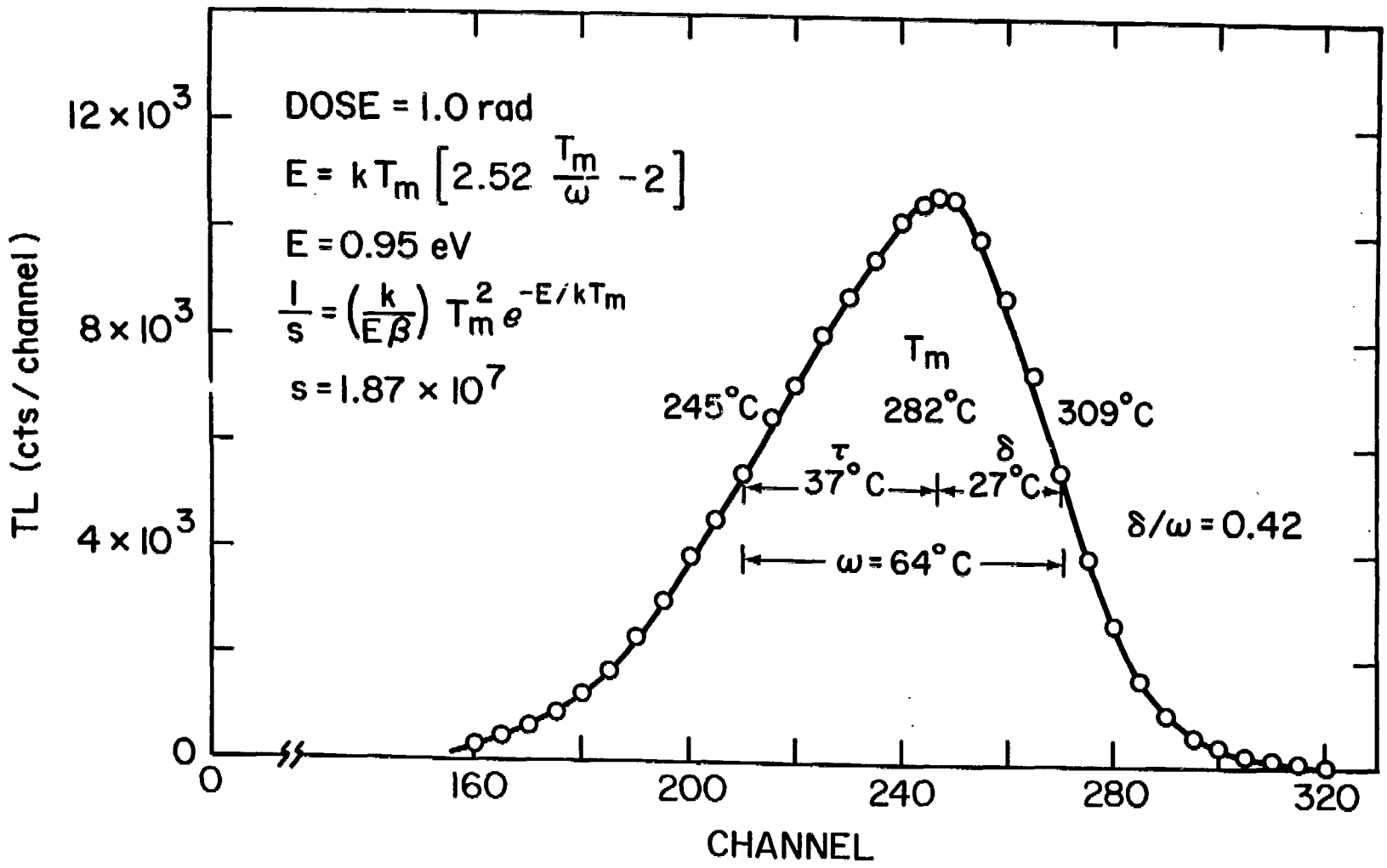
DOSE = 1.0 rad
$E = kT_m \left[2.52 \frac{T_m}{\omega} - 2\right]$
E = 0.95 eV
$\frac{I}{s} = \left(\frac{k}{E\beta}\right) T_m^2 e^{-E/kT_m}$
$s = 1.87 \times 10^7$
T_m
282°C
245°C
309°C
τ
37°C
δ
27°C
ω = 64°C
δ/ω = 0.42
12×10^3
8×10^3
4×10^3
0
TL (cts / channel)
0
160
200
240
280
320
CHANNEL

