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Theory of Thermally Stimulated Conductivity in a Previously Photoexcited Crystal*

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The theory of thermally stimulated conductivity (TSC) for a single trap depth in the presence of deeper traps, and a single type of recombination center, has been developed in detail without making the customary restrictive approximations and assumptions based on the relative importance of recombination or retrapping, or on the constancy of the lifetime. General conclusions about the shape of the TSC curve are presented, depending on the ratio of recombination to trapping probabilities, and on the ratio of the density of the traps of interest to that of deeper traps. The results of the theory are applied to the particular cases of first-order kinetics, strong retrapping with constant lifetime, and strong retrapping with varying lifetime. A critical discussion is given of the analysis of TSC data according to methods involving the quasi-Fermi-level, the half-widths of the TSC curve, varying heating rates, and the initial activation energy at the beginning of the TSC curve. It is concluded that the method of decayed TSC provides the most reliable determination of trap depth. The results of the theory can be readily adapted for application to systems involving more than one type of recombination center.

INTRODUCTION

A VARIETY of methods have been used for the determination of trapping parameters of imperfections in crystals. Among these various methods thermally stimulated conductivity (TSC) offers the advantage of experimental simplicity and potentially a high yield of information per unit time expended. This method consists of photoexcitation of a crystal at a low temperature, thus producing occupied traps from which the trapped carriers cannot be freed by the available thermal energy at that temperature. When the temperature is increased, usually at a linear rate, for convenience of analysis, these trapped carriers become free and contribute to the conductivity until they recombine with carriers of the opposite type. The conductivity measured in such a heating of the crystal, in excess of the normal dark conductivity, is called the thermally stimulated conductivity. For a single trap depth, information about the magnitude of the trap depth can be obtained from the temperature of the maximum TSC, about the density of traps from the area under the TSC curve, and about the capture cross section of the trap from the detailed shape of the TSC curve. It is the unambiguous derivation of this information from the experimental data that is of chief concern in the interpretation of TSC.

Since thermal stimulation was first proposed by Urbach[1] in connection with luminescence measurements (glow curves), several different models have been explored. The energy-level scheme has been basically the same for the different treatments, consisting of a single trap level, a recombination level, and the conduction band. Differences between the treatments have arisen because of different assumptions about the densities of the levels, their capture cross sections, and their ionization energies.

Two considerations are of primary importance: (1) which is the dominant process—capture of free electrons by recombination centers (lifetime dominant), or capture of free electrons by empty traps (retrapping dominant); and (2) is the lifetime constant during the TSC measurement or is it varying? The combination of these possibilities gives rise to four basic types of TSC curves, three of which have been treated in some detail; (a) lifetime both dominant and constant, giving rise to a first-order kinetics TSC curve[2]; (b) retrapping dominant and lifetime constant, giving rise to an "effective thermal equilibrium" TSC curve analyzable in terms of a quasi-Fermi-level[3,4]; (c) retrapping dominant and lifetime changing[5]; and (d) lifetime both dominant and changing. The only model of type (c) to be analyzed has been one in which the density of holes in recombination centers is equal to the density of trapped electrons (i.e., it is assumed that there are no deeper traps in the crystal and that the density of trapped electrons is much larger than that of free electrons).

Extensions of these basic models exist in the form of criteria by which to judge the shape of a TSC curve. Examples of these are the formulations of Grossweiner[6] relating the partial width of the TSC peak to the trap depth and the capture cross section, derived on a first-order kinetics model, and of Halperin and Braner,[7] and of Luschik,[8] who have expressions involving the

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half-width of the TSC peak for first-order kinetics and for strong retrapping cases.

There are also experimental variations of the simple TSC measurement that permit a determination of trap parameters by an analysis that is somewhat independent of the characteristics of the levels. The heating-rate methods[2,5] are based on the fact that the temperature of the maximum TSC depends on the heating rate used. The initial activation-energy method of Garlick and Gibson[9] assumes that at the beginning of the TSC curve, far below the maximum temperature, the density of free electrons has an activation energy equal to the trap depth. A variant of the preceding, the decayed TSC method, involves a preliminary heating to empty partially the trap of interest as well as to empty completely all shallower traps.

There have been several recent critical investigations of TSC with the purpose of establishing experimentally which of all the proposed methods is the most reliable. Dittfeld and Voigt[10] studied 11 ways of analyzing TSC curves and concluded that the quasi-Fermi-level analysis assuming retrapping dominant was superior to other methods for CdS crystals. At about the same time Nicholas and Woods[11] applied nine ways of analyzing TSC curves to CdS crystals and concluded that first-order kinetics was the most commonly encountered behavior, for which the quasi-Fermi-level approach was by definition completely inadequate. Bube *et al.*[12] concluded that the method of decayed TSC was the most reliable indication of trap depth in the absence of information about the importance of retrapping. For traps for which retrapping was dominant, trap depths determined from decayed TSC agreed with Fermi-level analysis; for traps for which retrapping was negligible, trap depths determined from decayed TSC agreed with decay-curve analysis.

It is the purpose of this paper to investigate the behavior of the classical simple level scheme with the additional consideration of the possibility of deeper filled traps, omitting all of the usual approximations and assumptions related to the characteristics of the levels until a final mathematical expression is at hand. It is in fact possible to do just this, and the results clarify the significance and the applicability of the different methods of analysis.

SOLUTION OF THE KINETIC EQUATIONS

In this section we shall calculate the density of free electrons n as a function of temperature T for a crystal with the energy-level scheme shown in Fig. 1.

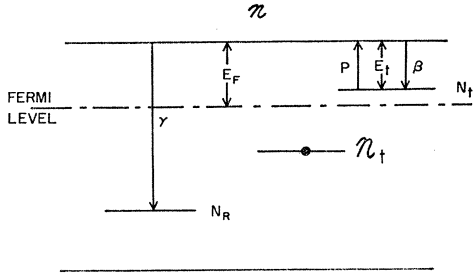

FIG. 1. The simple form of the energy-level diagram forming the model for the considerations of this paper. Included are n free electrons; a quasi-electron-Fermi-level located E_F below the conduction band; N_R recombination centers with a capture probability γ for free electrons; N_t traps with depth E_t, capture probability β for free electrons, and thermal emission probability P; and $\mathfrak{N}_t$ deep traps.

It is assumed that the crystal has two trap levels, a shallower level with density N_t and a deeper level with density $\mathfrak{N}_t$, and one recombination level with density $N_R \gg N_t + \mathfrak{N}_t$.[13] It is assumed that only the shallow traps have effective thermal interaction with the conduction band, and the deeper traps are introduced primarily as a reservoir of excited electrons (and hence of holes in the recombination centers) as a way of simulating different lifetime conditions.

We choose to treat the discrete trap case, in spite of the evidence that the physical situation commonly involves a distribution in energy,[12] in order to gain physical insight into the general nature of the problem and in recognition of the fact that discrete levels do occur even in real crystals.[11,12] The analysis presented here can be extended by extrapolation to a quasi-continuous trap distribution and can be used to clarify the results obtained experimentally in that case.

The kinetic equations based upon the model of Fig. 1 are

$$\dot{n} + \dot{n}_t = -\gamma n (n + n_t + \mathfrak{N}_t) = -n/\tau , \qquad (1)$$

$$\dot{n}_t = \beta n (N_t - n_t) - n_t P , \qquad (2)$$

where $P = \beta N_c \exp(-E_t/kT)$, N_c is the effective density of states in the conduction band, E_t is the shallow trap depth, n_t is the density of electrons trapped in shallow traps, τ is the lifetime for free electrons, γ is the capture probability of a recombination center occupied by a hole for a free electron, and β is the capture probability of an empty trap for a free electron.

The normal condition in high-resistivity crystals is for $n \ll n_t$ and for $\dot{n} \ll \dot{n}_t$. This latter condition is satisfied experimentally for normal heating rates of a fraction of a degree/sec as long as the lifetime is much less than 1 sec; the highest lifetimes encountered in photosensitive materials of CdS-type are less than 0.1 sec. With the additional assumption that N_c is independent of temperature (i.e., that we make negligible error by neglect-

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[13] This assumption is made only to avoid saturation of recombination centers.

ing the $T^{3/2}$ dependence of N_c), Eqs. (1) and (2) become

$$\dot{n}_t=-\gamma n(n_t+\mathcal{N}_t), \tag{3}$$

$$\dot{n}_t=\beta n(N_t-n_t)-n_t P. \tag{4}$$

Eliminating $\dot{n}_t$, we obtain

$$n=\frac{Pn_t}{\beta N_t+\gamma\mathcal{N}_t+(\gamma-\beta)n_t}, \tag{5}$$

and

$$n_t=\frac{(\beta N_t+\gamma\mathcal{N}_t)n}{(\beta-\gamma)n+P}=N_t\frac{\beta N_t+\gamma\mathcal{N}_t}{\beta N_t}\times\frac{1}{1-(\gamma/\beta)+\exp[(E_F-E_t)/kT]}, \tag{6}$$

where E_F is the depth of the Fermi level below the conduction band. Differentiating Eq. (5) with respect to t, setting $T=T_0+bt$, where b is the linear heating rate, we obtain

$$\frac{\dot{n}}{n}=\frac{bE}{kT^2}-\frac{\gamma P}{\beta}\left(\frac{\beta n}{P}\right)^2\left(1-\frac{\gamma}{\beta}+\frac{P}{\beta n}\right)-\frac{\beta\mathcal{N}_t}{\beta N_t+\gamma\mathcal{N}_t}\frac{\gamma P}{\beta}\left(\frac{\beta n}{P}\right)^2\left(1-\frac{\gamma}{\beta}+\frac{P}{\beta n}\right)^2. \tag{7}$$

It is not necessary at this state to assume a linear heating rate, and the calculation could be carried through in a general way for any heating program by retaining t as the variable. Since in practice, however, a linear heating rate is commonly used, we have introduced it here.

