Numerical solutions to the rate equations governing the simultaneous release of electrons and holes during thermoluminescence and isothermal decay

S. W. S. McKeever

Department of Physics, Oklahoma State University, Stillwater, Oklahoma 74078

Joanne F. Rhodes, V. K. Mathur, R. Chen,* and M. D. Brown

Naval Surface Weapons Center, White Oak, Silver Spring, Maryland 20910

R. K. Bull

Environmental and Medical Sciences Division, Atomic Energy Research Establishment, United Kingdom Atomic Energy Authority, Harwell, Didcot, Oxon OX11 0RA, United Kingdom

The usual, simple model for the analysis of thermoluminescence (TL) curves deals with just one trapping level and one recombination level and assumes that only one recombination pathway exists for the production of luminescence (e.g., the thermal release of trapped electrons to recombine with thermally stable, trapped holes). In this paper we examine a more complex model which allows for the thermal release of both charge carriers in the same temperature range. Known as the Schön-Klasens model, this charge-transfer scheme has been often suggested as a cause of the thermal quenching of luminescence in insulators. The set of four simultaneous differential equations which describe the flow of charge between the energy levels in the Schön-Klasens model is solved numerically without the use of approximations. The TL curve shapes so generated are then analyzed with use of the usual Randall-Wilkins, Garlick-Gibson, or general-order formalisms—i.e., the so-called "three-parameter" form of equations. In the cases examined, good fits between the generated TL curves and the curves expected using these approximate formulations were obtained. We conclude that a fit of an experimental glow curve to a "three-parameter" form of equation cannot be used to indicate that the simple "three-parameter" model is necessarily valid. Additional to curve fitting, the curves were also analyzed using the conventional initial-rise and heating-rate methods. The parameters calculated from these analyses were compared with the original parameters inserted into the model and conclusions drawn regarding the interpretations of the calculated values. Finally, with use of these calculated parameters the isothermal stabilities of the TL curves were predicted and compared with the stabilities calculated from the numerical solution to the differential equations. We conclude that a "three-parameter" type of analysis is not a reliable means of estimating the thermal stability of the TL when the Schön-Klasens model is applicable.

I. INTRODUCTION

A useful experimental method for studying the charge-transfer processes which can take place in insulators and semiconductors is to follow the thermally stimulated relaxation of a nonequilibrium defect distribution following the application of an external stimulus. Several experimental techniques exist within this category and among these thermoluminescence (TL) and thermally stimulated conductivity (TSC) have proved to be popular. These techniques monitor the thermally stimulated charge transfer between defects after irradiation of the material. A primary objective is to derive, from the luminescence or conductivity "glow curves," values for the various parameters associated with the charge-transfer process. To this end, most glow curves are analyzed purely on the basis of a phenomenological model involving localized energy levels within the band gap of the material (see, e.g., Refs. 1—3). For this type of model the relevant parameters include trap depths (E), frequency factors (s), capture cross sections, and densities of the various traps and recombination centers taking part in the process. Having arrived at

these values, however, we are still a long way from defining the point-defect model with which they are associated. Nevertheless, calculations of this type are considered to be a necessary step in arriving at an acceptable level of understanding of the underlying processes.

The major difficulty with this procedure is that without a prior knowledge of the actual point defects involved we have no way of knowing that the phenomenological model is, in fact, an accurate representation of the process. Most analyses of TL and TSC proceed on the basis of a simplified energy-level scheme involving just two energy levels (a "trap" and a "recombination center") and on the assumption that only one charge-carrier type is thermally activated in a given temperature regime. During TL the luminescence transition then involves the recombination of the mobile carrier with the trapped carrier of opposite sign, such that the intensity of the TL is described by

$$I_{\text{TL}} = -\frac{dm}{dt}, \tag{1}$$

where m is the number of recombination sites (i.e., the number of trapped oppositely charged carriers) and t is

time. If the recombination sites are trapped holes, then dm/dt is related to the free-electron concentration n_c by

$$\frac{dm}{dt} = -n_c m A_m ,$$ (2)

where A_m is the probability of recombination of electrons with trapped holes. In a similar fashion, the time dependences of n_c and of the trapped electron concentration n may be written

$$\frac{dn_c}{dt} = ns \exp\left[-\frac{E}{k_B T}\right] - n_c[(N-n)A_n + A_m m]$$ (3)

and

$$\frac{dn}{dt} = -ns \exp\left[-\frac{E}{k_B T}\right] + n_c(N-n)A_n .$$ (4)

In these equations, which were first written by Halperin and Braner,[4] N is the concentration of available electron traps and A_n is the retrapping probability for electrons. E and s are interpreted as the electron trap depth and the electron attempt-to-escape frequency factor, respectively.

At this point, two major assumptions are normally introduced, namely

$$n_c \ll n$$ (5a)

and

$$\frac{dn_c}{dt} \ll \frac{dn}{dt} .$$ (5b)

Taken together, these assumptions imply that free charge does not accumulate in the delocalized bands during the thermal stimulation of the trapped carriers. As a result of these assumptions, the so-called "Randall-Wilkins" and "Galick-Gibson" formalisms may be developed.[5,6] They are, respectively,

$$I_{TL} = sn_0 \exp\left[-\frac{E}{k_B T}\right]$$

$$\times \exp\left[-(s/\beta)\int_{T_0}^{T} \exp\left[-\frac{E}{k_B T}\right]dT\right]$$ (6)

and

$$I_{TL} = sn_0 \exp\left[-\frac{E}{k_B T}\right]$$

$$\times \left[(s/\beta)\int_{T_0}^{T}\exp\left[-\frac{E}{k_B T}\right]dT+1\right]^{-2} ,$$ (7)

where β is the heating rate.

