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Generalized description of thermally stimulated processes without the quasiequilibrium approximation

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An alternative mathematical description of thermally stimulated luminescence (TL) and thermally stimulated conductivity (TSC) is presented without the restrictions of the quasiequilibrium (QE) and kinetic-order (KO) approximations. The development is carried out within the framework of a model consisting of a single active trap in the presence of a large concentration of deep, thermally disconnected traps and recombination centers. The QE and KO approximations are removed and replaced by two new functions, $Q(T)$ and $P(T)$, both rigorously defined in terms of trap emptying and filling processes. The resulting generalized equations are capable of continuously describing the behavior of systems over a wide range of kinetic cases and very far from QE. From these, generalized initial-rise and Hoogenstraaten equations are derived from which previously unknown correction terms are identified. In addition, a modified version of the initial-rise analysis is presented and its range of validity addressed. The formalism presented provides much insight in that one may describe clearly the effects of common approximations and estimate if such approximations are warranted. Other results include a physical justification for why first-order (slow-retrapping) processes dominate in nature, a general TL-TSC relationship, the realization that the QE approximation is only valid at the temperature of the TSC peak maximum, and an experimental method for determining the shape of the $Q(T)$ function. The applicability of this analysis is illustrated using numerical solutions of the differential rate equations.

I. INTRODUCTION

The usual analysis of thermally stimulated luminescence (or thermoluminescence, TL) and thermally stimulated conductivity (TSC) are based on the traditional description of these processes discussed more than 40 years ago by Randall and Wilkins[1] and Garlick and Gibson.[2] The simplest model of the type discussed by these authors consists of a single localized state for electrons and one for holes. Charge trapped at these levels may be thermally freed and eventually undergo recombination. While in the delocalized bands, the free carriers give rise to transient conductivity (TSC) and during recombination they may yield luminescence (TL). Electrons are normally assumed to be the thermally freed carriers and to recombine with trapped holes in a Shockley-Read process, although the concept of free holes recombining with trapped electrons is equally acceptable.

Several theoretical exercises have been undertaken to examine the expected TL and TSC profiles. Early theories dealt only with the simplistic model described above (e.g., Haering and Adams[3] and Halperin and Braner[4]), but later analysis introduced an extra, thermally disconnected electron energy level (e.g., Dussel and Bube[5] and Saunders[6]) and continuous distributions of traps.[7] The work in TL and TSC theory is extensive with much work presented in the literature[8-14] and extensive review articles published.[15-17] Essentially, however, the fundamental approach has remained unchanged.

Common to all the above treatments is the establishing of models consisting of various traps and recombination centers consistent with charge neutrality. Models such as these provide a framework from which a phenomenological theory of TL and TSC can be presented, and thus one may qualitatively understand complicated TL and TSC spectra. However, it has been the quantitative understanding that has thus far been elusive. Once a model has been assumed, rate equations are developed that describe, in terms of the fundamental system parameters, the traffic of charge out of and into the various traps and delocalized bands. In principle, the solution of these equations may lead to expressions for the TL and TSC curves, comparison of which with experimental data may provide information concerning the fundamental trapping parameters. In practice, however, the rate equations usually become intractable (i.e., cannot be decoupled) so that exact analytical solutions are unobtainable for even the simplest of systems. Consequently, in all previous treatments approximations were used to obtain analytical solutions. From these approximate solutions, procedures were developed to determine the trapping parameters. The most common of these are the initial-rise analysis,[2] the heating rate method of Hoogenstraaten[18] and direct peak fitting (e.g., Mohan and Chen[19]). A whole array of other procedures involving the use of peak symmetries, inflection points, half-peak values, etc., have also been developed and have been reported in the literature.[15-22] The motivation for the development of these various procedures has been to obtain information concerning the fundamental trapping parameters from experimental TSC and/or TL spectra.

The problem of determining trapping parameters from TL and TSC has been the subject of several studies that employ direct numerical solutions of the rate equations. The conclusions reached are indeed pessimistic. The work of the Kelly, Laubitz, and Bräunlich[11] (and earlier work by Kelly and Bräunlich[9,10]) and also the work of Shenker and Chen[12] are of particular interest. Essentially these researchers concluded that as the theory presently stands, isolated measurements of thermally stimulated processes are valueless for determining trapping parameters. This conclusion was based partly on the fact that oversimplified models were used in the development of standard analysis techniques and partly on the fact that even within the framework of these simplified models parameter ranges could be found over which the approximate solutions simply are not adequate. A degree of "degeneracy" was also noticed, that is, it was found possible to analyze TL and TSC spectra based on any one of several models and obtain parameters that yield very similar TL or TSC curves.[11] Based on this evidence they conclude that unless a realistic model is known beforehand and unless at least some of the associated parameters are reasonably well known, isolated measurements of TL and/or TSC will not be very informative.

Reviewing the literature one finds that essentially the problem is threefold consisting of the following drawbacks.

1. *The model*: The simple model involving a single electron (or hole) level and a single recombination center with constant parameters from which most analysis techniques are based is inadequate. This model fails to describe the rich variety of experimentally observed TL and TSC phenomena.

2. *The inability of obtaining exact analytical solutions*: Because of the nonlinear coupling of the rate equations, exact analytical solutions have not been possible for even the simplest of models. Numerical studies have called into question the validity of the quasiequilibrium (QE) approximation which, when applied, effectively decouples the rate equations. The QE approximation is difficult to justify physically and, in fact, has never been shown to be rigorously applicable to any known system. In addition to this approximation, traditional presentations usually develop the equations into very specific cases in which one expresses the degree by which recombination processes dominate over retrapping (or vice versa) and in this way introduce the concept of kinetic order (KO). While it may be true for a particular TL or TSC peak that recombination or retrapping dominates over certain temperature ranges, this condition cannot be made *a priori*. Attempts have been made to generalize the concept of kinetic order by the introduction of a kinetic-order parameter[23,24] or by the introduction of mixed-order solutions that contain parameters to be adjusted so as to achieve an optimal fit of experimental data.[13,14] While this approach has been successful in the fitting of certain peak shapes, all physical meaning is lost. The concept of kinetic order may be of some use by itself, however, when used in conjunction with the QE approximation it serves only to compound the problem, since it is not at all clear whether these approximations are self consistant for any given system or over the entire temperature range of trap emptying.

3. *Analysis procedures*: Finally, since the analysis procedures used to obtain trapping parameters are derived from within the context of the QE and/or kinetic-order (KO) approximations, the validity of these approximations calls into question the validity of the analysis procedures. All methods that are developed from approximate solutions are susceptible to the breakdown of these approximations to one degree or another, and, since no truly general formal description exists, the degree of this breakdown has yet to be firmly established. This effect is no doubt responsible, in many cases, for the large variation in parameter values obtained from the different analytical methods. A possible exception is the initial-rise procedure, which has been shown in numerical studies to be widely applicable and somewhat consistent.[11] It is known that the initial-rise method is independent of KO and why this is so.[17] However, it is not known if this method is dependent on the QE approximation.

Clearly, if the problem is to be understood to any acceptable degree a truly general, formal description must be made available. In order to achieve this one must abandon the rigidity of the QE and KO approximations and present a mathematical description that is capable of dealing with intermediate cases. Any general description must be developed within the framework of a model that is flexible enough to support a wide variety of TL and TSC phenomena and would thus be capable of adequately predicting TL and TSC curves over wide variations of the fundamental parameters. It is to be accepted, however, that no single model exists that will explain all TL and TSC phenomena.

The purpose of this paper is to present an alternative mathematical description by the development of generalized forms of the TL and TSC equations. Instead of dealing only with the specific cases that the QE and KO approximations necessarily require, solution forms will be arrived at without these restrictions. Abandoned is the rigid concept of QE as an approximation. Its replacement consists of a physically meaningful and, in principle, experimentally measurable function [the $Q(T)$ function] rigorously defined in terms of trap emptying and filling processes. A kinetic-order function [the $P(T)$ function] is introduced and also defined in terms of physically meaningful processes. It significance as a measure of the degree of retrapping is retained; however, its generalization to a function allows for the kinetic order of a process to vary as traps are emptied. The removal of these approximations results in generalized equation forms that are capable of continuously describing a wide range of kinetic cases. From these, generalized initial-rise and Hoogenstraaten equations are derived. The approach is to first derive generalized expressions and then show that they reduce to the more familiar equations under various common approximation sets. In this way one is able to describe clearly the effects of certain approximations and estimate if such approximations are warranted, thus providing insight as to the range of validity of the simplified forms.

II. THE MODEL

The choice of a model places restrictions on the type and variety of TL and TSC phenomena that are possible and in itself represents a significant assumption. However, since it is impossible to develop any analysis procedure independent of the framework of a model, its choice becomes vitally important.

The model chosen here closely resembles one first considered by Dussel and Bube[5] and later by Saunders[6] and is shown schematically as Fig. 1. A model of this type was chosen because it has been used in the past to develop the traditional TL and TSC equations and, therefore, allows for the direct comparison of the results obtained here with those of previous authors. The model consists of the following types of levels: (1) the active electron traps (AT's), (2) a distribution of shallow electron traps (ST's), (3) a distribution of deep, thermally disconnected electron traps (DET's), and (4) a distribution of deep, thermally disconnected hole traps (DHT's).

The top of the valence band is denoted E_v, the concentration of free holes is $h_v(T)$, the bottom of the conduction band is denoted E_c, and the concentration of free electrons is $n_c(T)$. The Fermi energy, E_F, is located schematically in the center of the band gap.

