fiable for $\sigma<\sigma_c$),

$$t_d \doteq \sigma_c A^{-1} \exp\left[\alpha S \psi_c^{1/2} + \frac{\chi_c}{kT} - \left(\frac{1}{kT} - \frac{\alpha S}{4\psi_c^{1/2}}\right)\frac{V}{2+L/\gamma S}\right]. \quad (15)$$

Note that this expression can be written

$$t_d = \text{const} \exp(-V/V^*),$$

where

$$V^* = \left(2+\frac{L}{\gamma S}\right)\Big/\left(\frac{1}{kT} - \frac{\alpha S}{4\psi_v^{1/2}}\right).$$

Thus the trends and magnitudes predicted for the present device are remarkably similar to the experimental observations reported by Ovshinsky.[1] It should be emphasized that the explicit temperature dependence exhibited for V^* and V_T is not general but a consequence of the restricted applicability of Eq. (1) to $V_1<\chi_c$. As switching occurs for $V_1 \to \chi_c$, the temperature dependences of V^* and V_T tend to vanish. The recent experimental results on the time delay for switching of amorphous semiconducting devices recently reported by DeFeo and Calella[4] are in general agreement with the analytic results presented here except that V^* is slightly different from V_T and has a different temperature dependence.

[4] S. DeFeo and P. Calella, Bull. Am. Phys. Soc. **14**, 115 (1969).

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I. Phenomenological Theory of Thermoluminescence

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Thermoluminescence (TL) glow curves are investigated in detail for a single trap depth in the presence of thermally disconnected traps and a single type of recombination center. The different shapes of TL curves are discussed as they relate to the ratio of trapping probability to recombination probability, and to the densities of recombination centers and thermally disconnected traps. The influence of such equipment parameters as heating rate, initial occupancy of the traps, and initial temperature is also examined. As a result of our calculations, we conclude that TL by itself is not a suitable tool for determining trapping parameters of imperfections in crystals, that the simple experiments performed to date have not yielded unique values of the trapping parameters, and that even a sophisticated experiment is highly unlikely to yield unique values.

INTRODUCTION

THE experimental simplicity of thermoluminescence (TL) and thermally stimulated electrical conductivity (TSC) has led to numerous papers which advocate their use for determining trapping parameters of imperfections in crystals. Despite considerable effort in this field during the last two decades, however, there is still little evidence that consistent quantitative information on trap depths and probabilities for retrapping or escape can be obtained by TL or TSC methods. It is not the purpose of this paper to give a thorough review of the literature on the subject. As a typical example, we will mention here only some of the work done on CdS, which has been studied in this context more thoroughly than any other material. Dittfeld and Voigt,[1] e.g., determined the trapping parameters of CdS by utilizing 11 of the methods known for the analysis of experimental TSC data, while Nicholas and Woods[2] did similar work employing eight different methods. Bube and co-workers[3] performed an analysis of CdS/CdSe mixed crystals in which they also compared different methods. The disagreement in the conclusions reached by those workers is characteristic of the situation in which the investigation of thermally stimulated processes is at the present time. Dittfeld and Voigt found that all the traps they investigated in CdS empty under fast retrapping conditions. This result is based on the consistency they obtain with methods based on a quasi-equilibrium between trapped and free electrons. Nicholas and Woods arrive, in a similar way, at exactly the opposite conclusion. They find that all but one of

[1] H. J. Dittfeld and J. Voigt, Phys. Status Solidi **3**, 1941 (1963).

[2] K. H. Nicholas and J. Woods, Brit. J. Appl. Phys. **15**, 783 (1964).

[3] R. H. Bube, G. A. Dussel, C. Ho, and L. D. Miller, J. Appl. Phys. **37**, 2 (1966).

the traps in CdS empty under monomolecular conditions. Undoubtedly, differences in material may be responsible for some of the diasgreement.[3] However, there is evidence that other, more basic reasons, might render TL and TSC techniques unsuitable for the investigation of the kinetics of the processes occurring during thermal release of trapped carriers and during their subsequent recombination. This evidence may be grouped under two main points: (a) There is generally insufficient knowledge about which of the several recombination kinetics discussed in the literature[4] prevail in a certain material; and (b) even if for some reason a particular model is found to describe the thermally stimulated processes in a certain material, consistent quantitative information cannot be obtained on the various characteristic parameters of that model from TL and TSC experiments alone.

Obviously, both points need to be studied in more detail, and it is the purpose of this paper to present as a contribution to the task a complete phenomenological theory of TL.

The knowledge about different kinetical models aside from the classical "simple model"[5] is, at best, only fragmentary.[4] However, one important fact is established: It is not possible to decide between several "reasonable" models by simply calculating a theoretical glow curve which fits the experimental curve.[6] Too many unknown parameters are present to establish a best fit. By means of various optical and electrical measurements, the band structure of a material can be determined, and it usually is known whether the material is n type or p type. This information allows certain conclusions to be made about the recombination processes, especially in regard to which way the electrons released from the traps travel toward the recombination center. However, the values of transition coefficients are usually unknown. In addition, no safe conclusions are possible in most cases as to whether or not the trapped and free electrons are in thermal equilibrium. The attempts by Dittfeld and Voigt and Nicholas and Woods to gain information on just this point in CdS by analyzing TSC and photoconductivity data had to fail because, for a proper choice among the numerous different methods of analysis, knowledge is required about the relative importance of retrapping transitions as compared to recombination transitions. Because a good fit of calculated and measured TSC or TL glow curves does not provide sufficient knowledge of what kinetics prevail,[6] there is no way of finding out, from glow-curve experiments alone, which method of analysis should be used to obtain trapping parameters in a particular case.

