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II. Correlations Between Thermoluminescence and Thermally Stimulated Conductivity

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Correlations between corresponding thermoluminescence (TL) and thermally stimulated conductivity (TSC) glow curves are investigated in detail for a single trap depth in the presence of thermally disconnected traps (reservoir for trapped charge carriers) and a single type of recombination centers. As a result of our calculations, we conclude that both types of glow curves have identical shapes if the concentration of thermally disconnected traps is much greater than the concentration of thermally connected traps. We find pronounced differences if this inequality is not satisfied, and conclude (a) the customary practice of analyzing TSC data with the aid of methods developed for TL is inadequate if those methods are based solely on the shape of the glow peak; (b) simultaneous measurements of TL and TSC data by themselves do not provide sufficient information on all the relevant parameters entering the kinetic equations derived from the simple basic model; and (c) from correlated TL and TSC experiments, it is possible to decide (1) whether there is a charge carrier transport associated with the thermal release of trapped charged carriers and their subsequent recombination, and (2) whether there is a large concentration of thermally disconnected traps present. The validity of the customary assumptions, that the concentration of free charge carriers is much smaller than the concentration of trapped carriers, is discussed. In addition, the Dussel-Bube theory of TSC is completed by extending it to the case of low retrapping and small concentration of thermally disconnected traps.

INTRODUCTION

SIMULTANEOUS measurements of thermally stimulated conductivity (TSC) and thermoluminescence (TL) glow curves have been reported in a number of papers. Most of the work was done on pure or doped ZnS,[1–4] on some alkali halides,[5–8] and on TiO_2.[9] Such experiments determine whether a transport of charged carriers takes place during thermal stimulation or whether the carriers remain localized in a luminescence center.

We hoped that a detailed investigation of the correlations between TL and TSC based on the basic simple model (see Ref. 10, hereafter referred to as I) would yield new methods for the analysis of experimental data; then, relevant parameters entering the kinetics could be determined in a self-consistent way. We will show in the following sections that this appears to be impossible and that simultaneous experiments on TSC and TL do not yield sufficient information to determine the kinetical mechanism of the thermally stimulated recombination process without *a priori* knowledge of most of the trapping parameters.

KINETIC EQUATIONS

In order to investigate the usefulness of simultaneous TL and TSC experiments for the determination of trapping parameters, solutions of the kinetic equations for TL and TSC must be compared for typical combinations of the model parameters.

A detailed theory of TSC was presented by Dussel and Bube[11] (hereafter referred to as DB) and in I we have reported a similar phenomenological theory of TL. Both theories use the same kinetic equations which are derived from a model involving a single trap depth, a single type recombination center, a conduction band, and additional thermally disconnected traps which act merely as a reservoir for trapped charged carriers. Given this model, there are two parameters entering the kinetic equations which essentially determine the properties of a TSC or TL curve: (a) the ratio $R=\beta/\gamma$ of the retrapping coefficient β and the recombination coefficient γ; and (b) the ratio N/M of the concentration of thermally connected traps N and the concentration of thermally disconnected traps M.

DB point out that four basic types of TSC curves exist: (1) R small and N/M small, (2) R small and N/M large, (3) R large and N/M small, and (4) R large and N/M large. All four cases apply naturally also for TL curves. However, the DB classification of TSC curves is incomplete. Case (2) contains two different typical TSC shapes. That makes it necessary to extend the DB theory for a complete investigation of TSC/TL correlations.

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Let n_c be the concentration of free charge carriers, n the concentration of trapped carriers, N the concentration of thermally connected traps at a depth E, and M the concentration of thermally disconnected traps. The kinetic equations can be written as

$$\dot{n}=\beta n_c(N-n)-nP\,, \tag{1}$$

$$\dot{n}_c+\dot{n}=-\gamma n_c(n_c+n+M)\,, \tag{2}$$

where $P=P_0e^{-E/kT}$. As in I, we assume P_0 to be temperature-independent, and $n_c \ll n$ and $\dot{n}_c \ll \dot{n}$.[11]

For reasons stated in I, we will calculate $w=n/N$ from the formalism given there rather than using the DB theory of TSC directly; n_c is then found from the expression

$$\gamma n_c=PNw/[N(1-R)w+M+RN]\,. \tag{3}$$

Equation (3) is readily obtained from Eqs. (1) and (2) by considering the mentioned assumptions. The fundamental equation which provides the correlation between corresponding TL and TSC curves is

$$n_c=L/\gamma(M+Nw)\,, \tag{4}$$

which is obtained from Eq. (3), and the following formula from I for the TL intensity L:

$$L=PNw(M+Nw)[Nw(1-R)+NR+M]^{-1}\,. \tag{5}$$

The filling ratio w has values only in the region $0\leq w\leq 1$. The basic assumptions $n_c \ll n$ and $\dot{n}_c \ll \dot{n}$, used to derive Eq. (3), were considered by DB to be valid in high-resistivity crystals under normal experimental conditions as long as the lifetime τ of the free charge carriers is much less than 1 sec. Having calculated TSC curves for the cases $M=0$ and $M \ll NR$, we feel that the validity of those assumptions needs to be examined more closely. For that purpose, it is convenient to write Eq. (3) in the following form:

$$n_c/n\tau_0=P[(1-R)(n/n_0)+R(N/n_0)+(M/n_0)]^{-1}\equiv X\,, \tag{6}$$

where $\tau_0\equiv 1/(\gamma n_0)$ and n_0 is the concentration of trapped charge carriers at $T=T_0$. Given a set of parameters, the function $X(P,R,n/n_0,N/n_0,M/n_0)$ is completely determined by the methods of I for either a constant or nonlinear heating rate. Equation (6) provides us with a criterion to test the self-consistency of the TL and TSC theories discussed in I and in this paper. If the assumption $n_c \ll n$ holds, the following inequality must be satisfied:

$$\tau_0^{-1} \gg X\,. \tag{7}$$

It is important to point out that τ_0 may be selected within a wide range of values independently of the choice of the other parameters in Eq. (6). This fact enables one to calculate for a given τ_0 a critical temperature T_c up to which the condition $n_c \ll n$ is still satisfied[12] for a particular TSC curve obtained by the methods of I and Eq. (4). The theory breaks down for temperatures above T_c.

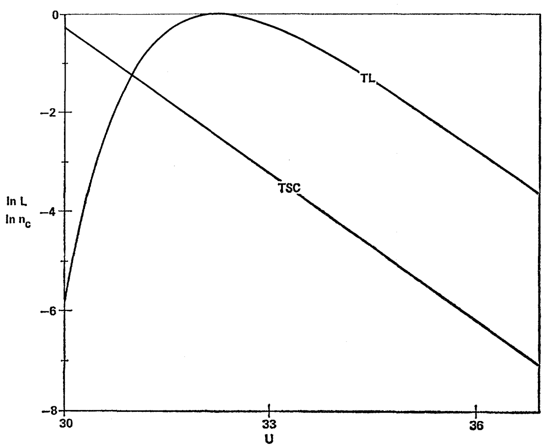

FIG. 1. Corresponding TL and TSC curves when there are no retrapping transitions and no thermally disconnected traps. The TSC curve does not depend on the heating program and has no maximum. The parameters are: $E/k=5\times10^{3}$°K, $P_0=10^{13}$ sec^{-1}, and $w_0=1$. The heating program is: $dT=\alpha T^2dt$, $\alpha=2\times10^{-5}$ (sec °K)$^{-1}$.

It is obvious from Eq. (4) that there is no difference between the shapes of corresponding normalized TL and TSC curves if $M \gg N$, and one can, therefore, conclude that in this case no additional information on the kinetic parameters can be obtained by simultaneous measurements of TSC and TL. Of interest, therefore, are cases where this inequality is not satisfied.

TL-TSC CORRELATIONS IN CASE $M=0$

The complete absence of thermally disconnected traps is relatively unlikely, as DB have pointed out. However, we believe it is legitimate to discuss this situation here as a limiting case since there must be, in any sample, a deepest trap and associated TSC and TL glow curves. With $M=0$, the only parameter to be varied now is R. If $R=0$, we have the classical "first-order" condition for which Randall and Wilkins[13] calculated the TL glow curve:

$$L=P_0N\exp[-U-F(U)]\,. \tag{8}$$

We use here the notations from (I).

The concentration of free charged carriers (TSC) is given by Eq. (3): $n_c=P_0e^{-U}$, independent of the heating program. In Fig. 1, the two curves are compared. The "pathological" shape of the TSC curve is in sharp contrast to the TL curve. Again, one could argue that $R=0$ is a very unlikely situation and simply regard this result as physically meaningless. However, even cases with $R\neq 0$ yield unusual TSC curves which may not even

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[12] It can be shown that $\dot{n}_c \ll \dot{n}$ if $n_c \ll n$.: For all cases of the parameters discussed in this paper this relation has been computed and found to hold.

[13] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) A184, 366, 390 (1945).