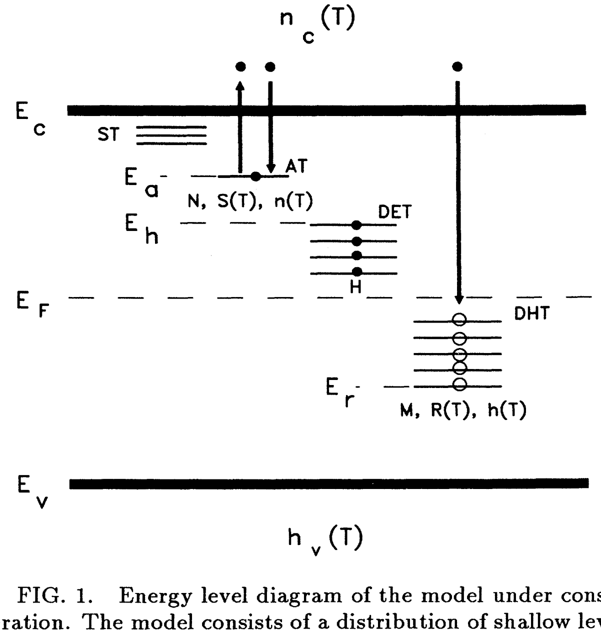

FIG. 1. Energy level diagram of the model under consideration. The model consists of a distribution of shallow levels (ST's), the active level (AT) at energy E_a, a distribution of deep thermally disconnected electron traps (DET's) from energies E_F to E_h, and a distribution of thermally disconnected hole traps (DHT's) from energies E_r to E_F.

The active electron traps are assumed to be of one defect type. They exist in concentration N and are located at energy E_a, thus having activation energy E, where $E = E_c - E_a$. Both E and N are assumed to be singular and temperature independent. The active temperature range (T_0–T_f) is defined as the temperature range over which these traps are thermally active, meaning that thermally induced transitions out of these traps are highly probable. Transitions taking place over the active temperature range will be the ones of primary interest in this paper. These traps are further characterized by the temperature-dependent functions $n(T)$ and $S(T)$, where the former represents the concentration of full traps and the latter represents the electron-capture cross section at any temperature T.

Shallow electron traps may exist as several defect types, but since the activation energies of these levels are less than E, these traps are empty over the active temperature range and do not constitute stable retrapping centers. For this reason they play little or no role in the later thermally induced redistribution of charge.

The remaining traps constitute all the remaining defect types responsible for the introduction of levels farther into the band gap. Over the active temperature range these levels are thermally disconnected, meaning that the probability of carrier release from these traps is negligible. Those levels having energies less than some energy E_h, where $E_h < E_a$, but greater than E_F, form a distribution of levels collectively labeled as the deep thermally disconnected electron traps. H characterizes the total concentration of these levels and is defined by

$$H = \int_{E_F}^{E_h} G(E)dE, \tag{1}$$

where $G(E)$ is the density of states function. Those levels with energy less than E_F but greater than some energy E_r form a distribution of levels collectively labeled as the deep thermally disconnected hole traps. M is the total concentration of these levels and is defined by the relation

$$M = \int_{E_r}^{E_F} G(E)dE. \tag{2}$$

It will be assumed that $E_c - E_a$ is less than $E_r - E_v$, so that over the active temperature range little or no simultaneous hole release is possible. By excluding direct band-to-band recombination as well, these hole traps function as the recombination centers for the system during the trap emptying process. These centers are further characterized by the temperature-dependent functions $h(T)$, the total concentration of full hole traps and $R(T)$, the average capture cross-section for electrons (i.e., the recombination cross-section). Formally $R(T)$ is given by

$$R(T) = \frac{1}{M} \sum_i M_i\, r_i(T), \tag{3}$$

where M_i is the concentration of hole traps of defect type i, and $r_i(T)$ is the capture cross section for electrons of a hole trap of defect type i. The sum is over all defect types that lead to energy levels less than E_F. Finally, this model requires that the concentration of trapped holes be somewhat greater than the concentration of trapped electrons so that over the active temperature range the deep electron traps remain full and therefore do not constitute retrapping centers for free electrons. This configuration means that the existence of deep electron traps enters the formalism only through the neutrality condition.

It should be noted that the establishment of a model that makes electrons the freed carrier during the trap emptying process in no way reduces the generality of the theoretical results as it pertains to carrier type. The theory of TL and TSC is essentially symmetric with respect to carrier type, and one could therefore define an analogous model making holes the freed carrier type during trap emptying.

III. THE THEORY

The particular scenario of interest is the following. The system, held at a temperature lower than T_0, is subjected to external excitation (illumination or radiation) of energy greater than the band gap. This excitation induces transitions across the band gap creating a large concentration of free electrons and holes, which then relax into the various traps. Trap filling is continued in this way until equilibrium is achieved (this ensures complete filling of the deep electron traps). The excitation is then removed and the system is heated according to a linear heating profile, $dT/dt \equiv \beta$, in the dark.

During heating the trap emptying process begins as electrons are thermally excited out of the shallow levels. However, over the active temperature range, the allowed transitions, as indicated in Fig. 1, show that electrons are excited into the conduction band from the active level with free carrier removal proceeding along two possible pathways, recombination and retrapping. Since the deeper electron traps do not empty until temperatures well past the active range, these traps remain full and therefore do not constitute potential trapping sites. Hence, transitions into these traps are forbidden. The thermal release probability function per unit time, $\mathcal{P}(T)$, is given by[1]

$$\mathcal{P}(T) = s(T) \exp\left(-\frac{E}{kT}\right), \tag{4}$$

where $s(T)$ is the frequency factor, E is the previously defined trap depth, T is the absolute temperature, and k is Boltzmann's constant.

In general, for any temperature range, the concentration of free and trapped electrons must equal the concentration of free and trapped holes, that is, charge neutrality must be preserved. For temperatures greater than T_0 this condition is expressed

$$n_c + n + H = h + h_v, \tag{5}$$

where all terms except H are temperature dependent. For convenience, notation expressing explicit temperature dependence has been suppressed. This practice will be used throughout the paper except when a symbol is first introduced or where it is necessary to avoid confusion or to highlight arguments where temperature dependency is explicitly being addressed.

If attention is restricted to include only the active temperature range, then a final assumption can be made. One may assume that

$$n + H \gg n_c - h_v, \tag{6}$$

since, in the active temperature range $h_v = 0$, this approximation consists of assuming that over this range the concentration of trapped electrons is always much greater than the concentration of free electrons. This approximation does not severely limit the applicability of this model, since in most physical systems the concentration of traps actually active at any temperature is small compared with the concentration of deeper inactive traps. With this approximation, Eq. (5) becomes

$$h \approx n + H, \tag{7}$$

meaning that the concentration of available hole centers must at least be equal to $N + H$. The recombination lifetime, τ, is then given by

$$\frac{1}{\tau(T)} = v_e(T) h R \approx v_e(T) R(n + H), \tag{8}$$

where v_e is the thermal velocity of an electron in the conduction band and is given approximately by

$$v_e = \sqrt{\frac{3kT}{m^*}}, \tag{9}$$

where m^* is the effective electron mass.

The rate equations governing the detrapping of charge over the active temperature range are[3]

$$\frac{dn}{dt} = -nN_c(T)Sv_e \exp\left(-\frac{E}{kT}\right) + n_c(N - n)Sv_e \tag{10}$$

and

$$\frac{dn_c}{dt} = -\frac{dn}{dt} - \frac{n_c}{\tau}, \tag{11}$$

where N_c is the effective density of states for the conduction band and is given by

$$N_c = 2\left(\frac{kTm^*}{2\pi\hbar^2}\right)^{3/2}, \tag{12}$$

where $\hbar$ is Planck's constant divided by 2π.

Equations (10) and (11) form a set of first-order, nonlinear, coupled differential equations. Since it is not possible to decouple them, these equations have no known, closed-form, analytical solution. At this point it will be worthwhile to briefly summarize the approximate solutions.

A. Summary of the approximate TL and TSC solutions

The first approximation made is that of quasiequilibrium. Formally this is expressed as

$$\frac{dn_c}{dt} \ll \frac{n_c}{\tau}, \tag{13}$$

or from Eq. (11) as

$$\frac{dn}{dt} \approx -\frac{n_c}{\tau}, \tag{14}$$

meaning that the overall rate of change of the concentration of free electrons is small compared to the rate of recombination. With this approximation one arrives at

$$n_c = \frac{n(T)\,(N_c S v_e)}{1/\tau + [N - n(T)]Sv_e} \exp\left(-\frac{E}{kT}\right), \tag{15}$$

from which, using $I_{\mathrm{TSC}}(T) = AFe\mu(T)n_c(T)$ and $I_{\mathrm{TL}}(T) = \eta n_c(T)/\tau(T)$ one gets

$$I_{\mathrm{TSC}} = \frac{AFe\mu ns}{1/\tau + (N-n)Sv_e} \exp\left(-\frac{E}{kT}\right), \tag{16}$$

$$I_{\mathrm{TL}} = \frac{\eta ns}{\tau(1/\tau + (N-n)Sv_e)} \exp\left(-\frac{E}{kT}\right), \tag{17}$$

where e is the modulus of the electronic charge, $\mu(T)$ is the electron mobility (which in general is temperature dependent; however, its temperature dependency is often weak and is usually ignored), A is the effective electrode area, F is the magnitude of any applied electric field, and η is the luminous efficiency of the recombination process (≤ 1). Also the frequency factor has been written as

$$s(T) = N_c(T)S(T)v_e(T). \tag{18}$$

Further approximations are normally introduced at this stage concerning the relative rates of retrapping and recombination. The results for the three cases usually considered are

(i) *Slow retrapping (first order),* $\tau^{-1} \gg (N-n)Sv_e$:

$$I_{\mathrm{TSC}} = AFe\mu\tau n_0 s(T) \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{1}{\beta}\int_{T_0}^{T} s(\Theta)\exp\left(-\frac{E}{k\Theta}\right) d\Theta\right], \tag{19}$$

$$I_{\mathrm{TL}} = \eta n_0 s(T) \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{1}{\beta}\int_{T_0}^{T} s(\Theta)\exp\left(-\frac{E}{k\Theta}\right) d\Theta\right], \tag{20}$$

(ii) *retrapping,* $\tau^{-1} = (N-n)Sv_e$:

$$I_{\mathrm{TSC}} = AFe\mu\tau n_0 \frac{s(T)}{2} \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{1}{2\beta}\int_{T_0}^{T} s(\Theta)\exp\left(-\frac{E}{k\Theta}\right) d\Theta\right], \tag{21}$$

$$I_{\mathrm{TL}} = \eta n_0 \frac{s(T)}{2} \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{1}{2\beta}\int_{T_0}^{T} s(\Theta)\exp\left(-\frac{E}{k\Theta}\right) d\Theta\right], \tag{22}$$

and (iii) *fast retrapping,* $\tau^{-1} \ll (N-n)Sv_e$:

$$I_{\mathrm{TSC}} = AFe\mu n_0 \frac{N_c}{N} \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{1}{\beta N}\int_{T_0}^{T} \frac{N_c}{\tau}\exp\left(-\frac{E}{k\Theta}\right) d\Theta\right], \tag{23}$$

$$I_{\mathrm{TL}} = \frac{\eta}{\tau} n_0 \frac{N_c}{N} \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{1}{\beta N}\int_{T_0}^{T} \frac{N_c}{\tau}\exp\left(-\frac{E}{k\Theta}\right) d\Theta\right]. \tag{24}$$

In the above equations n_0 is the initial concentration of electrons trapped at the active level. For the fast-retrapping case it has to be assumed that $n_0/N \ll 1$.