Figure 1

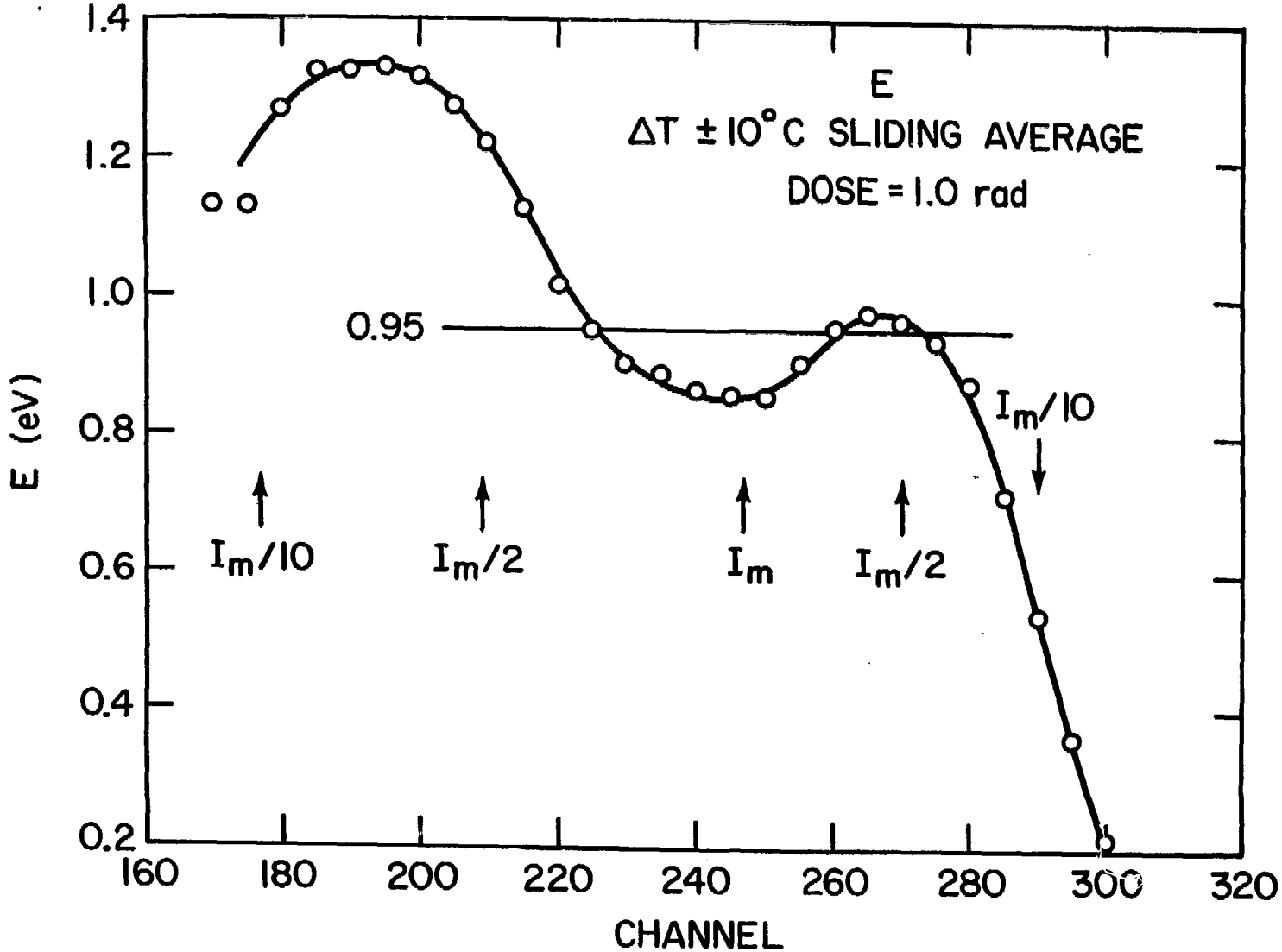
E
ΔT ± 10°C SLIDING AVERAGE
DOSE = 1.0 rad
0.95
E (eV)
CHANNEL
$I_m/10$
$I_m/2$
I_m
$I_m/2$
$I_m/10$
1.4
1.2
1.0
0.8
0.6
0.4
0.2
160
180
200
220
240
260
280
300
320

Figure 2

$-\frac{dn}{dt} = s\theta^{-E/kT} \cdot \frac{n}{\left[\frac{\sigma_r(n+m)}{\sigma_+(N-n)} + 1\right]}$
n+m
E
M, m
u, N, n
σ_r
σ_+
$s\theta^{-E/kT}$