Known as the "first-order" (no retrapping) and "second-order" (extensive retrapping) equations for TL, these expressions led directly to the development of the empirical "three-parameter" equation,[1,7] namely

$$I_{TL} = sn_0 \exp\left[-\frac{E}{k_B T}\right]$$

$$\times \left[\frac{(b-1)s}{\beta}\int_{T_0}^{T}\exp\left[-\frac{E}{k_B T}\right]dT+1\right]^{-b/(b-1)} .$$ (8)

The above expression is a general form of Eq. (7) and reduces to Eq. (6) in the limit as $b \to 1$. In all of the above relationships, n_0 is the initial concentration of trapped electrons, k_B is Boltzmann's constant, and T is temperature.

The three-parameters referred to in the description of Eq. (8) are E, s, and the kinetic order b. When $b=1$, Eq. (6) is used. When $b=2$, Eq. (7) is used. This last parameter relates to the probability that the thermally released carrier will be retrapped before it undergoes recombination.

Recently, however, Fillard, Gasiot, and colleagues[8−10] have presented experimental evidence to indicate that Eq. (1) is invalid in many cases. It appears that charge carriers are being removed from the recombination site by an additional route to the radiative recombination, and as a result, the analysis leading to the three-parameter equation is inappropriate in these cases.

In the material ZnSe:Al, Fillard et al.[9] argue that the thermal release of charge from the recombination site must be taking place. Thus, if electrons are being released from their traps to recombine with trapped holes, then, in ZnSe:Al, holes are also being thermally released in the same temperature range before the electrons can recombine with them. This model of simultaneous electron and hole release within the same temperature range was discussed previously by Schön[11,12] and by Klasens[13] and is thus described as the Schön-Klasens energy-level scheme. It is illustrated schematically in Fig. 1. In this figure n_c and p are the concentrations of free electrons and holes, respectively, n (and m) are the concentrations of trapped electrons (and holes), and N (and M) are concentrations of available electron (and hole) traps. The other terms are defined below.

The additional route by which m may decrease was included by Schön and by Klasens to explain the phenomenon of thermal quenching in those materials for which luminescence production involved transitions of the
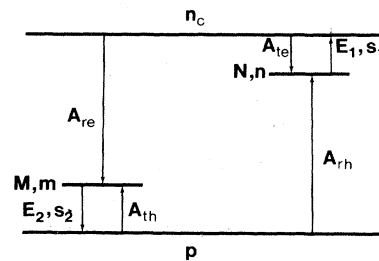

FIG. 1. Energy levels, trap depths, concentrations, and transition probabilities for the Schön-Klasens energy-level model.

charge carriers to the delocalized bands. Despite the fact that there are many reported cases of thermal quenching during TL production,[3] glow curves are nevertheless still analyzed primarily on the basis of the three-parameter equation. It should be noted that not all forms of thermal quenching can be described by the Schön-Klasens model, and neither are all causes of the breakdown of Eq. (1) due to the simultaneous thermal release of carriers. Nevertheless, there is such a large number of reported cases of thermal quenching that a consideration of the Schön-Klasens model becomes one of importance.

Bräunlich and Scharmann[14] developed an approximate analysis of the Schön-Klasens scheme by introducing several assumptions into the model. They defined two parameters, namely $R = A_{te}/A_{re}$ and $R^* = A_{th}/A_{rh}$, where, from Fig. 1, A_{te} and A_{th} are the retrapping probabilities, and A_{re} and A_{rh} are the recombination probabilities, for the electrons and holes, respectively. By assuming relative values for R and R^* and by introducing some simplifying assumptions (in particular, the assumption of a quasiconstant concentration of free charge in the delocalized bands), Bräunlich and Scharmann were able to arrive at approximate solutions to the rate equations. Specifically, for $R \approx 0$ and $R^* \approx 0$, for $R \approx 0$ and $R^* \gg 1$, and for $R \gg 1$ and $R^* \approx 0$, equations similar in form to Eq. (6) were derived, whereas for $R \gg 1$ and $R^* \gg 1$ an expression similar to Eq. (7) was produced. Thus, despite the introduction of an apparently more complex set of recombination pathways, the simple three-parameter type of equation could still be used to describe the glow-curve shape (leaving aside, for the moment, interpretations of the activation energy so calculated).

The assumption that the electron and hole populations in the conduction and valence bands are approximately constant is one of the cornerstones of the derivation of the Randall-Wilkins and Garlick-Gibson expressions, from which the three-parameter equation is developed. This is true no matter if the conventional, simplified energy-level scheme or the more complex Schön-Klasens scheme is adopted. However, Kelly et al.[15] have shown that this assumption has only a limited range of generality, and many sets of parameter values (i.e., numerical values for A_{te}, A_{re}, m, n, etc.) can be chosen for which the assumption becomes invalid. Under these circumstances, glow curves can be produced which should not be analyzed using the three-parameter form of equation.