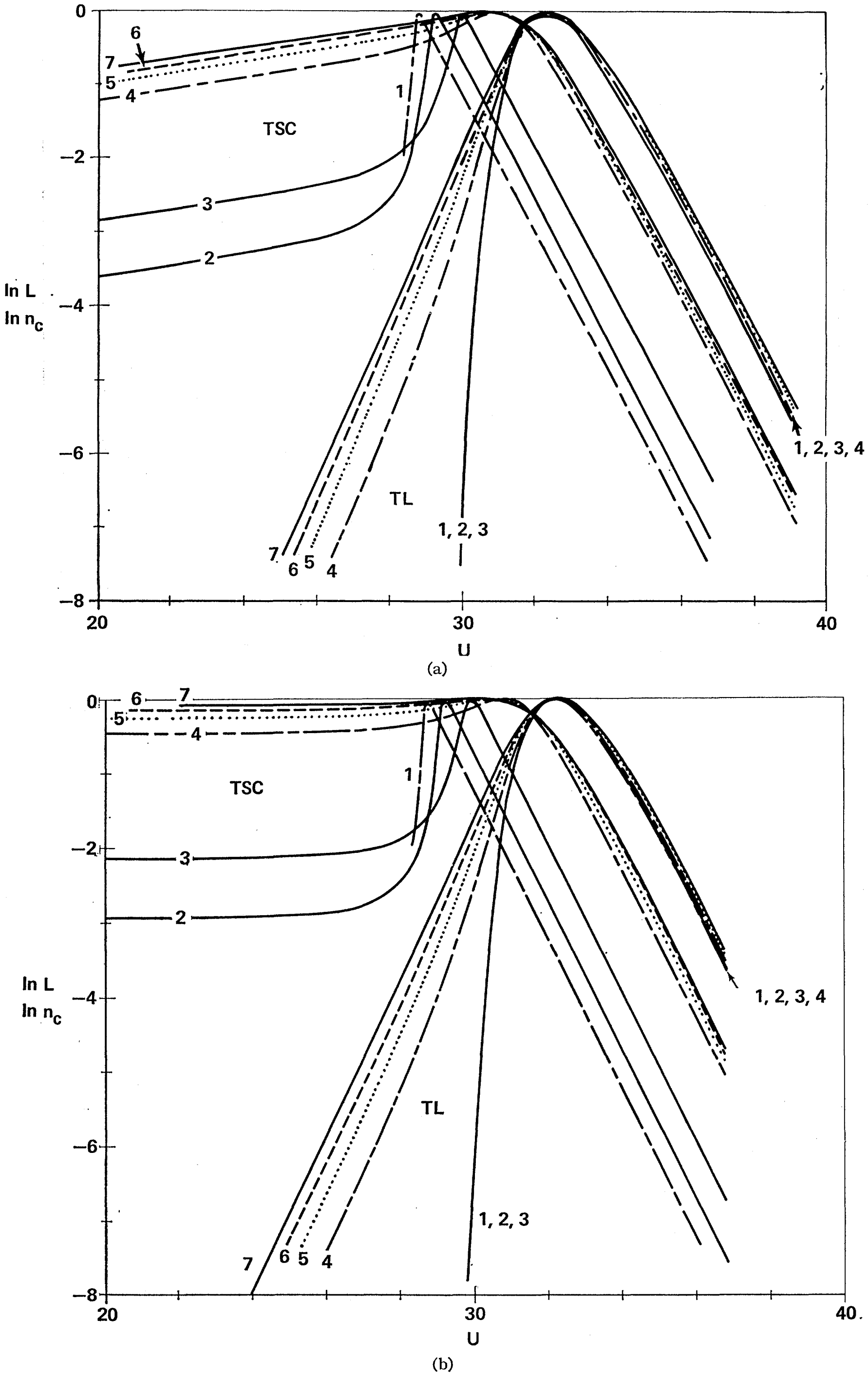

FIG. 2. Corresponding normalized TL and TSC curves for different values of the retrapping coefficient R in absence of thermally disconnected traps and criterion for validity of $n_c \ll n$. (a) Heating program $dT = q dt$; the heating rate q is constant and was chosen as described in (I). (b) Heating program $dT = \alpha T^2 dt$; $\alpha = 2 \times 10^{-5}$ (sec °K)$^{-1}$. The parameters are: $E/k = 5 \times 10^3$ °K, $P_0 = 10^{13}$ sec^{-1}, $w_0 = 1$, and $U_0 \gg U^*$. N does not affect the shape of the normalized glow curves. The R values for the curves are as follows—1: $R = 10^{-15}$, 2: $R = 10^{-10}$, 3: $R = 10^{-5}$, 4: $R = 10^{-1}$ for $q = 0.481$ °K sec^{-1}; and 5: $R = 0.2$ for $q = 0.483$ °K sec^{-1}, 6: $R = 0.3$ for $q = 0.485$ °K sec^{-1}, 7: $R = 0.4$ for $q = 0.489$ °K sec^{-1}. (c) Plot of U_c for different values of R as calculated from Eq. (6) according to the methods described in (I) and the condition $\tau_0^{-1} = 10X$. The parameters are $M = 0$, $E/k = 5 \times 10^3$ °K, $P_0 = 10^{13}$ sec^{-1}, and $\alpha = 2 \times 10^{-5}$ (sec °K)$^{-1}$. For a given τ_0, the critical temperature $T_c = E/kU_c$ is defined as the temperature up to which $n_c \ll n$ is valid. Above T_c, the simple TSC theory which is based on the assumption $n_c \ll n$ breaks down.

have a maximum. A set of TL and TSC curves for two different heating programs, (1) constant rate: $dT = q dt$; and (2) quadratic rate: $dT = T^2 dt$, are shown in Fig. 2. We have varied R in the interval $0 \leq R < 1$. We note again the dissimilarity between TSC and TL and the unusual shapes of the TSC curves. All TSC curves, with a constant heating rate, exhibit a maximum; it is possible, however, to maintain a constant concentration n_c after a certain temperature is surpassed simply by heating with a heating program $dT = \alpha T^2 dt$.[14] Curves with