Figure 3

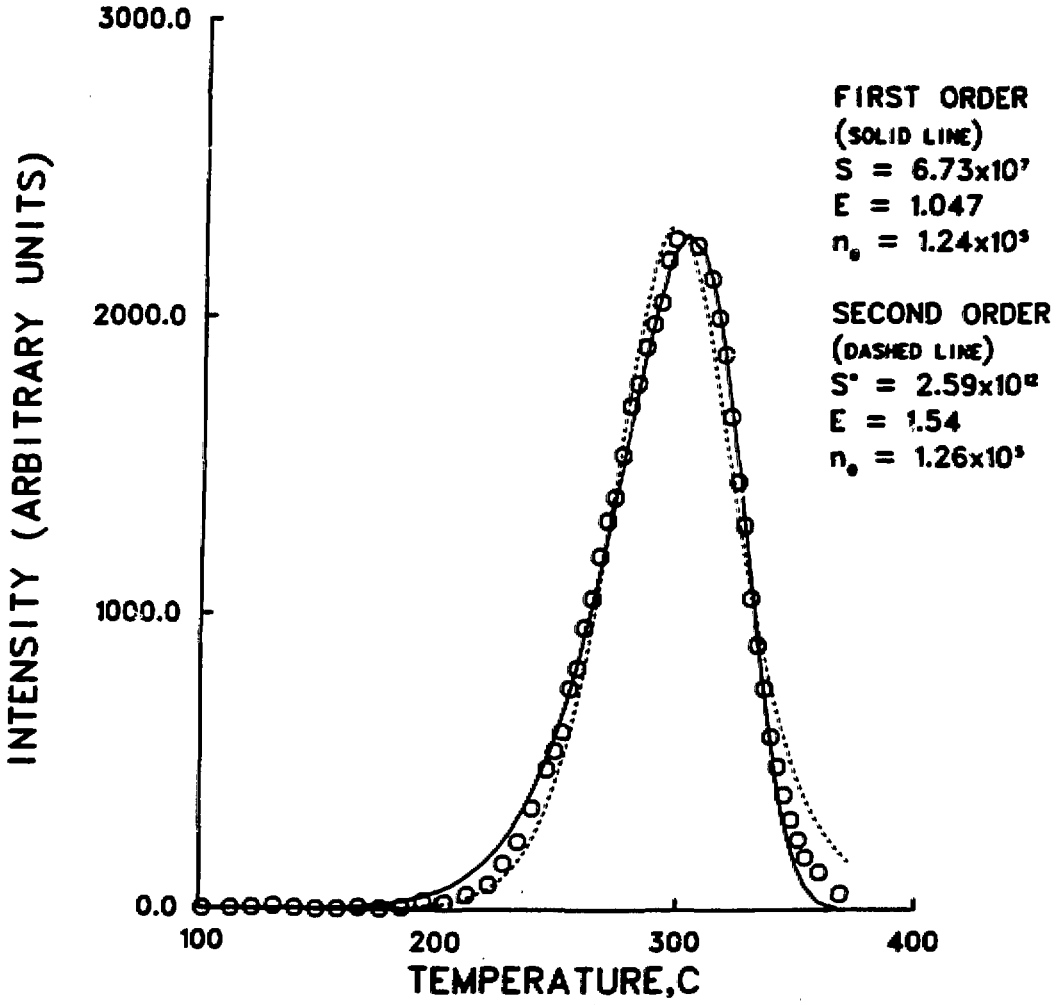
3000.0
2000.0
1000.0
0.0
INTENSITY (ARBITRARY UNITS)
100
200
300
400
TEMPERATURE,C
FIRST ORDER
(SOLID LINE)
S = 6.73x10⁷
E = 1.047
n₀ = 1.24x10⁵
SECOND ORDER
(DASHED LINE)
S' = 2.59x10¹²
E = 1.54
n₀ = 1.26x10⁵