This is also illustrated by the fact that the same analytical methods for experimental data may provide different parameters when various models are used. The methods based on glow-curve shapes provide examples. Although designed for the determination of a trap depth when the kinetics are described by the "simple model,"[5] they may yield the trap depth for hole traps if the model proposed by M. Schön[7,8] holds. Conversely, they may yield the energy difference between the ground and the excited state of a trap if the model discussed previously in the literature[6] describes the kinetics.

Currently, there is no method known which is completely independent of the kinetics. The knowledge of one or more key parameters is always required. This, in turn, explains at least partially the discrepancy of the results reported by Dittfeld and Voigt and Nicholas and Woods. However, a final word on the situation could not be given at the time of those experiments because there was no complete theory of TL and TSC available. Not even the kinetic equations derived from the simple model were completely solved for TL. Recently, though, Dussel and Bube[5] (hereafter referred to as DB) presented a detailed analysis of this model, but for the TSC only. One could, in principle, obtain solutions for TL using their results. However, as we will show, their analysis is not complete. Further, they introduce a quasi-Fermi level. This imposes restrictions and requires assumptions, which one wishes to eliminate. By using a more direct approach, it is possible to develop a complete theory of TL based on the simple model. This will be done in the following sections. It is also possible to complete the DB theory of TSC.[9] After this has been accomplished, we are in a position to make the following statement: It appears impossible to obtain relevant quantitative information on the trapping parameters by any method of evaluating experimental TL or TSC data unless the electron kinetics is known in detail. TL and TSC data may then provide a way to check experimental data obtained otherwise. If one can assume that the simple model discussed in this paper is a good description of the kinetical processes occurring during the thermal release of trapped charged carriers, only a sophisticated analysis of TL and TSC will reveal enough information to characterize the parameters. This would require a measurement of the shape of a peak over many orders of magnitude with various initial trap fillings.

PHENOMENOLOGICAL THEORY OF TL

The kinetic equations obtained by considering the charge carrier traffic in terms of the typical model[5] are usually solved with the aid of two assumptions. The first is that the concentration of free charge carriers

[4] G. Bonfiglioli and P. Bräunlich, in *Thermoluminescence of Geological Materials*, edited by D. J. McDougall (Academic Press Inc., London, 1968) (these articles list additional references on the subject).

[5] G. A. Dussel and R. H. Bube, Phys. Rev. **155**, 764 (1967).

[6] P. Bräunlich and A. Scharmann, Z. Physik **177**, 320 (1964).

[7] P. Bräunlich, Ann. Physik **12**, 262 (1963).

[8] M. Schön, Tech. Wiss. Abhandl. Osram-Ges. **7**, 175 (1958); *Halbleiterprobleme*, edited by W. Schottky (Friedrich Vieweg and Sohn, Braunschweig, 1958), Bd. IV, p. 282.

[9] The results are presented in paper II.

(n_c) is always much smaller than the concentration of trapped charge carriers (n), and the second is that the time rate of change of the free carrier concentration ($\dot{n}_c$) is much smaller than the time rate of change of the trapped carrier concentration ($\dot{n}$): That is,

$$n_c \ll n \tag{1}$$

and

$$\dot{n}_c \ll \dot{n}. \tag{2}$$

The range of validity of (1) and (2) will be discussed in paper II; as shown there, the results presented in this paper are not affected by these assumptions.

SOLUTIONS OF KINETIC EQUATIONS

The basic kinetic equations are

$$\dot{n} = \beta n_c (N-n) - Pn, \tag{3}$$

$$\dot{n}_c + \dot{n} = -\gamma n_c (n_c + n + M), \tag{4}$$

where β is the retrapping coefficient, γ is the recombination coefficient, N is the density of thermally connected traps, M is the density of thermally disconnected traps (deep traps), and $P = P_0 \exp(-E/kT)$, the probability of escape, with k the Boltzmann constant and T the absolute temperature. Thermally connected traps are those which deliver charge carriers to the empty band during the glow-curve experiment. P_0 is assumed to be temperature-independent (see Ref. 5).

Inequalities and Eqs. (1)–(4) immediately yield[10]

$$-\dot{n} = (M+n)Pn/[(1-R)n + M + RN] \tag{5}$$

and

$$n_c = Pn/\gamma[(1-R)n + M + RN], \tag{6}$$

with $R = \beta/\gamma$.

These equations yield a measure of TL, since the TL intensity is proportional to $-\dot{n}$, and a measure of TSC since the latter is proportional to n_c. The thermoluminescence intensity can be calculated from

$$L(T) = -\dot{n} \equiv -\dot{w}N, \tag{7}$$

and one obtains readily

$$L(T) = PNw(M+Nw)/[(1-R)Nw + M + RN]. \tag{8}$$

The fraction of filled traps w is defined in the interval $0 \leq w \leq 1$; $w=0$, corresponds to empty traps, and $w=1$ corresponds to completely filled traps. The luminous efficiency is taken to be unity in Eq. (7); however, as long as the efficiency can be assumed to be constant over the temperature range of the TL peak, the results are unchanged

Integration of Eq. (8) yields implicit expressions for w. A function which correlates time and temperature (heating program) has to be introduced at this point. In practice, a constant heating rate is generally used ($dT = q\,dt$), but in some cases quadratic heating rates have been employed ($dT = \alpha T^2 dt$).[8,11] The result of the integration with either rate is given by

$$F(U) = (B-A)\ln[(M+Nw)/(M+Nw_0)] - B\ln(w/w_0), \quad M \neq 0 \tag{9a}$$

$$= A\ln(w_0/w) + R(w^{-1} - w_0^{-1}), \quad M = 0 \tag{9b}$$

where

$$F(U) \equiv P_\alpha (e^{-U} - e^{-U_0}) \quad \text{for} \quad dT = \alpha T^2 dt$$

$$\equiv \int_{U_0}^{U} P_q e^{-U} dU \quad \text{for} \quad dT = q\,dt, \tag{10}$$

with

$$P_\alpha \equiv P_0 k/\alpha E,$$

$$P_q \equiv P_0 E/qkU^2,$$

$$U \equiv E/kT,$$

$$w_0 \equiv n(T=T_0)/N,$$

and

$$w \equiv n/N,$$

$$A \equiv 1-R,$$

$$B \equiv 1 + RN/M.$$

We omit at this point any further duscussion of the case $M \equiv 0$ since we show that the case $N/M \gg 1$ contains this limiting case.