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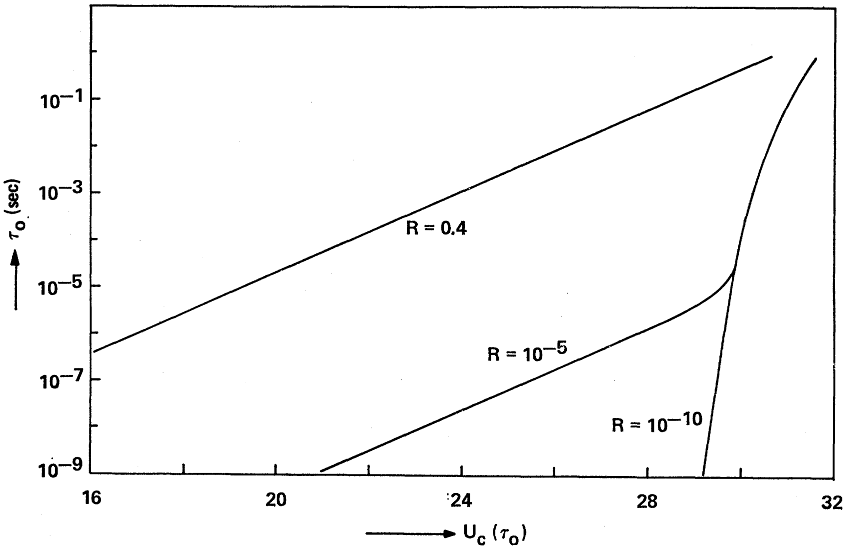
[14] For physical reasons, the TSC curve must start to descend eventually. It turns out that this occurs only at U values for which the present theory is not valid because the assumption $n_c \ll n$ breaks down.



(c)

FIG. 2. (*continued*)

$R \geq 1$ and quadratic heating rate have no maximum. The unusual shapes of the TSC curves shown in Figs. 1 and 2 require a test of relation (7). Since $M=0$, the parameter τ_0 has a simple meaning: It is the recombination lifetime[15] of the free charge carriers determined at T_0. The lifetime τ_0 is for a given combination of parameters R, M, N, n_0, $P(T_0)$ determined by γ or the cross section for recombination. This cross section is independent of the trapping parameters. Lifetimes encountered in materials which exhibit TSC range from 0.1 sec[11] down to less than 1 nsec. We have calculated X for the glow curves shown in Figs. 1 and 2. Choosing τ_0^{-1} to be at least 10 X in order for the assumption $n_c \ll n$ to be valid, we derived from that calculation a critical value $U_c(\tau_0)$, so that the solutions of Eqs. (4) and (5) for TSC and TL are consistent with the basic assumptions only in the region $U \geq U_c$. In Fig. 2(c), U_c is plotted as a function of τ_0 for the cases $M=0$ and $0 \leq R \leq 0.4$ with $w_0=1$, $P_0=10^{13}$ sec^{-1}, $E/k=5\times10^3$ °K, and $\alpha=2\times10^{-5}$ (sec °K)$^{-1}$. Those are the most critical parameter combinations, since according to Eq. (6), X decreases with increasing R and M. The U_c values for $\tau_0=10^{-9}$ sec indicate that the TSC curves in Figs. 2(a) and 2(b) with $R \geq 10^{-5}$ and $M=0$ peak in the allowed region of U values and that, therefore, they cannot be simply disregarded as being mathematically meaningless. If $R<10^{-6}$ and $M=0$, the TSC theory described here appears to be inadequate because the assumption $n_c \ll n$ may not be justified. This does not apply to the corresponding TL theory, as can be seen from Figs. 1 and 2. All TL curves peak in the allowed region of U values.

The characteristic features of TSC curves with $M=0$ are as follows: The curve starts at U_0 linear in U with a slope of about -1, passes a maximum, and reaches a constant value at $n_c=P_0/\gamma R P_\alpha$ for quadratic heating rates [Fig. 2(b)]. The onset of that constant part occurs at larger values of U as R increases. If a constant heating rate is used, we note a slightly different slope of the initial rise and a distinctly different behavior of the decreasing part of the glow curve after the maximum. The constant part is replaced by the slowly varying function $\ln(n_c) \propto \ln(qkU^2/\gamma E)$. All curves exhibit a maximum and broaden enormously as R increases [Fig. 2(a)]. (A full discussion of the behavior of the TSC curves is given in Ref. 16).

A set of curves, calculated from Eq. (4) by the methods of I, with different initial filling ratios $w_0 = n_0/N$ is shown in Fig. 3. While the TL curve changes from a first-order shape to a second-order shape as w_0 decreases, the TSC curve changes drastically. It exhibits no maximum for $0<R<1$ if w_0 is sufficiently small and if a quadratic heating rate is used.[14] According to Eq. (6), the critical value U_c for a given τ_0 becomes smaller as w_0 decreases from $w_0=1$ to smaller initial filling ratios, so that the TSC curves in Fig. 3 represent valid solutions of Eq. (3).

TSC-TL CORRELATIONS IN CASE $M<NR$

We will concern ourselves in this section with the case $M/N \leq 1$ only. This is done because (a) here again we have a striking dissimilarity between the shapes of the first-order TL peak and the corresponding TSC peak, and (b) calculations of TSC curves of this type are required to complete the DB theory.

Equations (3) and (9) of I yield TSC curves, the characteristic features of which are shown in Fig. 4

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[15] The lifetime of free charge carriers is $\tau=1/\gamma(n_c+n+M)$. Assuming T_0 to be low enough so that $n_c(T_0) \ll n_0$, it is $\tau=1/\gamma n_0$ if the concentration M of thermally disconnected traps is very small.