The integration of Eq. (7) can be expressed formally as

$$\ln\left(\frac{n}{n_0}\right)=y_0-y-I=y_0-y-\ln\left(\frac{x}{x_0}\right), \tag{8}$$

where

$$y=E_t/kT, \tag{9}$$

$$y_0=E_t/kT_0, \tag{10}$$

$$x=\exp\left(\frac{E_F-E_t}{kT}\right)=\frac{P}{\beta n}, \tag{11}$$

$$x_0=\exp\left(\frac{E_{F0}-E_t}{kT_0}\right)=\frac{P(T_0)}{\beta n_0}, \tag{12}$$

$$I=\ln\left(\frac{x}{x_0}\right)=\int_{T_0}^{T}\frac{\gamma P}{b\beta}\left(\frac{\beta n}{P}\right)^2\left(1-\frac{\gamma}{\beta}+\frac{P}{\beta n}\right)\times\left(1+\frac{N_t}{\mathcal{N}_t}+\frac{P}{\beta n}\right)\frac{\beta\mathcal{N}_t}{\beta N_t+\gamma\mathcal{N}_t}dT'. \tag{13}$$

According to Eqs. (11) and (12), Eq. (13) can be written as

$$I=\frac{\beta\mathcal{N}_t}{\beta N_t+\gamma\mathcal{N}_t}\int_{T_0}^{T}\frac{\gamma P}{b\beta}x^{-2}\left(1-\frac{\gamma}{\beta}+x\right)\times\left(1+\frac{N_t}{\mathcal{N}_t}+x\right)dT'. \tag{14}$$

Then we can calculate

$$\frac{dI}{dT}=\frac{\beta\mathcal{N}_t}{\beta N_t+\gamma\mathcal{N}_t}\frac{\gamma P}{b\beta}\frac{(1-\gamma/\beta+x)(1+N_t/\mathcal{N}_t+x)}{x^2}=\frac{1}{x}\frac{dx}{dT}=-\frac{dx}{dy}\frac{k}{E_t}\frac{y^2}{x}, \tag{15}$$

from which it is possible to obtain $x=x(T)$ as an implicit function,

$$-\left[1-\frac{\gamma}{\beta}\right]\ln\left(\frac{1-\gamma/\beta+x}{1-\gamma/\beta+x_0}\right)+\left(1+\frac{N_t}{\mathcal{N}_t}\right)\times\ln\left(\frac{1+N_t/\mathcal{N}_t+x}{1+N_t/\mathcal{N}_t+x_0}\right)=\frac{\gamma N_c}{b}\frac{E_t}{k}F(y), \tag{16}$$

where

$$F(y)=\int_{y}^{y_0}y^{-2}e^{-y}dy. \tag{17}$$

The solution of Eq. (16) substituted into Eq. (8) gives the density of free electrons as a function of the temperature; neglecting the temperature dependence of mobility, this is then the desired solution for the TSC.

GENERAL CONSIDERATIONS

Before considering detailed calculations in a later section, a general discussion of the properties of the above equations is fruitful.

Equation (16) shows that the characteristics of the TSC curve are determined by three relationships between parameters. (1) The ratio γ/β, which is related to the relative importance of recombination and retrapping, (2) the ratio $N_t/\mathcal{N}_t$, which is related to the change in lifetime during the TSC measurement, and (3) the ratio $\gamma N_c E_t/bk$, which determines the temperature for the maximum TSC, since $\ln F(y)$ is almost a simple linear function of y. If these parameters are specified, together with the initial conditions described by x_0, the solution is completely determined.

Initial Conditions

In terms of the variable x, Eq. (6) becomes

$$\frac{n_t}{N_t}=\frac{\beta N_t+\gamma\mathcal{N}_t}{\beta N_t}\frac{1}{1-\gamma/\beta+x}. \tag{18}$$

Table I. Initial conditions for an initially filled trap.

$\frac{\gamma}{\beta}$	$\frac{\mathfrak{N}_t}{N_t}$	$\frac{\gamma\mathfrak{N}_t}{\beta N_t}$	x_0	Physical description
>1	>1	>1	>1	No retrapping; constant lifetime
>1	<1	>1	>1	No retrapping; changing lifetime
<1	>1	>1	>1	No retrapping; constant lifetime
<1	>1	<1	<1	Strong retrapping; constant lifetime
<1	<1	<1	<1	Strong retrapping; changing lifetime

Since n_t can never be greater than N_t, a lower limit for x_0 is established by the conditions of Eq. (18). If we set $n_{t0}=N_t$, i.e., the traps are initially filled,

$$x_0=\frac{\gamma}{\beta}\left[1+\frac{\mathfrak{N}_t}{N_t}\right]. \tag{19}$$

If the result of Eq. (19) is applied to Eq. (15), it is seen that $(dx/dy)_0$ is negative, which means that x is increasing with decreasing y, such that for y less than y_0, dx/dy is always negative. Thus x is a monotonically increasing function of temperature.

Table I summarizes the initial conditions in the case of an initially filled trap for different relations between the parameters, emphasizing the physical situation of each case. These conditions should hold if the quasi-Fermi level is above the trap level of interest under excitation at low temperatures.

It is of interest to note that when $\gamma<\beta$, the first-order kinetics TSC peak can be "imitated" by a trap with strong retrapping, simply by initially emptying the trap sufficiently for x_0 to become much larger than unity. This results because Eq. (16) does not depend on the ratio $\gamma\mathfrak{N}_t/\beta N_t$, which is the only difference between the two cases. This is the reason that Haering and Adams[2] obtain the same shape for the first-order kinetics and the strong retrapping cases. In order to be able to integrate the system of kinetic equations, these authors assume that strong retrapping is dominant over recombination from the beginning; such a situation can occur only if the trap is sufficiently empty.

If the trap is initially filled, the strong retrapping curve starts as a nonretrapping case. Since the capture cross section, and hence the thermal emission probability, is relatively high, however, the curve appears at lower temperatures than it would for a real nonretrapping situation. When the emptying of the trap has proceeded sufficiently so that retrapping becomes important, an effect that may be thought of as equivalent to a decrease in the effective net thermal emission rate, the whole curve is shifted toward higher temperatures, thus producing a broader peak. For a trap that was initially almost completely empty, the capture is not affected by further emptying of the trap, so that the effective net thermal emission depends on temperature in the usual way and gives a first-order kinetics TSC peak.

Relevance of the Quasi-Fermi-Level

The expression for n_t/N_t given in Eq. (18) may be compared with that obtained for steady-state photoexcitation for the same trap,

$$n_t/N_t=1/(1+x). \tag{20}$$

Equation (18) gives directly the effect of recombination on the occupancy of the trap. In the case where $\gamma/\beta\ll1$, and $\beta N_t/\gamma\mathfrak{N}_t\gg1$, i.e., retrapping dominant over recombination, the quasi-Fermi-level is a useful quantity.

If a quasi-Fermi-level E_{Ft} for traps during the TSC is defined,[14] so that

$$n_t/N_t=1/(1+x'), \tag{21}$$

where $x'=\exp[(E_{Ft}-E_t)/kT]$, then equating Eqs. (18) and (21), one obtains

$$x=\frac{\gamma}{\beta}\left(1+\frac{\mathfrak{N}_t}{N_t}\right)+\left(1+\frac{\gamma\mathfrak{N}_t}{\beta N_t}\right)x'=x_0+\left(1+\frac{\gamma\mathfrak{N}_t}{\beta N_t}\right)x'. \tag{22}$$

Since all the coefficients in Eq. (22) are positive, and since the coefficient of x' is always larger than or equal to 1, we may conclude that $x>x'$, and that $E_F>E_{Ft}$. For the nonretrapping cases ($\gamma/\beta\gg1$, or $\gamma\mathfrak{N}_t/\beta N_t\gg1$), it is also true that $E_F>E_t$, ($x>1$). Since Eq. (18) is particularly valid at the maximum of the TSC curve, where $\dot{n}=0$, this result is another way of showing that the first-order kinetics peak is characterized by a quasi-Fermi-level for electrons lying below the trap level. It is evident that although under various circumstances E_F and E_{Ft} may be almost coincident, they are never exactly equal.

Shape of the TSC Curve

Equation (8) can be rewritten as

$$\ln n=\ln N_c-y-\ln x, \tag{23}$$

and in terms of x and y, Eq. (7) is

$$\dot{n}=\left(\frac{nbky^2}{E_t}\right)\left[1-\left(1-\frac{\gamma}{\beta}+x\right)\left(1+\frac{N_t}{\mathfrak{N}_t}+x\right)x^{-2}G(y)\right], \tag{24}$$

where

$$G(y)=\frac{\beta N_cE_t}{(\beta N_t/\gamma\mathfrak{N}_t+1)bk}y^{-2}e^{-y}. \tag{25}$$

Let us simplify the notation by defining

$$g(x)\equiv x^2(1-\gamma/\beta+x)^{-1}(1+N_t/\mathfrak{N}_t+x)^{-1}, \tag{26}$$

so that

$$\frac{\dot{n}}{n}=\left(\frac{bky^2}{E_t}\right)\left(1-\frac{G(y)}{g(x)}\right)=\left(\frac{bky^2}{E_t}\right)\left(1+x^{-1}\frac{dx}{dy}\right). \tag{27}$$

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[14] G. A. Dussel and R. H. Bube, J. Appl. Phys. **37**, 2797 (1966).

It has been previously pointed out that dx/dy is always negative, so that x is a monotonically increasing function of T or t; with T increasing, therefore, $g(x)$ tends to 1 while $G(y)$ increases. For sufficiently low T, $G(y) \ll g(x)$, and the Garlick and Gibson[9] activation energy from the slope may be obtained by integrating Eq. (27). Further conditions for the validity of this approach will be discussed later.

The condition

$$G(y)=g(x) \tag{28}$$

defines through Eq. (8) the loci of the points in the $(\ln n,y)$ plane that are solutions of $\dot{n}=0$, i.e., the extrema of the function $n(y)$. Whether the extrema obtained in this way are maxima or minima can be established as follows. At constant y, i.e., fixed $G(y)$, if upon increasing x over the value corresponding to Eq. (28) [i.e., according to Eq. (23), decreasing n], $g(x)$ increases, then $\dot{n}>0$; if $g(x)$ decreases, $\dot{n}<0$. Since Eq. (28) separates the $(\ln n,y)$ plane into two regions with different signs of the slopes, the whole behavior of the TSC curve will be determined by the dependence of $g(x)$ on x. $G(y)$ has a simple behavior with y; changing the parameters simply displaces the curve but leaves the shape unchanged.

Since, according to Eq. (19), $x \geq (\gamma/\beta)(1+\mathfrak{N}_t/N_t)$, all points lying above the line

$$\ln n_{\max}=\ln N_c-y-\ln[(\gamma/\beta)(1+\mathfrak{N}_t/N_t)] \tag{29}$$

are not attainable with a given set of parameters, unless of course another set of traps exists that can maintain such a point. Thus, given a crystal, all possible solutions corresponding to a particular trap are restricted to the semi-plane lying below the line of Eq. (29).

