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THERMOLUMINESCENCE KINETICS IN MATERIALS EXPOSED TO THE LOW DOSES APPLICABLE TO DATING AND DOSIMETRY

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THERMOLUMINESCENCE KINETICS IN MATERIALS EXPOSED TO THE LOW DOSES APPLICABLE TO DATING AND DOSIMETRY*

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ABSTRACT

Thermoluminescence (TL) kinetics have been investigated for low dose situations applicable to dating, dosimetry, and recent geological deposits. Studied were the general one-trap kinetic equation, which reduces to the well known 1st and 2nd order kinetic equations when various assumptions apply, and the interactive kinetic equations, which describes TL in materials exhibiting more than one glow peak. In materials with one glow peak the peak area varies linearly with dose; however, peak height is not linear with dose unless the TL obeys 1st order kinetics at all doses. In materials with two or more glow peaks neither peak height nor peak area varies linearly with dose, except in special situations. In fact, many peak height vs. dose curves will be supralinear with the initial low-slope region occurring at relatively low doses. These considerations indicate: 1) Dating and dosimetry techniques based on assumed linear peak height vs. dose curves will usually underestimate the accumulated dose. 2) Dating techniques can be improved and/or made more reliable by determining the TL kinetics of the glow peaks measured.

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INTRODUCTION

The thermoluminescence (TL) kinetics that applies to the low dose situations occurring in archaeometry, dosimetry, geology of recent deposits, etc. has been investigated. It cannot be stated that the conclusions described here are developed from the results described in recent papers (Levy 1979, 1982a, 1982b, 1983, 1984a, 1984c). Rather, historically, logically, and pedagodically, almost all of the results given here precede the previous publications. The more recent efforts include demonstrations showing that both the kinetic equation for a single glow peak, called the general one-trap (GOT) kinetic equation and the kinetics describing materials with more than one peak, called interactive kinetics, apply to the low dose cases encountered in dating and dosimetry and the low, moderate, and even high dose cases encountered in geological applications.

MATERIALS EXHIBITING A SINGLE GLOW PEAK: THE GENERAL ONE-TRAP KINETIC EQUATION

As is well established, the equation called here, the general one-trap (or GOT) thermoluminescence kinetic equation was introduced by Randall and Wilkins (1945) and Garlick and Gibson (1948). The derivation of this equation, as well as its application to experimental results, requires numerous assumptions. Some of these assumptions have been stated explicitly but others, which are equally important, are implicit, i.e., not stated. Space is not available for a detailed discussion of all these assumptions; only those essential for an understanding of thermoluminescence (TL) kinetics at low doses, i.e. low premeasurement trapped charge concentrations, are included here.

First, the general one-trap (GOT) kinetic equation applies to TL materials that exhibit only one glow peak or, if more than one glow peak occurs, it applies only if the peaks do not interact, i.e. if they are completely independent. If more than one glow peak is observed it is likely that some interaction must occur. From a practical viewpoint this interaction may be negligible. However, the nature of the TL process makes it unlikely that the interaction is zero. When interactions between different types of traps occur, i.e. when more than one glow peak is present and charges released from one type of trap can be trapped on other types of traps, the TL kinetics can be described by the interactive kinetics discussed in the next section. Second, to simplify this discussion it will be assumed that Eq. (1), given below, describes a material with one type of electron trap, one type of hole trap that is also the electron-hole recombination center emitting light during a TL measurement, that only electrons are thermally released during measurement, and that the number of hole-trap recombination-centers is greater than the number of electron traps. Third, it will be assumed that all thermally released electrons enter into light emitting recombination with holes. Under certain circumstances this is an important assumption. TL kinetics for cases in which this assumption does not apply will be described elsewhere (Levy, 1984b). Fourth, the concentration of premeasurement trapped electrons will be assumed equal to the concentration of trapped holes. Cases in which this assumption does not apply have been described previously (Levy 1982a, 1982b, 1983, 1984a). A number of additional assumptions that are important under certain circumstances will not be described.

Using these assumptions, the equation that describes the trapped electron concentration during heating is:

$$I(t) = -\frac{dn}{dt} = n\, s \exp(-E/kT)\left[1 - \frac{\sigma_t(N-n)}{\sigma_t(N-n) + \sigma_r n_r}\right) \text{, where} \qquad (1)$$

$I(t)$ = TL intensity at time, t

n = trapped electron concentration at time, t

n_0 = trapped electron concentration at time $t = 0$

s = preexponential, attempt-to-escape, frequency

E = thermal activation energy, in eV

N = trap concentration (traps/cm^3)

k = Boltzmann's constant

T = temperature (°C for plots, K for computations)

σ_t = cross section for electron retrapping

σ_r = cross section for light emitting electron-hole recombination

n_r = trapped hole concentration at time t

n_{ro} = trapped hole concentration at time $t = 0$

β = heating rate (degrees/unit time)

$\sigma = \sigma_t/\sigma_r$ = retrapping-recombination cross section ratio

and the TL intensity is given by

$$I(t) = -\frac{dn}{dt} = -\frac{dn_r}{dt} \qquad (2)$$

In the *GOT* equation, i.e. (1), the term before the bracket describes the release of electrons to the conduction band, the bracket gives the fraction of released electrons <u>not</u> retrapped, i.e. the fraction contributing to the TL intensity.

1st and 2nd order kinetics: If retrapping is negligible then $\sigma = 0$ and (1) becomes

$$I(t) = -dn/dt = s\, n \exp(-E/kT) \tag{3}$$

which, when solved using the usual linear heating rate equation $T = T_0 + \beta t$ becomes the well known 1st order TL equation

$$I(T) = n_0\, s \exp(-E/kT)\exp\left(-\int_0^T \frac{s}{\beta} \exp(-E/kT)dT\right). \tag{4}$$

If retrapping occurs and both of the following apply: $\sigma_t = \sigma_r$ and $n = n_r$ (or equivalently $n_0 = n_{r0}$) then (1) becomes

$$I(t) = -dn/dt = (n^2 s/N) \exp(-E/kT), \tag{5}$$

which, using $T = T_0 + \beta t$ becomes the well known 2nd order TL kinetic equation

$$I(T) = \frac{n_0\, s^* \exp(-E/kT)}{\left(1 + \frac{s^*}{\beta}\int_0^T \exp(-E/kT)dt\right)^2} \quad \text{where } s^* = \frac{n_0}{N} s. \tag{6}$$

The General One-Trap Equation at High and Low Doses -- High Dose Case: If $\sigma(=\sigma_t/\sigma_r) \ll 1$ and if n $(=n_r)$ is large, so that $N-n$ is small, then $n + \sigma(N-n) \approx n$ and Eq. (1) is approximated by Eqs. (3) and (4), the 1st order kinetic equations. In other words, at high initial trapped charge levels, i.e. high doses, the GOT equation would produce a glow curve corresponding to a 1st order curve, except for the extreme high temperature "wing."