From these equations further analytical procedures have been developed to arrive at estimates of the activation energy. It should be recognized that each of the above equations reduces to

$$I = \text{const} \times \exp\left(-\frac{E}{kT}\right) \tag{25}$$

when $T \approx T_0$, where I is the TL or TSC intensity during the initial rise part of the TL or TSC peak. This recognition led to the development of the initial-rise analysis, since a plot of $\ln(I)$ versus $1/T$ over the initial rise part of the peak would result in a straight line of slope $-E/k$ (Ref. 2).

Similarly, Hoogenstraaten[18] made use of the observation that the temperature of the TL or TSC peak maximum, T_m, shifted to higher values as the heating rate is increased. By setting $dI(T)/dT = 0$ at T_m for the slow-retrapping case, he showed that

$$\ln\left(\frac{T_m^2}{\beta}\right) = \frac{E}{kT_m} - \ln\left(\frac{E}{ks}\right), \tag{26}$$

where it was assumed that the frequency factor is constant.

It has been recognized for some time that in reality TL or TSC signals may not be described adequately by the set of assumptions described above. The QE approximation is particularly contentious in that it places stringent restrictions upon how the model will behave. The conclusion of the numerical studies was that the QE approximation is only valid in special sets of circumstances and does not have any general validity.[9-12]

B. The general TL and TSC equations

As already mentioned, the QE approximation is difficult to justify physically. Thus, instead of this approximation, we introduce the quasiequilibrium function, $q(T)$, defined by the relation

$$q(T)\left(\frac{n_c}{\tau}\right) \equiv \frac{dn_c}{dt}. \tag{27}$$

Using Eq. (11), this can be written as

$$Q(T)\left(\frac{n_c}{\tau}\right) = -\frac{dn}{dt}, \tag{28}$$

where $Q(T) \equiv q(T) + 1$. The form and properties of the $Q(T)$ function will be of great importance in the generalized theory of TL and TSC. So as not to disrupt the continuity of the present derivation, detailed discussion of the $Q(T)$ function will be left to a later section.

Using Eq. (10) in Eq. (28), one can solve for n_c yielding

$$n_c = \frac{n\,(N_c S v_e)}{Q/\tau + (N-n)Sv_e} \exp\left(-\frac{E}{kT}\right). \tag{29}$$

Substituting n_c back into Eq. (28) produces,

$$\frac{1}{n}\frac{dn}{dt}[Q + \tau(N-n)Sv_e] = -Q(N_c S v_e)\exp\left(-\frac{E}{kT}\right), \tag{30}$$

which is a differential equation in $n(T)$ only.

It is at this point that one traditionally develops the equations using specific values for the kinetic order. However, these separate cases can be unified by the definition of the kinetic-order function, $P(T)$, defined by the relation

$$P(T) \equiv \tau(N-n)Sv_e. \tag{31}$$

Just as for the $Q(T)$ function, the form and properties of $P(T)$ will play an important role in the generalized description of TL and TSC; however a detailed analysis of the $P(T)$ function will again be left for a later section.

Using the definitions of both $Q(T)$ and $P(T)$ along with Eq. (8), Eq. (29) can be written as

$$n_c = \frac{S}{R}\frac{N_c}{Q+P}\frac{n}{n+H}\exp\left(-\frac{E}{kT}\right) \tag{32}$$

and Eq. (30) as

$$\frac{1}{n}\frac{dn}{dT} = -\frac{Q\,(N_c S v_e)}{\beta\,(Q+P)}\exp\left(-\frac{E}{kT}\right). \tag{33}$$

Integration of this equation gives

$$n = n_0 \exp\left[-\frac{1}{\beta}\int_{T_0}^{T}\left(\frac{Q(\Theta)}{Q(\Theta)+P(\Theta)}\right) s(\Theta)\exp\left(-\frac{E}{k\Theta}\right) d\Theta\right]. \tag{34}$$

Substitution of Eq. (34) into Eq. (32) to yield an expression for n_c can now be accomplished. Before this is done, however, it is useful from an operational standpoint, to employ the expansion

$$\frac{n}{n+H} = \sum_{j=1}^{\infty}(-1)^{j+1}\left(\frac{n}{H}\right)^j, \tag{35}$$

provided $H > n(T)$. Then with the substitution of Eq. (34), Eq. (32) becomes

$$n_c(T) = \frac{S}{R}\frac{N_c}{Q(T)+P(T)}\exp\left(-\frac{E}{kT}\right)\sum_{j=1}^{\infty}(-1)^{j+1}\left(\frac{n_0}{H}\right)^j \exp[-j\,g(T)],$$

where

$$g(T) = \frac{1}{\beta}\int_{T_0}^{T}\left(\frac{Q(\Theta)}{Q(\Theta)+P(\Theta)}\right) s(\Theta)\exp\left(-\frac{E}{k\Theta}\right) d\Theta. \tag{36}$$

Since I_{TSC} is related to $n_c(T)$ by $Ae\mu(T)F$, Eq. (36) could be properly referred to as the general form of the general order TSC equation for a single level system in the presence of thermally disconnected traps.

The number of terms used in the series to accurately represent a TSC peak depends on the relative magnitude of n_0 to H and on the magnitude of $g(T)$. Since $g(T)$ appears in the exponential, its magnitude is the chief determining factor in establishing rate of convergence. The fact that $g(T)$ is evolving in temperature, growing larger as T is increased, means that the number of terms taken to describe the peak shape will change as different temperature regions are sampled. Generally speaking, however, the lower the temperature, the more terms will be needed. For example if T is close to T_0, $g(T)$ is approximately zero, and the expansion will need all the terms becoming $n_0/(n_0+H)$. If $T \gg T_0$, then $g(T)$ will take on larger values, meaning that the series could accurately be approximated by the first term, becoming $(n_0/H)\exp[-g(T)]$. In general, however, one expects this series to always converge rather quickly.

To arrive at an expression for TL it is unnecessary to specify τ, and for this reason the general expression for TL takes on the simpler form

$$I_{\rm TL} = \eta\left(\frac{n_c}{\tau}\right) = \eta\,\frac{ns}{Q+P}\,\exp\left(-\frac{E}{kT}\right); \tag{37}$$

then using Eq. (34) results in

$$I_{\rm TL}(T) = \eta n_0\,\frac{s(T)}{Q(T)+P(T)}\,\exp\left(-\frac{E}{kT}\right)\,\exp[-g(T)]. \tag{38}$$

Equation (38) represents the general form of the general order TL equation for a single level system in the presence of thermally disconnected traps. It should be noticed that, since it is not necessary to specify τ, the $n+H \gg n_c - h_v$ approximation is not needed in its derivation; therefore, this equation is more general than the TSC equation.

Without explicit knowledge of the $Q(T)$ and $P(T)$ functions Eqs. (36) and (38) cannot, as they stand, be used as fitting equations for TL and TSC curves. They do, however, represent general solution forms and will be useful in the understanding of various properties of the system. They will be used as a starting point in the derivation of equations relating to the initial-rise and Hoogenstraaten analysis techniques and in the derivation of reduced forms of the TL and TSC equations obtained under various approximation sets. With respect to reduction under approximations, Eqs. (36) and (38) will form the basis from which one could systematically apply approximations, observe the effects and determine if the approximations are mathematically warranted.

C. The general TL-TSC relationship

From the results of the preceding section a general relationship between TL and TSC can be obtained. Using Eqs. (36) and (38) this relationship can be expressed as

$$I_{\rm TSC}(T) = I_{\rm TL}(T)\,\frac{AFe}{\eta H}\,\frac{\mu(T)}{R(T)v_e(T)} \times \sum_{j=0}^{\infty}\left(-\frac{n_0}{H}\right)^j \exp[-j\,g(T)]. \tag{39}$$

It should be noted that if $H \gg n_0$ (large numbers of thermally disconnected traps or a small initial trap concentration) then one may approximate the series expansion by the first term. Furthermore, if one also assumes that $\mu(T)/[R(T)v_e(T)]$ ≈const then the TL and TSC peaks will have the same peak temperature and indeed will have the same shape. This is in agreement with numerical studies.[10,11] It should also be noted that Eq. (39) can be expressed in closed form as

$$I_{\rm TL}(T) = \eta H\, I_{\rm TSC}(T)\left(\frac{AFe\mu(T)}{R(T)v_e(T)} - \frac{I_{\rm TSC}(T)\,[Q(T)+P(T)]}{s(T)\,\exp(-E/kT)}\right)^{-1}. \tag{40}$$

From Eq. (39) one can easily determine the general form of the recombination lifetime,

$$\tau(T) = \frac{1}{HR(T)v_e(T)}\sum_{j=0}^{\infty}\left(-\frac{n_0}{H}\right)^j \exp[-j\,g(T)]. \tag{41}$$

Considering the case where $T \approx T_0$ then $g(T) \approx 0$ so that the TL-TSC and recombination lifetime expressions become

$$I_{\rm TSC}(T) = \frac{AFe}{\eta(n_0+H)}\,\frac{\mu(T)}{R(T)v_e(T)}\,I_{\rm TL}(T)$$

and (42)

$$\tau(T) = \frac{1}{(H+n_0)R(T)v_e(T)}.$$

If $T \gg T_0$ then $\exp[-g(T)] \approx 0$, and these relations reduce to

$$I_{\rm TSC}(T) = \frac{AFe}{\eta H}\,\frac{\mu(T)}{R(T)v_e(T)}\,I_{\rm TL}(T)$$

and (43)

$$\tau(T) = \frac{1}{HR(T)v_e(T)}.$$

Thus for temperatures close to the high and low limits of the active temperature range, the TL-TSC relationship takes on a particularly simple form with $I_{\rm TSC}$ and $I_{\rm TL}$ being highly correlated differing only by a constant and any temperature dependency $\mu(T)/[R(T)v_e(T)]$ might have. Notice that these limiting expressions are independent of $Q(T)$ and $P(T)$.