In view of this, it becomes instructive to analyze the Schön-Klasens scheme *numerically*, without the use of any assumptions regarding the relative values of the different parameters. In the following section we discuss the relevant rate equations describing the flow of charge during thermal stimulation using the Schön-Klasens model. From these equations we produce numerical solutions which describe the shape of the TL glow curves. It is the primary purpose of this paper to describe an analysis of the glow curves so generated using the three-parameter type of equation [viz., Eqs. (6)—(8)]. These equations are those which are used in almost every analysis of real TL curves that we have seen in the published literature, and it is our intent to point out the limitations of such analyses when a scheme of the Schön-Klasens type is suspected.

II. THE SCHÖN-KLASENS MODEL

As described in the Introduction, the Schön-Klasens model concerns the simultaneous release of charge from trapping levels for electrons and holes (Fig. 1) located near the demarcation levels within the band gap of an insulator or semiconductor.

The four rate equations which describe the flow of charge carriers between the various energy levels in this model have been discussed by Bräunlich and Scharmann[14] and are rewritten here thusly

$$\frac{dn}{dt} = -s_1 n \exp\left[-\frac{E_1}{k_B T}\right] + A_{te} n_c (N-n) - A_{rh} p n \ , \quad (9a)$$

$$\frac{dn_c}{dt} = s_1 n \exp\left[-\frac{E_1}{k_B T}\right] - A_{te} n_c (N-n) - A_{re} n_c m \ , \quad (9b)$$

$$\frac{dm}{dt} = -s_2 m \exp\left[-\frac{E_2}{k_B T}\right] + A_{th} p (M-m) - A_{re} n_c m \ , \quad (9c)$$

$$\frac{dp}{dt} = s_2 m \exp\left[-\frac{E_2}{k_B T}\right] - A_{th} p (M-m) - A_{rh} p n \ . \quad (9d)$$

The set of equations includes the neutrality condition

$$\frac{dn}{dt} + \frac{dn_c}{dt} = \frac{dm}{dt} + \frac{dp}{dt} \ . \quad (9e)$$

Similar sets of simultaneous differential equations describing trap filling[16,17] and trap emptying,[15,18] but for the simple energy-level scheme, have been solved numerically in the past. The present set of equations for the Schön-Klasens model has so far been solved analytically only with the use of simplifying approximations.[14] In this paper we solve for the first time the complete set of equations numerically without any simplifying assumptions. Two programs were utilized in the solution, one a second-order predictor-corrector routine and the other a sixth-order Runge-Kutta predictor-corrector routine. Both programs gave the same results for the range of values of input parameters discussed in this paper. The calculations were performed on IBM 370 and Control Data Corporation Cyber 170/720 computers.

In the analysis we allow for one of two transitions, or for both simultaneously, to yield TL. The allowed radiative transitions are (i) free electron to bound hole (e-h), for which the TL intensity is

$$I_{TL} = A_{re} n_c m \ , \quad (10a)$$

(ii) free hole to bound electron (h-e), giving

$$I_{TL} = A_{rh} p n \ , \quad (10b)$$

and (iii) both transitions (i) and (ii), giving

$$I_{TL} = A_{re} n_c m + A_{rh} p n \ . \quad (10c)$$

All other transitions are assumed to be nonradiative, or, if radiative, not detected. It is to be noted that each of Eqs. (10a)—(10c) means that $I_{TL} \neq -dm/dt$ [viz., Eq. (1)].

In a previous numerical solution to these equations[19] we

preferred to limit the complexity and, therefore, the generality of the solutions by considering only free-electron to bound-hole transitions to be radiative, and to ignore hole retrapping. In this paper we remove these restrictions in an effort to increase the generality and applicability of the results, although we are still necessarily dealing with a relatively unsophisticated case and are ignoring, for instance, the existence of a multiplicity of electron and/or hole traps.[20]

The earlier results[19] showed that while the three-parameter equation could be used as a rather accurate description of the glow-peak shape, even in this complex case, anomalously high values for the frequency factors s could be obtained, along with an apparent order of kinetics of less than one. (Both of these situations have been reported in the literature.[3])

Since there are many aspects of such a complex model that could be examined, we have limited our attention to the following: examining the validity of certain aspects of the Bräunlich and Scharmann[14] analysis, examining the degree to which the produced glow curves can be described by the three-parameter analysis, interpreting the meaning of the E values so obtained, and, finally, testing the ability of the three-parameter analysis to predict the thermal behavior (i.e., the isothermal decay rates) of the glow peaks. This latter item was thought to be of importance because of the use to which TL is put in the fields of radiation dosimetry, archaeology, and geology, wherein the isothermal stability of a particular glow peak is often predicted on the basis of a three-parameter examination.

III. RESULTS AND DISCUSSION

We have selected parameter values which, for the simple energy-level model, would yield either first- or second-order kinetics. We have done this (i) for the situation where carrier accumulation in the delocalized bands is prevented [thereby ensuring that the assumptions inherent in the development of Eqs. (6)—(8) are valid], and (ii) for the case where some carrier accumulation does occur. The purpose of the latter case is to produce a situation in which the constancy of the electron and hole populations is not achieved and thus the three-parameter type of analysis should be inappropriate, irrespective of the energy scheme adopted.