Low Dose Case: At sufficiently low doses $n \ll N$ and $n + \sigma(N-n) \approx \sigma N$. For this approximation Eq. (1) becomes

$$I(t) = -dn/dt = (n^2 s/N\sigma)\exp(-E/kT). \tag{7}$$

This is the precise form of the 2nd order equation, namely Eq. (5), and when solved using $T = T_0 + \beta t$ will produce the 2nd order glow curve

equation, Eq. (6), with one important difference. Instead of containing the lumped constant $s^* = s\, n_0/N$ it will contain a different lumped constant $s^o = s n_0/N\sigma$. This difference has important practical applications that are illustrated by the following example. If a measured one peak glow curve is fitted to (6), the 2nd order glow curve equation, one can obtain a best value (in the best-fit sense) that corresponds to either $s^* = s\, n_0/N$ or to $s^o = s\, n_0/N\sigma$. The best-fit procedure will not differentiate between these two obviously different lumped constants.

These comments on the difference between s^* and s^o provide an immediate explanation for some, but not necessarily all, of the physically unrealistic s, $s'(= s/N)$, or s^* values obtained from a variety of measurements. For example, $s = 10^{12}$, $n_0 = 10^{14}$ and $N = 10^{16}$ are physically realistic values that yield $s' = s/N = 10^{-4}$, or $s^* = 10^{10}$. However, $s^* > 10^{14}$, which is the physically realistic upper limit, is often obtained on the basis that the kinetic procedure is determining s^*. As described above, the kinetic procedure may be determining s^o, not s^*. Thus, if $\sigma = 10^{-5}$ the determined constant would be $s^o = n_0 s/N\sigma = 10^{15}$, a quantity that is physically unrealistic if attributed to s^*, but quite reasonable if attributed to s^o. This observation can account for numerous abnormal s, s', or s^* determinations.

PROPERTIES OF THE GENERAL ONE-TRAP TL KINETIC EQUATION FOR VARYING DOSE

All of the properties of the GOT kinetic equation described above, and a demonstration of the properties of this equation as a function of dose, i.e. the premeasurement trapped charge concentration, are de-

scribed in Fig. 1. In this figure, all of the solid line glow peaks were computed from Eq. (1), the GOT kinetic equation, using the indicated values, and a particularly low value of σ, namely $\sigma = 10^{-6}$. It is important to note that n_0 ranges from 10^8 to 10^{13} charges/cm^3, but that the glow area has been made constant by multiplying by the necessary scale factor. Superimposed on the $n_0 = 10^{13}$ GOT curve, which is very close to the $n_0 = 10^{12}$ GOT curve, is a curve, indicated by the plus (+) signs, computed from the 1st order expression, Eq. (4). This demonstrates that this GOT glow peak is very accurately described by first order kinetics. Also, the $n_0 = 10^8$ GOT curve is accurately described by the curve, indicated by the "X" signs, computed from the 2nd order expression, Eq. (6). Thus this, and all curves with $n_0 < 10^8$, are accurately described by 2nd order kinetics. For $n_0 > 10^8$, as the values of n_0 increase, the GOT curves increasingly deviate from 2nd order curves. This is demonstrated by the $n_0 = 10^9$ and 5×10^9 curves shown in Fig. 1. Thus, as described above and exemplified by Fig. 1, at high doses the GOT curve is indistinguishable from 1st order curves, at low doses it is indistinguishable from 2nd order curves and at intermediate doses the glow curves are not approximated by either 1st or 2nd order kinetics. In other words, over a sufficiently large increasing premeasurement dose range the measured glow curves would appear to change from 2nd order to GOT to 1st order kinetics.

Relation to Partial Order Kinetics: As summarized by Chen and Kirsh (1981), many glow curves have been analyzed on the basis that they are described by the partial order TL kinetic equation

$$I(t) = -dn/dt = -s\, n^P \exp(-E/kT) \qquad (8)$$

where p is $\neq 1$, or $\neq 2$. For this equation to be meaningful, or consistent with, the GOT formulation, it would be necessary for the following term in Eq. (1)

$$n\left(1 - \frac{\sigma(N-n)}{\sigma(N-n) + n_r}\right) \qquad (9)$$

to be equal to n^p. By expanding the fraction it can be seen that Eq. (9) cannot be expressed as n^p. Thus partial order kinetics is not consistent with the GOT kinetics, Eq. (1). As far as can be determined, partial order TL kinetics is an empirical concept and does not have a physical basis (Chen and Kirsh, 1981). More specifically, Eq. (8) has not been derived from any of the normal physical mechanisms giving rise to TL.

It has been reported that TL glow curves, analyzed by partial order TL kinetics, change from first order to second order as the premeasurement dose is decreased, e.g. see Kuthuria and Sunta (1979). Such a transition from 1st to 2nd order is the same as that described by the GOT kinetic equation and exemplified by Fig. 1. However, the transition associated with the GOT kinetic equation has a physical basis, i.e. this transition need not be associated with the empirical partial order TL kinetics. As far as can be determined, the 1st to 2nd order transition has not been observed in a TL material exhibiting a single glow peak. Consequently, it is possible that this discussion on the 1st to 2nd order transition may <u>not</u> apply to materials with more than one glow peak. However such materials are described by more general kinetics, such as the interactive kinetics outlined below.

Peak Height vs. Dose Properties of the 1st and 2nd Order and General One-Trap (GOT) TL kinetics:

It is known, but not as well as it should be, that the height of 1st order glow peaks is proportional to the premeasurement trapped charge concentration n_0, i.e. the premeasurement dose. As emphasized previously (Levy 1979, 1982b), this is a consequence of the fact that the shape of 1st order glow peaks do not change as n_0 changes, i.e., the intensity, or height, is proportional to n_0. Also, it is known, but often ignored, that the height of 2nd order glow peaks is not proportional to n_0; the glow peak shape changes, as n_0 changes. The dependence of peak height on dose for glow peaks described by GOT kinetics is demonstrated by Fig. 2. This figure is obtained from numerous plots such as Fig. 1. More specifically, glow curves have been computed from Eq. (1) using the parameters $N = 10^{16}$ traps/cm^3, $E = 1.0$ eV, and $s = 10^{10}$ for a variety of n_0 values in the range 10^8 to 10^{13} and for $\sigma(=\sigma_t/\sigma_r)$ ranging from 10^{-6} to 10, including the 1st order curves, $\sigma = 0$, and the 2nd order curves, $\sigma = 1$. From these glow curves the peak height vs. n_0 curves in Fig. 2 were obtained.