In general,

$$g(x)=x^2(a+x)^{-1}(c+x)^{-1}, \tag{30}$$

where

$$-\infty<a\equiv 1-\gamma/\beta<1, \tag{31}$$

$$1<c\equiv 1+N_t/\mathfrak{N}_t<\infty\,. \tag{32}$$

Equation (30) for $g(x)$ has two poles at $x=-a$ and $x=-c$, a double zero at $x=0$, and extrema at $x=0$ and $x=-2ac/(a+c)$. The derivative of $g(x)$ with respect to x is

$$\frac{dg(x)}{dx}=x[2ac+(a+c)x](a+x)^{-2}(c+x)^{-2}. \tag{33}$$

All points of physical interest correspond to the region

$$x \geq x_0 \geq \frac{\gamma}{\beta}\left(1+\frac{\mathfrak{N}_t}{N_t}\right) \equiv (1-a)\frac{c}{c-1} > \left\{\begin{matrix} 0 \\ -a \\ -c \\ \gamma/\beta \\ \gamma\mathfrak{N}_t/\beta N_t \end{matrix}\right\}. \tag{34}$$

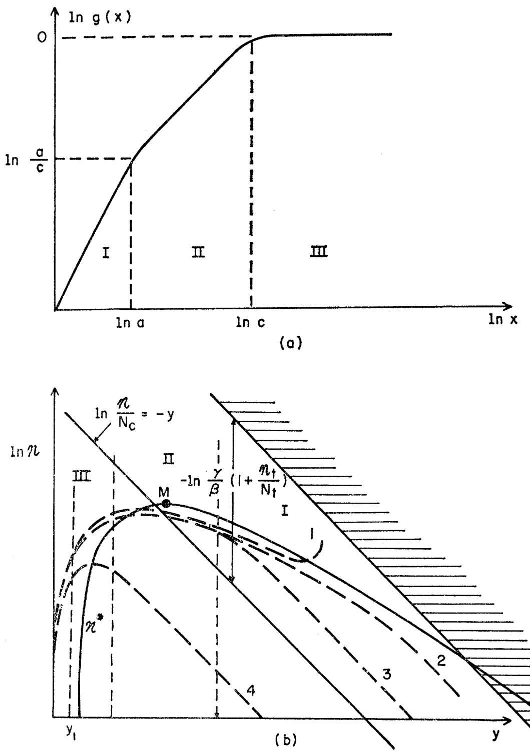

FIG. 2. (a) Plot of $g(x)$ as a function of x according to Eq. (30) for $a>0$ and $c>0$. (b) Corresponding free-electron density n in a TSC measurement as a function of y, according to Eq. (27). n^* are those values of n for which $\dot{n}=0$. Dashed curves 1, 2, 3, and 4 represent cases of decreasing initial occupancy of the trap. The curves are not drawn to scale, features having been exaggerated to emphasize the tendencies.

Thus the poles and zeros of Eq. (30) are excluded, but not necessarily the extremum in $g(x)$. There are just three physically meaningful cases: (a) $a>0$ and $c>0$. $g(x)$ is a monotonically increasing function of x. (b) $a<0$ and $(a+c)>0$. For small values of x, $g(x)$ may be a decreasing function of x [$dg(x)/dx$ from Eq. (33) <0]. The function has a minimum at $x=-2ac/(a+c)$, and then increases with x. (c) $a<0$ and $(a+c)<0$. $g(x)$ is a monotonically decreasing function of x.

These three cases may be discussed in somewhat more detail to get a complete picture of the shape of the TSC curve.

(*a*) $a>0$ *and* $c>0$. Let n^* be the value of n that satisfies the condition of Eq. (28) ($\dot{n}=0$) in the $(\ln n,y)$ plane. $g(x)$ increases continuously with x, but has three different dependences: (i) for $x<a$, $g(x)\propto x^2$ [region I of Fig. 2(a)]; (ii) for $a<x<c$, $g(x)$ is a linear function of x [region II of Fig. 2(a)]; (iii) for $x>c$, $g(x)$ is practically a constant with value unity [region III of Fig. 2(a)]. Since $G(y)$ is very nearly a simple exponential function, $n^* \propto \exp[-(y/2)-\ln y]$ in region I, n^* is nearly constant in region II and n^* decreases rapidly in region III. The parameters, besides influencing the location of the curve on the y axis, also determine the extension of

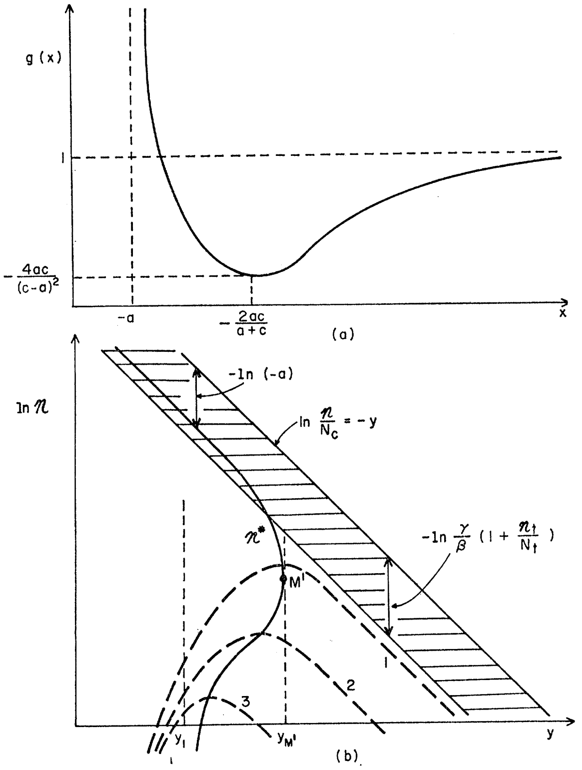

FIG. 3. (a) Plot of $g(x)$ as a function of x according to Eq. (30) for $a<0$ and $(a+c)>0$. (b) Corresponding free-electron density n in a TSC measurement as a function of y, according to Eq. (27). n^* are those values of n for which $\dot{n}=0$. Dashed curves 1, 2, and 3 represent cases of decreasing initial occupancy of the trap. The curves are not drawn to scale, features having been exaggerated to emphasize the tendencies.

region II, which depends on the ratio a/c as shown in Fig. 2(a).

Since $g(x)$ is an increasing function of x, points above n^* have $\dot{n}<0$, while points below n^* have $\dot{n}>0$. Thus points corresponding to n^* to the right of M in Fig. 2(b) represent minima, while points corresponding to n^* to the left of M represent maxima. This means that if an initial point lies above n^*, the effect of increasing the temperature will cause it to move down till it crosses n^* horizontally ($\dot{n}=0$); then n will increase with increasing T until it crosses n^* again to the left of point M, after which it will decrease. The latter crossing point is the maximum of the TSC curve under the given initial conditions. If the initial point lies below n^*, and if the vertical distance to n^* is large [x_0 much larger than the value satisfying Eq. (28) for the given y], then it moves upwards with a slope of -1 until it either comes close to n^* to the right of M, in which case the slope now reduces to about $-\frac{1}{2}$ until the solution emerges to the left of M, or if the initial value of x_0 is large enough, the solution can cross n^* directly without having a region of $-\frac{1}{2}$ slope. These cases are all illustrated in Fig. 2(b).

Because of the uniqueness of the solutions, curves with $x_0<1$ must exhibit a region with a slope of approximately $-\frac{1}{2}$. Thus a fully excited strong retrapping trap must exhibit a smaller activation energy in a Garlick-Gibson[9]–type measurement than when decay of the trap population has been permitted at a temperature close to or above the TSC maximum before measuring the activation energy. The shift in the temperature of the TSC maximum following decay to different temperatures should also be appreciable. In contrast, a first-order kinetics nonretrapping trap ($x_0>1$) can exhibit only a single activation energy regardless of the degree of decay since the point M now lies in the forbidden region. Also, since the maximum of the TSC occurs in the region of the steep decrease of n^*, the shift of the temperature of the TSC maximum should be hardly observable.

(*b*) $a<0$ *and* $(a+c)>0$. The dependence of $g(x)$ on x is shown in Fig. 3(a), and the general form of n^* in Fig. 3(b). For $x>-2ac/(a+c)$, $g(x)$ increases with x and hence $\dot{n}>0$ for $n<n^*$. For $x<-2ac/(a+c)$, $g(x)$ is a decreasing function of x and $\dot{n}>0$ for $n>n^*$. If the initial point lies to the right of n^*, the TSC can have only a maximum; if the point lies to the left of n^*, the TSC has no extrema at all and decreases monotonically with increasing temperature.

Since $a<0$ implies that $\gamma/\beta>1$,

$$x_{\min}=(\gamma/\beta)[1+(\mathfrak{N}_t/N_t)]>1.$$

This implies that the branch of n^* above the point M' can be reached from initial points to the right of n^* only under very unusual circumstances. In fact, to have an extremum above M' requires at least that

$$x_{\min}=\frac{(1-a)c}{c-1}<x_{M'}=-\frac{2ac}{(a+c)},$$

or $(a-c)(1+a)>0$. Since $a<0$ and $c>1$, this implies $1<-a$, or $\gamma/\beta>2$, which corresponds to a lifetime dominant over retrapping situation. Since, in addition, for this case to exist at all, $(a+c)>0$, or $N_t/\mathfrak{N}_t>[\gamma/\beta-2]$, the lifetime must in general be not only dominant but changing with T as well.