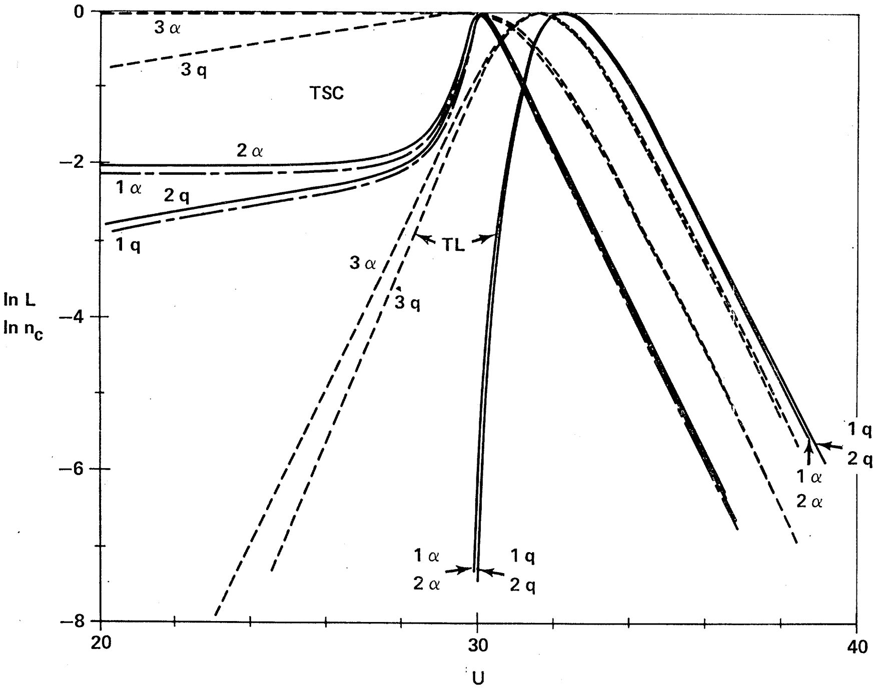

FIG. 3. Normalized TL and TSC curves for different filling ratios w_0 in the absence of thermally disconnected traps. The curves were obtained for the two different heating programs (1) $dT=qdt$; and (2) $dT=\alpha T^2dt$. They are labeled accordingly by the subscripts q and α. The parameters are: $M=0$; $R=10^{-5}$; $E/k=5\times10^3$ °K; $U_0 \gg U^*$; $P_0=10^{13}$ sec^{-1}; and $\alpha=2\times10^{-5}$ (sec °K)$^{-1}$; for N, see caption of Fig. 2. The w_0 values for the curves are as follows— 1: $w_0=1$ for $q=0.481$ °K sec^{-1}; 2: $w_0=0.5$ for $q=0.481$ °K sec^{-1}; 3: $w_0=10^{-5}$ for $q=0.514$ °K sec^{-1}.

for constant and quadratic heating rates together with corresponding TL curves. While the TL curves exhibit typical properties of first-order curves, we obtain again unusual shapes of the TSC curves [Fig. 4(a)]. Mathematical expressions for $n_c(U)$ in the four regions indicated in Fig. 4(a) are given in Ref. 16. The influence of M on the shape of the TSC curves is shown in Fig. 4(b). Note that region III narrows as M increases until regions IV and II merge, for $M/RN\geq 1$, a case discussed by DB.

The influence of w_0 on the shape of the TSC curve is found from the formulas for w and n_c given in Ref. 16 and is shown in Fig. 5. As w_0 decreases, the initial linear part of $\ln(n_c)$ shifts from region I in Fig. 4(a) toward region IV. A first-order glow peak is obtained if $w_0 < M/N$. If one assumes that τ_0 in (7) may be again as small as 1 nsec, the region on the U axis for which the assumption $n_c \ll n$ is still justified extends to the values $U\geq U_c=21$ for the parameter combination considered in Figs. 4 and 5. The cases discussed in the last two sections are of interest in as much as under typical first-order conditions a distinct deviation from a typical first-order shape[13] of the TSC curve is obtained. Corresponding TSC and TL curves are completely different. Further, it is found that under certain conditions, the solutions of Eqs. (1) and (2) do not even exhibit a maximum.

CORRELATIONS BETWEEN TSC AND TL FOR CASES $M>RN$, $R<1$, AND $M<RN$, $R>1$

These are the two typical cases left to be discussed within DB's classification. The solutions of Eqs. (1) and (2) are known from the work of DB and from I. Since here we are not interested in cases where $M \gg N$ (perfect correlation), we will discuss the case $M>RN$ for $R<1$ and $M\leq N$ only. Typical examples of TSC and TL curves for constant and quadratic heating rates are presented in Fig. 6.

$M>RN$, $R<1$, and $M\leq N$

Under those conditions, the TL curve is the first-order type. The assumptions of this section permit the derivation of formulas for both curves.[16] The results only are illustrated here. In Fig. 6, corresponding TSC and TL curves are plotted for that case (TSC curves 1α and 1q). We note the differences in the shapes of those two curves. The TSC curve has not the Randall-Wilkins shape despite the typical first-order conditions. The two types of curves are identical only if $w_0 < M/N$. The assumption $n_c \ll n$ is not critical in this particular case.

$M<NR$, $R>1$

Examples of TL and TSC curves for that case and two different heating programs are shown in Fig. 6. We note that both types of curves have a very large half-width and that one obtains a large section of the TSC curve which is temperature-independent if a quadratic heating rate is employed. Both types of curves were discussed in detail by DB or in I, respectively.