Figures 1 and 2 contain a very large amount of information of which only the more important conclusions are mentioned here:

1) Only the 1st order curve is a linear function of dose. (The other curves may be straight lines in certain ranges but they have slopes different from 1, i.e. they have the form Const(dose)^q where $q \neq 1$.

2) Many of the peak height vs. dose (n_0) curves will appear to be linear, especially over small n_0 ranges.

3) At low n_0 values the GOT curves differ appreciably from being linear. This point is illustrated by Fig. 3, discussed below.

4) Saturation effects caused by filling, or nearly filling, the available traps appear to be important only at very high doses. This is illustrated by the "bending-over" of the curves in the insert.

5) In a sense, Fig. 2 explains why TL dating works as well as it does. For glow curves containing a single glow peak a large fraction of the peak height vs. dose curves will be in the region between the upper and lower curves shown, may be expected to be roughly linear, and be somewhat independent of kinetics.

6) Most importantly, Figs. 1 and 2 demonstrate that an accurate dating or dosimetry procedure - using a material containing only one glow peak - requires that one or both of the following be utilized: a) the peak area, not the peak height, be used. Or, b) if the peak height is used a reliable curve of intensity vs. dose must be established. A meaningful or precise extrapolation to zero dose can be made only if this information is available.

It is important to reiterate, the discussion in this section is concerned with peak height, not peak area. This can be illustrated by emphasizing the fact that development given here is based on the assumption that the initial charge concentrations, the n_0's, are assumed to be directly proportional to dose. The dependence of premeasurement charge on dose, or more precisely exposure, has important consequences for dating and dosimetry and will be discussed elsewhere (Levy 1984b).

Peak Height vs. Dose Curves: To illustrate the peak height vs. dose curves obtained from the GOT kinetics, Fig. 3 was constructed from the

information in Fig. 1. The linear dependence applies to 1st order kinetics, or to curves of total glow peak area, vs. dose. The other curves are typical of the curves applying to dating or dosimetry not strictly obeying 1st order kinetics. It is apparent that an extrapolation to zero dose, of the peak height curve, will underestimate the dose received by the sample. If it can be established 1) that the glow curve being measured contains a single glow peak and 2) if the TL kinetics of the peak can be determined then in principle it is possible to determine the shape of the peak height vs. dose curve. In other words, in principle, it is possible to determine the correction that must be applied to determine the actual dose imparted to the sample.

Also shown in this figure are points corresponding to GOT glow peaks that are well approximated by the 2nd order kinetic expression with, however, the usual $s^* = s\, n_0/N$ is replaced by the $s^o = s\, n_0/N\sigma$ obtained from GOT kinetics. The extrapolation to zero dose is straightforward for materials clearly exhibiting 2nd order kinetics. Lastly, the peak height vs. dose curve shows an initial low dose region that can be approximated as linear and, at higher doses, a transition to a second "linear" region at a higher slope. Thus glow curves described by the GOT kinetic equation exhibit a peak height vs. dose characteristic that can be called supralinear. In other words, supralinearity is a natural property of the GOT kinetics. However, as mentioned above, curves of peak area vs. dose, for glow peaks described by GOT kinetics, will be linear and will not exhibit supralinearity.

MATERIALS EXHIBITING MORE THAN ONE GLOW PEAK: THE INTERACTIVE KINETIC EQUATIONS

The nature of the physical processes responsible for TL makes it unlikely that the glow peaks occurring in a glow curve containing more than one glow peak will be described by 1st order or 2nd order kinetics. More specifically the TL process involves the thermal release of electrons to the conduction band, the possibility that the charges in the conduction band may be retrapped on the type of trap from which they originate, retrapped on other types of traps, or undergo radiative or non-radiative recombination. If more than one type of trap is present, the possibility that an electron in the conduction band is subject to a variety of competing processes makes it unlikely that 1st or 2nd order kinetics will be observed. TL kinetics, in which all of these competing processes occur, has been described elsewhere (Levy 1982a, 1982b, 1983, 1984a, and 1984c). Called interactive TL kinetics, their properties have been investigated by computing glow curves — from the equations given below — using nominal values for the parameters, regarding the computed curves as "data," and analyzing them by fitting to the usual 1st and 2nd order kinetic equations using computerized "best-fit" procedures.

The results of fitting the computed interactive kinetics glow curves to 1st and 2nd order kinetics have many consequences for dosimetry and dating applications and for TL studies in general.

1) The computed glow peaks are well fitted by 1st and/or 2nd order kinetics over the upper 60 percent or so but not in the "wings." Very often the interactive kinetics glow peaks match the 1st and/or 2nd order

curves very well at the peak and at half maximum height. Thus if the mismatch in the "wings" is ignored, or data curves are analyzed by methods that depend on peak temperature, full width at half maximum, either the high or low temperature half width at half maximum, etc., one obtains erroneous information suggesting that the glow peaks are described by 1st or 2nd order kinetics. Thus to exclude the possibility that data curves are described by kinetics other than 1st or 2nd order it is essential to demonstrate that the entire glow peak is fitted by the 1st or 2nd order kinetic expression.

2) The relative height and the shape of glow curves in interactive kinetic systems depends on the level and distribution of the premeasurement trapped charge distribution. The importance of this conclusion for low dose applications is described below.

3) The properties of the interactive kinetics glow peaks depend strongly on the kinetic parameters, particularly the retrapping to recombination cross section ratios, $\sigma_1 = \sigma_{t1}/\sigma_r$.

4) Often the 1st and 2nd order kinetic expressions fit the interactive glow peaks very well but the kinetic parameters obtained are not physically realistic.

5) Often, especially at low initial trapped charge concentrations, the glow peak computed from interactive kinetics cannot be fitted well by either 1st or 2nd order kinetics.

Space is not available to list additional properties of the interactive kinetics equations.