D. The $Q(T)$ and $P(T)$ functions

Before proceeding, it will be necessary to discuss in detail the form and properties of the QE and KO functions. The $Q(T)$ function represents an alternative to the QE approximation, however, as conditions of QE are approached Eqs. (14) and (28) show that $Q(T)$ approaches unity. From the definitions of $I_{\rm TL}$ and $I_{\rm TSC}$, $Q(T)$ can be expressed as

$$Q(T) = \frac{\eta\beta}{AFe\mu(T)I_{\mathrm{TL}}(T)} \left(\frac{dI_{\mathrm{TSC}}(T)}{dT} - \frac{I_{\mathrm{TSC}}(T)}{\mu(T)} \frac{d\mu(T)}{dT} \right) + 1. \tag{44}$$

If it is assumed that $\mu(T) = \mu$ =const then this equation becomes

$$Q(T) = \frac{\eta\beta}{AFe\mu I_{\mathrm{TL}}(T)} \frac{dI_{\mathrm{TSC}}(T)}{dT} + 1. \tag{45}$$

It is clear from this equation that $Q(T_{\mathrm{mc}}) = 1$, where T_{mc} is the temperature of the TSC peak maximum. Using the rate equations, $Q(T)$ can also be expressed as

$$Q(T) = \frac{S}{R(n+H)} \left[\frac{nN_c}{n_c} \exp\left(-\frac{E}{kT}\right) + n - N \right]. \tag{46}$$

Note that during the initial rise of a TL or TSC peak, $n(T) \approx n_0$ and $n_c(T) \approx 0$, therefore Q(T) starts at infinity for T close to T_0 and drops quickly to unity as the peak temperature is approached. The above equation can be rewritten in the form

$$Q(T) = \frac{1}{R_{\mathrm{recom}}(T)} [R_{\mathrm{ex}}(T) - R_{\mathrm{recap}}(T)], \tag{47}$$

where

$R_{\mathrm{recom}}(T) \equiv$ the rate of recombination $= n_c/\tau = n_c v_e R(n+H)$,

$R_{\mathrm{ex}}(T) \equiv$ the rate of excitation $= n(N_c S v_e) exp(-E/kT)$,

$R_{\mathrm{recap}}(T) \equiv$ the rate of trap recapture $= n_c(N-n)Sv_e$.

Note that $R_{\mathrm{recom}}(T)$, $R_{\mathrm{ex}}(T)$ and $R_{\mathrm{recap}}(T)$ are defined so as to be positive quantities. Equation (47) expresses the $Q(T)$ function in terms of physically meaningful processes. There are several points to be noted.

1. The imposition of the QE approximation means setting $Q(T) = 1$ for all T, which in turn means $R_{\mathrm{recom}}(T) = R_{\mathrm{ex}}(T) - R_{\mathrm{recap}}(T)$. So physically speaking, *the QE approximation requires that, for all T, the net rate of charge removal from the active trap must be equal to the rate of removal from the conduction band by recombination processes.*

2. For $\mu(T)$ =const, $Q(T) - 1$ is directly proportional to $(dI_{\mathrm{TSC}}/dT)/I_{\mathrm{TL}}$; therefore, in the case where simultaneous knowledge of TL and TSC is available, *Eq. (45) could be used to experimentally determine the shape of the Q(T) function and test for the applicability of the QE approximation.*

3. For $\mu(T)$ =const, $Q(T_{\mathrm{mc}}) = 1$, in general. Therefore the temperature of the TSC peak maximum can be characterized as that temperature for which $R_{\mathrm{recom}}(T_{\mathrm{mc}}) = R_{\mathrm{ex}}(T_{\mathrm{mc}}) - R_{\mathrm{recap}}(T_{\mathrm{mc}})$ holds, meaning that *the QE approximation is only valid at the temperature of the TSC peak maximum.*

The $P(T)$ function represents a generalization of the concept of kinetic order. From Eqs. (8) and (31) the $P(T)$ function can be written as

$$P(T) = \frac{S}{R} \frac{(N-n)}{(n+H)} = \frac{R_{\mathrm{recap}}(T)}{R_{\mathrm{recom}}(T)}. \tag{48}$$

Thus, unlike previous treatments involving kinetic order, $P(T)$ maintains a physical interpretation in that it expresses, at any temperature T, the degree by which retrapping processes compare to recombination processes. From Eq. (47) it can be shown that

$$Q(T) + P(T) = \frac{R_{\mathrm{ex}}(T)}{R_{\mathrm{recom}}(T)} \tag{49}$$

and

$$\frac{Q(T)}{P(T)} + 1 = \frac{R_{\mathrm{ex}}(T)}{R_{\mathrm{recap}}(T)}. \tag{50}$$

Thus the $Q(T)$ and $P(T)$ functions provide the functional link between the three processes involved in TL and TSC. The standard kinetic order cases can be considered by making $P(T)$ take on certain *constant* values. From the definition of the $P(T)$ function: $P(T) \ll 1$ for the slow-retrapping (first-order) case, $P(T) = 1$ for the retrapping case, and $P(T) \gg 1$ for the fast-retrapping case.

Before proceeding, it will be informative to discuss briefly, within the context of the $Q(T)$ and $P(T)$ functions, some of the physical implications involved in making the QE and KO approximations.

Consider first the case of a traditional derivation in which both QE and fast-retrapping conditions are assumed. In this case $Q(T) = 1$ and $P(T) \gg 1$. From Eq. (50) it is apparent that for all T, $R_{\mathrm{ex}}(T) \approx R_{\mathrm{recap}}(T)$. If this condition were rigorously true the traps would not empty. Since the traps must empty for some finite T, the only conclusion is that QE and the fast-retrapping approximations do not form a consistent set of approximations over the entire active temperature range. The retrapping case with $Q(T) = 1$ and $P(T) = 1$ requires that $R_{\mathrm{recom}}(T) = R_{\mathrm{recap}}(T)$. While this case would conceivably allow for the emptying of traps, one would always expect $R_{\mathrm{recap}}(T)$ to go to zero before $R_{\mathrm{recom}}(T)$ as the end of the active temperature range is approached. So, while it is unlikely that valid parameter ranges could be found in nature that would exhibit this type of behavior over the entire active temperature range, physical systems may be found that approximate this behavior with discrepancies appearing near the end of the peak. From a physical standpoint, the QE, slow-retrapping combination seems the most plausible. This case requires $Q(T) = 1$ and $P(T) \ll 1$, which then results in $R_{\mathrm{recom}}(T) \gg R_{\mathrm{recap}}(T)$ and $R_{\mathrm{ex}}(T) \gg R_{\mathrm{recap}}(T)$ thus allowing for the emptying of traps at finite T and the physically motivated restriction that $R_{\mathrm{recap}}(T)$ must die off faster than $R_{\mathrm{recom}}(T)$. So, while it should be considered overly restrictive to make assumptions concerning the values of $Q(T)$ and $P(T)$ *a priori* , it should be noted that of the QE and KO cases traditionally considered, the slow-retrapping case best satisfies the basic requirements of any physically realizable system. It is then perhaps no coincidence that the vast majority of observed TL and TSC curves have been categorized as slow-retrapping processes.

With the $Q(T)$ and $P(T)$ functions defined, it is now possible to discuss the reduction of the general TL and TSC equations under some approximations. For the reasons stated above, special consideration will be given to the slow-retrapping approximation. Since the retrapping and fast-retrapping cases can easily be obtained by requiring $P(T) = 1$ or $P(T) \gg 1$, respectively, these results will not be presented.

To consider the slow-retrapping approximation one only needs to set $P(T) = 0$. Doing this in Eq. (36) for TSC and Eq. (38) for TL gives

$$n_c(T) = \frac{SN_c}{RQ(T)} \exp\left(-\frac{E}{kT}\right) \sum_{j=1}^{\infty}(-1)^{j+1}\left(\frac{n_0}{H}\right)^j \exp\left(-\frac{j}{\beta}\int_{T_0}^{T} s(\Theta)\, e^{-E/k\Theta} d\Theta\right), \tag{51}$$

$$I_{\mathrm{TL}}(T) = \frac{\eta n_0 s(T)}{Q(T)} \exp\left(-\frac{E}{kT}\right) \exp\left(-\frac{1}{\beta}\int_{T_0}^{T} s(\Theta)\, e^{-E/k\Theta} d\Theta\right). \tag{52}$$

Note that under these circumstances,

$$I^{\mathrm{QE}}_{\mathrm{TSC}}(T) = Q(T) I_{\mathrm{TSC}}(T)$$

and (53)

$$I^{\mathrm{QE}}_{\mathrm{TL}}(T) = Q(T) I_{\mathrm{TL}}(T),$$

where $I^{\mathrm{QE}}_{\mathrm{TSC}}(T)$ and $I^{\mathrm{QE}}_{\mathrm{TL}}(T)$ are the slow-retrapping TSC and TL functions under conditions of QE. So, under conditions of slow-retrapping, the expressions for TL and TSC obtained with the QE approximation are the same obtained without this approximation modified by a factor $Q(T)$. Furthermore, with Eq. (45) it can be shown that

$$I^{\mathrm{QE}}_{\mathrm{TSC}}(T) = \tau\beta\, \frac{dI_{\mathrm{TSC}}(T)}{dT} + I_{\mathrm{TSC}}(T)$$

and (54)

$$I^{\mathrm{QE}}_{\mathrm{TL}}(T) = \frac{\eta\beta}{AFe\mu}\, \frac{dI_{\mathrm{TSC}}(T)}{dT} + I_{\mathrm{TL}}(T).$$

From Eq. (51) one observes that the ratio n_0/H is instrumental in determining the rate of convergence of this series in the initial rise portion of the peak where $g(T)$ is still close to zero. For systems where the concentration of deep thermally disconnected traps is much greater than the concentration of active levels then $H \gg n_0$ and one could accurately approximate the TSC function for all temperatures by taking just the first term in this series. With this done, it can be shown that the TSC equation will take on the same form as the TL equation (which is invariant under this approximation). This is true regardless of kinetic order.