The lower branch of n^* below M' is contained between the limiting values of y given by

$$y_{M'}^{-2}e^{-y_{M'}}=\frac{bk}{E_t}\frac{4}{\gamma N_c}\frac{(\gamma/\beta-1)(1+N_t/\mathfrak{N}_t)}{(\gamma/\beta+N_t/\mathfrak{N}_t)}$$

$$=y_1^{-2}e^{-y_1}\frac{4(\gamma/\beta-1)(1+N_t/\mathfrak{N}_t)}{(\gamma/\beta+N_t/\mathfrak{N}_t)^2}, \quad (35)$$

and

$$y_1^{-2}e^{-y_1}=\frac{bk}{E_t}\frac{1}{\gamma N_c}\left(\frac{\gamma}{\beta}+\frac{N_t}{\mathfrak{N}_t}\right), \quad (36)$$

since

$$G(y_M')=g(x_{\min})=-\frac{4ac}{(c-a)^2}; \quad G(y_1)=g(x\rightarrow\infty)=1.$$

Thus the larger the value of $N_t/\mathfrak{N}_t$ relative to γ/β,

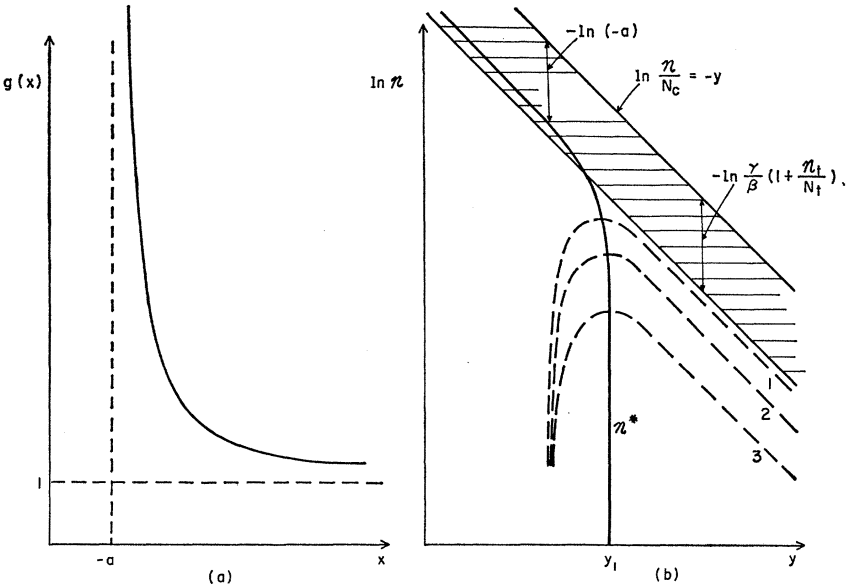

FIG. 4. (a) Plot of $g(x)$ as a function of x according to Eq. (30) for $a<0$ and $(a+c)<0$. (b) Corresponding free-electron density n in a TSC measurement as a function of y, according to Eq. (27). n^* are those values of n for which $\dot{n}=0$. Dashed curves 1, 2, and 3 represent cases of decreasing initial occupancy of the trap. The curves are not drawn to scale, features having been exaggerated to emphasize the tendencies.

$(c \gg a)$, the larger the shift in the TSC with decay at different temperatures.

For $1 \leq \gamma/\beta \leq 2$, the forbidden region includes the point M', so that only the lower branch of n^* is observable for this case. For these values of γ/β any value of $N_t/\mathfrak{N}_t > 0$ satisfies the relation $(a+c)>0$.

For an initial point to the right of n^*, the solution moves along a line of slope -1 since $g(x) \gg G(y)$, until it approaches n^*, where it represents the maximum of the TSC.

Differences between case (b) and case (a) can be summarized. 1. In case (b), decaying to temperatures below the maximum does not alter the curve shape. This is the result of the fact that the decay component in $\dot{n}$ is negligible until the maximum is reached, so that the trap is in the same initial condition after decay at temperatures below the maximum. In case (a), on the other hand, after heating to a temperature $T_1 < T_m$, a slope of -1 appears in the TSC until a temperature close to T_1 is reached, whereupon the slope decreases to approximately $-\frac{1}{2}$. 2. If $N_t/\mathfrak{N}_t \gg \gamma/\beta$, heating close to or slightly above the temperature of the maximum TSC produces only very slight decrease in the temperature at the maximum while the current (n) decreases much more rapidly. This is quite different from case (a). 3. When TSC curves are measured after decaying to above the TSC maximum, an increased shift of the peak toward higher temperatures is found until it finally stabilizes at the temperature corresponding to y_1. In case (a), heating above the initial maximum produces almost no change in the temperature of the peak, although of course this peak is shifted with respect to the undecayed curve. 4. There is no minimum at the beginning of the TSC, unless there is a shallow trap which is still emptying. 5. There is no region with slope of $-\frac{1}{2}$.

(c) $a<0$ *and* $(a+c)<0$. These conditions apply whenever lifetime is dominant and constant with $\gamma/\beta > 2$, or dominant and changing with $\gamma/\beta > [2+N_t/\mathfrak{N}_t]$. Corresponding $g(x)$ and n^* curves are given in Figs. 4(a) and 4(b), respectively. Since $g(x)$ is a decreasing func-

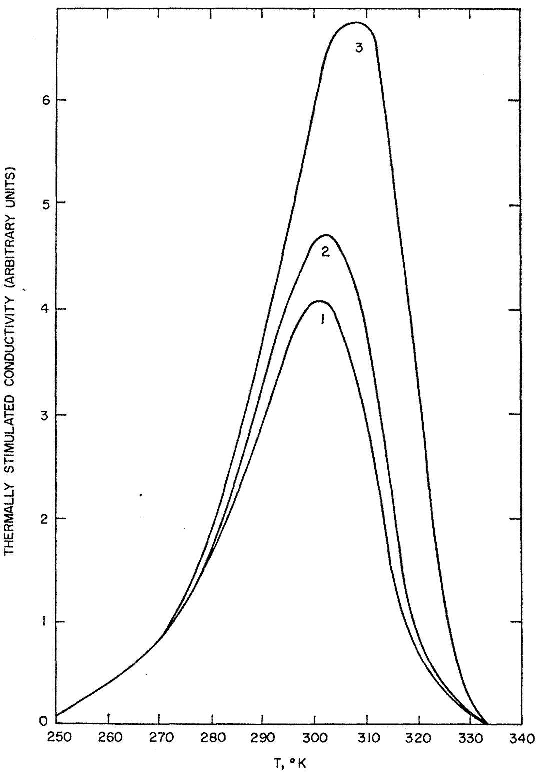

FIG. 5. Typical TSC curves for nonretrapping cases. Plotted for $A=10^{12}$ and $E_t=0.55$ eV. (1) Eq. (39) or Eq. (40) with $x_0=10$; (2) Eq. (37); (3) Eq. (16) with $\mathfrak{N}_t/N_t \ll 1$, and $\gamma\mathfrak{N}_t/\beta N_t \gg 1$.

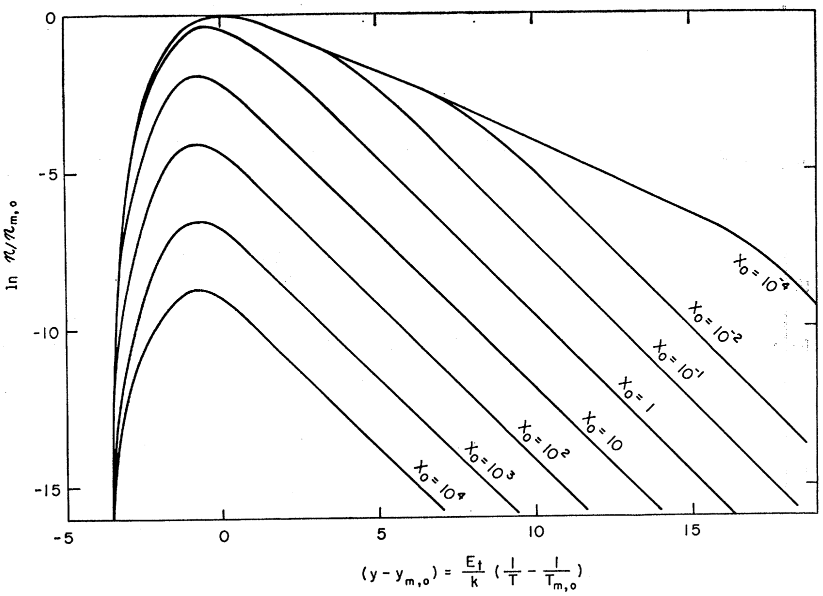

FIG. 6. Variation of the shape of the TSC curve for the case of strong retrapping with lifetime constant, as a function of the initial occupancy of the traps. The ln of the ratio of n to the value $n_{m,0}$ is plotted as a function of the difference between y and $y_{m,0}$, where the subindex "m,0" refers to the maximum of the TSC for the completely filled trap.

tion of x, points to the right of n^* have $\dot{n}>0$, while points to the left of n^* have $\dot{n}<0$. This case is quite similar to (b) except that the lower branch of the n^* curve does not exist. Thus in measurements of decayed TSC, only shifts toward lower temperatures can be observed, if detectable. The most favorable conditions to observe such "negative" shifts are when $\gamma/\beta\gg1$ and $N_t/\mathfrak{N}_t\ll1$, i.e., lifetime dominant and constant.

APPLICATION TO PARTICULAR CASES

First-Order Kinetics

The first-order kinetics case corresponds to a situation of constant lifetime ($\mathfrak{N}_t\gg N_t$) and no retrapping ($\gamma\mathfrak{N}_t/\beta N_t\gg1$). The usual derivation neglects the term corresponding to capture in the expression for $\dot{n}_t$ given in Eq. (2). With this approximation

$$\ln\left(\frac{x}{x_0}\right)=\frac{\beta N_cE_t}{bk}F(y), \tag{37}$$

whereas a first-order kinetics peak derived from Eq. (16) under the above conditions leads to slightly different expressions. According to Table I there are two situations capable of producing a first-order kinetics peak, one in which the nonretrapping arises from $\gamma>\beta$, and a second in which retrapping is made less than recombination because $\mathfrak{N}_t\gg N_t$ in spite of the fact that $\gamma<\beta$. The corresponding approximations are

$$\gamma/\beta\gg1,$$

$$\ln\left(\frac{1+x}{1+x_0}\right)-\left(\frac{\gamma}{\beta}-1\right)[(1+x)^{-1}-(1+x_0)^{-1}]=\frac{\beta N_cE_t}{bk}F(y); \tag{38}$$

$$\gamma/\beta\ll1,\quad \gamma\mathfrak{N}_t/\beta N_t\gg1,$$

$$\ln\left(\frac{1+x}{1+x_0}\right)+[(1+x)^{-1}-(1+x_0)^{-1}]=\frac{\beta N_cE_t}{bk}F(y). \tag{39}$$

The fact that a trap gives a first-order kinetics TSC peak does not prove in itself that the capture cross section of recombination centers is much larger than that of the trap; the first-order kinetics peak could be due to the presence of a high-density deeper trap.

In the first-order kinetics case, the temperature for maximum TSC is almost completely independent of the initial occupancy of the trap. A very small shift toward higher temperatures should occur with decreasing initial occupancy of the trap, Examples of such behavior have been reported.[12]

As long as the lifetime is constant ($\mathfrak{N}_t/N_t\gg1$), the shape of the curves given by Eqs. (37), (38), and (39) is practically the same. The principal difference is a slight rounding of the maximum, which gives a slightly different half-width for the three cases. This is much more pronounced for the changing-lifetime case ($\mathfrak{N}_t/N_t\ll1$; $\gamma\mathfrak{N}_t/\beta N_t\gg1$), in which the increase in lifetime maintains the exponential increase in n much longer. Examples are given in Fig. 5.