The Interactive Kinetic Equations: As emphasized in the Introduction, the 1st, 2nd, and General One-Trap, or GOT, kinetic equations are

based on the implicit, or unstated, assumption that glow curves containing more than one glow peak do not include, or allow for, the possibility that charges released from one type of trap — traps characterized by a single set of N, s, E, and σ parameters — are not retrapped on other types of traps. A number of generalizations can be formulated in which charges released from one type of trap can be retrapped on the original type and on other types of traps. The formulation described previously (Levy 1982a, 1982b, 1983, and 1984a), and the one whose low dose or low initial trapped charge properties are described here, was chosen on the basis that it represents the simplest possible extension of the 1st and 2nd order and GOT kinetic equations that can describe glow curves in which interactions between different types of traps can occur. This particular kinetic formulation has an additional advantage; it minimizes the number of adjustable parameters that have to be determined when the interactive kinetic equations are fitted to measured glow curves.

The interactive kinetic equations are:

$$\frac{dn_i}{dt} = -n_i s_i e^{-E_i/kT} + \left(\sum_{i=1}^{j} n_i s_i e^{-E_i/kT}\right)\left(\frac{\sigma_i(N_i-n_i)}{n_r + \sum_{i=1}^{j} \sigma_i(N_i-n_i)}\right) \qquad (10)$$

$$I(t) = -\frac{dn_r}{dt} = -\sum_{i=1}^{j} \frac{dn_i}{dt} \qquad (11)$$

$$\sigma_i = \sigma_{ti}/\sigma_r \qquad (12)$$

where the symbols are strictly analogous to those given above and j refers to the number of different types of traps. Note that only the σ_i

can be determined; since σ_{ti} and σ_r always appear as ratios they cannot be determined separately.

Properties of the Interactive Kinetic Equations at low doses or low initial trapped charge concentrations: The interactive kinetic equations have not been solved analytically using the linear temperature rise condition, $T = T_0 + \beta t$. As mentioned above these properties have been determined from numerical solutions of Eqs. (10), (11), and (12). One set of solutions, computed using the constants $N_1 = N_2 = N_3 = 10^{16}$; $s_1 = s_2 = s_3 = 10^{10}$; $\sigma_1 = \sigma_2 = \sigma_3 = 0.1$; $E_1 = 1.0$, $E_2 = 1.25$, $E_3 = 1.50$, and the $n_{01} = n_{02} = n_{03}$ values indicated, is shown in Fig. 4 for the n_{oi} ranging from 10^8 to 5×10^{15}. Such a range should encompass most dosimetry, archaeological, and geological applications.

The properties of interactive kinetics that are important at low doses, and are illustrated by Fig. 4, include the following:

1) Increasingly so, as the initial trapped charge decreases the retrapping of thermally released charges reduces the intensity of the lower temperature peaks in comparison with the highest temperature peak. Thus, measured glow curves may give the impression that they contain only one high temperature glow peak while, in reality, they contain one or more additional peaks that are not detected.

2) Depending on the kinetic parameters describing the glow peaks, the glow curves may not be separable into individual glow peaks. In these cases there may not be a meaningful way to determine the glow peak area, other than to arbitrarly separate the peaks at the intervening minimum.

3) It is apparent, even if glow peak areas can be determined, curves of "area" vs. initial charge concentration, n_0, i.e. dose, will not be linear. The transfer of charge from low temperature traps to high temperature traps decreases as n_0 increases.

4) Curves of peak height vs. n_0, i.e. dose will not be linear. This is illustrated, for the glow peaks shown in Fig. 4, by the curves in Fig. 5. For such curves an extrapolation of the approximately linear region, for the two low temperature peaks, to zero height will lead to an underestimate of the dose imparted to the sample. This will apply even if the peak shapes are closely approximated by 1st order kinetics. To determine the dose received by such a sample it is necessary to establish the peak height vs. dose curve at low enough doses to determine the "off-set" or "extrapolation error."

5) The curves shown in Fig. 5 exhibit supralinearity. Thus this little understood property is a characteristic of interactive kinetics.

MEASURED GLOW PEAKS DESCRIBED BY GOT AND INTERACTIVE TL KINETICS

The single glow peak exhibited by CaF_2:Mn dosimeter material exposed to doses of 100 rad or less at room temperature is not accurately described by either 1st or 2nd order kinetics. However, it is quite well described by GOT kinetics (Hornyak, et al. 1984). Also, when the CaF_2:Mn dosimeter material is exposed to similar doses at liquid nitrogen temperatures (≈80K) two glow peaks are observed. The high temperature peak corresponds to the one described above and is much better fitted by GOT kinetics than by 1st or 2nd order kinetics. The low temperature peak, which occurs at approximately 185K, is also best fitted by

GOT kinetics. However, both peaks are fitted as well or even better by a two peak version of the interactive kinetic equations (Mathur, et al. 1984). As far as can be determined, these CaF_2:Mn results are the first examples of measured glow peaks that appear to be better described by GOT and Interactive Kinetic equations, than the well-known 1st and 2nd order kinetics.

APPLICATIONS TO DATING AND DOSIMETRY

The TL kinetics described above provide a number of conclusions that are applicable to dating, dosimetry, and geological applications. Almost all of these applications require the preparation of a TL intensity, or response, curve vs. dose that is extrapolated to zero intensity. The precision of such an extrapolation requires that the shape of the response curve is known. If it is assumed that the trapped charge concentration, present before the TL measurement is made, increases linearly with dose the shape of the response curve is governed by the TL kinetics described above. This leads to numerous conclusions of which only the most important are included here.

Materials exhibiting a single TL glow peak: A plot of peak area vs. dose will be linear, no matter what kinetics describes the glow peak. Also, peaks described by 1st order kinetics at all doses will provide linear peak height vs. dose curves. Peaks described by GOT or 2nd order kinetics may appear to be linear in certain dose ranges. Unfortunately, it appears that materials exhibiting a single glow peak are very rare; and perhaps single glow peaks occur only at very low doses.

Materials Exhibiting Two or More Glow Peaks: In materials exhibiting more than one glow peak, curves of peak height and peak area will in-

crease linearly with dose only if 1st order kinetics is obeyed. In other cases it is likely that interactive kinetics, or some similar kinetics will apply. If interactive kinetics applies, in most cases curves of peak height or peak area will not vary linearly with dose. If care is taken to measure the total glow curve area, including a correction for emission occurring at temperatures where the "oven-glow" is too intense to make accurate measurements, the total glow curve area will increase linearly with dose.