The comparison of corresponding TL and TSC curves in Fig. 6 reveals considerable dissimilarities in their shapes. Half-width, peak temperature, and initial rise

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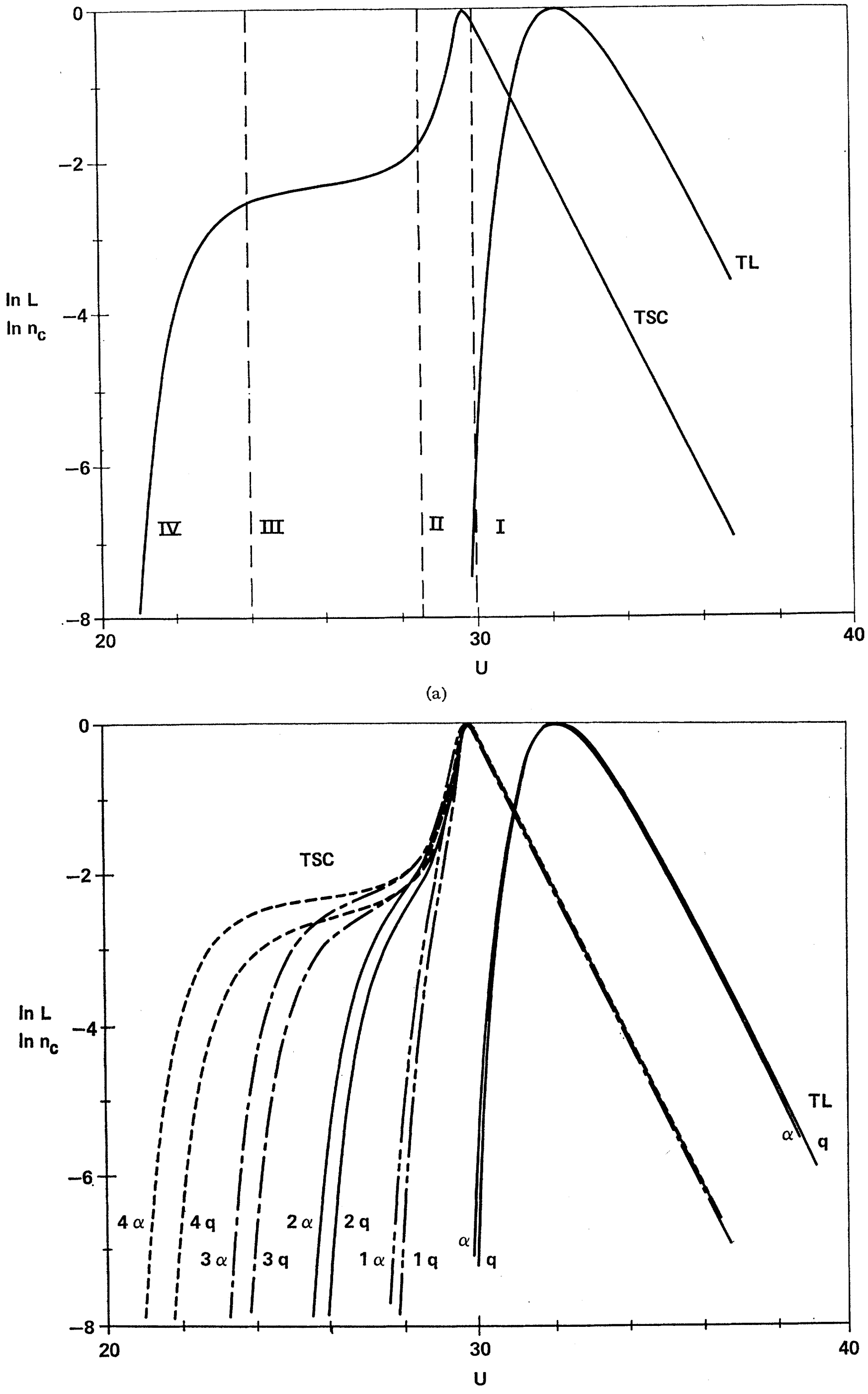
[16] NRC Report No. 11000, 1969 (unpublished); this report may be obtained free of charge by writing to Dr. P. Kelly, NRC, Building M36, Ottawa, Canada.



(a)

(b)

FIG. 4. TL and TSC curves for the first-order case $M<NR$, $R<1$. (a) A typical TSC and TL curve obtained with the heating program $dT=\alpha T^2 dt$. (b) Corresponding TSC and TL curves for different concentrations of thermally disconnected traps and two different heating programs. In the limit $M\to 0$, the TSC curves have the shape shown in Fig. 2. The parameters are: $E/k=5\times 10^3$ °K, $P_0=10^{13}\ \text{sec}^{-1}$, $R=10^{-6}$, $q=0.481$ °K sec^{-1}, and $\alpha=2\times 10^{-5}$ (sec °K)$^{-1}$. The N/M values for the curves are 10^7, 10^8, 10^9, and 10^{10} for curves 1, 2, 3, and 4, respectively. The ratio N/M does not influence the TL curves. Curves labeled by the subscript α are obtained with the heating program $dT=\alpha T^2$ and the ones labeled by the subscript q are with $dT=qdt$.

of both TSC and TL curves depend critically on w_0, and only for $w_0\ll 1$ are the curves identical and of first-order type.