A. Curve fitting

The results corresponding to case (i) are shown in Fig. 2. For each of the curves illustrated in this figure the electron trap depth E_1 is held constant at 0.8 eV and the hole trap depth E_2 is varied, as indicated in the figure caption. As can be seen, first-order [Fig. 2(a)] and second-order [Fig. 2(b)] curves are produced by varying the relative values of the recombination and trapping coefficients, as indicated. The important point is that the three-parameter type of equation can be used to describe accurately the curve shape, despite the fact that the curves were generated using a more complex model than these equations are meant to describe. (We leave aside, until later, a discussion of what the fitted parameters mean in a
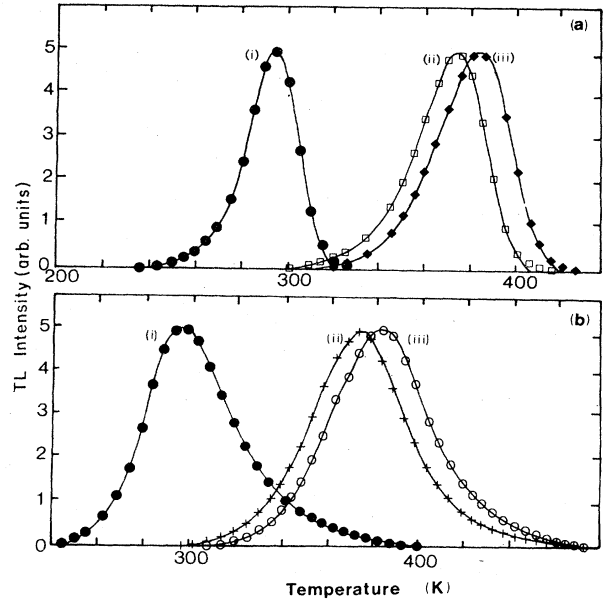

FIG. 2. (a) First-order TL curves (data points) generated from Eqs. 9(a)—9(e) with $E_1 = 0.8$ eV and (i) $E_2 = 0.6$ eV, (ii) $E_2 = 0.8$ eV, and (iii) $E_2 = 1.0$ eV. The other parameter values are $m_0 = n_0 = 1.0 \times 10^9$ cm^{-3}, $M = N = 1.0 \times 10^{10}$ cm^{-3}, $n_{c0} = p_0 = 0$, $s_1 = s_2 = 1.0 \times 10^{10}$ s^{-1}, $A_{re} = A_{rh} = 1.0 \times 10^7$ cm^{3}s^{-1}, and $A_{te} = A_{th} = 1.0 \times 10^9$ cm^{3}s^{-1}. Heating rate $= 5$ K s^{-1}. The solid lines are the fitted curves using Eq. (8). For (b) the parameters are the same, except $A_{te} = A_{th} = A_{re} = A_{rh} = 1.0 \times 10^8$ cm^{3}s^{-1} and the kinetics are approximately second order. e-h transitions are radiative.

physical sense.) In Fig. 3 we find that even when moderate charge-carrier accumulation in the delocalized bands is allowed [case (ii)], the equations *still* accurately describe the curve shape. For this case carrier accumulation was induced by making the retrapping probabilities for both energy levels very much less than the recombination probabilities, as indicated in the figure caption. The
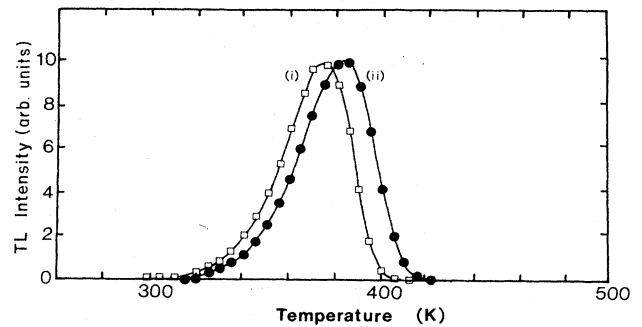

FIG. 3. First-order TL curves generated using the parameters listed in Table II, except for $M = N = 1.0 \times 10^9$ cm^{-3}, $A_{re} = A_{rh} = 1.0 \times 10^{-7}$ cm^{3}s^{-1}, and $A_{te} = A_{th} = 1.0 \times 10^{-18}$ cm^{3}s^{-1}. Moderate free-carrier accumulation is allowed. For each curve $E_1 = 0.8$ eV. For curve (i), $E_2 = 0.6$ eV, and for curve (ii), $E_2 = 1.0$ eV.

TL peak produced is very well described by a first-order curve.

The free-carrier accumulation in these latter cases is moderate only. For example, in Fig. 3 the free carrier to trapped carrier ratio is only $\sim 10^{-2}$ at the TL peak, and thus inequality (5a) is still approximately true. However, dn_c/dt and dp/dt can be rather large compared with dn/dt and dm/dt, respectively [viz., inequality (5b)]. In more extreme cases of carrier pile up we obtained TL peaks with extremely long high-temperature tails. These TL peaks could not be fitted by equations of the type (6)—(8). Carrier pile up can be induced if both the retrapping coefficients and the recombination coefficients are small, or if the initial trapped charge densities are low.

In a treatment similar to that offered here, but for the simple energy-level model, Kelly et al.[15] illustrated that when the parameter values were such that the assumptions inherent in the derivation of the approximate solutions were invalid, TL and TSC curve shapes were obtained which could not be described by the approximate solutions. Here, for the more complex Schön-Klasens model, we see that the approximate solution can be a good description of the curve shape but only under similar restrictions to those dealt with by Kelly et al.[15] Although we have only demonstrated this for a limited number of cases (there are many combinations and permutations of the various parameter values that could be tried), we have no reason to suspect that these cases are in any way unique.