Figure 4

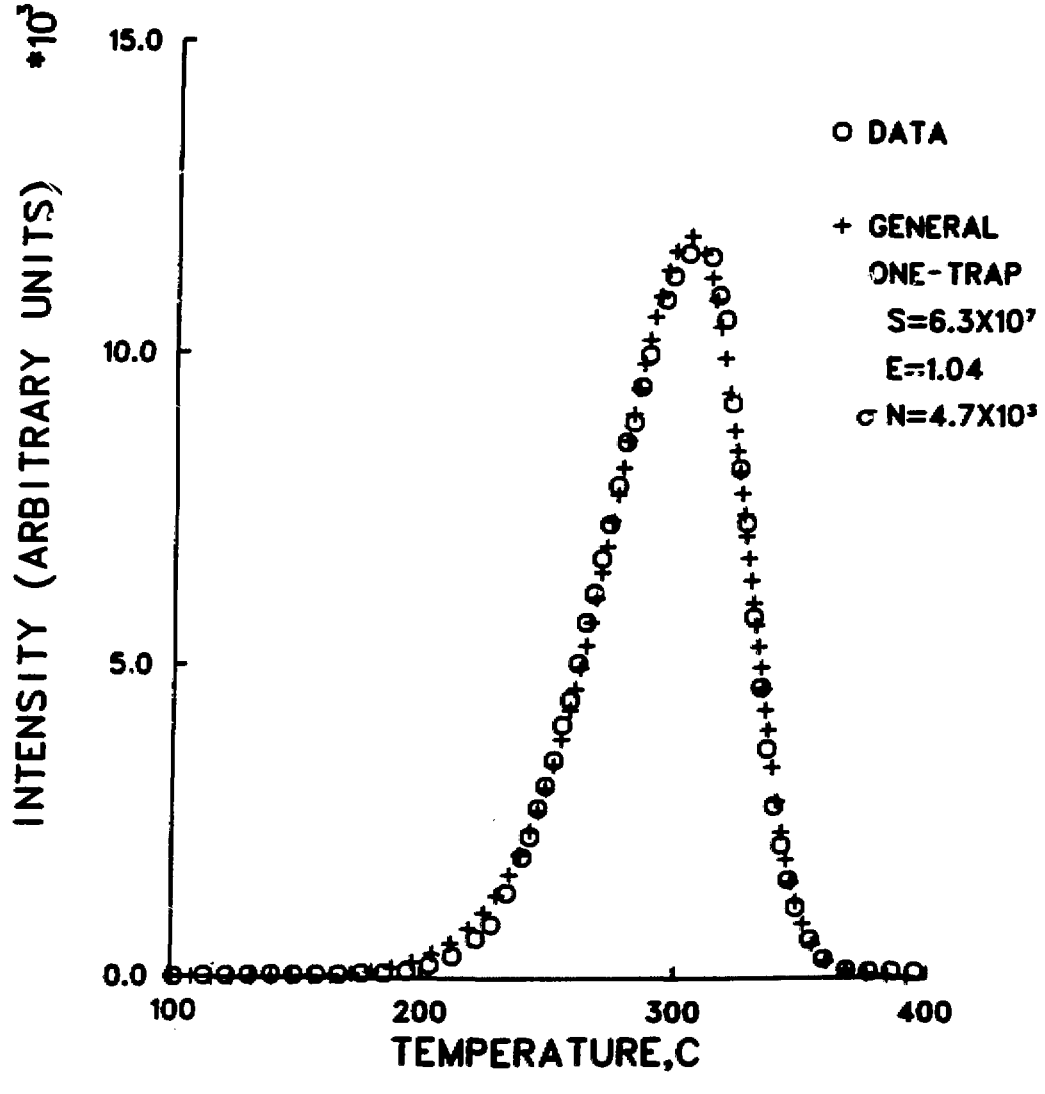
INTENSITY (ARBITRARY UNITS)
*10³
15.0
10.0
5.0
0.0
100
200
300
400
TEMPERATURE,C
O DATA
+ GENERAL ONE-TRAP
S=6.3X10⁷
E=1.04
σ N=4.7X10³