DISCUSSION

The present calculation of TSC curves reveals a number of new TSC shapes. Under certain conditions there is no maximum.[14] Corresponding TL and TSC curves exhibit remarkable differences in shape and location of the maximum on the temperature scale whenever the inequality $M\gg N$ is not valid. We found further that under typical first-order conditions, for which the TL curve has the classical Randall-Wilkins shape,[13] the TSC curve departs considerably from this shape. We con-

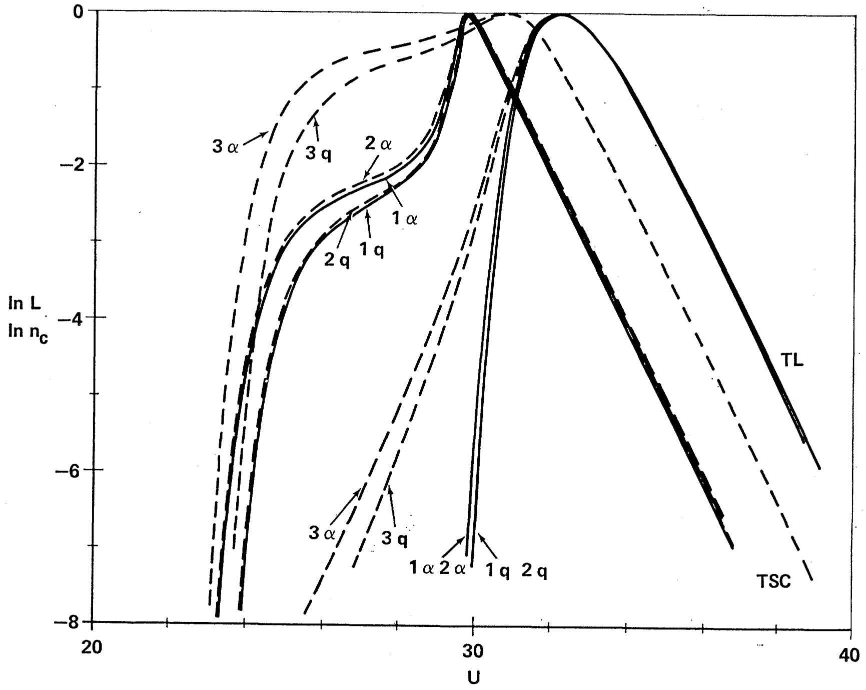


FIG. 5. Normalized TL and TSC curves for different filling ratios in case $M<NR$ and $R<1$. Again, corresponding curves for the two heating programs are compared. [Curves are labeled by the subscripts α and q (see Fig. 3).] The curves reveal the basic shapes which are typical for that case. However, because of the normalization, the shift of the linear part of $\ln n_c$ with decreasing w_0 is reversed. A shape like that of the TSC curve 1 in Fig. 6 (modified first-order shape) is obtained if $w_0<M/N$. The parameters are: $E/k=5\times10^3$ °K; $P_0=10^{13}$ sec^{-1}, $q=0.481$ °K sec^{-1}, $\alpha=2\times10^{-5}$ (sec °K)$^{-1}$, $M/N=10^{-9}$, and $R=10^{-6}$. The w_0 values for the curves are 1, 0.5, and 10^{-5} for curves 1, 2, and 3, respectively.

clude from this fact, e.g., that Grossweiner's method[17] for the determination of E from first-order TL glow curves cannot be employed to TSC curves unless $M\gg N$. The factor Δ_- (DB notation)[18] in his formula changes from 0.726 for $R=10^{-15}$ to 1.346 for $R=0.1$ in the case $M=0$, $w_0=1$, and from 0.788 for $w_0=1$ to 1.38 for $w_0=10^{-5}$ in the case $R=10^{-6}$ and $M/N=10^{-9}$. The application of this formula to first-order kinetic TSC can, therefore, be in error up to 50%. All other *shape* methods derived for TL are erroneous also, if applied to TSC,[19,20] unless $M\gg N$. Moreover, there can be no method based on the shape of the curve, the location of the maximum, or its initial rise which does not require specific knowledge of the parameters in Eqs. (1) and (2) as one can see from DB, I, and the present calculations.[21] Even methods which one can derive from TL-TSC correlations, by utilizing the differences in the maximum temperature or half-width of the two corresponding curves, depend critically on the parameters. The only method which gives a consistent value for an activation energy is, as pointed out by DB and in I, the initial rise method[22] for it requires only that $w_0<1$, which is experi-