Equations (51) and (52) represent the TSC and TL expressions for slow-retrapping without the QE approximation. If this approximation is made [by setting $Q(T) = 1$] the TL expression reduces to the Randall and Wilkins form [Eq. (20)]; however, the TSC expression does not. One must, in addition, assume that $H \gg n_0$ in order to obtain the traditional form [Eq. (19)]. This additional requirement is necessary, since the model of Randall and Wilkins does not include deep thermally disconnected traps. Instead, their model assumes a very large concentration of recombination centers as compared to the concentration of full active levels (that is, $h_0 \gg n_0$). The formalism presented here replaces h_0, via charge neutrality, by $H + n_0$. Therefore, the condition that $H \gg n_0$ is equivalent to the requirement that $h_0 \gg n_0$. Of course, the expression for TL does not need this requirement, since for TL it is unnecessary to specify the form of τ.

E. The initial-rise equations

The initial-rise procedure involves the analysis of the relationship between $\ln(I_{\mathrm{TSC}})$ or $\ln(I_{\mathrm{TL}})$ and $1/T$ over the initial-rise portion of the peak. However, this procedure has traditionally been developed within the context of the QE approximation.

To obtain the general form of the TSC initial-rise equation, one starts with the general TSC equation and makes the approximation that $T \approx T_0$. With this approximation, $g(T) \approx 0$ and equation (36) takes the form

$$n_c(T) = \frac{S}{R}\, \frac{N_c}{Q(T) + P(T)} \exp\left(-\frac{E}{kT}\right) \frac{n_0}{n_0 + H}. \tag{55}$$

Similarly for T close to T_0, $P(T)$ becomes

$$P(T) = \frac{S}{R}\, \frac{(N - n_0)}{(n_0 + H)}, \tag{56}$$

so that Eq. (55) can be written as

$$\begin{aligned}\ln[n_c(T)] = {}& \ln(N_c f_0 \alpha) \\ & - \ln[Q(T)(f_0 + \gamma) + \alpha(1 - f_0)] - \frac{E}{kT},\end{aligned} \tag{57}$$

where $f(T) \equiv n(T)/N$, $\alpha(T) \equiv S(T)/R(T)$, and $\gamma \equiv$

H/N. For TL the procedure is much the same. Starting with Eq. (38) and making the $T \approx T_0$ approximation, the resulting TL initial-rise equation is

$$\ln[I_{\rm TL}(T)] = \ln\left(\frac{\eta N_c f_0 \alpha}{\tau_0}\right) - \ln[Q(T)(f_0+\gamma)+\alpha(1-f_0)] - \frac{E}{kT}, \tag{58}$$

where $\tau_0(T) = 1/[v_e(T)R(T)(n_0+H)]$.

These general forms bring to light those terms that could adversely effect the application of the initial-rise procedure. The above equations are similar to the traditional initial-rise equations except that now temperature-dependent correction terms are included. Since this procedure requires that the slope of an Arrhenius plot be considered, it is the temperature dependency of the leading logarithmic terms that introduces errors into the analysis. While the above equations show that the analysis is independent of the amount of retrapping, i.e., the kinetic order, it also shows that the analysis is critically dependent upon the behavior of $Q(T)$. To further demonstrate the effects of the various temperature-dependent terms upon the slope of an Arrhenius plot, it best to consider the form of $d\ln(I)/d\delta$, where $\delta \equiv 1/T$. Under this operation Eqs. (57) and (58) become

$$\frac{d\ln(I_{\rm TSC})}{d\delta} = -\frac{1}{k}\left(\frac{3k}{2\delta} + \frac{k}{Q}\frac{dQ}{d\delta} + E\right) = -\frac{1}{k}E_{\rm eff}^{\rm TSC}(\delta) \tag{59}$$

and

$$\frac{d\ln(I_{\rm TL})}{d\delta} = -\frac{1}{k}\left(\frac{(2-b)k}{\delta} + \frac{k}{Q}\frac{dQ}{d\delta} + E\right) = -\frac{1}{k}E_{\rm eff}^{\rm TL}(\delta), \tag{60}$$

where it has been assumed that $N_c(T) = \text{const} \times T^{3/2}$, $v_e(T) = \text{const} \times T^{1/2}$, $R(T) = \text{const} \times T^{-b}$, $\alpha(T) = \alpha = \text{const}$, $\mu(T) = \mu = \text{const}$, and also that excitation was carried to saturation so that $f_0 = 1$. It should be emphasized that these conditions need not be satisfied over the entire active temperature range but only need to be approximately correct in the initial-rise region.

Equations (59) and (60) show that when one measures the slope of an Arrhenius plot one does not measure E; what is actually measured is $E_{\rm eff}(\delta)$, which is slightly different for TL and TSC. In both cases $E_{\rm eff}$ consists of E plus two temperature-dependent correction terms. The form of these equations suggests an alternative initial-rise method. Rewriting them as

$$-k\left(\frac{d\ln(I)}{d\delta} + \frac{a}{\delta}\right) = \frac{k}{Q}\frac{dQ}{d\delta} + E, \tag{61}$$

where $I = I_{\rm TSC}$ and $a = \frac{3}{2}$ for TSC, and $I = I_{\rm TL}$ and $a = 2-b$ for TL, shows that plotting $-k[d\ln(I)/d\delta + a/\delta]$ versus δ will produce a curve that will be constant (i.e., equal to E) if and only if $(1/Q)dQ/dT \approx 0$. Thus, strictly speaking, the initial-rise analysis is only valid for $Q(T)$ =const, and therefore the QE approximation [$Q(T) = 1$] represents only a special case. In the analysis section examples of TL and TSC curves will be discussed for which $Q(T)$ is approximately constant but > 1 (sometimes $\gg 1$), and in doing so the general validity of the initial-rise method will be addressed.

F. The Hoogenstraaten heating rate analysis

Another important and commonly used analysis technique is that originally developed by Hoogenstraaten.[18] This technique stems from the observation that TL and TSC peak maximum temperatures, $T_{\rm ml}$ and $T_{\rm mc}$ respectively, shift under variations in the heating rate. From the generalized TL and TSC equations one can calculate $dI_{\rm TL}/dT$ and $dI_{\rm TSC}/dT$ and set these equal to zero at the peak maximum temperatures. This procedure for TSC gives

$$\ln\left(\frac{T_{\rm mc}^2}{\beta}\right) = \frac{E}{kT_{\rm mc}} + \ln\left(\frac{E}{ks(T_{\rm mc})}\right) - \ln\left(\frac{H}{n_0\ \exp[-g(T_{\rm mc})]+H}\ \frac{1}{1+P(T_{\rm mc})} + \frac{(d/dT)\ \ln\{[Q(T)+P(T)]R(T)/S(T)\ N_c(T)\}_{T_{\rm mc}}}{[s(T_{\rm mc})/\beta]\ \exp(-E/kT_{\rm mc})}\right), \tag{62}$$

and the same procedure for TL yields

$$\ln\left(\frac{T_{\rm ml}^2}{\beta}\right) = \frac{E}{kT_{\rm ml}} + \ln\left(\frac{E}{k\ s(T_{\rm ml})}\right) - \ln\left(\frac{Q(T_{\rm ml})}{Q(T_{\rm ml})+P(T_{\rm ml})} + \frac{(d/dT)\ \ln\{[Q(T)+P(T)]/s(T)\}_{T_{\rm ml}}}{[s(T_{ml})/\beta]\ \exp(-E/kT_{\rm ml})}\right). \tag{63}$$

Use was made of the fact that $Q(T_{\rm mc}) = 1$, which from Eq. (44) means that the $\mu(T)$ ≈const assumption was made near $T_{\rm mc}$ [note that $Q(T_{\rm ml})$ does not equal one in general].

Equations (62) and (63) represent the generalized Hoogenstraaten relations. They are to be distinguished from the traditional equation [Eq. (26)] in that they involve no assumptions concerning QE or KO and differ from the traditional forms by a correction term. If one again assumes that $H \gg n_0$ and that $\mu(T)/[R(T)v_e(T)]$ ≈const, then $T_{\rm mc} = T_{\rm ml} = T_m$ [refer to Eq. (39)] and the TL and TSC Hoogenstraaten equations take on the same form. If one then imposes the particular set of assumptions, $s(T)$=s =const,

$Q(T) = Q$ =const (near T_m), and $P(T) \ll 1$ (i.e., slow-retrapping), then the correction terms equate to zero. Thus only under these rather special circumstances do the generalized equations (62) and (63) reduce to the standard form

$$\ln\left(\frac{T_m^2}{\beta}\right) = \frac{E}{kT_m} + \ln\left(\frac{E}{k\,s}\right), \tag{64}$$

valid for both TL and TSC.

If instead of $P(T) \ll 1$, one assumes that $P(T) \approx 1$ (i.e., retrapping), then the equations reduce to

$$\ln\left(\frac{T_m^2}{\beta}\right) = \frac{E}{kT_m} + \ln\left(\frac{2E}{k\,s}\right), \tag{65}$$

valid for both TL and TSC. Thus even in the case where significant retrapping takes place, a plot of $\ln(T_m^2/\beta)$ versus $1/T_m$ will still produce a straight line of slope E/k.

However, if $P(T) \gg 1$(i.e., fast retrapping) then the equations reduce to

$$\ln\left(\frac{T_m^2}{\beta}\right) = \frac{E}{kT_m} + \ln\left(\frac{E\,P(T_m)}{k\,s}\right), \tag{66}$$

for both TL and TSC. In this case some curvature may be observed in the Hoogenstraaten plot.