Strong Retrapping: Lifetime Constant

Applying the appropriate assumptions as listed in Table I to Eq. (16) reduces it to

$$\ln\left(\frac{1+x}{1+x_0}\right)+[(1+x)^{-1}-(1+x_0)^{-1}]=\frac{\beta}{1+\beta N_t/\gamma\mathfrak{N}_t}\frac{N_cE_t}{bk}F(y). \tag{40}$$

Since the shape of the curve is practically unchanged by a displacement in the position of the maximum [corresponding to a different value of the constant multiplier of $F(y)$ in Eq. (40)], a family of curves can be drawn with x_0 as varying parameter, representing Eq. (40) as a function of $y - y_{m\,0}$, where $y_{m,0}$ is the position of the maximum for the initially completely filled trap. Such a family is given in Fig. 6. Figure 7 shows[15] the way in which the position of the maximum (y_m) depends on the value of the constant multiplier. The shift of the peak due to different initial conditions is much larger in this case than in the first-order kinetics case, of the order of one unit of y [Fig. 7(a)]. The curve is also much broader than in the first-order case, as will be discussed further on.

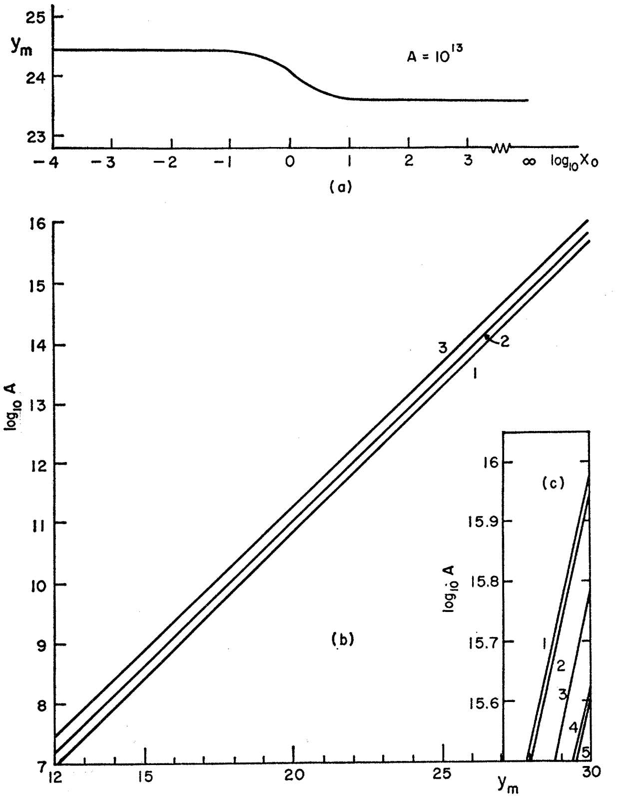

FIG. 7. Case of strong retrapping with lifetime constant. (a) Variation of the temperature of the maximum of the TSC with initial occupancy of the traps for a value of the constant multiplier of $F(y)$ in Eq. (40), $A = 10^{13}$. (b) Dependence of the temperature of the maximum of the TSC on value of A. Curve 1 is for $x_0 = 10^{-4}$, curve 2 for $x_0 = 1$, and curve 3 for $x_0 = 10^2$. (c) Detail of (b) showing variation of temperature for maximum TSC on the value of A for $\infty < x_0 \leq 10^2$ (curve 1), $x_0 = 10$ (curve 2), $x_0 = 1$ (curve 3), $x_0 = 10^{-1}$ (curve 4), and $x_0 = 10^{-4}$ (curve 5).

Strong Retrapping: Lifetime Changing

This case has been treated in some detail by Böer *et al.*,[5] for the case $\mathfrak{N}_t = 0$. In that case Eq. (16) reduces to

$$-\ln\left(\frac{1+x}{1+x_0}\right) + x - x_0 = \frac{\gamma N_c E_t}{bk} F(y). \qquad (41)$$

Figures 8 and 9 show respectively the shape of the curve and the position of the maximum as a function of the constant multiplier of $F(y)$ in Eq. (41), using the initial occupancy of traps (x_0) as a varying parameter. The peak has broadened enormously because of the increase in lifetime, and a large shift of the maximum of the TSC to higher temperatures is found for decreasing initial occupancy.

In actual fact the situation described by Eq. (41) is relatively unlikely, since it assumes there are no deeper traps in the material. The presence of some deeper trap, however small its density, will alter the shape of the TSC curve in a radical way. When the trap

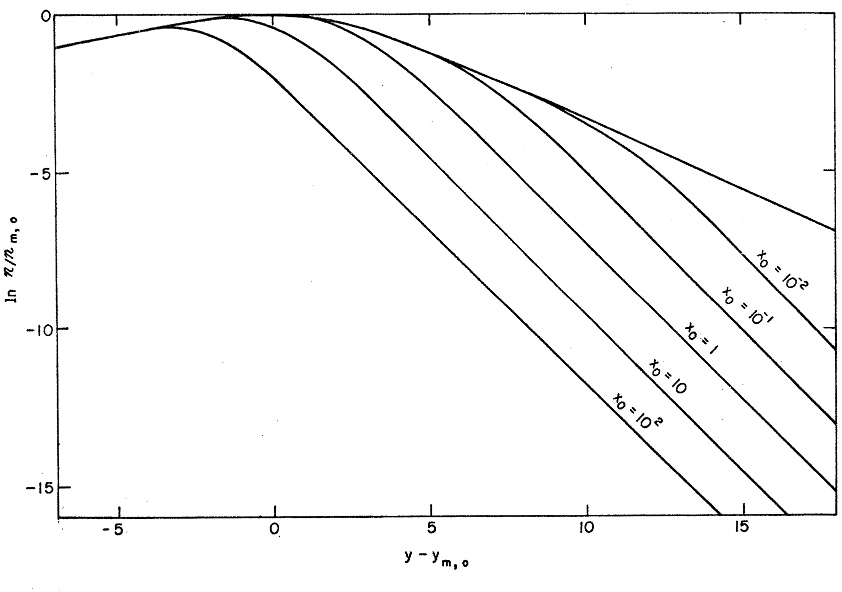

FIG. 8. Variation of the shape of the TSC curve for the case of strong retrapping with lifetime changing without limit, as a function of the initial occupancy of the traps. The ln of the ratio of n to the value $n_{m,0}$, is plotted as a function of the difference between y and $y_{m,0}$, where the subindex "m,0" refers to the maximum of the TSC for the completely filled trap.

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[15] Obtained by eliminating x_m between Eqs. (44) and (46), with the approximations of this section.

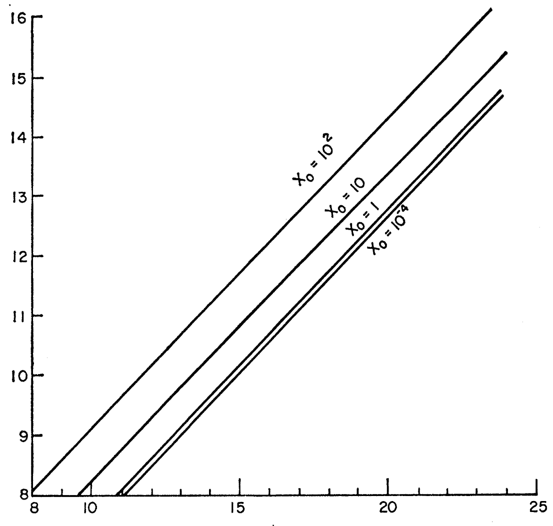

FIG. 9. Case of strong retrapping with lifetime changing without limit. Dependence of the temperature of the maximum of the TSC on the value of the constant multiplier A in Eq. (41), for different values of initial occupancy of the trap.

has emptied to such an extent that its density of trapped electrons becomes comparable to the density of trapped electrons in deeper traps, the lifetime becomes constant and the curve will terminate with a shape corresponding to those given in Fig. 6. Figure 10 shows a family of curves generated from Eq. (16) by changing the ratio $N_t/\mathfrak{N}_t$, so as to go from the case of completely constant lifetime to the case of completely changing lifetime ($\mathfrak{N}_t \approx 0$). For comparison two constant-lifetime cases with different lifetimes are also shown, these being chosen so that one of them has the lifetime corresponding to an "intermediate" changing-lifetime case at the beginning of the TSC (determined by N_t), while the other has the lifetime corresponding to the end of the "intermediate" case (determined by $\mathfrak{N}_t$). Since any "intermediate" case must go between two constant-lifetime cases, an estimate of the shift in the temperature of the maximum with different initial occupancy, as well as of the half-width of the peak, can be obtained from Figs. 6 and 7. Evidently the half-width of such an "intermediate" peak must be larger than that corresponding to a constant-lifetime case.

Another illustration of the effect of the ratio of deep traps to traps being observed on the properties of the TSC curve, Fig. 11 shows six TSC curves calculated for fixed values of all parameters except the ratio of $\mathfrak{N}_t$ to N_t. The effect of changing $\mathfrak{N}_t/N_t$ from 10^7 to 10^{-2} is to change the character of the peak from first-order kinetics, through strong retrapping with constant lifetime, to strong retrapping with changing lifetime. By changing the ratio $\mathfrak{N}_t/N_t$ by a factor of 10^9, the temperature of the peak is increased by a factor of over 2 and the half-width is increased by a factor of about 10. Even relatively small changes in the lifetime (one or two orders of magnitude) such as might be quite normal in experiments with different crystals, change the temperature of the maximum by 15 to 20%. This implies that comparison of the results of different workers on "similar" crystals, using the temperature of the maximum as a criterion, is not a reliable procedure.

CRITICAL DISCUSSION OF SOME METHODS

Quasi-Fermi-Level Analysis

One method that has been used to estimate the trap depth from a measurement of TSC is to equate the trap depth desired with the value of the quasi-Fermi level at the TSC maximum. In a previous section we have shown the general nature of the approximation involved in this procedure. Now we investigate this approximation in more detail.