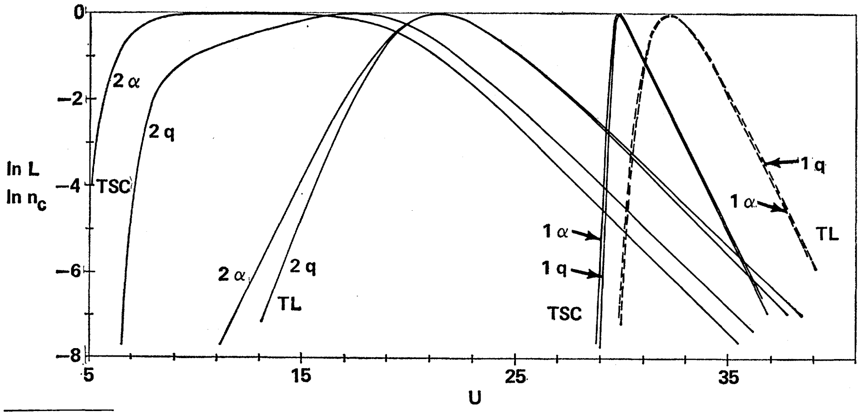


FIG. 6. Comparison of normalized TL and TSC curves for (1) $M\geq NR$, $R<1$: first-order conditions, TL and TSC curves 1α and 1q. While the TL curve has the characteristic Randall-Wilkins shape, the TSC curve is shifted to higher temperatures, has an extended linear initial rise, and descends steeper on the high-temperature side. (2) $M<NR$, $R>1$: Curves 2α, 2q. Both types of curves have large half-widths and exhibit a linear rise with the slope of $-\frac{1}{2}$ if $w_0\approx1$. The parameters are: $E/k=5\times10^3$ °K, $w_0=1$, $P_0=10^{13}$ sec^{-1}, $\alpha=2\times10^{-5}$ (sec °K)$^{-1}$, and $q=0.481$ °K sec^{-1}. For curves 1α and 1q, $N/M=10^6$ and $R=10^{-6}$. For 2α and 2q, $N/M=10^6$, and $R=10^5$.

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[17] L. J. Grossweiner, J. Appl. Phys. **24**, 1306 (1953).

[18] The factor Δ_- is defined as the so-called lower temperature "half-width"; $\Delta_-=T^*-T_1$, where T_1 is the temperature on the low-temperature side of the peak at which the intensity is half the maximum intensity.

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

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

[21] This is also the case for the so-called "Fermi-level analysis" (Ref. 11), which requires for proper application that trapped and free carriers are in quasithermal equilibrium. That means the rate of recombination transitions must be much smaller than the retrapping rate. Therefore, at least information on R is needed.

[22] G. F. Garlick and A. F. Gibson, Proc. Roy. Soc. (London) **60**, 544 (1948).

mentally easily achievable. But all other parameters remain unknown. One gains, therefore, no significant information on the kinetical process by studying TL, TSC, or TSC-TL correlations alone. It appears even doubtful whether a consistent value obtained for E is of relevance, since there seems to be no way to check the applicability of the simple basic model for a particular crystal by measuring and analyzing TSC and TL glow curves. Other conceivable models must be investigated, e.g., those which consider two activation energies.[6,23,24] By looking at those models, it appears questionable if the initial rise of a glow curve is always determined solely by the depth of a trap. Detailed investigations of some of the more relevant models are needed and will be presented in a later paper, with the goal to answer these questions.

We conclude that TSC and TL experiments are not adequate tools for measuring trapping parameters in contrast to statements on the subject in the literature. Isolated experiments on glow curves are of little value unless the pertinent parameters are measured by some other experimental technique, in which case TL and TSC may provide an excellent means of checking the results.

ACKNOWLEDGMENTS

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Far-Infrared Donor Absorption and Photoconductivity in Epitaxial n-Type GaAs

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Donor-state absorption and photoconductivity spectra of n-type epitaxial GaAs layers with carrier concentrations in the range 10^{14}–10^{16}/cm^3 are reported. The essentially effective-mass-like behavior of the impurity spectra is confirmed, and ionization energies of 6.08, 5.81, 5.89, and 6.10±0.025 meV are reported for Ge, Si, Se, and S donors. The influence of impurity-banding upon the values of E_D is considered. Central-cell corrections to donor ground-state energies are discussed.

THE effective mass of an electron in the $\mathbf{k}=0$ minimum of the conduction band of GaAs has recently been reported as $(0.0665\pm0.0005)m_0$.[1] The binding energy E_{H} predicted by effective-mass theory for the ground state of a simple donor near $\mathbf{k}=0$ will, therefore, be small, $E_{\mathrm{H}}=5.79$ meV.[2] Many older estimates of donor binding energies, based mainly upon electrical measurements of fairly impure bulk-grown material, are in the region of 2–5 meV.[3] As it is difficult to envisage a potential field that will produce such shallow isolated donors in a III-V semiconductor, it is highly probable that these estimates are influenced by donor-impurity banding.

Epitaxial growth techniques now produce GaAs layers of a purity not previously available, and thus it is of interest to investigate by direct means the question of donor binding energies in n-type GaAs. Very recently, spectroscopic determinations of donor ionization energies E_D of 4.6,[4] ~5.1,[5] 6.8,[6] 6.0,[7] and ~6.5 meV[8] have been reported. Direct chemical identifications have not

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[2] The measurement of ϵ_0 in GaAs seems to have posed several problems and consistent values are simply not available. [See low-frequency determinations reported for ϵ_0; K. S. Champlin *et al.*, Appl. Phys. Letters **11**, 348 (1967); N. Braslau, *ibid.* **11**, 350 (1967); S. Jones and S. Mao, *ibid.* **11**, 351 (1967); C. B. Rodgers *et al.*, *ibid.* **11**, 353 (1967). We reverse the procedure by noting that our result for Si in GaAs puts an upper limit on E_H, and therefore, a (lower) bounded value on ϵ_0. This bounded value is in good agreement with a room-temperature static determination of 12.5±0.3 for ϵ_0. We have thus used $\epsilon_0=12.5$ and $m^*=0.0665\pm0.0005$ as the most consistent and best values available to calculate the hydrogenic donor binding energy in GaAs. We obtain $E_{\mathrm{H}}=13.6m^*/\epsilon_0^2=5.79\pm0.28$ meV.

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