Figure 5

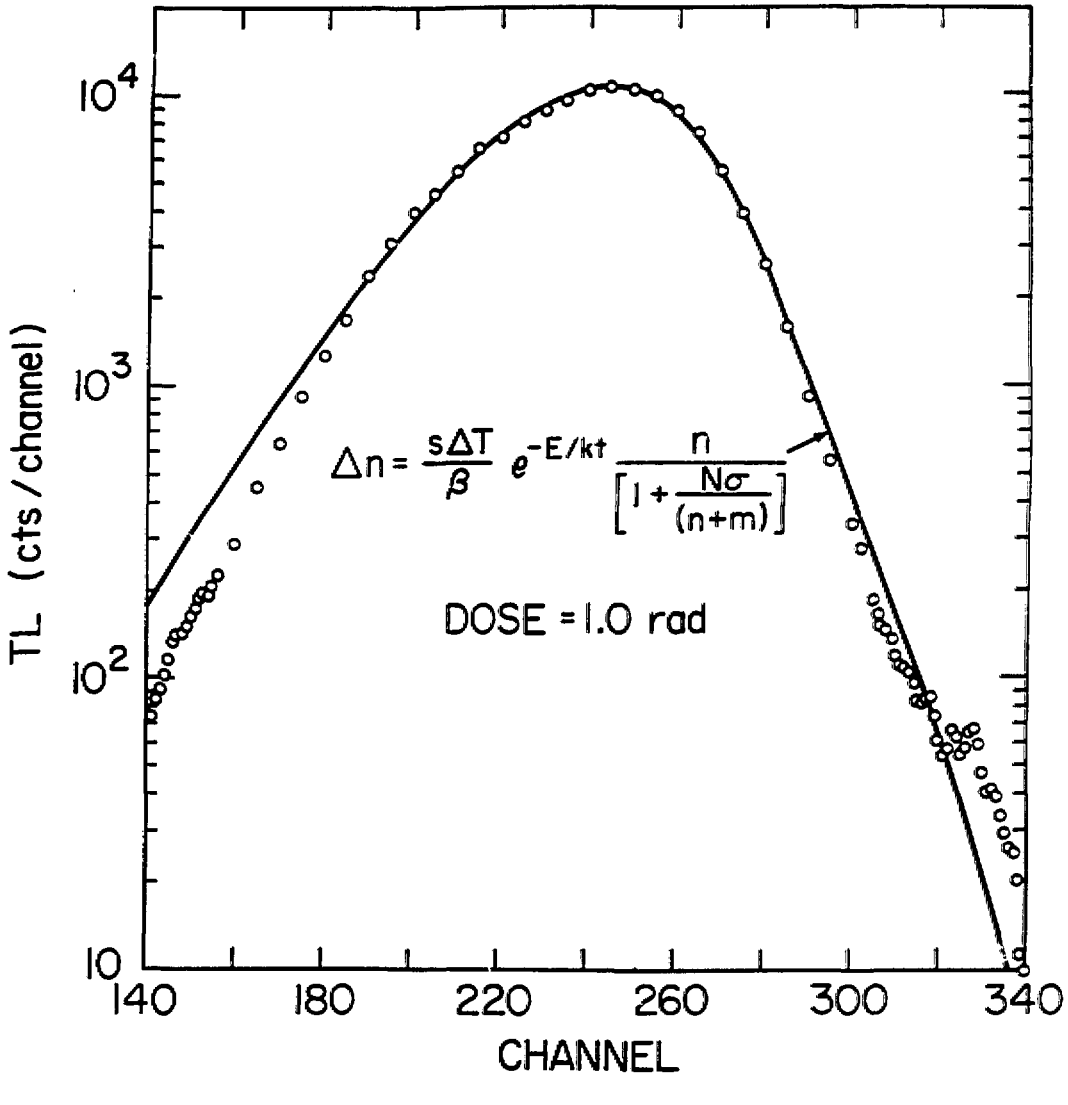
TL (cts/channel)
10^4
10^3
10^2
10
$\Delta n = \frac{s\Delta T}{\beta} e^{-E/kt} \frac{n}{\left[1+\frac{N\sigma}{(n+m)}\right]}$
DOSE = 1.0 rad
140
180
220
260
300
340
CHANNEL

Figure 5

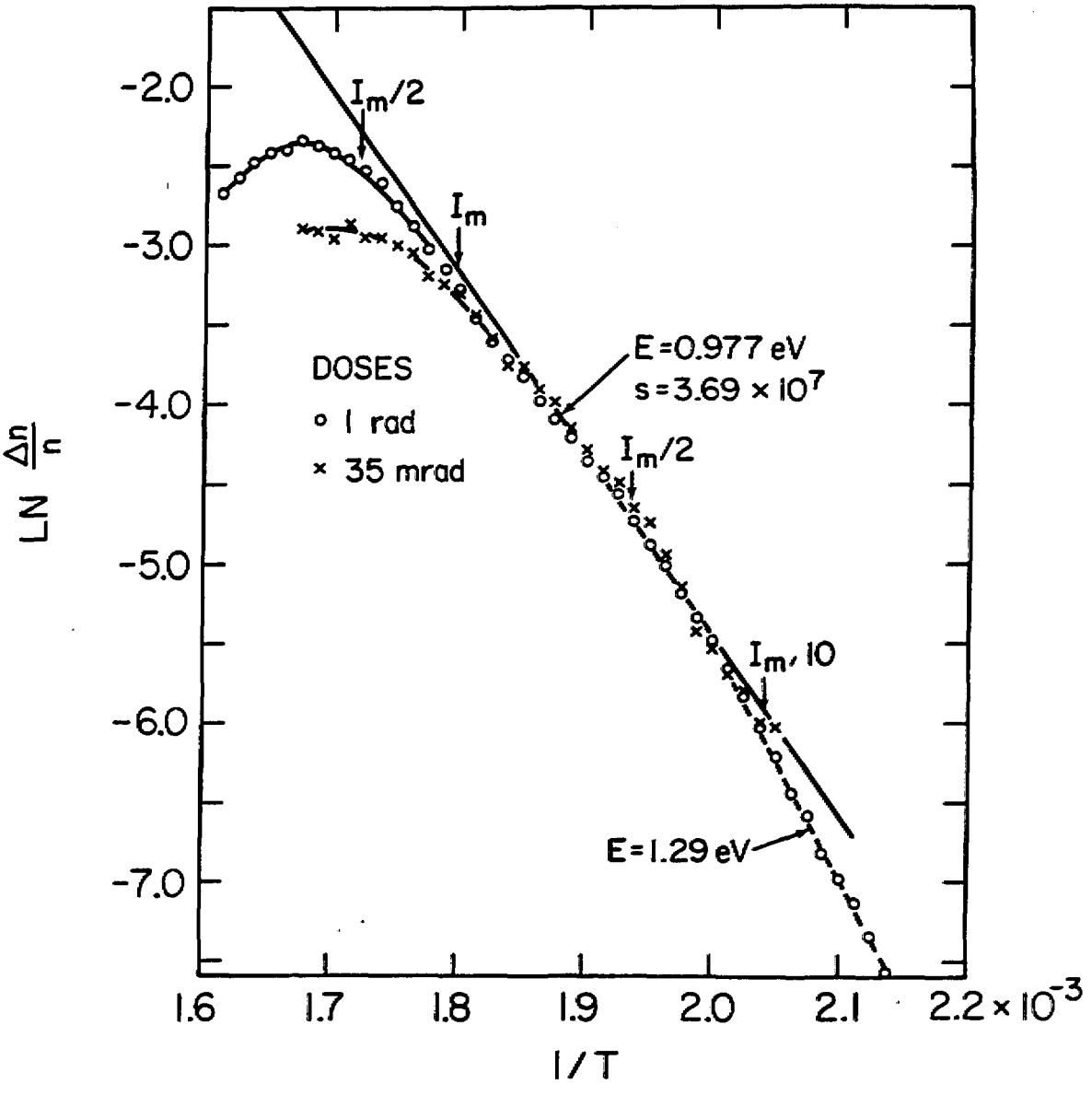
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
LN Δn/n
$I_m/2$
I_m
E=0.977 eV
s=3.69 × 10^7
DOSES
o 1 rad
× 35 mrad
$I_m/2$
I_m, 10
E=1.29 eV
1.6
1.7
1.8
1.9
2.0
2.1
2.2 × 10^-3
1/T