The maximum of the TSC curve is characterized by the condition that $\dot{\mathfrak{n}}_m = 0$. From Eq. (27).

$$\dot{\mathfrak{n}}_m = 0 = (\mathfrak{n}_m b k y_m^2/E_t)(1 + x^{-1} dx/dy)_m, \qquad (42)$$

or

$$(dx/dy)_m = -x_m. \qquad (43)$$

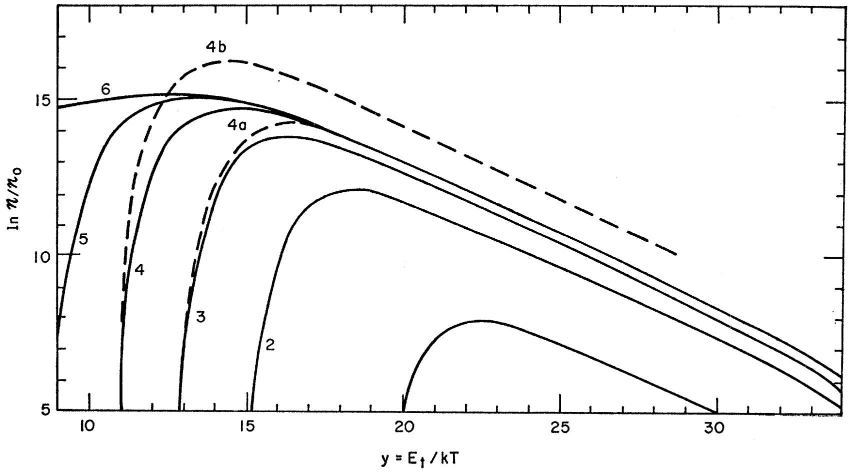

FIG. 10. A family of TSC curves generated from Eq. (16) by changing the ratio $N_t/\mathfrak{N}_t$, so as to go from the case of completely constant lifetime to the case of completely changing lifetime. Curves are plotted for $\gamma/\beta = 10^{-6}$ and $\gamma N_c E_t/bk = 10^9$, with $N_t/\mathfrak{N}_t$ given by (1) 10^{-3}, (2) 10^{-1}, (3) 1, (4) 10, (5) 10^2, (6) ∞. Curves 4a and 4b represent constant-lifetime cases with $\beta N_c E_t/\{[1 + (\beta N_t/\gamma \mathfrak{N}_t)]bk\} = 10^{10}$ and 10^9, respectively.

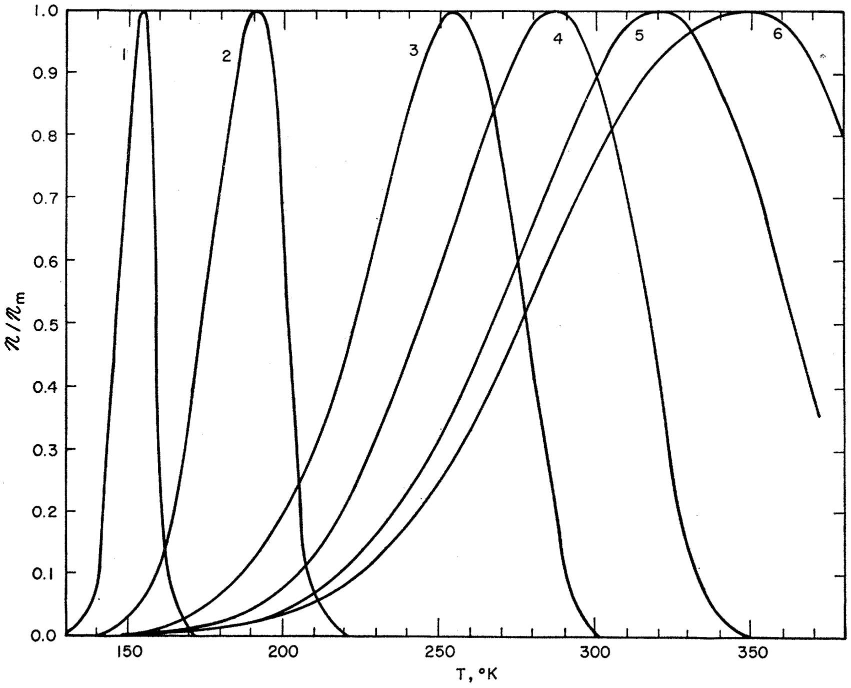

FIG. 11. A family of TSC curves all of which correspond to $E_t=0.40$ eV, $b=0.23°/\text{sec}$, $N_c=10^{19}\ \text{cm}^{-3}$, $\gamma=5\times10^{-14}\ \text{cm}^3/\text{sec}$, and $\beta=5\times10^{-9}\ \text{cm}^3/\text{sec}$. The family parameter is the ratio $\mathcal{N}_t/N_t$ which has the values: (1) 10^7, (2) 10^4, (3) 10, (4) 1, (5) 10^{-1}, (6) 10^{-2}. Note that n_m is different for the different curves.

From Eq. (15),

$$\frac{x_m^2}{(1-\gamma/\beta+x_m)(1+N_t/\mathcal{N}_t+x_m)} = \frac{\gamma N_c E_t}{bk} y_m^{-2} e^{-y_m} \left(\frac{\gamma}{\beta}+\frac{N_t}{\mathcal{N}_t}\right)^{-1}. \qquad (44)$$

The intersection of Eq. (16) and Eq. (44) gives the desired position of the maximum. One procedure we have used in our calculations is to express $F(y)$ as a function of $y^{-2}e^{-y}$ through

$$F(y)=y^{-2}e^{-y}\Sigma(y), \qquad (45)$$

where the function $\Sigma(y)$ can be obtained directly as the ratio between the numerical computation of $F(y)$ and the corresponding values of $y^{-2}e^{-y}$ or approximated as indicated in the Appendix. The function $\Sigma(y)$ is plotted in Fig. 12.

Replacing Eq. (45) in Eq. (16), and using Eq. (16) in Eq. (44) gives

$$-\left(1-\frac{\gamma}{\beta}\right)\ln\left(\frac{1-\gamma/\beta+x_m}{1-\gamma/\beta+x_0}\right) +\left(1+\frac{N_t}{\mathcal{N}_t}\right)\ln\left(\frac{1+N_t/\mathcal{N}_t+x_m}{1+N_t/\mathcal{N}_t+x_0}\right) =\sum(y_m)\frac{x_m^2(\gamma/\beta+N_t/\mathcal{N}_t)}{(1+N_t/\mathcal{N}_t+x_m)(1-\gamma/\beta+x_m)}. \qquad (46)$$

Solving Eq. (46) gives x_m as a function of y_m, x_0, γ/β, and $N_t/\mathcal{N}_t$.

Now the results of Eq. (46) for x_m, expressed as

$$\frac{\Delta E_t}{E_t}=\frac{(E_{Fm}-E_t)}{E_t}=y_m^{-1}\ln x_m, \qquad (47)$$

give the relative error in assuming that the quasi-Fermi-level at the maximum of the TSC is equal to the trap depth. Figure 13 gives the results from Eq. (47) for different initial conditions, for the two strong retrapping limiting cases (totally constant and totally changing lifetime), and also the points corresponding to the peaks of "intermediate" changing lifetime shown in Fig. 10.

For the "ideal" first-order kinetics curve (no retrapping at all), there is no correlation between the quasi-Fermi-level and the trap depth. For the real nonretrapping cases ($x_0\geq1$), the relation between the quasi-Fermi-level and the trap depth is the same as that for the strong retrapping case, under the same initial conditions. From Fig. 13 it is observed that the quasi-Fermi-level is always below the trap level at the TSC maximum ($x_m\geq1$), and that the quasi-Fermi-level approximation differs from the real trap depth by less than 5% for the constant-lifetime case with strong retrapping (and even for lifetimes comparable with retrapping). For the "intermediate" changing lifetime cases, the quasi-Fermi-level remains a good approximation to the trap depth as long as the lifetime does not change too much during the peak. For the nonretrapping cases, since x_m must be larger than x_0, which in turn is larger than unity, the quasi-Fermi-level approximation can give large errors.

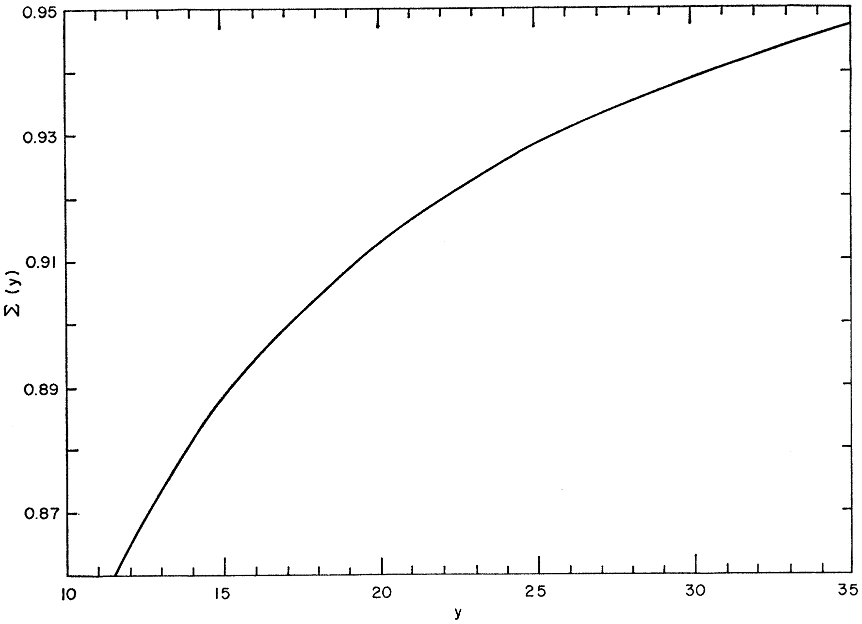

FIG. 12. The function $\Sigma(y)$, defined in terms of Eqs. (17) and (45).