Thus if $H \gg n_0$ and if both $s(T)$ and $Q(T)$ are approximately constant then the traditional slow-retrapping Hoogenstraaten relation seems to introduce only small errors when applied to cases other than slow retrapping. This cannot be said, in general; however, it is in agreement with the observations of Chen and Winer.[25]

IV. EXAMPLE SOLUTIONS AND FURTHER DISCUSSION

It can be seen from the foregoing sections that the introduction of the $Q(T)$ and $P(T)$ functions does not allow one to actually solve the differential rate equations, but it does allow one to arrive at general forms of the solutions. These general forms are valuable in that one may then make physical arguments about the behavior of $Q(T)$ and $P(T)$ and thereby gain information about the actual solutions in various cases.

To achieve this, various TL and TSC curves have been generated using extreme cases of retrapping and recombination by numerically solving the rate equations. For these cases the shapes and values of the $Q(T)$ and $P(T)$ functions are examined as well as how they vary as functions of the initial level of trap filling n_0 and the heating rate β. Also discussed is how well the initial-rise and Hoogenstraaten analysis hold up under these differing sets of circumstances.

Six different cases based on the relative values of H and N, and S and R were chosen. The actual values for these cases, labeled A through F, are given in Table I and were chosen to span the range from slow to fast retrapping. For all cases the value of E was chosen to be 0.3000 eV, the value of the electron effective mass was chosen to be the free-electron mass and, in addition, power-law temperature-dependent functions were chosen for $S(T)$ and $R(T)$ of the form CT^{-d}; $d = 1.5$ and DT^{-b} ; $b = 1.5$, respectively. For each of these cases TL and TSC curve shapes were calculated as well as their corresponding $Q(T)$ and $P(T)$ functions. Variations in these for changes in n_0 (actually $f_0 = n_0/N$) and β were examined. The cases covered in Table I include $H \gg N$ and $H = N$.

These calculations generated a large amount of data from which several trends could be observed. Figures 2(a)–2(d) show typical results for case A in Table I. Figure 2(a) shows the TL curves, Fig. 2(b) shows the TSC curves, Fig. 2(c) shows the $Q(T)$ function, and Fig. 2(d) shows the $P(T)$ function, as the initial occupancy f_0 varies from 0.005 to 1.0. Figures 3(a)–3(d) show the same data, but with f_0 fixed at 1.0 and β varied from 4.0 K/min to 9.0 K/min. Figures 4(a)–4(d) and Figs. 5(a)–5(d) show similar data generated using the parameters of case F. Cases A and F represent extreme situations of slow and fast retrapping, and therefore comparison of these two data sets will be of particular interest in the discussion. Based on the data the following observations regarding the behavior of the $Q(T)$ and $P(T)$ functions can be made.

For T very close to T_0, $n_c \approx 0$, and R_{recap} and R_{recom} are both approximately zero. In this region $Q(T)$ is very large but is dropping rapidly. $P(T)$ starts off as $S(N-n_0)/R(n_0+H)$, which is zero for $n_0 = N$ ($f_0 = 1$). As T increases slightly past T_0, the value of $Q(T)$ then levels off for temperatures approximately a third of the way into the peak. Over this same region $P(T)$ also re-

TABLE I. Summary of the system parameters used for the calculation of TL, TSC, $Q(T)$, and $P(T)$ curves. Power-law temperature dependencies, $R(T) = DT^{-b}$; $b = 1.5$ and $S(T) = CT^{-d}$; $d =$ 1.5, were assumed for the capture and recombination cross sections.

Case		$H(\mathrm{m}^{-3})$	$N(\mathrm{m}^{-3})$	$D(\mathrm{K}^b\mathrm{m}^2)$	$C(\mathrm{K}^d\mathrm{m}^2)$
A	$(H \gg N,\, S \ll R)$	1.0×10^{12}	1.0×10^{9}	1.0×10^{-15}	1.6×10^{-17}
B	$(H \gg N,\, S = R)$	1.0×10^{12}	1.0×10^{9}	1.6×10^{-17}	1.6×10^{-17}
C	$(H \gg N,\, S \gg R)$	1.0×10^{12}	1.0×10^{9}	1.0×10^{-19}	1.6×10^{-17}
D	$(H = N,\, S \ll R)$	1.0×10^{9}	1.0×10^{9}	1.0×10^{-15}	1.6×10^{-17}
E	$(H = N,\, S = R)$	1.0×10^{9}	1.0×10^{9}	1.6×10^{-17}	1.6×10^{-17}
F	$(H = N,\, S \gg R)$	1.0×10^{9}	1.0×10^{9}	1.0×10^{-19}	1.6×10^{-17}

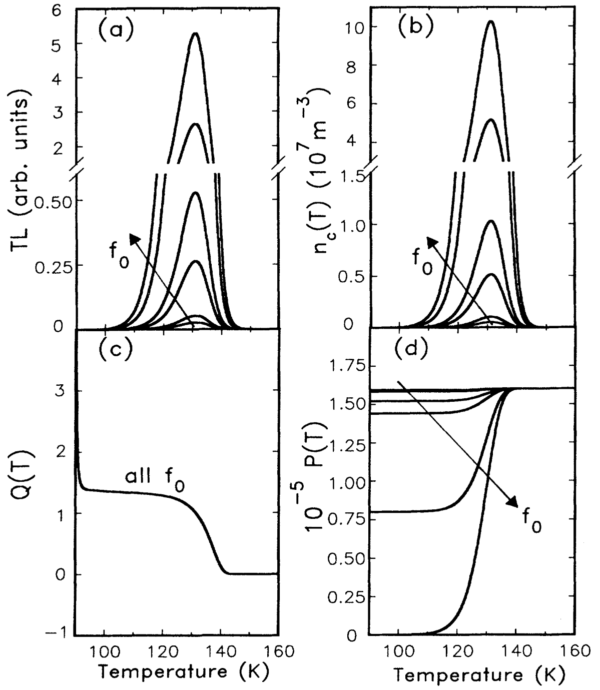

FIG. 2. Curve shapes obtained from numerically solving the differential rate equations (10) and (11) using the parameters of case A. This figure shows (a) TL, (b) $n_c(T)$ (TSC), (c) $Q(T)$, and (d) $P(T)$ for $\beta = 4.0$ K/min with f_0 taking the values 0.005, 0.01, 0.05, 0.1, 0.5, and 1.0.

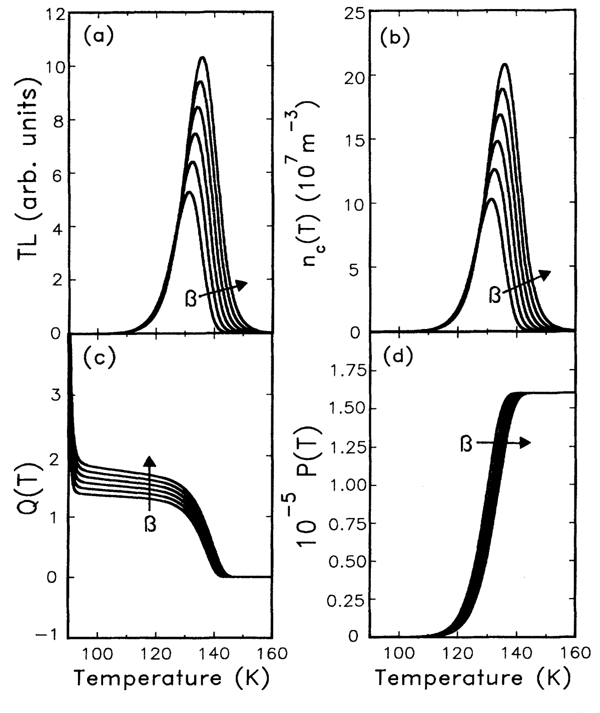

FIG. 3. Curve shapes obtained from numerically solving the differential rate equations (10) and (11) using the parameters of case A. This figure shows (a) TL, (b) $n_c(T)$ (TSC), (c) $Q(T)$, and (d) $P(T)$ for $f_0 = 1.0$ and with β taking the values 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0 K/min.

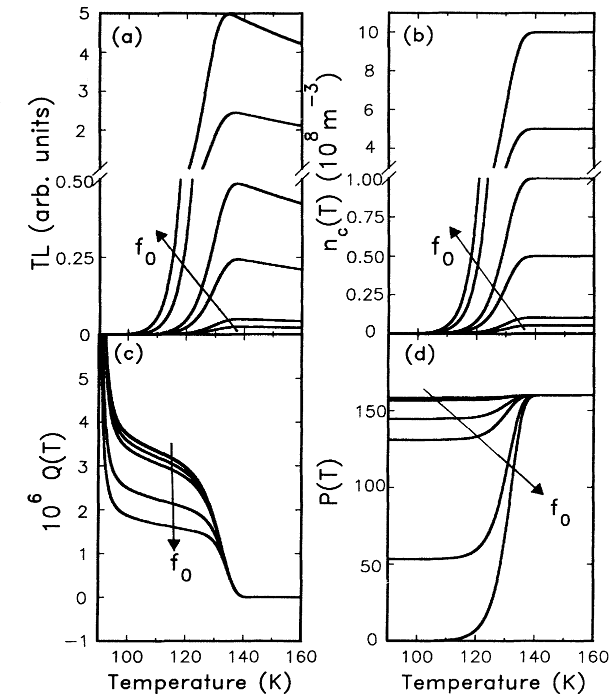

FIG. 4. Curve shapes obtained from numerically solving the differential rate equations (10) and (11) using the parameters of case F. This figure shows (a) TL, (b) $n_c(T)$ (TSC), (c) $Q(T)$, and (d) $P(T)$ for $\beta = 4.0$ K/min with f_0 taking the values 0.005, 0.01, 0.05, 0.1, 0.5, and 1.0.