The solution of Eqs. (8)–(10) for L as a function of U is determined by the initial concentration $w_0 = n_0/N$ at T_0, the retrapping factor R, and the ratio N/M.

We proceed now to discuss the expected behavoir of TL glow curves in terms of a wide variation of these parameters.

DISCUSSION OF TL CURVE SHAPES

We now consider the expected shape of TL curves as predicted by Eqs. (7)–(10) using the approach of DB. We limit the present discussion to curves obtained with the rate $dt = \alpha T^2 dt$ since there is less algebraic complexity. In the next section, we show that there is no fundamental difference in the shape of a glow curve obtained with either a constant heating rate or this nonlinear rate.

The basic idea of the DB method as applied to the case of TL is to find the characteristic shape of a TL curve for a particular set of parameters (T_0, T, N/M, R, and P) without solving Eqs. (7)–(10) and without elaborate calculations. First, an extremum condition is discussed. It provides the possible location of extrema of a TL glow curve. Thus, we obtain the regions of posi-

[10] The assumed inequalities effectively decouple the basic kinetic equations (3) and (4). All our attempts to solve the basic equations numerically have been unsuccessful. However, in the accompanying paper, we discuss the relevance of these assumptions.

[11] A. Halperin, M. Leibowitz, and M. Schlesinger, Rev. Sci. Instr. **33**, 1168 (1962); W. Arnold and H. Sherwood, J. Chem. Phys. **62**, 2 (1959); P. J. Kelly and M. J. Laubitz, Can. J. Phys. **45**, 311 (1967).

tive and negative slopes of the TL glow curve in an L-U plane.

All parameters except the filling ratio w are fixed. Considering $w_0=1$ yields the envelope of all glow curves with the same set of parameters and smaller w_0. The extremum condition is obtained from Eqs. (8) and (9):

$$\dot{I}/I=\{[G(U)/g(w)]-1\}P_0/P_\alpha, \tag{11}$$

with

$$G(U)\equiv P_\alpha \exp(-U),$$
$$I\equiv L/M,$$

and

$$g(w)\equiv\frac{[(N/M)Aw+B]^2}{[(N/M)Aw+B]wN/M+B[1+(N/M)w]}.$$

Obviously,

$$G(U^*)=g(w) \tag{12}$$

defines the location U^* of the extrema of $I(U)$ in the I-U plane.

Extrema are possible only in the region between $U^*(w=1)\equiv U_1^*$ and $U^*(w=0)\equiv U_0^*$. The curve $I^*(U^*)$ defined by Eqs. (8) and (12) divides the plane between two lines through U_1^* and U_0^* parallel to the I axis in two parts: one for which $\dot{I}>0$ and one for which $\dot{I}<0$. The function $g(w)$ is always positive for the values of w in the allowed range $0\leq w\leq 1$. It is monotonically decreasing with increasing w. We note further that $I(U)$ decreases with decreasing w and fixed U. With this, we can now establish where the sign of $\dot{I}$ is positive and where it is negative. Assume a fixed point on $I^*(U^*)$. For fixed U, $I(U)$ increases upon increasing w and we reach a point above the curve I^*. At the same time, $g(w)$ decreases and, in Eq. (11), $\dot{I}$ becomes positive. $I^*(U^*)$ decreases rapidly as U^* approaches U_0^* so that for $U<U_0^*$ the slope of the TL curve $I(U)$ is always positive. The slope of $I(U)$ for $U>U_1^*$ depends on the parameters and will be discussed separately. Having tried all combinations of the parameters, there are only three distinct sets of parameters, we need to discuss—I: $R<1$, $M<NR$; II: $R>1$, $M<NR$; III: $M>RN$. In the following section, we give a summary of the results obtained for these cases. (A complete discussion of this procedure is given in Ref. 12. Mathematical expressions for the glow curves reported here are derived as well.)

Case I: $R<1$, $M<NR$

There are three different dependencies of I^* on U^*, as illustrated by regions, I, II, and III of Fig. 1(a).

Assuming the initial condition $U_0\gg U_1^*$, it is possible to construct a glow curve which is an envelope for all other glow curves with the same parameters. This curve is the one which is obtained for $w_0=1$ (completely filled traps at U_0). All other glow curves (with $w_0<1$) have lower TL intensities at any temperature and the curve $I(w_0=1)\equiv I_0$ is, therefore, an upper limit. The typical TL glow curve of this section starts with a linear slope of -1 at the right of U_1^*. As it approaches I^*, the slope increases until it crosses the curve I^* horizontally. The maximum temperature shifts considerably with decreasing w_0 until for $w_0\ll 1$ the curve crosses in region III. The decreasing part of the TL curves $\ln I(U)$ have a positive slope and lie, therefore, between $I_0(U)$ and $I^*(U^*)$. We note an interesting feature of this part of the glow curve: If U^* of a TL curve lies in region I, which is the case of $w_0\simeq 1$, the curve decreases first steeper (as it would in a typical first-order peak), later less steep again with a constant slope of $+1$, and, finally, we have a characteristic steep decrease.