More general TL kinetics and alternative dating and dosimetry methods: It should be emphasized that 1st and 2nd order, GOT, and interactive kinetics are based on numerous assumptions and are undoubtedly restrictive cases of more general kinetics. The conclusions given here are based on the assumption that these kinetics apply to the TL materials being studied. While it is likely that a large number of TL emitters will be described by these kinetics, it is possible that some emitters will be described by other kinetics. Lastly, the conditions under which alternative techniques, e.g. the pre-dose methods, will be reliable and/or precise have yet to be established.

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Figure Captions

Fig. 1 The solid line glow curves were computed from the General One-Trap (GOT) kinetic equation, (1) in the text, using the parameters shown. The plus signs (+) are the well-known 1st order and the crosses (x) 2nd order glow curves. All curves have been adjusted to the same area by applying a scale factor. This plot demonstrates that the GOT glow curves are approximated by 1st order kinetics at high doses, 2nd order at low doses, and by neither at intermediate doses.

Fig. 2 Curves of peak height vs. initial trapped change concentration, n_0, i.e. dose, computed from 1st order ($\sigma = 0$), 2nd order ($\sigma = 1$), and GOT kinetics for the σ values shown. The other parameters are shown on Fig. 1. Only the 1st order curve is precisely linear. At certain n_0 levels some of the GOT curves differ appreciably from linear, see Fig. 3.

Fig. 3 Peak height vs. n_0, or dose, curves obtained from the GOT curve for $\sigma = 10^{-6}$ in Fig. 2. The insert shows part of the computed curve plotted in the usual fashion with linear axes. These curves appear to be linear at restricted dose ranges. They demonstrate that an extrapolation of the apparently linear region to zero peak height will usually lead to an underestimate of the dose imparted to the sample. Also, these curves indicate that both GOT and 2nd order peak height vs. dose curves are supralinear.

Fig. 4 Glow curves computed from interactive kinetics, Eqs. (10) and (11) in the text, using $N_1 = 10^{16}$, $s_1 = 10^{10}$, and $E_1 = 1.0$, $E_2 = 1.25$, $E_3 = 1.50$ eV and the parameters shown. The more obvious properties of interactive kinetics glow curves are listed in the text.

Fig. 5 Peak height vs. n_0, or dose, curves for the three glow peaks shown in Fig. 4. Obviously none of these curves are linear and an extrapolation of the apparently linear region of the two lower temperature peak height vs. dose curves to zero peak height will lead to an underestimate of the dose imparted to the sample. Also, curves of peak "area" vs. dose are not linear. Lastly, these curves exhibit supralinearity.

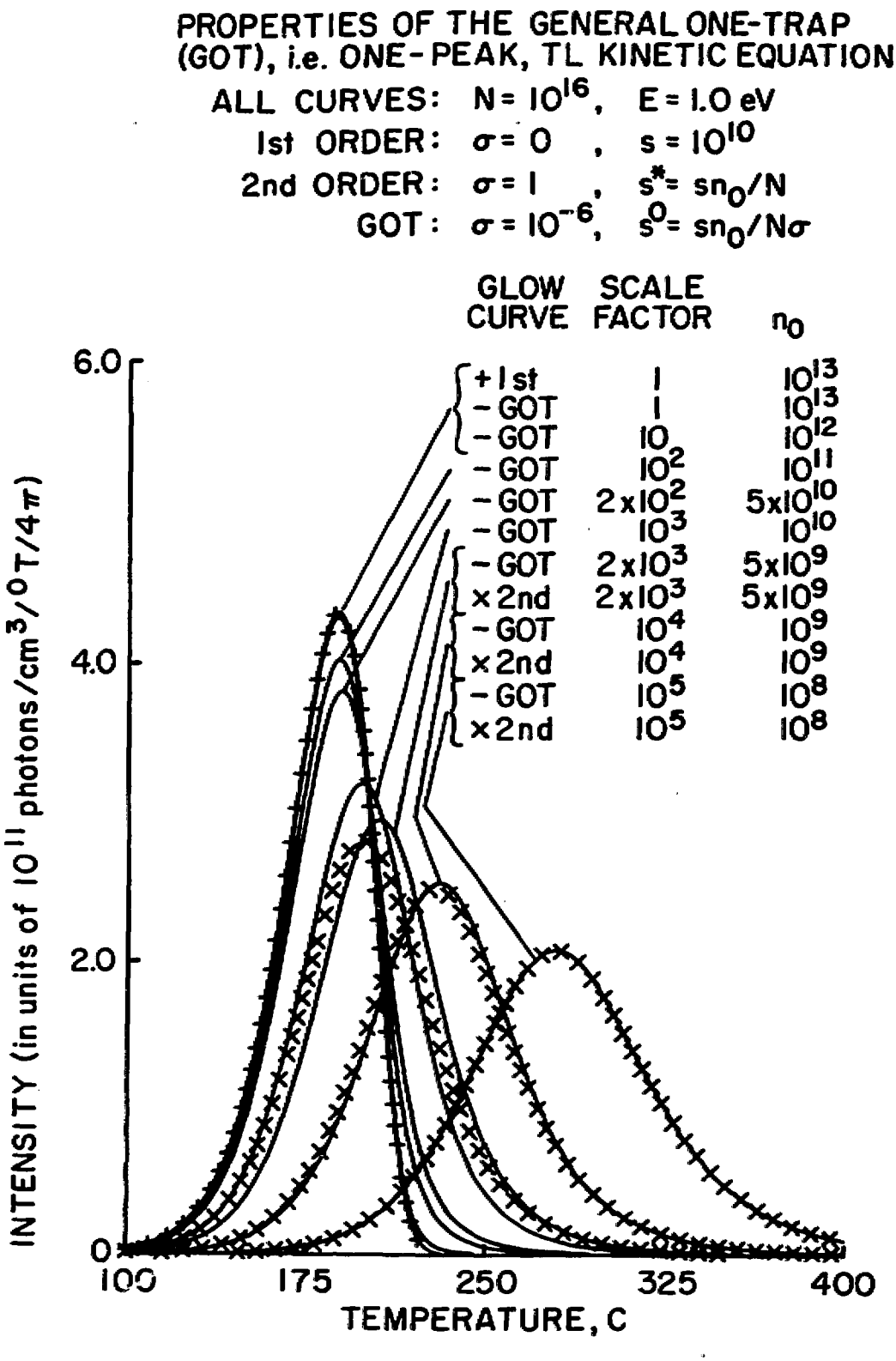
PROPERTIES OF THE GENERAL ONE-TRAP (GOT), i.e. ONE-PEAK, TL KINETIC EQUATION
ALL CURVES: N = 10^16, E = 1.0 eV
1st ORDER: σ = 0, s = 10^10
2nd ORDER: σ = 1, s* = sn0/N
GOT: σ = 10^-6, s^0 = sn0/Nσ
GLOW CURVE
SCALE FACTOR
n0
+1st 1 10^13
-GOT 1 10^13
-GOT 10 10^12
-GOT 10^2 10^11
-GOT 2x10^2 5x10^10
-GOT 10^3 10^10
-GOT 2x10^3 5x10^9
×2nd 2x10^3 5x10^9
-GOT 10^4 10^9
×2nd 10^4 10^9
-GOT 10^5 10^8
×2nd 10^5 10^8
INTENSITY (in units of 10^11 photons/cm^3/0T/4π)
6.0
4.0
2.0
0
100
175
250
325
400
TEMPERATURE, C