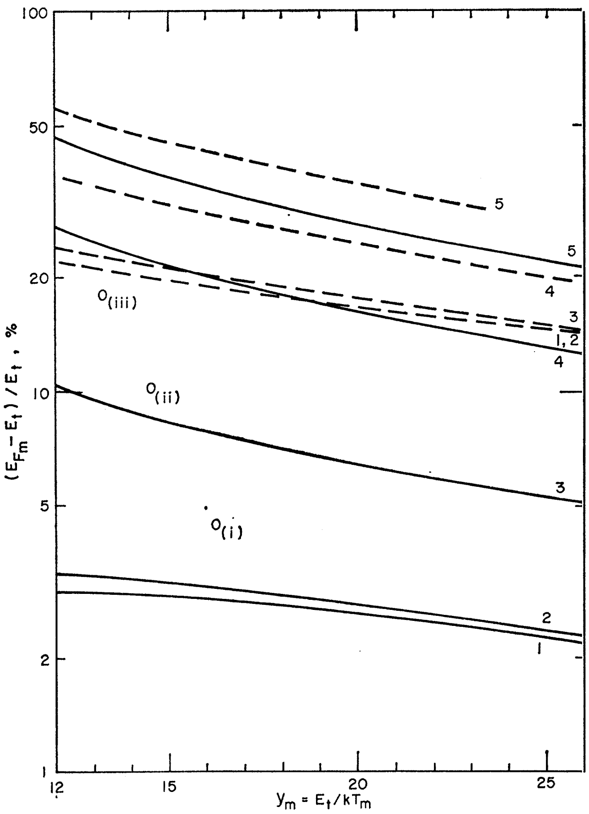

FIG. 13. Error involved in assuming that the trap depth is given by the value of the quasi-Fermi-level at the maximum of the TSC curve. Solid curves are for lifetime constant $(\tau^{-1}=\gamma\mathcal{N}_t)$ and the following values of x_0: (1) 10^{-4}, (2) 10^{-1}, (3) 1, (4) 10, and (5) 10^2. Dashed curves are for lifetime changing without limit $(\tau^{-1}=\gamma n_t)$ and the following values of x_0: (1) 10^{-4}, (2) 10^{-1}, (3) 1, (4) 10, and (5) 10^2. The points correspond to the maxima of "intermediate" changing-lifetime cases from Fig. 9 as follows: (i) curve 3 of Fig. 9, (ii) curve 4 of Fig. 9, (iii) curve 5 of Fig. 9.

Methods Based on the Half-Width

Except for the "ideal" first-order kinetics case, we have not been able to obtain a simple expression for the half-width of the peak as a function of the trapping parameters. Using the fact that the shape of the peak is almost unchanged by variations in the trapping parameters, we have determined graphically from Figs. 6 and 8 the corresponding half-widths for the strong retrapping cases as a function of the initial occupancy of the trap. As before, values of $x_0>1$ represent real nonretrapping cases for constant lifetime. The difference between the corresponding values of y is a convenient way to designate the half-width, since

$$\Delta_{1,2}=y_1-y_2=E_t(T_2-T_1)/T_1T_2, \qquad (48)$$

from which

$$E_t=\Delta_{1,2}\frac{T_1T_2}{T_2-T_1}. \qquad (49)$$

In Fig. 14 are shown three such differences, the total half-width Δ, the lower temperature "half-width" Δ_-, and the higher temperature "half-width" Δ_+. Some values for "intermediate" changing-lifetime cases are also included.

The value of Δ_- for large values of x_0 should be coincident with the value given by Grossweiner,[6] $\Delta_-=1.51$. This value is in error according to our results. The calculation of the half-width for the "ideal" first-order kinetics case can be expressed in a relatively simple way. The position of the maximum is given by

$$(\beta N_c E_t/bk)y_m^{-2}e^{-y_m}=1. \qquad (50)$$

By subtracting the values for n_m and $\frac{1}{2}n_m$ in Eq. (8), we

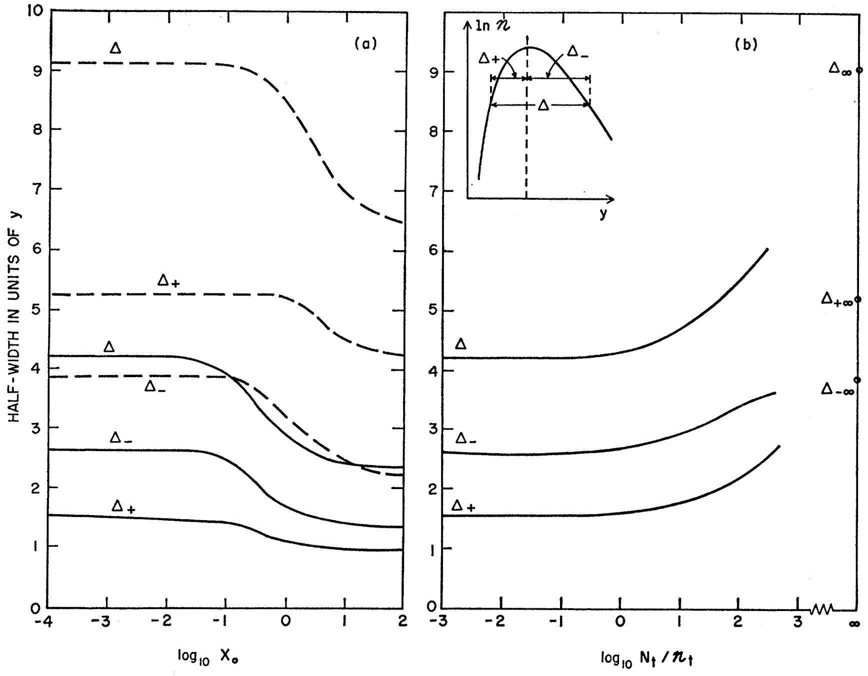

FIG. 14. Values of the various half-widths of the TSC curve, as defined in the inset. (a) Solid curves are for constant lifetime ($\tau^{-1}=\gamma\mathfrak{N}_t$) determined for $A=\beta\gamma N_tN_cE_t/[(\gamma\mathfrak{N}_t+\beta N_t)bk]=10^{12}$, for various values of x_0. Dashed curves are for lifetime changing without limit ($\tau^{-1}=\gamma n_t$) for various values of x_0. (b) Variation of half-widths with ratio of $N_t/\mathfrak{N}_t$ for "intermediate" changing-lifetime cases, for $x_0=10^{-4}$.

obtain

$$\ln 2=\Delta_- - A[F(y_m)-F(y_-)], \qquad (51)$$

where $A=\beta N_cE_t/bk$. From Eqs. (45) and (50),

$$AF(y_m)=Ay_m^{-2}e^{-y_m}\Sigma(y_m)=\Sigma(y_m),$$

and ($y_-=y_m+\Delta_-$),

$$AF(y_-)=[1+\Delta_-/y_m]^{-2}\exp(-\Delta_-)\Sigma(y_-),$$

we obtain

$$\ln 2+\Sigma(y_m)=\Delta_- +(1+\Delta_-/y_m)^2\exp(-\Delta_-)\Sigma(y_-). \qquad (52)$$

Since $\Sigma(y_m)$ is a slowly varying function of y, the value of Δ_- is readily obtained for a given y_m through an iterative calculation. Results are quite consistent with the above described graphical determination, and the variation of the lower half-width Δ_- with position of the peak is quite small. Table II gives some values for Δ_- for selected values of y_m. The results indicate that the Grossweiner value is in error by about 7%.

All these results show that the half-width of the peak is not a reliable method for the determination of trap depth, unless it is known by some independent means what kind of a trap is being analyzed. Some insight can be obtained from the ratios between any two of the three characteristic half-widths, since these are independent of trap depth, but these ratios do depend on whether the lifetime is constant or changing during the peak. A knowledge of the value of the initial position of the quasi-Fermi-level can be of further help in this case, since then one is able to determine what trap depth gives a value of x_0 consistent with the above ratios and the absolute values of the half-widths (as calculated from the assumed value of trap depth and the known temperatures). On the other hand, if the trap depth is known from some previous analysis of another method, a knowledge of x_0 and the half-widths give useful information in determining the other trapping characteristics.

TABLE II. Calculated values for the lower "half-width" Δ_-.

$y_m=E_t/kT_m$	$\Delta_-=y_- - y_m$
17	1.4022±0.0003
22	1.4145±0.0001
26	1.4208±0.0001

It is difficult to compare these results in general with those of Halperin and Braner,[7] or Luschik.[8] These authors express the trap depth as a function of $T_m^2/\Delta T$; comparison would require a point-by-point calculation.

Heating-Rate Methods

These methods are based on the shift of the TSC maximum with different heating rates. Three ways of plotting the results have been proposed: (a) $\ln\sigma_m$ versus $1/T_m^2$, (b) $\ln T_m^2/b$ versus $1/T_m$,[5,16] and (c) $\ln b^{-1}$ versus $1/T_m$.[5] In each case the activation energy is taken to be E_t.

From our analysis, (a) implies via Eq. (8) that x_m is independent of the position of the peak in temperature; (b) implies via Eq. (44) that a function of x_m is constant, independent of the position of the peak, which is equivalent to implying that x_m is constant; (c) implies via Eq. (44) that $x_m^2y_m^2(1-\gamma/\beta+x_m)$

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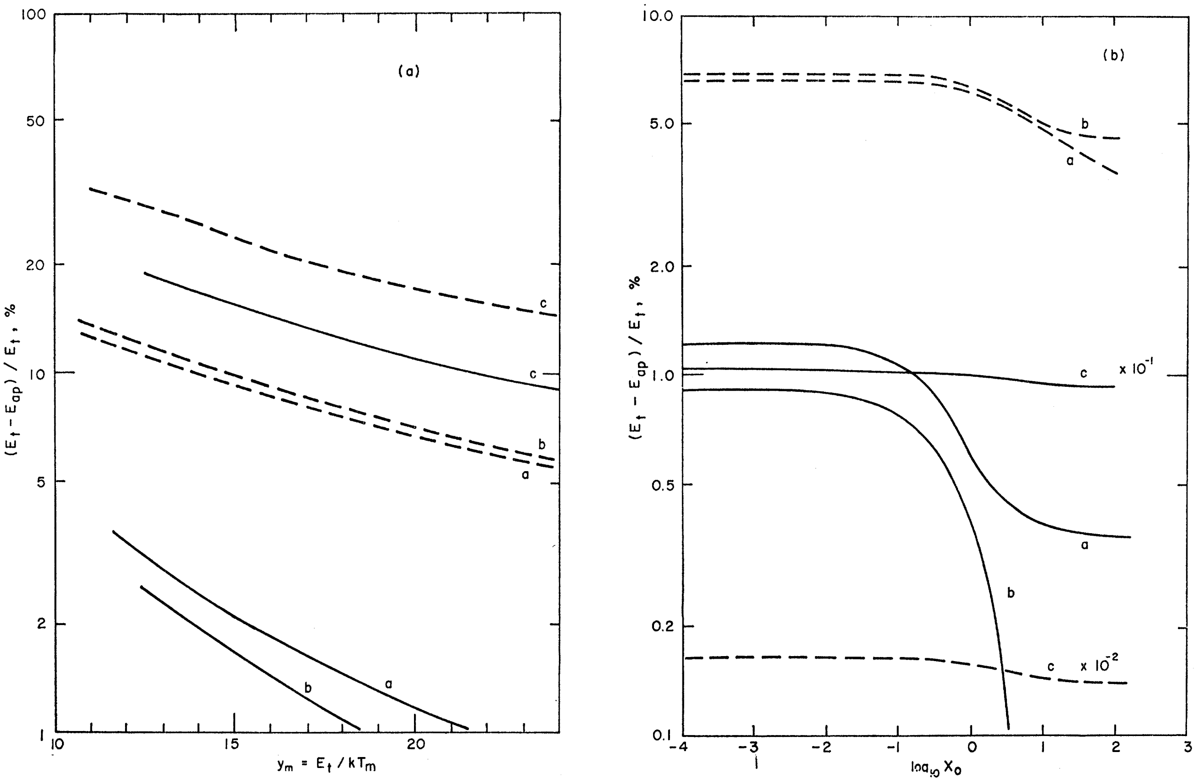
[16] R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1960), p. 295.