Figure 7

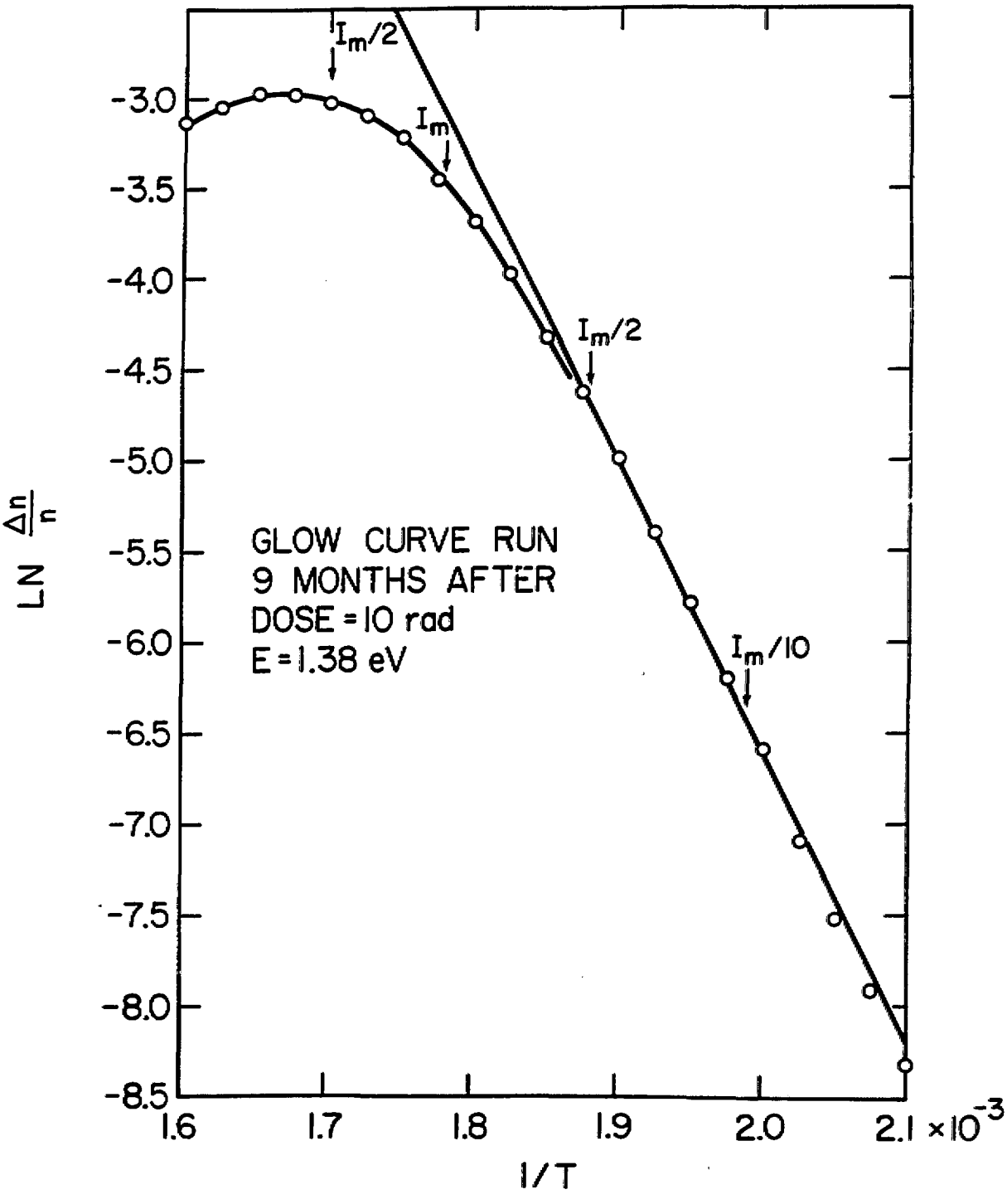
$I_m/2$
I_m
$I_m/2$
$I_m/10$
GLOW CURVE RUN
9 MONTHS AFTER
DOSE = 10 rad
E = 1.38 eV
LN $\frac{\Delta n}{n}$
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
-6.0
-6.5
-7.0
-7.5
-8.0
-8.5
1.6
1.7
1.8
1.9
2.0
2.1 $\times 10^{-3}$
1/T