From the above results it becomes clear that the fact that the approximate three-parameter type of equation can be used to describe accurately the glow-curve shape obtained in a TL or TSC experiment should *not* be regarded as evidence that the energy-level system under investigation is described by the simple energy-level scheme from which Eqs. (6)—(8) were developed.

B. Parameter analysis

The above discussion leads naturally to the question regarding the interpretation of the derived parameters, when the approximate solution is used to analyze the results.

As seen in expressions (6)—(8), these equations contain a single activation energy E and a single frequency factor s. However, the Schön-Klasens model contains two activation energies, E_1 and E_2, and two frequency factors, s_1 and s_2. In what follows, we compare the parameter values obtained from the three-parameter curve fitting, and those obtained from the initial-rise[6] and heating-rate[21] methods of analysis, with the actual values for E_1, E_2, s_1, and s_2 inserted into the program. Tables I—III list some of the results of this analysis. Several possibilities regarding the luminescent transition have been considered, namely those described in Eqs. (10a)—(10c). For the variable-heating-rate analysis, heating rates of 5, 10, 50, and 100 $\mathrm{K\,s^{-1}}$ were used.

It emerges from these data that if we consider only the e-h transition as radiative then the initial-rise method of analysis yields an accurate value for the trap depth of the electron trap. Conversely, if the h-e transition is radiative, the hole trap depth can be found with similar accuracy. However, if both transitions are radiative, assuming an identical quantum efficiency for each, then the initial-rise analysis gives the trap depth of the least thermally stable trap.

The different-heating-rates method, however, always appears to give an activation energy which is a somewhat less accurate (typically ~ 5—10%) reflection of the least stable trap, irrespective of the radiative transition, or transitions, involved. The reason for the greater inaccuracy with this method is probably due to the fact that the heating-rate analysis as described by Hoogenstraaten[21] and as used in this paper is an approximation and only in a strict first-order case will it yield an accurate value of E. Additionally, and possibly more importantly, we are dealing with a more complex system than that described by Hoogenstraaten. In view of this, the inaccuracies in the results of this method should not be considered surprising.

As a first step at understanding these results it is useful to examine the approximate solutions to the rate equations for the Schön-Klasens model, derived by Bräunlich and Scharmann.[14] For illustrative purposes we select the situation of $R \gg 1$ and $R^* \gg 1$, and rewrite the TL equation developed by Bräunlich and Scharmann using the nomenclature adopted in this paper; thus,

TABLE I. No free-carrier accumulation; e-h transition radiative.

Parameters	E_2 values (eV)	Three-parameter fit E (eV)	s (s^{-1})	b	Initial rise E (eV)	s (s^{-1})	Heating rate E (eV)	s (s^{-1})
(i) As for Fig. 2(a)	(a) $E_2=0.6$	0.741	2.33×10^{12}	1.17	0.791	1.85×10^{13}	0.597	6.92×10^9
	(b) $E_2=0.7$	0.761	1.04×10^{11}	1.09	0.795	2.68×10^{11}	0.701	1.05×10^{11}
	(c) $E_2=0.8$	0.808	2.62×10^{10}	1.04	0.798	1.92×10^{10}	0.803	2.38×10^{10}
	(d) $E_2=0.9$	0.798	1.02×10^{10}	1.02	0.798	9.88×10^9	0.819	1.99×10^{10}
	(e) $E_2=1.0$	0.803	1.10×10^{10}	1.03	0.796	9.17×10^9	0.803	1.15×10^{10}
(ii) As for Fig. 2(b)	(a) $E_2=0.6$	0.709	4.04×10^{11}	2.93	0.789	1.16×10^{13}	0.543	5.67×10^8
	(b) $E_2=0.7$	0.777	8.17×10^{10}	2.33	0.795	2.45×10^{11}	0.634	8.84×10^8
	(c) $E_2=0.8$	0.803	2.38×10^{10}	2.01	0.796	1.88×10^{10}	0.754	5.96×10^9
	(d) $E_2=0.9$	0.805	1.47×10^{10}	2.04	0.798	1.06×10^{10}	0.740	2.40×10^9
	(e) $E_2=1.0$	0.798	9.7×10^9	2.01	0.798	9.93×10^9	0.731	2.29×10^9

TABLE II. No free-carrier accumulation; h-e transition radiative.