TL curves which cross $\ln I^*$ in region II still have the constant slope after the maximum. Note that the quadratic heating rate chosen for the discussion, in this section is not the reason for that constant slope of a glow curve which has its maximum occurring in region III. A linear heating rate produces a similar effect.

Computed examples of TL glow curves are shown in Fig. 1(b), which illustrates the predicted behavior for case I.

Case II: $R>1$, $M<NR$

There are three different dependencies of I^* on U^*, as illustrated by regions I, II, and III of Fig. 2(a).

Again, we can construct a largest of all possible glow curves I_0 with the same initial condition of case I, that is $U_0\gg U_0^*$. It is an envelope for all other glow curves with $w_0\leq 1$, In the region $U>U_1^*$. the function $\ln(I_0)$ has a constant slope of -1 because w is still nearly unity. The curve approaches U_1^* with a linear slope and has a value[12] at U_1^* which is below $\ln[I^*(U_1^*)]$. Thus, the curve $\ln(I_0)$ bends over to a smaller slope. It must remain below the curve $\ln(I^*)$ until it crosses it at $U^*<U_m^*$. From now on, the condition $w<\frac{1}{2}$ is fulfilled and the curve decays linearly until $w<M/N$. The curve decreases rapidly for $w<M/N$. All other glow curves ($w_0<1$) cross the vertical line through U_1^* at lower values than $\ln(I_0)$ does and have a slope of $-\frac{1}{2}$ only, if w_0 is still close to one. The decreasing part will have the slope $+1$ if the crossing occurs in region II because all curves must be between $\ln(I_0)$ and $\ln(I^*)$ in this region.

The remarkable features of curves with the characteristic parameters of this section are the slope of $-\frac{1}{2}$ during the "initial rise" if $w_0\simeq 1$ and the slope of $+1$ after the maximum for $w>M/N$. A family of computed TL glow curves is shown in Fig. 2(b) which illustrates the predicted behavior of this case. Again, note that the intensity becomes smaller and the TL maximum shifts to higher temperatures as the filling ratio w_0 is decreased from unity.

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[12] NRC Report No. 10999, 1969 (unpublished); this report may be obtained free of charge by writing to Dr. P. Kelly, NRC, Bldg. M36, Ottawa, Canada.