Figure 8

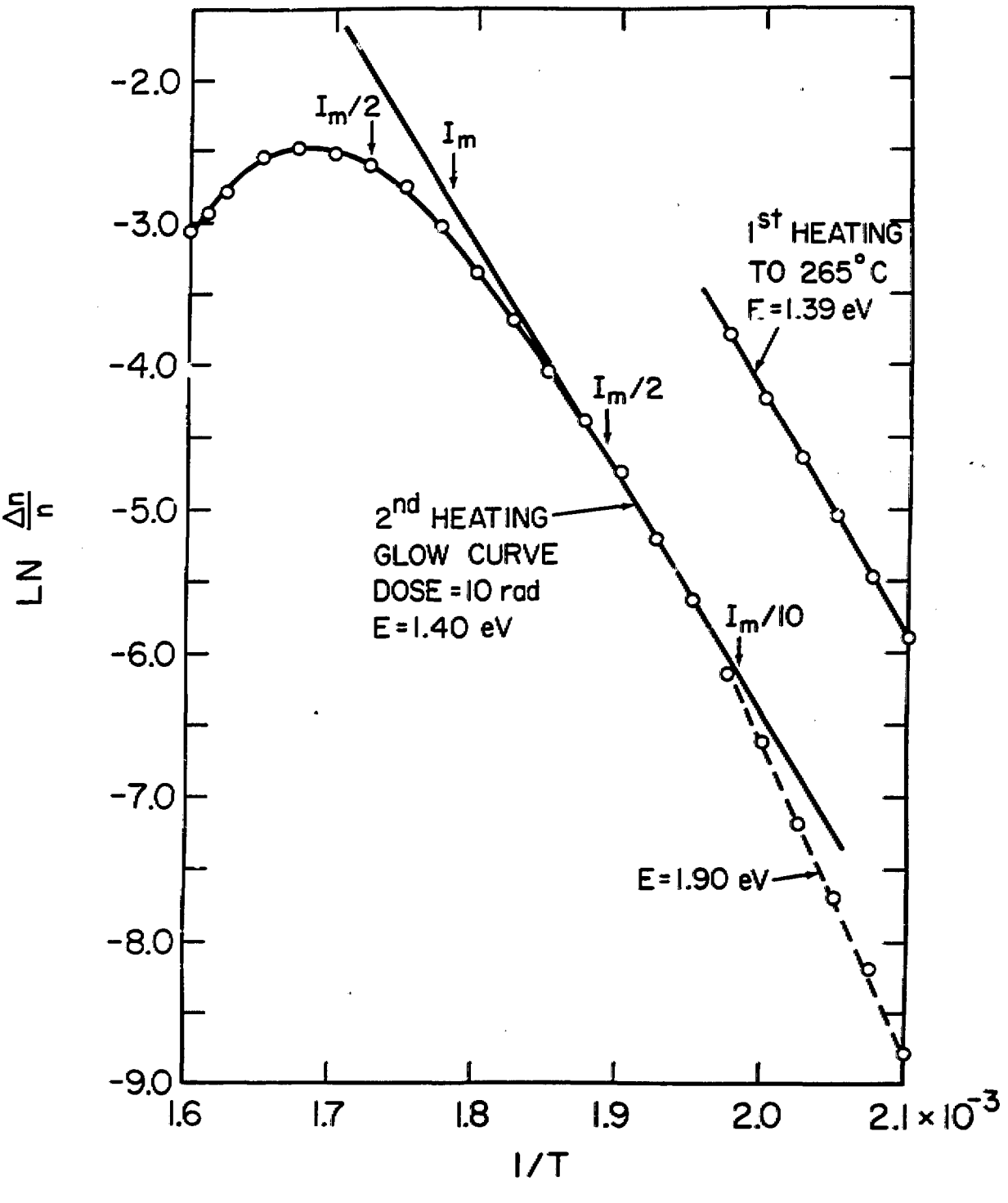
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
LN Δn/n
1.6
1.7
1.8
1.9
2.0
2.1 × 10⁻³
1/T
Im/2
Im
Im/2
Im/10
1st HEATING
TO 265°C
E=1.39 eV
2nd HEATING
GLOW CURVE
DOSE = 10 rad
E=1.40 eV
E=1.90 eV