Parameters	E_2 values (eV)	Three-parameter fit E (eV)	s (s^{-1})	b	Initial rise E (eV)	s (s^{-1})	Heating rate E (eV)	s (s^{-1})
(a) $\beta=5\mathrm{K\,s}^{-1}$, $n_{c0}=p_0=0$	(a) $E_2=0.6$	0.618	2.18×10^{10}	1.23	0.600	1.04×10^{10}	0.542	2.17×10^{9}
$m_0=n_0=1.09\times10^9$ cm^{-3}	(b) $E_2=0.7$	0.726	2.80×10^{10}	1.20	0.699	1.06×10^{10}	0.647	1.95×10^{9}
$s_1=s_2=1.0\times10^{10}$ s^{-1}	(c) $E_2=0.8$	0.804	2.39×10^{10}	1.05	0.797	1.91×10^{10}	0.778	1.09×10^{10}
$A_{re}=A_{rh}=1.0\times10^8$ cm^{3}s^{-1}	(d) $E_2=0.9$	0.853	4.77×10^{10}	1.06	0.892	1.88×10^{11}	0.811	1.30×10^{10}
$A_{te}=A_{th}=1.0\times10^{11}$ cm^{3}s^{-1}	(e) $E_2=1.0$	0.936	5.33×10^{11}	1.16	0.986	2.56×10^{12}	0.803	9.64×10^{9}
$M=N=1.0\times10^{10}$ cm^{-3}								
$E_1=0.8$ eV								
(b) As above, except	(a) $E_2=0.6$	0.602	1.11×10^9	2.05	0.597	9.90×10^8	0.618	2.42×10^9
$A_{re}=A_{rh}=A_{te}=A_{th}$	(b) $E_2=0.7$	0.702	1.14×10^9	2.01	0.697	1.06×10^9	0.736	4.53×10^9
$=1.0\times10^8$ cm^{3}s^{-1}	(c) $E_2=0.8$	0.793	1.89×10^9	2.26	0.797	2.02×10^9	0.840	8.06×10^9
	(d) $E_2=0.9$	0.860	1.85×10^9	2.26	0.910	2.64×10^{10}	0.832	2.84×10^9
	(e) $E_2=1.0$	0.920	1.92×10^{10}	2.67	0.998	1.45×10^{11}	0.803	7.75×10^8

$$I_{\mathrm{TL}}=n\left[s_1\exp\left(-\frac{E_1}{k_BT}\right)+s_2\exp\left(-\frac{E_2}{k_BT}\right)\right]\exp\left\{-\frac{1}{\beta}\int_{T_0}^{T}\left[s_1\exp\left(-\frac{E_1}{k_BT}\right)+s_2\exp\left(-\frac{E_2}{k_BT}\right)\right]dT\right\}. \tag{11}$$

If the thermal stimulation of holes is neglected, this equation reduces to the first-order version of the three-parameter equation [namely, Eq. (6)].

Equation (11) describes the TL produced assuming both e-h and h-e transitions are radiative. If we were to consider e-h transitions only, the second term in the first pair of large parentheses would be ignored. Alternatively, to consider the h-e radiative transitions only, the first term in the first pair of large parentheses would be ignored. Thus, the initial-rise analysis, which considers the terms in the first pair of large parentheses only, calculates E_1 for e-h transitions, E_2 for h-e transitions, or the smaller of E_1 and E_2 if both transitions are radiative.

Similarly, the heating-rate analysis places importance on the terms within the large curly braces and thus always calculates the smaller of E_1 and E_2, irrespective of the radiative transition. If $E_1=E_2=E$, then E is calculated. If $E_1\ll E_2$, E_1 is calculated. If $E_2\ll E_1$, E_2 is calculated. However, if E_1 and E_2 are different, but similar, the E value calculated is a "weighted average" of the two (i.e.,

weighted by the rate of recombination of each species at the peak temperature). Similar discussions can be made for the other situations examined by Bräunlich and Scharmann.[14]

As stated above, the glow curves produced can be described very well by the simple three-parameter form of equation. However, interpretation of the activation energy obtained from a curve-fitting procedure using this equation is not straightforward. Both the first and second terms of the three-parameter type of equation contain just one energy term E, where two energies are actually involved (E_1 and E_2). From a consideration of the data in Tables I—III it emerges that the three-parameter fitting procedure yields values for the smaller of E_1 and E_2 if both transitions are radiative (viz., Table III). For e-h transitions, it gives E_1 if $E_1<E_2$, and it gives a value somewhere between E_1 and E_2 if $E_2<E_1$ (viz., Table I), and vice versa for h-e transitions. Clearly, without independent evidence to indicate which transition is radiative and which trap depth is the smallest, interpretation of

TABLE III. No free-carrier accumulation; both h-e and e-h transitions radiative.

Parameters	E_2 values (eV)	Three-parameter fit E (eV)	s (s^{-1})	b	Initial rise E (eV)	s (s^{-1})	Heating rate E (eV)	s (s^{-1})
As Table II,	(a) $E_2=0.6$	0.618	2.03×10^{10}	1.22	0.599	1.03×10^{10}	0.542	2.17×10^9
part (a)	(b) $E_2=0.7$	0.709	1.44×10^{10}	1.13	0.701	1.75×10^{10}	0.657	4.50×10^9
	(c) $E_2=0.8$	0.804	2.39×10^{10}	1.05	0.797	1.91×10^{10}	0.778	1.09×10^{10}
	(d) $E_2=0.9$	0.805	1.47×10^{10}	1.12	0.801	1.09×10^{10}	0.759	6.79×10^9
	(e) $E_2=1.0$	0.808	1.33×10^{10}	1.15	0.789	7.39×10^9	0.745	2.86×10^9
As Table II,	(a) $E_2=0.6$	0.602	1.10×10^9	2.05	0.598	1.02×10^9	0.618	2.42×10^9
part (b)	(b) $E_2=0.7$	0.707	1.36×10^9	2.05	0.699	1.12×10^9	0.727	2.90×10^9
	(c) $E_2=0.8$	0.793	1.89×10^9	2.00	0.797	2.02×10^9	0.840	8.06×10^9
	(d) $E_2=0.9$	0.811	1.48×10^9	2.05	0.809	1.64×10^9	0.829	3.16×10^9
	(e) $E_2=1.0$	0.801	1.08×10^9	2.03	0.793	9.18×10^8	0.818	2.02×10^9

the activation energy physically means is of minor importance. It is only important to know if the calculated energy will provide for an accurate prediction of the peak's thermal behavior. Thus, although there may be some uncertainty regarding the understanding of the activation energy calculated from a three-parameter type of fit, the fact that this type of equation is a good description of the curve shape raises the possibility that it may be used profitably to determine the isothermal stability.