(a) (b)

FIG. 15. Error involved in determining the trap depth from the heating-rate methods. (a) Solid curves are for lifetime constant ($\tau^{-1}=\gamma\mathcal{N}_t$) and $x_0=10^{-14}$. For a, the error is positive, for b and c it is negative. The letters a, b, and c, refer to the three ways of plotting heating-rate data, as discussed in the text. Dashed curves are for lifetime changing ($\tau^{-1}=\gamma n_t$) and same x_0. (b) Variation of error in different heating-rate methods as a function of initial occupancy of traps. Description of curves is the same as in (a). Calculated for $y_m=20.83$. Note that the error for method c has been multiplied by a reduction factor in plotting.

$\times(1+N_t/\mathcal{N}_t+x_m)$ is constant. Since in all real cases x_m depends on the initial conditions (x_0), it is essential that the initial occupancy be the same in applying these methods. The simplest way to assure this is to be certain that the traps are completely filled initially, i.e., that the quasi-Fermi level lies above the trap level and that steady-state conditions have been achieved.

The errors found in application of the heating-rate methods are summarized in Fig. 15. The three cases can be expressed as

$$f(x)=\mp y+\delta, \tag{53}$$

where $f(x)$ is $\ln\sigma_m$, $\ln T_m^2/b$, and $\ln b^{-1}$ in (a), (b), and (c), respectively; the $-$ sign is for case (a), and the $+$ sign for cases (b) and (c). If δ is a constant, the activation energy is E_t. Otherwise the measured E_{ap} will be related to E_t by

$$\frac{E_t-E_{ap}}{E_t}=\pm\frac{\Delta\delta}{\Delta y}, \tag{54}$$

where $+$ is for (a), $-$ for (b) and (c). Since $\Delta\delta/\Delta y$ is always greater than 0, this implies that $E_t>E_{ap}$ for (a), while for (b) and (c), $E_t<E_{ap}$. The large error in case (c) agrees well with published results of Böer *et al.*[5] and of Dittfeld and Voigt.[10] There is a definite tendency for the error to decrease as the kinetics tend toward first order (x_0 increasing).

Garlick and Gibson Method

Except for the strong-retrapping cases with the trap substantially filled initially, the Garlick and Gibson[9] initial activation energy of the TSC curve gives the actual trap depth. Thus decayed TSC curves should always give the correct trap depth if decay has been carried out at a temperature close enough to the maximum, or greater than the maximum. If there is interference from a second trap with a different activation energy, a simple argument shows that the curve should show two slopes, the one with the smaller activation energy dominating at low currents and the one with the larger activation energy dominating at high currents. With different initial decays, these two portions should shift with respect to one another, and it should be possible to identify both traps from such a shift.

Equation (7) can be rewritten as

$$\dot{n}_{\mathrm{TSC}}=nbE_t/kT^2+\dot{n}_{\mathrm{decay},T}, \tag{55}$$

where $\dot{n}_{\rm TSC}$ is the time variation of n during a TSC measurement (increasing T), and $\dot{n}_{{\rm decay},T}$ is the variation with time of n at the given temperature T. Thus $\dot{n}_{\rm TSC}$ is given as a resultant of two competing factors, one a term corresponding to thermal excitation and the other a decay component which is always negative. Since the Garlick and Gibson slope appears whenever the first term on the right side of Eq. (55) is dominant, the slope should represent the energy of the trap depth, as long as the decay term is negligible, even in cases in which the lifetime is changing in a different way from those discussed in this paper. Even under a nonlinear heating rate, the Garlick and Gibson slope should give the trap depth.

GENERAL DISCUSSION

From Eq. (16) for the TSC curve, it is seen that using reasonable values for the parameters, the peak should be defined by approximately

$$15 \leq y_m \leq 26. \tag{56}$$

The estimate of $y_m = 25$, given by Randall and Wilkins,[17] is thus seen to be a little high. The range of Eq. (56) is in good agreement with estimates by Voigt[18] and previous publications of the authors.[12]

For a determination of trap depth, it is clear that the most reliable method is that of decayed TSC. Using this method it is possible to eliminate contributions to the TSC from other traps, and to obtain the trap depth correctly regardless of the trapping or lifetime kinetics. Experimentally this method does require a good knowledge of the mobility as a function of temperature if accurate trap depths are to be obtained, as well as reliable Ohmic contacts over the temperature ranges needed.

The heating-rate methods, especially plotting $\ln n_m$ versus $1/T$, give reliable results with less requirement of knowledge of mobility dependence on temperature, and on the temperature range over which Ohmic contacts are required, since the shift of the peak with different heating rates is relatively small. The presence of a nearby TSC peak, however, can lead to completely incorrect analysis, and in this case it is not possible to remove the effects of the other trap by decay. Attempts to achieve the latter change the initial conditions and the heating-rate method is no longer applicable. Also, for nonretrapping cases the small value of β makes it experimentally difficult to obtain the same initial degree of filling of traps.

Once the position of the trap level is known, the other parameters of the trap can be determined from knowledge of the location of the quasi-Fermi-level at the TSC maximum, the half-widths of the TSC curve, and the shift in temperature of the maximum with different initial conditions. It must be noted, however, that the trap density never appears independently, but is always related to the lifetime. Since the lifetime during TSC can be different from that under steady photoexcitation,[19] some uncertainty in determinations of trap density may be present.

Although the model treated considers explicitly only the single possibility of recombination through one set of recombination centers, according to the definition of lifetime in Eq. (1), the conclusions can be applied more generally to a system involving two sets of recombination centers, one with a small electron-capture cross section (sensitizing centers) and the other with a large electron-capture cross section. As long as the temperature is low enough so that thermal excitation of holes to the valence band can be neglected, there are the following possibilities within the framework of the theory: (1) The fast recombination centers will be filled faster by electron capture, and since (by definition) the holes are principally in the sensitizing centers, holes in the fast centers may be completely exhausted in the decay period prior to the TSC heating, or at most during the very initial states of TSC heating. (2) If the density of holes in fast centers is comparable to or less than the density of the traps of interest, an "intermediate" changing-lifetime case would be observed corresponding to the change in recombination path from fast to sensitizing centers. (3) If the density of holes in fast centers is greater than the density of traps of interest, then the TSC corresponds to a constant-lifetime case. In all these cases, if sufficient care is taken to choose the appropriate parameters, the TSC can be described in terms of the theory given in this paper.

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APPENDIX

To calculate the integral

$$F(y) = -\int_{y0}^{y} y'^{-2} e^{-y'} dy' = \frac{k}{E_t} \int_{T0}^{T} \exp(-E_t/kT') dT',$$

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[17] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **184A**, 365 (1945).

[18] J. Voigt, Diplomarbeit, Berlin, 1958 (unpublished).

[19] G. A. Dussel and R. H. Bube, J. Appl. Phys. **37**, 934 (1966).

where the lower limit is $y=E_t/kT$ and the upper limit is $y_0=E_t/kT_0$ ($T>T_0$), integrate by parts

$$-\int_{y_0}^{y} y'^{-2}e^{-y'}dy'=(y'^{-2}e^{-y'})\Big|_{y_0}^{y}+2\int_{y_0}^{y} y'^{-3}e^{-y'}dy'$$

$$=\cdots=y'^{-2}e^{-y'}\sum_{n=0}^{k}[(-1)^n(n+1)!y'^{-n}]\Big|_{y_0}^{y}$$

$$+(-1)^{k+2}(k+2)!\int_{y_0}^{y} y'^{-(k+3)}e^{-y'}dy'. \quad \text{(A1)}$$

After integrating by parts a sufficient number of times, both terms in the expression for the integral begin to compensate one another. Thus it is possible to approximate the integral by a series, within a given accuracy, by taking the optimum number of terms in the series.

If we define

$$f_k(y)\equiv y^{-2}e^{-y}\sum_{0}^{k}[(-1)(n+1)!y^{-n}], \quad \text{(A2)}$$

and

$$F_k(y)\equiv f_k(y)-f_k(y_0), \quad \text{(A3)}$$

then

$$\Delta_kF=F(y)-F_k(y)=(-1)^{k+2}(k+2)!\int_{y_0}^{y} y'^{-(k+3)}e^{-y'}dy'$$

$$\leq(-1)^{k+2}\frac{(k+2)!}{y^{k+3}}e^{-y}. \quad \text{(A4)}$$

For $y<y_0$, so that $f_k(y)\gg f_k(y_0)$, we can approximate by setting $F_k(y)\approx f_k(y)$, and obtain

$$\left|\frac{\Delta F}{F}\right|\approx\left|\frac{\Delta_kF}{F_k}\right|\leq\frac{(k+2)!}{y^{k+1}\Sigma_k(y)}, \quad \text{(A5)}$$

where

$$\Sigma_k(y)=\sum_{0}^{k}[(-1)^n(n+1)!y^{-n}]. \quad \text{(A6)}$$

The error decreases by increasing the number of terms in the series until $k+2\geq y$, neglecting the dependence of $\Sigma_k(y)$ on k. As a matter of fact, for the ranges of interest in y the series is close to unity as shown in Fig. 12, and is a slowly varying function of y. An estimate of the error in approximating the integral by the series for low values of y is given in Table III. In our calculations we used Σ_k obtained through the series for $y\geq 15$, and for $10\leq y\leq 15$, we used

$$\Sigma_k(y)=\frac{\int_{y_0}^{y} y'^{-2}e^{-y'}dy'}{y^{-2}e^{-y}},$$

where the integral was obtained by numerical integration using a computer. For $y\geq 15$ our results checked with the computer results to the fourth decimal.

TABLE III. Error made in approximating $F(y)$ by series with k terms.

y	k	$\Delta F/F$
10	7	4×10^{-3}
15	7	1.5×10^{-4}
15	12	5×10^{-5}
20	10	4×10^{-6}
20	17	3×10^{-7}