FIG. 1

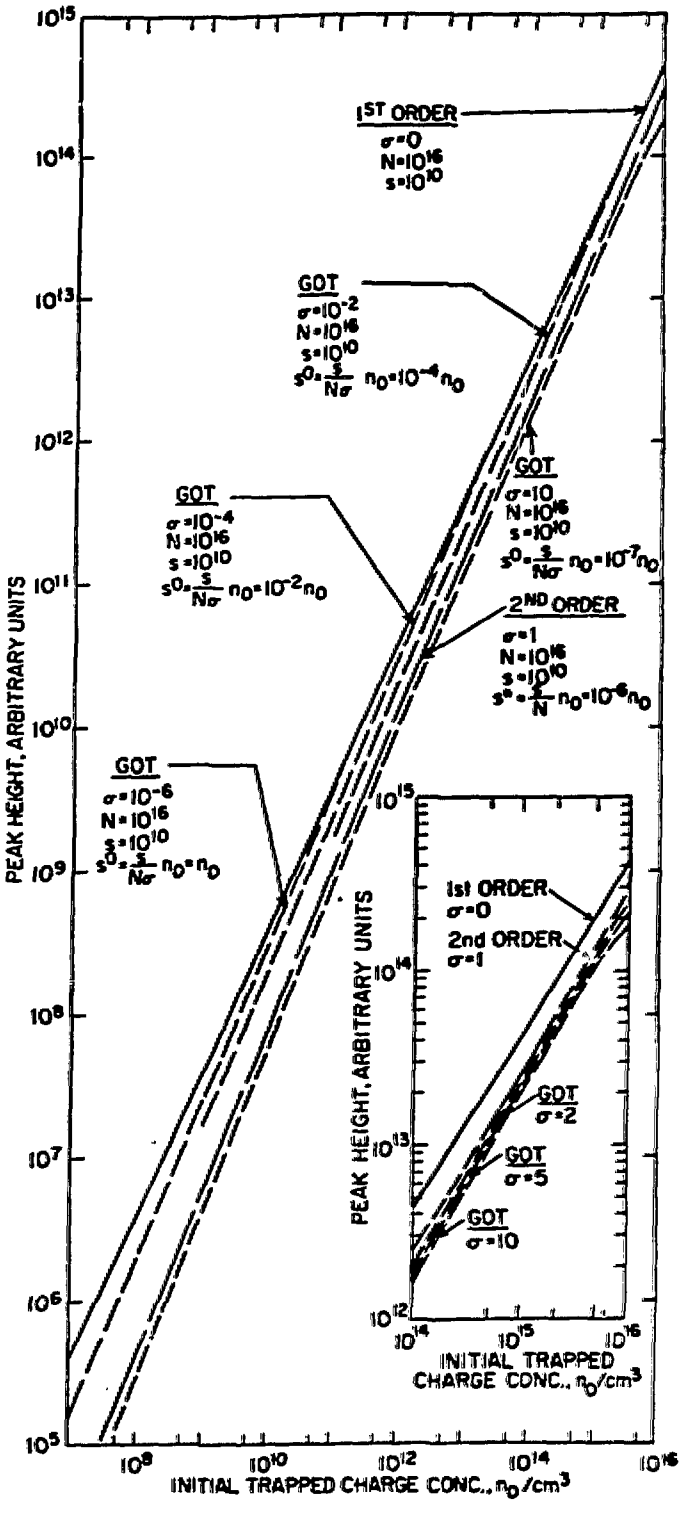
PEAK HEIGHT, ARBITRARY UNITS
INITIAL TRAPPED CHARGE CONC., n_0/cm^3
1ST ORDER
$\sigma=0$
$N=10^{16}$
$s=10^{10}$
GOT
$\sigma=10^{-2}$
$N=10^{16}$
$s=10^{10}$
$s^0=\frac{s}{N\sigma}$ $n_0=10^{-4}n_0$
GOT
$\sigma=10^{-4}$
$N=10^{16}$
$s=10^{10}$
$s^0=\frac{s}{N\sigma}$ $n_0=10^{-2}n_0$
GOT
$\sigma=10$
$N=10^{16}$
$s=10^{10}$
$s^0=\frac{s}{N\sigma}$ $n_0=10^{-7}n_0$
2ND ORDER
$\sigma=1$
$N=10^{16}$
$s=10^{10}$
$s^0=\frac{s}{N}$ $n_0=10^{-6}n_0$
GOT
$\sigma=10^{-6}$
$N=10^{16}$
$s=10^{10}$
$s^0=\frac{s}{N\sigma}$ $n_0=n_0$
1st ORDER
$\sigma=0$
2nd ORDER
$\sigma=1$
GOT
$\sigma=2$
GOT
$\sigma=5$
GOT
$\sigma=10$
PEAK HEIGHT, ARBITRARY UNITS
INITIAL TRAPPED CHARGE CONC., n_0/cm^3