To examine this point we have numerically calculated the isothermal decay curves for several sets of data by setting the heating rate β to zero. We then compared the curves obtained with those expected using the results of the three-parameter analysis. For this test we chose the data relevant to Fig. 2 (Table I). The results are shown in Figs. 4 and 5. For the decay temperature a value 20 K less than the peak position (produced at a heating rate of 5 $K s^{-1}$) was chosen (viz., Fig. 2). In Fig. 4 panels (a), (b), and (c) correspond to the values given in Table I, part (i), (a), (c), and (d), respectively. Similarly, Figs. 5(a)—(c) correspond to Table I, part (ii), (a), (c), and (d), respectively.

In only two cases [Figs. 4(b) and (c)] can the calculated decay be said to be a reasonable approximation to the actual decay. In each of the other cases, a poor correspondence between the calculated and actual decay rates is observed. No meaningful significance can be attached to

FIG. 4. TL decay curves generated using the Schön-Klasens scheme and the parameters listed in Table I (●●●). These are compared with the predicted decay rates calculated using the three-parameter curve fit (———), the initial-rise analysis (— — —), and the heating-rate analysis (· · · ·). The kinetics are first order and the differences between diagrams (a), (b), and (c) are described in the text.

the E values obtained from curve fitting is not possible in the Schön-Klasens scheme. If one energy is much smaller than the other (e.g., $E_1 \ll E_2$) for e-h transitions, then the term containing $E_1/k_B T$ will dominate the equation and a reasonably accurate value for E_1 will emerge. However, if the $E/k_B T$ terms are not too different, an E value corresponding to neither E_1 nor E_2 will emerge. Furthermore, the value of the kinetic order b will be of little meaning in this latter case. Both of these situations can be seen, for example, in Table I.

C. Thermal stability

A remaining question concerns not the interpretation of the calculated activation energy, but its usefulness in predicting the thermal behavior of the glow peak. Often during the application of TL to the fields of archaeology, dosimetry, and geology, it is useful to be able to predict the thermal stability of a TL peak from the activation energy calculated using one or another of the methods discussed above. In this regard, our interpretation of what
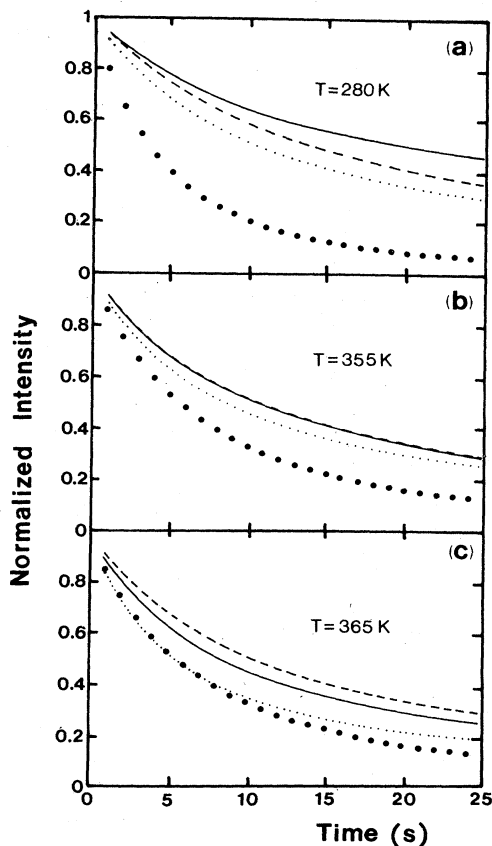

FIG. 5. Same as for Fig. 4, but for second-order kinetics. See text for further description.

this observation and no obvious trends or patterns emerge. We conclude that the estimation of the decay rate for TL using analyses based on Eqs. (6)—(8) must be performed with extreme caution if premature judgements are to be avoided.

IV. CONCLUSIONS

The main conclusions drawn from this work are the following:

(i) Glow curves generated using the Schön-Klasens model of simultaneous hole and electron release can have the same shape as those expected from the simple Randall-Wilkins and Garlick-Gibson energy-level schemes. The three-parameter form of equation which results from these simplified models is seen to fit the curves for the Schön-Klasens case with a high degree of accuracy if the assumptions inherent in the derivation of the three-parameter type of equation (primarily the constancy of the free-carrier concentrations) are shown to apply. Although similar conclusions were arrived at in earlier work, using approximations, this is the first time that this has been demonstrated using exact solutions to the appropriate rate equations without the restrictive assumptions. The ability of Eqs. (6)—(8) to describe an experimental glow-curve shape should not, therefore, be contemplated as a test of the applicability of the simplified energy-level scheme in any given material.

(ii) The activation energy calculated from a fit of the three-parameter type of equation of the glow curve is not straightforward to interpret. For the case where e-h transitions are radiative,, the fitting procedure yields a value for the electron trap depth if $E_1 < E_2$, and vice versa if the h-e transitions are radiative. However, if the trap depth of the opposite charge carrier is low (i.e., $E_2 < E_1$), an inaccurate figure is obtained.