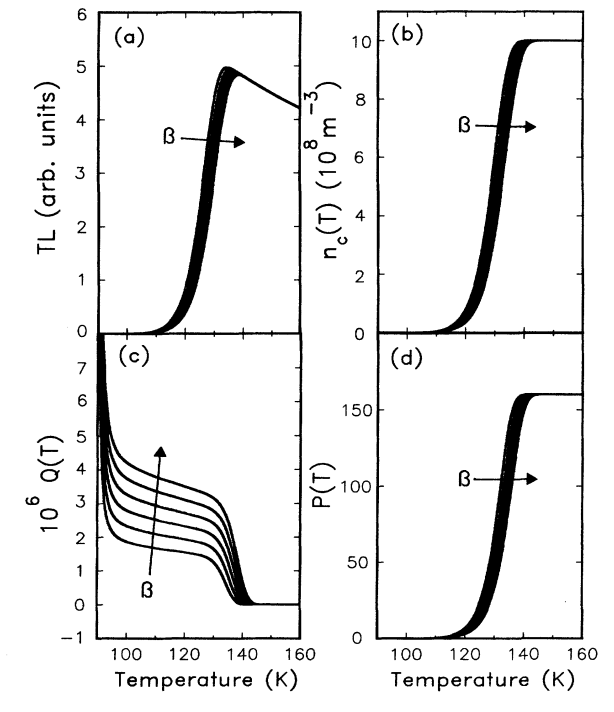

FIG. 5. Curve shapes obtained from numerically solving the differential rate equations (10) and (11) using the parameters of case F. This figure shows (a) TL, (b) $n_c(T)$ (TSC), (c) $Q(T)$, and (d) $P(T)$ for $f_0 = 1.0$ and with β taking the values 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0 K/min.

mains approximately level. These characteristics define the initial-rise region of the peak. The occurrence and width of this region does not appear to vary significantly with H,N, S, R, f_0, or β. The values of $Q(T)$ and $P(T)$, however, are critically dependent upon the values of these parameters. Comparison of Figs. 2(a)–2(d) (case A) with Figs. 4(a)–4(d) (case F) illustrate this. Case F represents an extreme case with little recombination, so no TSC peak actually forms. Nevertheless, the $Q(T)$ and $P(T)$ functions still display the same basic shape as before, but with their numerical values very much larger than their counterparts in Fig. 2. Thus, while changing the ratios H/N or S/N changes the numerical values of $Q(T)$ and $P(T)$, they still remain relatively constant over the initial rise region. That is, in this region, $(1/Q)dQ/dT$ and $(1/P)dP/dT$ are small in both cases. *This property with regard to the $Q(T)$ function is what gives the initial-rise analysis a wide range of validity encompassing even systems very far away from QE and showing a high degree of retrapping.*

An important point to note in the initial-rise assumption is that $f \approx f_0$ =const over the initial-rise region. Note, however, that, for temperatures very close to T_0, $Q(T)$ is changing rapidly [refer to Eq. (46) and the discussion relating to this equation]. Thus f ≈const is a necessary condition for the initial-rise analysis to work, but it is not a sufficient one. It is only during the region of relatively constant $Q(T)$ [i.e., $(1/Q)dQ/dT \approx 0$] that the initial-rise plot will produce a straight line. This was found to be true for all the calculations attempted, and thus it is believed to be true independent of retrapping kinetics.

The $P(T)$ function in all cases starts from a low value determined by f_0 and the H/N and S/R ratios. As T increases, f decreases and $P(T)$ increases monotonically toward the constant value SN/RH indicating an increase in the degree of retrapping. The factor $R_{\rm recom}\,SN/RH$ represents an upper bound to the rate of retrapping [refer to Eq. (48)]. So, while it is clear that the kinetic order of the system varies as a function of temperature, it is also important to note that if $SN/RH \ll 1$ then $P(T) \ll 1$ for all temperatures, and the system would display only slow-retrapping characteristics. Case A is an example of this situation with Fig. 2(d) showing that $P(T)$ approaches the maximum value of 1.6×10^{-5} indicating that even for high temperatures $R_{\rm recap} \ll R_{\rm recom}$. On the other hand, case F shows a marked increase in kinetic order as higher temperatures as reached. In Fig. 4(d) one observes that for $f_0 = 1$ $P(T)$ starts at zero then after a region of relative constant values rises quickly to $SN/RH = 160$ indicating that past the peak maximum retrapping is the dominant process. Thus not only are the values of $P(T)$ higher than case A but also the variation with temperature is greater. Figure 4(d) shows that in the initial rise region the peak is best characterized by slow-retrapping kinetics; however, for higher temperatures the peak takes on the characteristics of fast retrapping. All these features are in accordance with expectations, but the figures graphically illustrate that the assumption of constant kinetic order throughout the TL or TSC peak is invalid. Nevertheless, this assumption can be taken as a good approximation if $SN/RH \ll 1$.

Referring to the $Q(T)$ function, it was found that $Q(T_{\rm mc}) = 1$ in all cases. For case F the $Q(T)$ values are extremely large ($\sim 10^6$ for $T < T_m$) and so the system is very far from QE. *The conclusion here is that the use of the QE approximation in the derivation of the fast-retrapping TL and TSC equations is entirely without merit and therefore the traditional fast-retrapping TL and TSC equations should be considered worthless.*

Finally, it should be noted that for all cases where $H \gg N$, the $Q(T)$ function is independent of f_0, regardless of the value of S/R. The value of the $P(T)$ function, however, varies linearly with f_0 in the initial rise region. This can be seen from the definition of the $P(T)$ function, which in the initial rise region can be written as

$$P(T) = \frac{S}{R}\,\frac{1-f_0}{f_0 + H/N}. \tag{67}$$

For $H \gg N$, however, this becomes

$$P(T) = \frac{SN}{RH} - \frac{SN}{RH}\,f_0\,, \tag{68}$$

and the f_0 dependence of $P(T)$ can be understood.

For $H = N$, however, both $Q(T)$ and $P(T)$ have some f_0 dependency. Under these conditions it can be demonstrated that both vary with f_0 as $1/[f_0\,C(T) + 1]$ in the initial-rise region. The temperature-dependent function, $C(T)$, is independent of f_0 and is the same for both $Q(T)$ and $P(T)$.

V. THE INITIAL-RISE ANALYSIS

The modified version of the initial-rise analysis as outlined in Sec. III E was applied to TL and TSC curves for all the cases presented in Table I. In order to access the effect of the correction term, $-ka/\delta$, in Eq. (61), plots of $-k[d\ln(I)/d\delta + a/\delta]$ versus δ were constructed for $a = 0$ and $\frac{1}{2}$ for TL (because for these curves $b = \frac{3}{2}$) and for $a = 0$ and $\frac{3}{2}$ for TSC. Figures 6(a) and 6(b) show the results for TL and Figs. 7(a) and 7(b) show the results for TSC. The curves presented in these figures represent $(k/Q)dQ/d\delta + E$. For high δ these curves have very large values and are increasing rapidly. This region corresponds to the regions in the previous figures in which, for low T, $Q(T)$ is very large and is decreasing rapidly. As δ lowers, the values of the curves in Figs. 6 and 7 reduce and reach an inflection point or level off briefly before dropping again. This region corresponds to the relatively level regions in the $Q(T)$ plots for which $(1/Q)dQ/dT \approx 0$. The final reduction of the curves in Figs. 6 and 7 is the result of the breakdown of the initial-rise approximations.

It has been shown that in the initial-rise region of a TL or TSC peak $(1/Q)dQ/dT \approx 0$. This appears to be a general characteristic of the Q(T) function and has been

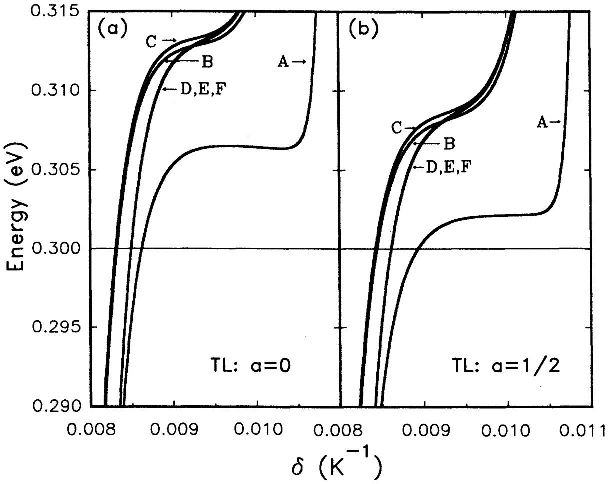

FIG. 6. Illustration of the modified version of the initial-rise analysis showing plots of $-k[d\ln(I_{\mathrm{TL}})/d\delta + a/\delta]$ vs δ in the initial rise region for (a) $a = 0$ and (b) $a = \frac{1}{2}$. Cases A–F ($f_0 = 1$, $\beta = 4.0$ K/min) are shown.