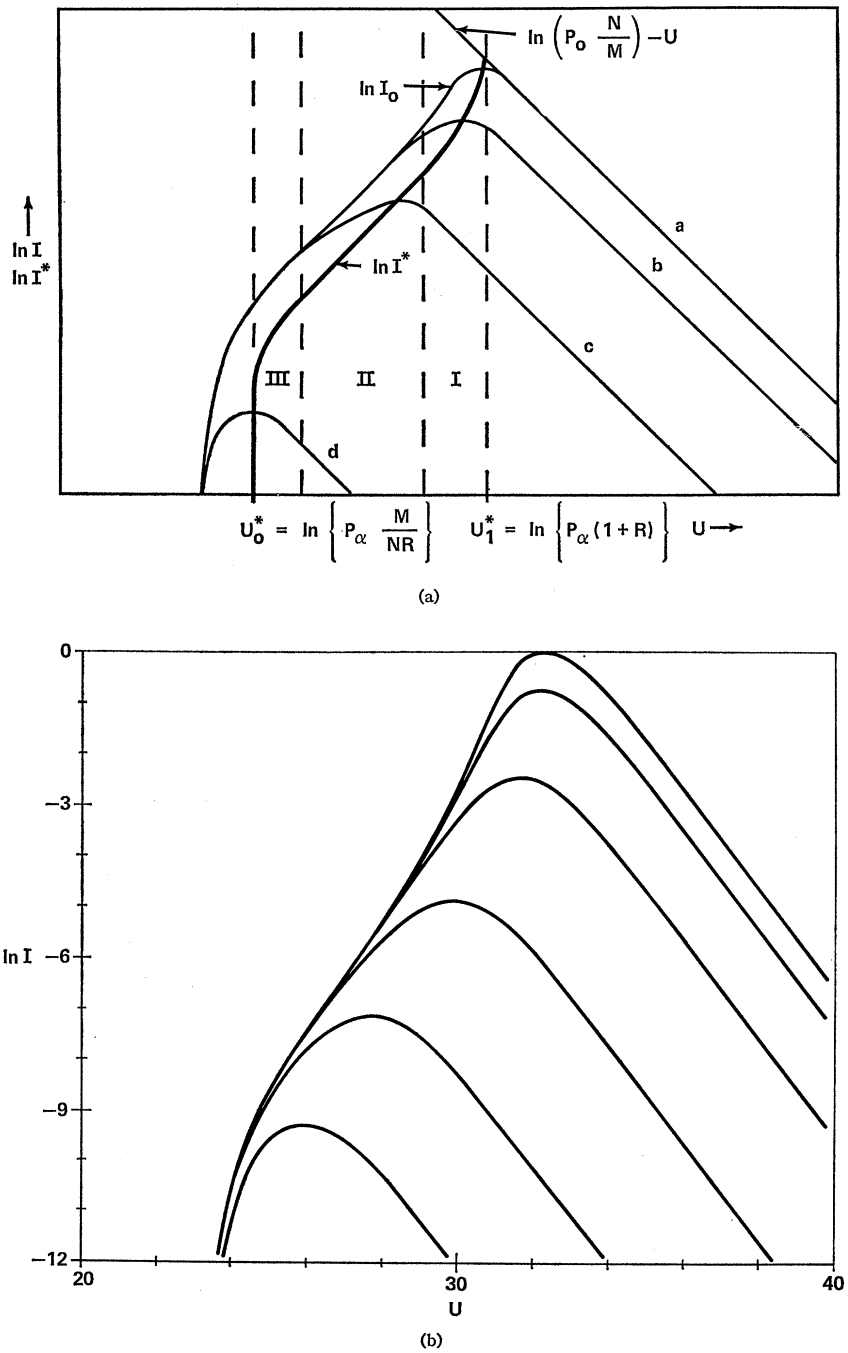

FIG. 1. (a) The function I^* (location of glow maxima) and TL glow curves. I_0 represents the curve with complete initial filling of the traps ($w_0=1$) and the curves a, b, c, and d are glow curves with decreasing initial occupancy w_0. (b) A set of TL glow curves characteristic for case I, calculated from Eqs. (8)–(10) with a quadratic heating rate and $R=0.1$, $M/N=10^{-4}$, $E/k=5\times10^3$ °K, $\alpha=2\times10^{-5}$ (sec °K)$^{-1}$, $P_0=10^{13}$ sec^{-1}, and $U_0\gg U^*$. The initial occupancy w_0 of the traps N is 1, 0.5, 0.1, 10^{-2}, 10^{-3}, and 10^{-4} in order of decreasing intensity at the maximum of the curves.

Case III: $M>RN$

As illustrated in Fig. 3, the conditions imposed by this case yield the first-order Randall-Wilkins shape.[13] There is no noticeable shift of the TL maximum if w_0 varies between zero and one.

[13] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) A184, 366 (1945).

COMPARISON OF TL CURVES OBTAINED WITH DIFFERENT HEATING RATES

We now show that there exists little or no difference between the shapes of computed TL glow curves obtained with the rate αT^2 or the rate q. In order to obtain a meaningful comparison we chose, arbitrarily, two temperatures T_0 and T^*, so that the glow curves started at the same temperature and peaked at the same temperature.

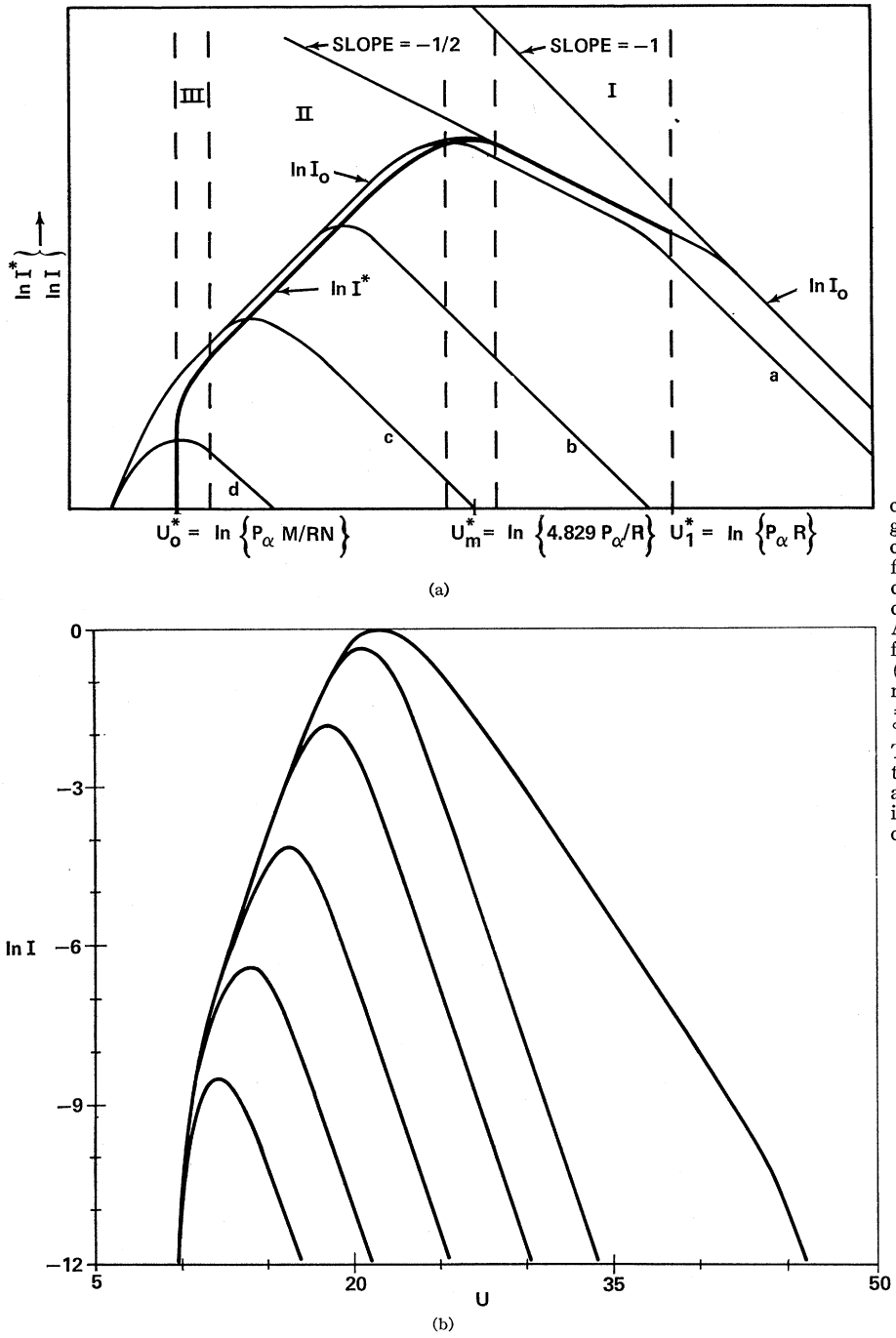

FIG. 2. (a) The function I^* (location of the extrema) and TL glow curves. I_0 represents the curve with complete initial trap filling ($w_0=1$) and the curves a, b, c, and d are glow curves with decreasing initial occupancy w_0. (b) A set of glow curves characteristic for case II, calculated from Eqs. (8)–(10) with quadratic heating rate and $R=10^5$, $M/N=10^{-4}$, $E/k=5\times10^3$ °K, $\alpha=2\times10^{-5}$ (sec °K)$^{-1}$, $P_0=10^{13}$ sec^{-1}, and $U_0\gg U^*$. The initial occupancy w_0 of the traps N is 1, 0.5, 0.1, 10^{-2}, 10^{-3}, and 10^{-4} in order of decreasing intensity at the maximum of the curves.