The initial-rise method of analysis, however, is easier to interpret. If only e-h transitions are radiative, a good value for the trap depth of the electron trap is obtained. The method gives the hole trap depth if h-e transitions produce luminescence. If both transitions are radiative, the trap depth of the least thermally stable trap is obtained.

The heating-rate method always produces a value (albeit 5—10 % inaccurate) for the activation energy of the least stable trap irrespective of the radiative transition involved.

Wintle[22] has advocated the use of both the initial-rise and the heating-rate methods for phosphors in which thermal quenching is taking place. For the Schön-Klasens model for thermal quenching, according to Wintle's arguments, the heating-rate method should yield the electron trap depth, if e-h transitions yield TL, and the initial-rise method should give the *difference* between the electron trap depth and the hole trap depth. However, Wintle only introduces the temperature dependence of the luminescence efficiency into the TL equation *after* this equation has been derived, when, in fact, it ought to be introduced before the derivation by accounting for it in the original rate equations. When this is done, as performed by Bräunlich and Scharmann[14] and in this work, the true meaning of the discrepancy between the results of the initial-rise and heating-rate methods comes to light, as discussed above. If independent evidence exists regarding which transition produces the luminescence, then, by a careful application of the initial-rise and heating-rate methods, one should be able to calculate at least one of the two trap depths, and, in favorable circumstances, both of them.

(iii) Although it is possible to describe the glow peak produced using the Schön-Klasens model by the conventional three-parameter form of equation, it is *not* possible, using this equation, to predict confidently the long-term thermal stability of the TL peak. Often such analyses are used as a means of assessing the thermal-decay characteristics of a TL signal in many different fields. However, the present analysis indicates that this is an unsatisfactory procedure.

(iv) Finally, the present work highlights the importance of using several different techniques to calculate the trap depths from a set of glow curves. In particular, curve fitting, the initial-rise method, the heating-rate method, and isothermal-decay analysis should all be carried out. Only when good agreement between each of these methods is achieved [as appears to be the case, for example, in LiF:Mg (Refs. 23—25)] can one be reasonably certain that the Schön-Klasens energy-level scheme does not apply. If, on the other hand, these methods yield different results (e.g., in quartz[22,26]), then one should suspect that a more complex energy-level scheme such as the Schön-Klasens model may be more appropriate. In such instances, independent evidence regarding thermal quenching, etc.[3] should be sought before any interpretations are attempted.

*Permanent address: Department of Physics and Astronomy, Tel-Aviv University, Ramat-Aviv, 69978 Tel-Aviv, Israel.

[1] R. Chen and Y. Kirsh, *Analysis of Thermally Stimulated Processes* (Pergamon, Oxford, 1981).

[2] *Thermally Stimulated Relaxation in Solids*, edited by P. Bräunlich (Springer, Berlin, 1979).

[3] S. W. S. McKeever, *Thermoluminescence of Solids* (Cambridge University Press, Cambridge, 1985).

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

[5] J. T. Randall and M. H. F. Wilkins, Proc. R. Soc. London, Ser. A 184, 390 (1945).

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

[7] C. E. May and J. A. Partridge, J. Chem. Phys. 40, 1401 (1964).

[8] J. Gasiot and J. P. Fillard, J. Appl. Phys. 48, 3171 (1982).

[9] J. P. Fillard, J. Gasiot, and J. C. Manifacier, Phys. Rev. B 18, 4497 (1978).

[10] J. P. Fillard, J. Gasiot, J. Jimenez, L. F. Sanz, and J. A. De Saja, J. Electrost. 3, 133 (1977).

[11] M. Schön, J. Phys. Radium 17, 689 (1956).

[12] M. Schön, Z. Phys. 119, 463 (1942).

[13] H. A. Klasens, Nature (London) 158, 306 (1946).

[14]P. Bräunlich and A. Scharmann, Phys. Status Solidi 18, 307 (1966).

[15]P. Kelly, M. J. Laubitz, and P. Bräunlich, Phys. Rev. B 4, 1960 (1971).

[16]S. W. S. McKeever, R. Chen, P. J. Groom, and S. A. Durrani, Nucl. Instrum. Methods 175, 43 (1980).

[17]R. Chen, S. W. S. McKeever, and S. A. Durrani, Phys. Rev. B 24, 4931 (1981).

[18]D. Shenker and R. Chen, J. Comput. Phys. 10, 272 (1972).

[19]R. Chen, V. K. Mathur, Joanne, F. Rhodes, M. D. Brown, S. W. S. McKeever, and R. K. Bull, Phys. Status Solidi B 126, 361 (1984).

[20]P. W. Levy, Radiat. Eff. 72, 259 (1983).

[21]W. Hoogenstraaten, Philips Res. Rep. 13, 315 (1958).

[22]A. G. Wintle, Geophys. J. R. Astron. Soc. 41, 107 (1975).

[23]S. W. S. McKeever, Phys. Status Solidi A 62, 331 (1980).

[24]G. C. Taylor and E. Lilley, J. Phys. D 11, 567 (1978).

[25]R. G. Fairchild, P. L. Mattern, K. Lengweiler, and P. W. Levy, J. Appl. Phys. 49, 4523 (1978).

[26]P. W. Levy, PACT (Journal of the European Study Group on Physical, Chemical and Mathematical Techniques Applied to Archeology) 3, 466 (1979).