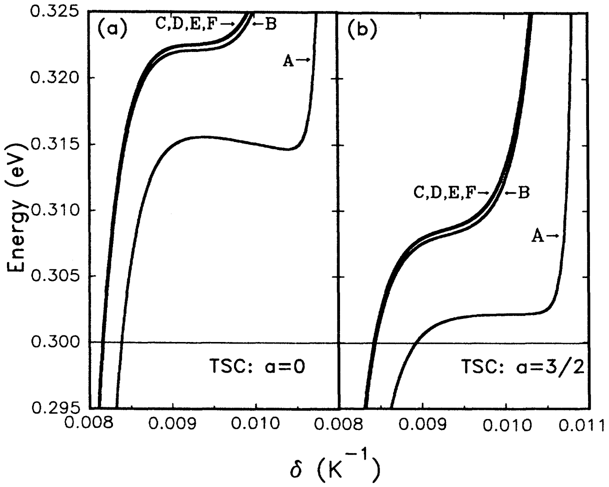

FIG. 7. Illustration of the modified version of the initial-rise analysis showing plots of $-k[d\ln(I_{\mathrm{TSC}})/d\delta + a/\delta]$ vs δ in the initial rise region for (a) $a = 0$ and (b) $a = \frac{3}{2}$. Cases A–F ($f_0 = 1$, $\beta = 4.0$ K/min) are shown.

shown to be true for a wide range of kinetic cases involving even systems very far from QE. In this region $|(k/Q)dQ/d\delta|$ is minimized resulting in a curve with a slope close to zero. The best values of E, therefore, are those chosen from the most level regions of these curves or from the inflection point when no clear level region is observed. The curves in Figs. 6 and 7 serve to illustrate nicely the boundaries of the initial-rise region and serve as a measure of the applicability of the initial-rise analysis. The energies obtained in this way are presented in Table II. The first and third columns ($a = 0$) contain values that one might obtain from a traditional initial-rise analyses. From the results presented it should be noticed that systems configured for higher Q(T) values generally give larger values of the energy. This is related to slight variations in the value of $(1/Q)dQ/dT$ in the initial-rise region. However, this effect is small and when the $-ka/\delta$ correction term is accounted for, the energy obtained for all cases agrees with the actual energy, 0.3000 eV, to within ±0.009 eV. So while it is apparent that the initial-rise analysis is independent of the KO approximation, we have shown that it does depend upon how close the system is to QE, but it does not depend upon the $Q(T)$ function as such. Instead, the important term governing its use is the rate of change of the logarithm of $Q(T)$; the effect of which can be minimized by a judicious choice of where to read off the energy. Hence one may obtain real information concerning the system without having explicit knowledge of the $Q(T)$ and $P(T)$ functions. However, for TL it is still necessary to obtain an approximate value for b. By subtracting Eq. (60) from (59) one obtains

$$\ln\left(\frac{I_{\mathrm{TSC}}}{I_{\mathrm{TL}}}\right) = \left(b - \tfrac{1}{2}\right)\ln(T) + \mathrm{const}, \qquad (69)$$

valid only in the initial rise region. Therefore, an approximate value for b can be determined from the slope of a $\ln(I_{\mathrm{TSC}}/I_{\mathrm{TL}})$ versus $\ln(T)$ plot.

VI. HOOGENSTRAATEN'S HEATING RATE ANALYSIS

Figures 8(a) and 8(b) show Hoogenstraaten plots for cases A and F as applied to TSC curves. In each is

TABLE II. Summary of activation energies obtained from the initial-rise analysis with and without the correction term. All energies are expressed in eV. In all cases the actual value of E was 0.3000 eV.

Case	TL ($a = 0$)	TL ($a = \frac{1}{2}$)	TSC ($a = 0$)	TSC ($a = \frac{3}{2}$)
A	0.306	0.302	0.315	0.302
B	0.313	0.308	0.322	0.308
C	0.313	0.309	0.323	0.309
D	0.313	0.309	0.323	0.309
E	0.313	0.309	0.323	0.309
F	0.313	0.309	0.323	0.309

plotted $\ln(T_{mc}^2/\beta)$ versus $1/T_{mc}$, and $\ln(T_{mc}^2/\beta)$ minus the correction term versus $1/T_{mc}$. [The correction term was discussed in relation to Eqs. (62) and (63).] In both cases the lines shown are linear regression fits to the data points with the slope of this fit producing values of E. For the uncorrected plots, frequency factors where calculated from the intercept of this fit. Table III summarizes the results obtained from the uncorrected plots for all the cases for both TL and TSC. Errors in the calculation of E and s were found to result from errors in picking off the actual peak temperature. The errors in choosing T_m were estimated to be ±0.15 K leading to errors of ±0.0006 to ±0.0007 eV in E and of the order of 1% in s. The slopes of the corrected plots gave values of $E = 0.3000 \pm 0.0006$ eV in all cases. While it is necessary to have considerable knowledge concerning the system in order to calculate the correction term, the point here is that by ignoring the correction term one introduces, in some cases, significant error into the evaluation of E (beyond just the error associated in determining T_m). The following observations concerning the values in Table III can be made: (i) The Hoogenstraaten plots from the TL curves tend to give more accurate E values than from the TSC curves; (ii) for both TL and TSC, the cases where $H = N$ appear to work better than $H \gg N$; (iii) overall the trend is that the higher the degree of retrapping, the higher the energy; and (iv) for all TSC cases the calculated frequency factor is about two orders of magnitude less than the real frequency factor.

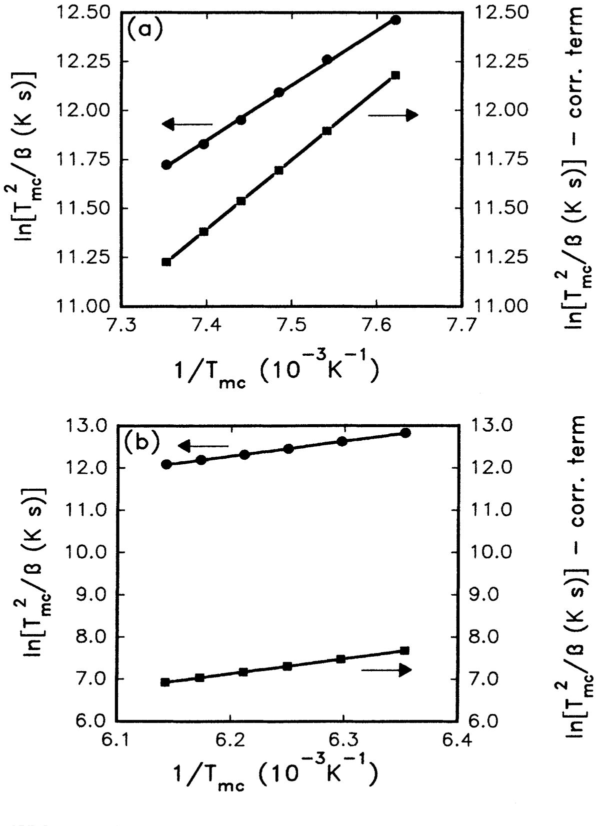

FIG. 8. TSC Hoogenstraaten plots for (a) case A ($f_0 = 1$) and (b) case F ($f_0 = 1$). When the correction term is ignored (line through circles) the slope and intercept can differ significantly from when the correction term is accounted for (line through boxes). The lines through the symbols are linear regression fits from which the activation energy is calculated. The slope of the corrected plots gave values of $E = 0.3000 \pm 0.0006$ eV in all cases.

Due to the complexity of the correction terms in Eqs. (62) and (63), simple interpretations of these results is difficult. Detailed analysis of these terms will be the subject of future work.

VII. FINAL COMMENTS AND PRACTICAL IMPLICATIONS

In this paper two new functions, $Q(T)$ and $P(T)$, have been introduced into the analysis of the thermally stimulated processes, TL and TSC. The clear message emerging from this analysis is that the treatment of TL and TSC using the assumption of QE and fixed KO throughout the TL and TSC curves is dubious. In some cases (for example case A) the use of the QE approximation and the simplified slow-retrapping TL and TSC equations are unlikely to lead to serious errors. In other cases, however, the use of the QE approximation is meaningless (for example the fast-retrapping case F).

Since both $Q(T)$ and $P(T)$ are defined in terms of physically meaningful processes (i.e., rates of excitation, recombination, and retrapping) connection with the physical system is always maintained, thus leaving open the

TABLE III. Summary of the activation energies and frequency factors obtained from the Hoogenstraaten heating rate analysis.

Case	Energy (eV)[a]	Frequency factor (s^{-1})[a]
	TSC	
A	0.2418	2.10×10^7
B	0.2468	1.14×10^7
C	0.2723	5.22×10^7
D	0.2616	2.68×10^7
E	0.2818	9.83×10^7
F	0.3032	4.88×10^7
	TL	
A	0.2507	4.84×10^7
B	0.2654	6.82×10^7
C	0.3031	1.50×10^9
D	0.3045	3.37×10^9
E	0.3188	1.18×10^{10}
F	0.3188	1.18×10^{10}

[a] In all cases the actual values of E and $s(T)$ were 0.3000 eV and $5.21 \times 10^8\ T^{1/2}\ s^{-1}$ respectively. With $T = T_m \approx 135$ K, $s \approx 6.05 \times 10^9\ s^{-1}$. The errors in the calculation of E vary from $\pm$ 0.0006 to $\pm$ 0.0007 eV and result from errors in picking the actual peak temperature. Errors in this are estimated to be ±0.15 K. The associated errors in s are of the order of 1%.

possibility that, for any given system configuration, $Q(T)$ and $P(T)$ can be required to take on specific forms on physical grounds. In general, however, one does not have specific knowledge of these functions, nevertheless, the general formalism clearly shows how these functions effect the shape and characteristics of TL and TSC curves as well as the applicability of the initial-rise and Hoogenstraaten relations. In short, the analysis presented in this paper provides a general framework from which more specific assumptions and approximations can be intelligently applied and in the process provide valuable insight into the nature of the system under study.

It should be emphasized that experimentally one can estimate the validity of the QE approximation by using Eq. (44) or Eq. (45), and here we suggest how this can be done. The shape of the $Q(T)$ function can be determined from simultaneous measurement of TSC and TL, using Eq. (45). Clearly, since the leading constants in this equation are unknown, this procedure will give only the shape of the $Q(T)$ function, but if it is recalled that the value of $Q(T)$ at high temperatures is zero, and that the value of $Q(T_{\text{mc}}) = 1$, then an estimate of the numerical value of $Q(T)$ may be obtained by scaling. Further work concerning the experimental determination of the $Q(T)$ function is presently being pursued.

The present analysis also demonstrates that as long as $(1/Q)dQ/dT$ is small the initial-rise analysis gives an estimate of the activation energy. However, one may obtain more accurate estimates if a modified version of this analysis is performed with the inclusion of the correction term, $-ka/\delta$. The conditions of validity for the initial-rise analysis are that $f \approx f_0 = \text{const}$ and that $(1/Q)dQ/dT$ is small. This is true, independent of the numerical value of $Q(T)$ and therefore independent of how close the system is to QE. Similarly the Hoogenstraaten heating rate analysis is only able to give an estimate of the activation energy. The departure of the calculated values from the actual values is complex, and no simple correction term can be applied. Further analysis of the Hoogenstraaten procedure as well as the extension of the general formalism to include systems containing more than one active level is the subject of continuing research.

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