The parameters (E/k, P_0, α, R, M, N, w) completely determine a particular glow curve. After selecting a set of these parameters, the steps outlined in the Appendix were taken to compute glow curves.

We now present some computed cases with typical sets of the parameters: Figure 4 contains the TL glow curves with two heating rates ($q, \alpha T^2$) for the parametric combination considered in the last sections. For these combinations of parameters, where three distinct behaviors can be obtained, we note that there is little or no difference observed in the shapes, due to the different heating programs.

The special case of a solid containing no thermally disconnected traps ($M=0$) is illustrated in Fig. 5. Again, there is little or no difference observed between glow curves obtained with the two different heating

rates. The influence of the filling ratio w_0 on a curve of that type ($R \ll 1$) is easily explained with the aid of Eq. (9b). A first-order shape[13] is obtained for $w_0 > R$ since the logarithmic term is dominant in a wide range of values for U. As w decreases, this range narrows and finally a perfect second-order[14] shape results for $w_0 < R$.

EFFECT OF EXCITATION TEMPERATURE ON TL GLOW-CURVE SHAPES

Figure 6 illustrates the effect of the choice of various U_0 on the shape of a TL glow curve characterized by a set of parameters from case II ($R=10^5$, $N/M=10^{-4}$, $w_0=1$). Note that, under certain conditions, a TL glow curve can exhibit a minimum. This can be understood with the aid of Fig. 2(b). If U_0 is selected in region I and the traps are filled to the rates w_0 for which $I(U_0,w_0) > I^*(U^*)$, the glow curve starts in a region where it must have a positive slope. It decays with decreasing, U until it crosses I^* horizontally. At the crossover point, the TL curve exhibits a minimum. The slope of the curve now becomes negative until it crosses I^* horizontally again, at which point the maximum is reached.

With reference to Figs. 1(b) and 3, it is obvious that for cases I and III such behavior cannot occur.

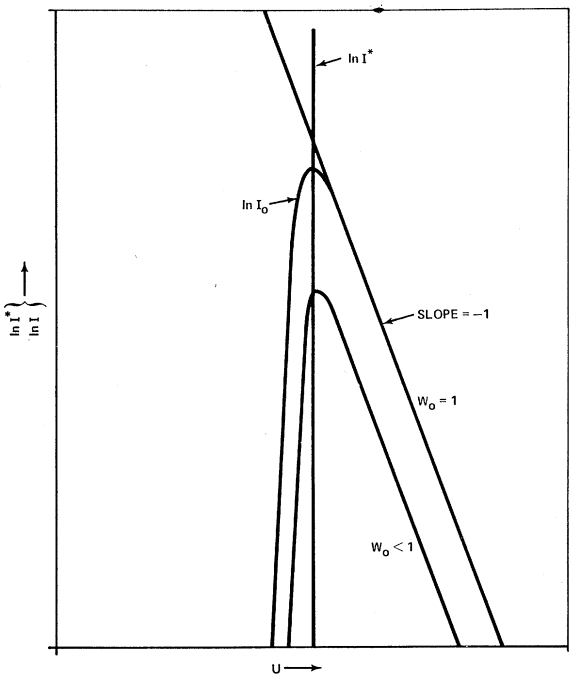

FIG. 3. The function I^* and TL glow curves for $w_0=1$ and $w_0<1$. All curves of this type have the shape characteristic for first-order kinetics and there is very little shift of the maximum temperature with changing w_0.

DISCUSSION

In the preceding sections, we have presented TL curves for a specific simple model which describes a solid through the parameters R, M, N, E, and P_0. Knowledge of these parameters, and the experimental parameters w_0, T_0, and q or α, predicts uniquely TL phenomena. The question we would like to discuss now