FIG. 2

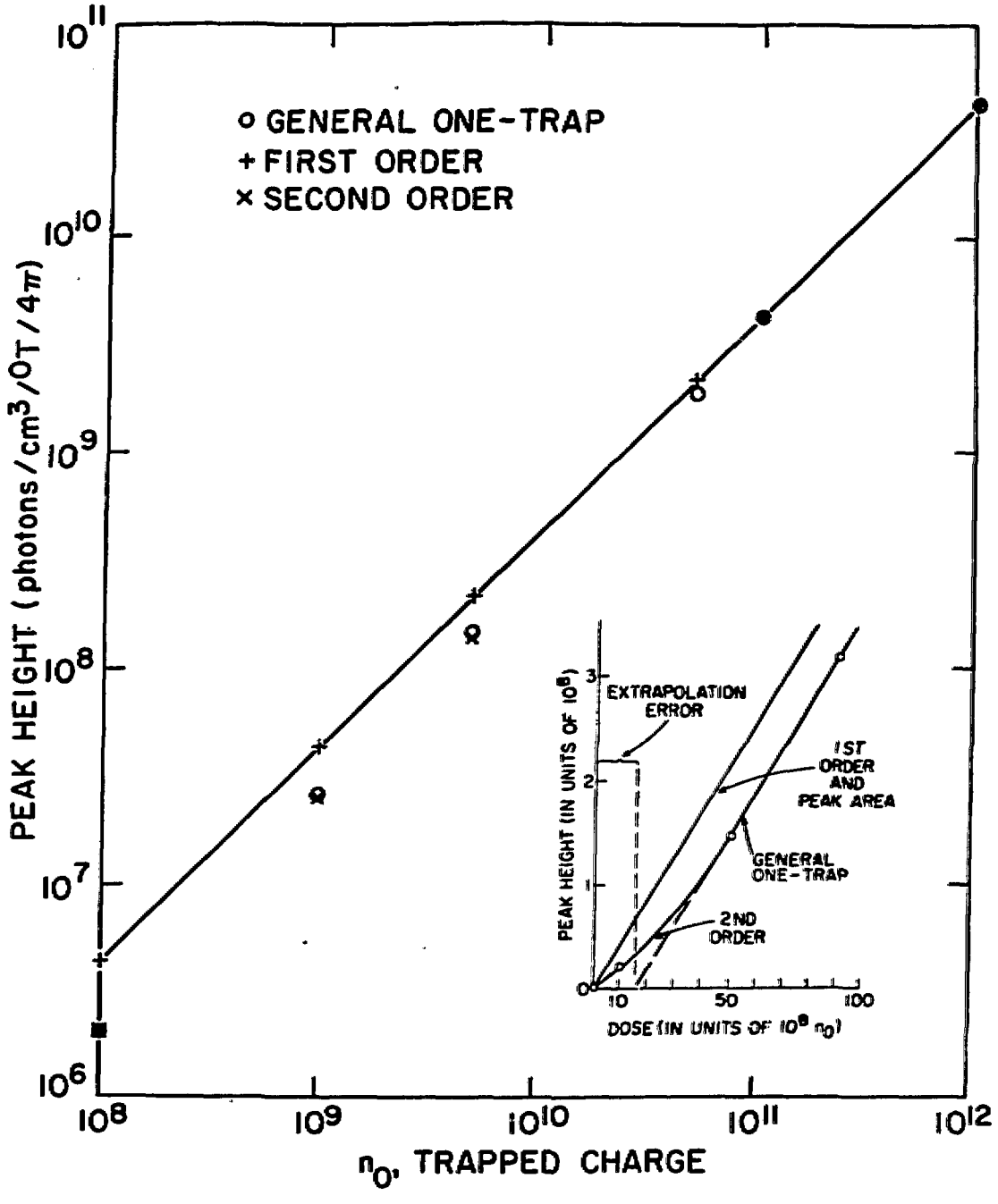
o GENERAL ONE-TRAP
+ FIRST ORDER
× SECOND ORDER
PEAK HEIGHT (photons/cm³/σT/4π)
10¹¹
10¹⁰
10⁹
10⁸
10⁷
10⁶
10⁸
10⁹
10¹⁰
10¹¹
10¹²
n₀, TRAPPED CHARGE
EXTRAPOLATION ERROR
1ST ORDER AND PEAK AREA
GENERAL ONE-TRAP
2ND ORDER
PEAK HEIGHT (IN UNITS OF 10⁸)
DOSE (IN UNITS OF 10⁸ n₀)
0
1
2
3
10
50
100

FIG. 3

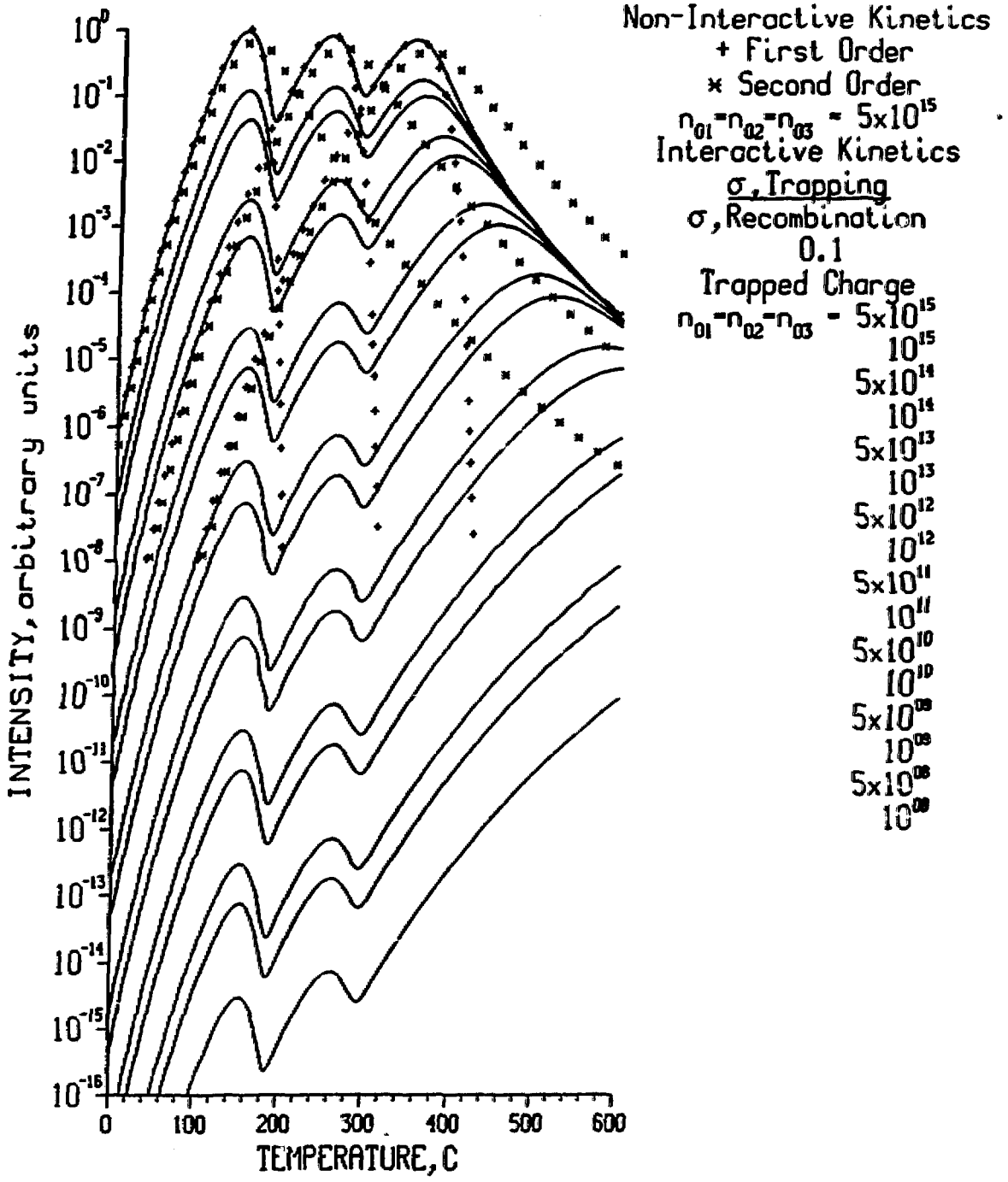
Non-Interactive Kinetics
+ First Order
× Second Order
$n_{01}=n_{02}=n_{03}$ = 5×10^{15}
Interactive Kinetics
σ, Trapping
σ, Recombination
0.1
Trapped Charge
$n_{01}=n_{02}=n_{03}$ = 5×10^{15}
10^{15}
5×10^{14}
10^{14}
5×10^{13}
10^{13}
5×10^{12}
10^{12}
5×10^{11}
10^{11}
5×10^{10}
10^{10}
5×10^{09}
10^{09}
5×10^{08}
10^{08}
INTENSITY, arbitrary units
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
0
100
200
300
400
500
600
TEMPERATURE, C