Figure 9

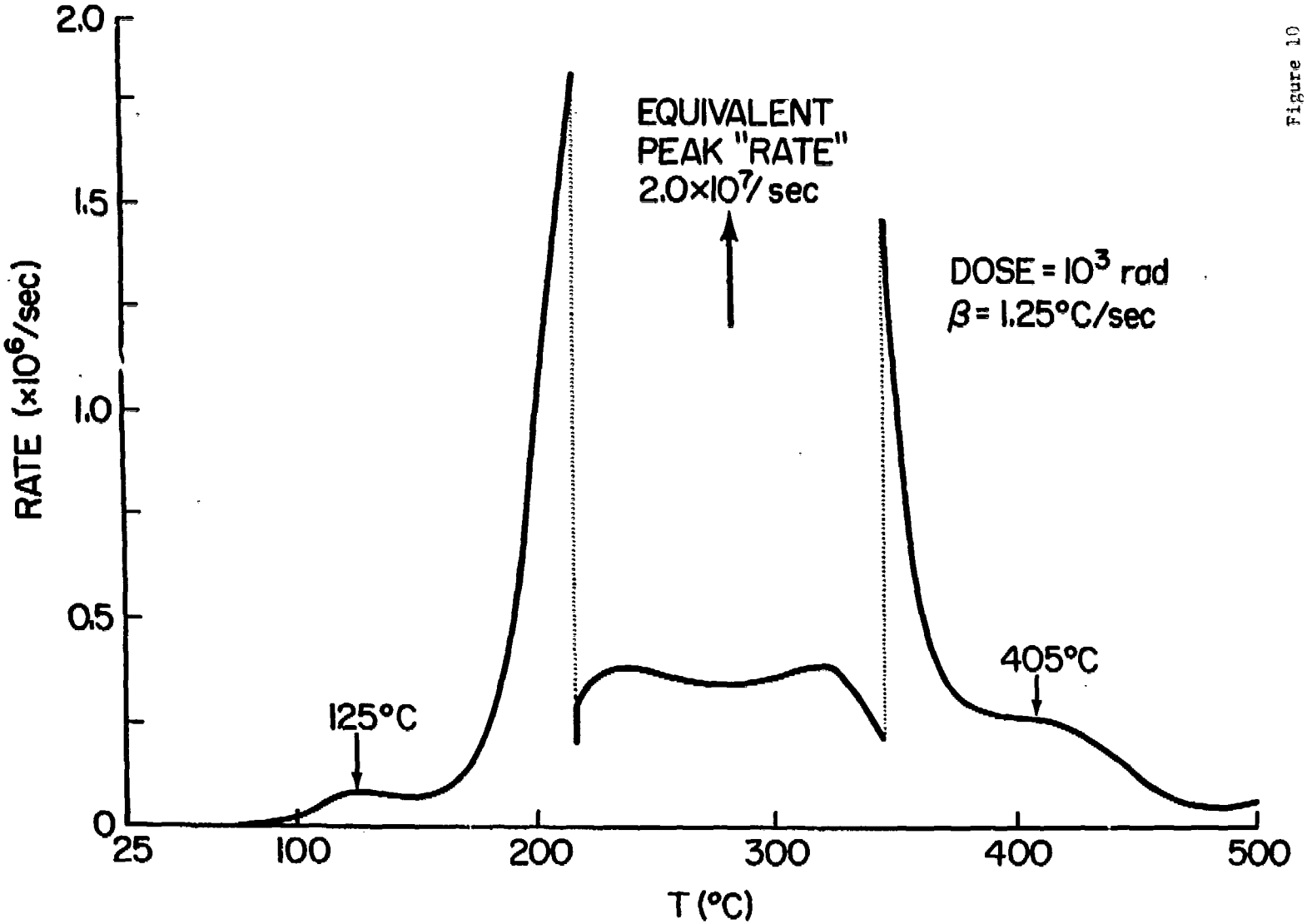
2.0
1.5
1.0
0.5
0
RATE (×10⁶/sec)
EQUIVALENT
PEAK "RATE"
2.0×10⁷/sec
DOSE = 10³ rad
β = 1.25°C/sec
125°C
405°C
25
100
200
300
400
500
T (°C)

Figure 10