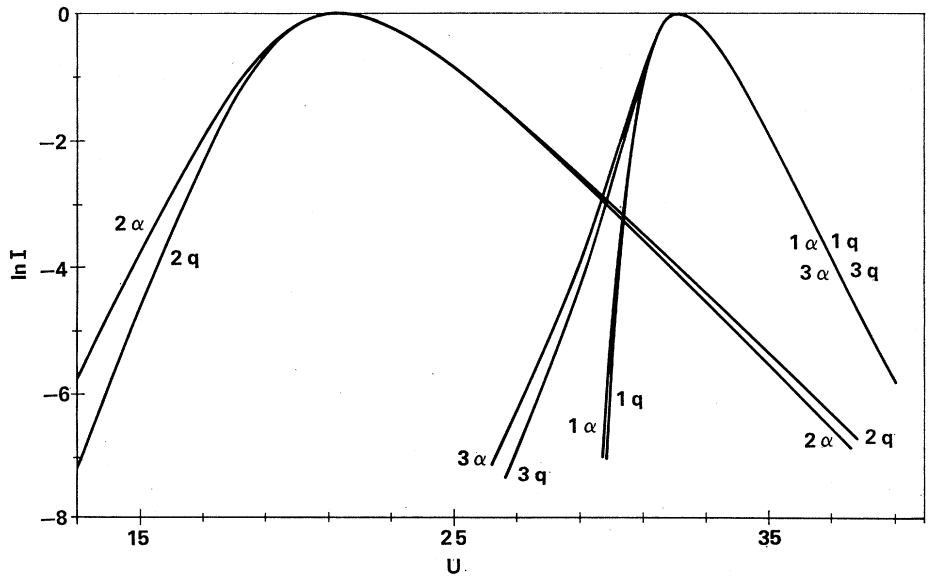

FIG. 4. Comparison of normalized typical TL glow curves for the two heating rates αT^2 (quadratic rates) and q (contant rate). The parameters were selected so that each of the three discussed characteristic cases is represented. The parameters common to all curves are $E/k=5\times10^3$ °K, $P_0=10^{13}$ sec^{-1}, $w_0=1$, and $U_0 \gg U^*$. The remaining ones are: $1q$—$M/N=10^5$, $R=0.1$, $q=0.481$ deg sec^{-1} (case III); $2q$—$M/N=10^{-6}$, $R=10^5$, $q=0.431$ deg sec^{-1} (case II); $3q$—$M/N=10^{-5}$, $R=0.1$, $q=0.481$ deg sec^{-1} (case I). The corresponding curves with quadratic heating rates (subscript α) were calculated with $\alpha=2\times10^{-5}$ (sec °K)$^{-1}$.

[14] G. F. J. Garlick and A. F. Gibson, Proc. Roy. Soc. (London) **A60**, 574 (1948).

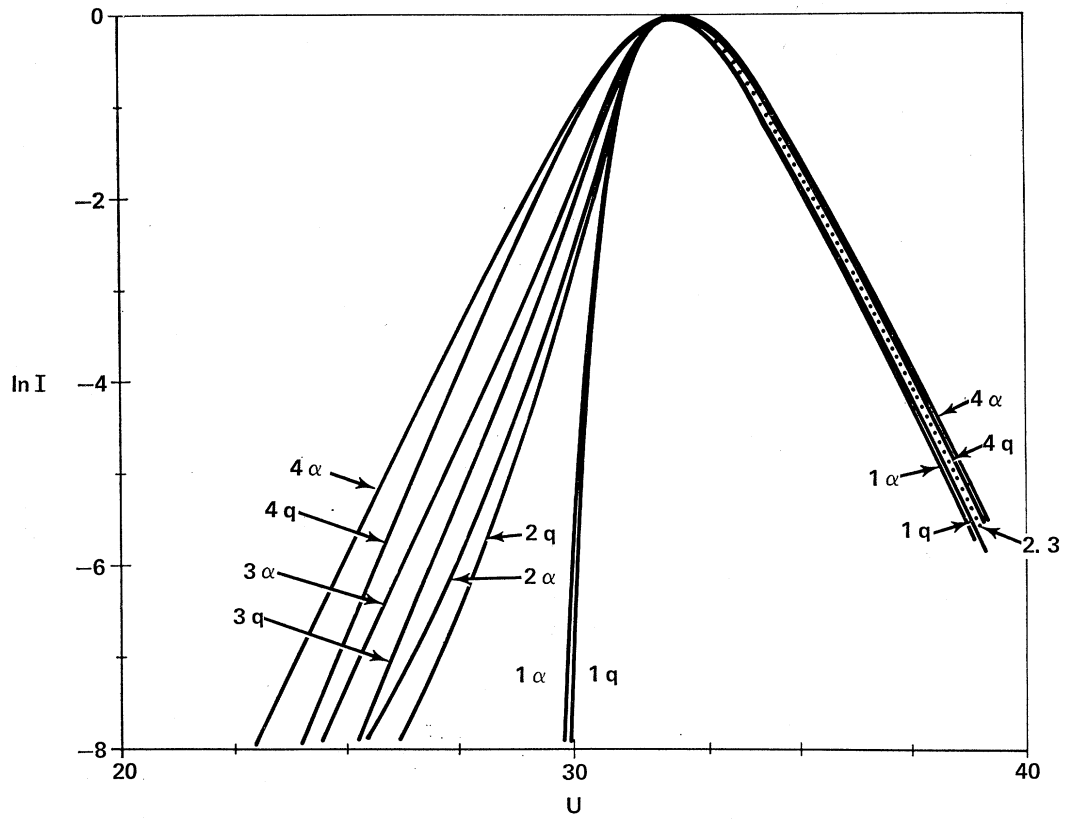

FIG. 5. Comparison of normalized TL glow curves with quadratic and constant heating rates for the special case $M=0$. The common parameters are $E/k=5\times10^3$ °K, $P_0=10^{13}$ sec^{-1}, $w_0=1$, and $U_0\gg U^*$. The values of the retrapping factor R and of q (in deg sec^{-1}), are $1q$—$R=10^{-5}$, $q=0.481$; $2q$—$R=10^{-1}$, $q=0.481$; $3q$—$R=0.3$, $q=0.486$; $4q$—$R=1.0$, $q=0.509$. The corresponding curves with quadratic heating rate (subscript α) were calculated with $\alpha=2\times10^{-5}$ (sec °K)$^{-1}$.

is the converse of the above: What can we learn about the solid from thermoluminescence? And, to anticipate, the answer is "precious little," unless we know, *a priori*, something about the parameters characterizing the

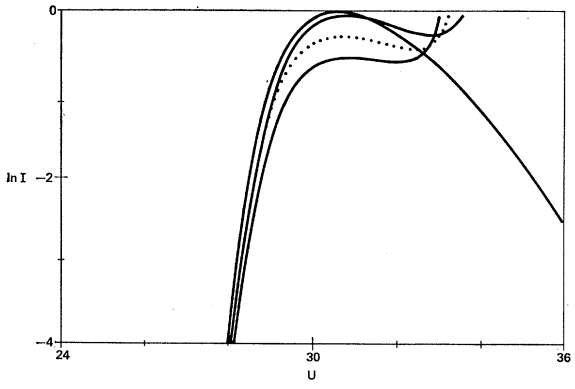

FIG. 6. Comparison of TL glow curves with different values of U_0. The parameters were selected from case II and are: $R=10^5$, $M/N=1$, $\alpha=2\times10^{-5}$ (sec °K)$^{-1}$ and $E/k=5\times10^3$ °K. The ratio U_0/U^* for those curves is in order of decreasing intensity at the maximum 100, 1.010999, 1.01090, and 1.0180. The curves show that under certain conditions TL glow curves may exhibit a minimum.

kinetics of the solid, and more importantly, if we know that the assumed model is applicable to the solid.