FIG. 4

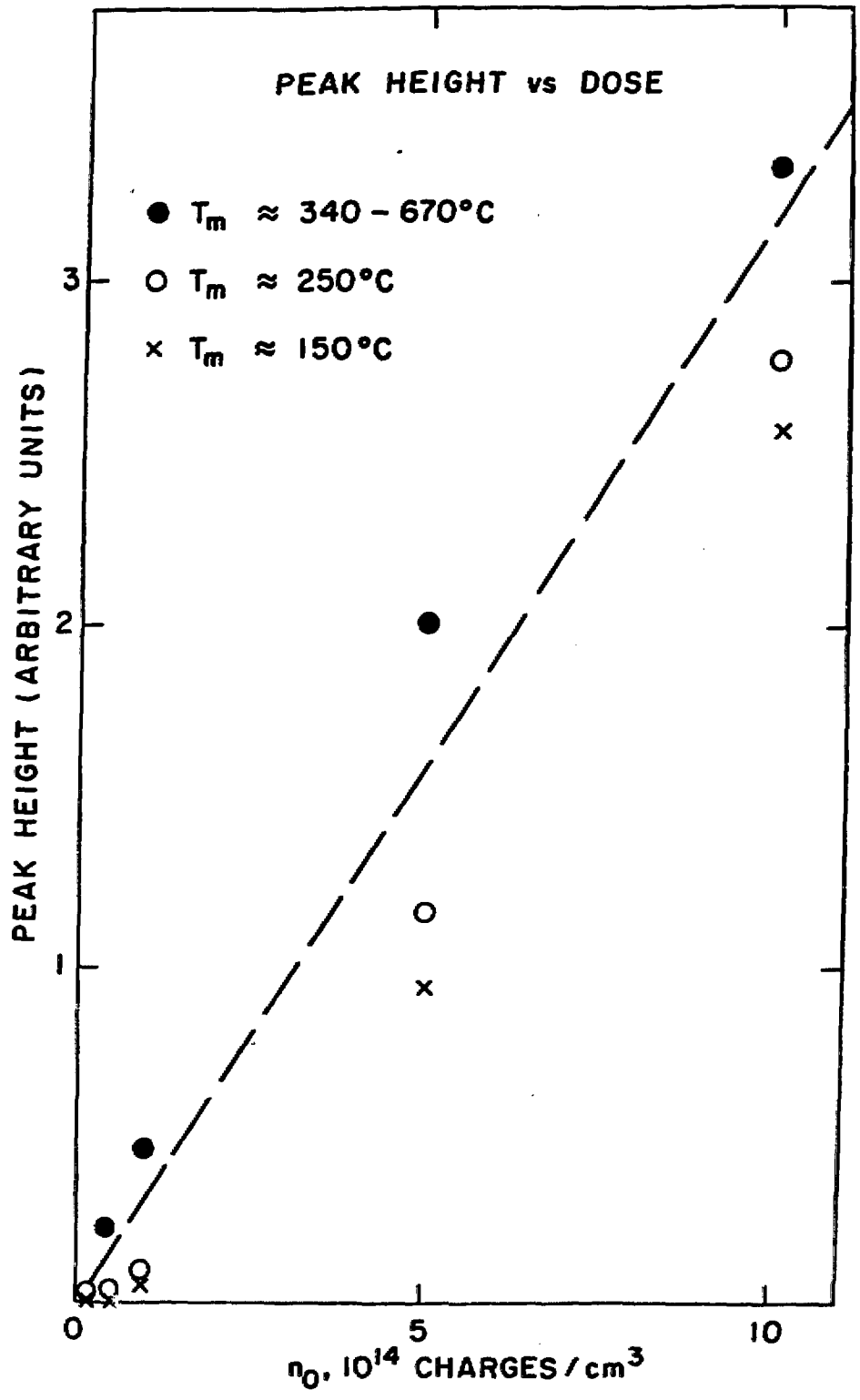
PEAK HEIGHT vs DOSE
● $T_m \approx 340 - 670°C$
○ $T_m \approx 250°C$
× $T_m \approx 150°C$
PEAK HEIGHT (ARBITRARY UNITS)
3
2
1
0
5
10
n_0, 10^{14} CHARGES / cm^3

FIG. 5