To reach this conclusion, we have to examine the various methods of analysis of glow curves. Three basic approaches have been used: (1) methods which use directly the shape of the glow peak, (2) "heating rate methods," where the heating rate of the specimen is varied, and (3) "initial rise" methods. The first two approaches actually depend upon the detailed shape of the peak: In the experiments, as they have been done and continue to be done right now, the TL intensity is measured only over two, or at most three, orders of magnitude. Even a casual perusal of Figs. 1–5 reveals that, barring the widths, the shape of the tops of the curves, the first two or three orders of magnitude, are not very sensitive to the parameters R, M, and N characterizing our model, and, thus, yield no information about them; this is especially true when no account of w_0 is taken. As the width of the curve is conventionally taken to be a measure of the trap depth E, then this quantity can be seriously in error when determined from the glow curve without a prior knowledge of R, M, and N.

The characteristic features of the TL glow curves

discussed in the previous sections may permit one to categorize a particular measured glow peak as belonging to one of the three cases. If this can be achieved than it might be possible to pick from the many existing analytical methods appropriate ones and, thus, one or more of the trapping parameters could be determined. However, clear evidence is required that the simple model used in the present work describes the kinetics. Also, the experiment needed for that task is necessarily much more elaborate than any TL experiment described in the literature. The light intensity of a single undisturbed peak would have to be measured over more than five orders of magnitude for filling ratios w_0 varying between 1 and 10^{-5} and for different initial temperatures. According to our results, only then will it be possible, e.g., to distinguish between the first-order shape of the curves with $w_0 \ll 1$ in cases I and II and the typical first-order shape of case III. The mentioned requirements and the unlikely chance to find an undisturbed peak or a peak that can be "cleaned" with known techniques throw serious doubt on the usefulness of shape methods as direct tools for the determination of trapping parameters. In addition, and this is an important point, preliminary studies indicate that other models, on the basis of quite different parameters, yield TL curves of the same shape as given by the model here considered. No unique information can, therefore, be obtained from the shape of the TL curve above. As a particular consequence, elaborate analyses of the conventional "first-order"[13] and "second-order" kinetics[14] (which are nothing but very special cases $M=0$, $N=1$, R much less than 1, and $M=0$, $N=1$, $R=1$ of our simple model) as have, for instance, been recently published by Chen,[15] seem to us at this state of the development of the field to be of rather limited value.

The only positive information can be obtained from the third approach, the initial rise method. This approach always yields an activation energy E (even for case II with $w_0 \approx 1$, where the initial slope of the curve has the wrong value, a second experiment with a different w_0 can be performed to obtain the correct E). The problem still remains, however, that with no model of the solid established, to what does this activation energy pertain?

The conclusion, therefore, is that whereas a model of the solid with given kinetic parameters uniquely specifies the TL curve, the TL curve, by itself, gives little or no information about the model or the parameters. TL can only be useful where previous information on the solid already exists. Whether such information can be obtained from other experiments is a moot point: In the next paper, we investigate the combined case of TL and TSC, and show that in that particular case the answer is no. It remains to be seen if other combinations of experiments prove more useful.

[15] R. Chen, J. Appl. Phys. **40**, 570 (1969).

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APPENDIX: STEPS TAKEN TO COMPUTE TL GLOW CURVES

Although it is possible to use standard numerical analysis techniques on the equations in the text, the following steps were taken to compute TL glow curves because of a saving in computer time.

(1) Equation (12) was solved for the value w^* with the condition $U_0 \gg U^*$. This yields a value of U^* from the relation $G(U^*) \equiv P_\alpha \exp(-U^*)$. $G(U^*)$ is here equivalent of $F(U^*)$ in Eq. (10).

(2) Now we arbitrarily choose a value for U_0 which is ten times the value of U^* obtained in step 1 in order to solve for a value of U^* in the most general manner. We generalize the extremum condition, Eq. (12), to $g(w^*) = F(U^*)$. This is solved for a new value of U^*. In practice, the choice of $U_0 \geq 2U^*$, with U^* from step 1, leaves the value U^* unchanged.

(3) For values of w_i in the range $10^{-15} \leq w_i \leq 1$, we solve Eq. (9) for the corrseponding value of U_i.

(4) Computed values of $\ln[I(U_i)/I(U^*)]$ were plotted versus the values of U_i. The accuracy of steps 1–4 was $\pm 10^{-15}$.

(5) In order to compute the curves with a constant rate, we first eliminate the quantity q from Eqs. (9) and (14) and solve for $w_q{}^*$ as in step 3. This yields a value for q as well. The heating rate q is computed rather than arbitrarily chosen in order to permit a meaningful comparison of glow-curve shapes with different rates, as mentioned previously.

(6) The above steps are repeated with the equations modified for a constant heating rate. Because of the numerical evaluation of the integral in Eq. (9), the accuracy of steps 4 and 5 is reduced to $\pm 10^{-10}$.