

New approach to thermally stimulated transients: Experimental evidence for ZnSe:Al crystals

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Thermal stimulation is often used as method of characterizing electronic processes in solid insulators. Thermally stimulated conductivity or luminescence in particular are more closely investigated in this study. The conventional method for interpreting these assisted relaxations is to start from the differential equations describing a detailed balance relative to a three-level scheme. We show how the deduced formula refers to a restricted model and approximation; the necessary critical feedback on the starting hypothesis is not often found in experimental work. In the particular case of thermoluminescence it will be demonstrated that most of the time the equation $J_{\text{TSL}} = -dm/dt$ does not apply. We propose a new approach to these transients: We show that the exact expression for a thermal stimulation parameter does not involve an algebraic function of temperature but rather a "functional" consideration of the "history" of the experiment. Such a general expression for thermally stimulated conductivity (TSC) and luminescence (TSL) leads to the elimination of the density n_c of electrons in the conduction band, the most difficult parameter to evaluate under transient conditions. When both phenomena (TSC and TSL) are observed in the same experiment under fractional-emptying evolution, a method is proposed to analyze the ratio $R = J_{\text{TSC}}/J_{\text{TSL}}$. This leads to two pieces of information. The first is related to the electronic properties of the material and is expressed by a conventional function $f(T)$; the second describes the evolution of the density of available recombination centers m . It is shown in the particular case of ZnSe:Al samples how this can be worked out. Taking a constant mobility for electrons in this material, we deduce from $f(T)$ the temperature behavior of the recombination capture cross section. This is in fair agreement with a tunnel effect through a repulsive Coulomb barrier. From the evolution of m it is also deduced that a strong hole emission from the radiative recombination centers takes place at low temperature. This emission is quantitatively evaluated and shown to be in accordance with a phenomenon of continuous thermal quenching as can be seen from dc measurements of photoconductivity and luminescence. The good experimental agreement of the data encourages further investigations of the "functional" expression of thermal stimulation and also emphasizes the necessity for a more critical use of conventional formulations.

I. INTRODUCTION

For a long time the analysis of solid-state materials by thermally stimulated relaxation has been used to characterize photoelectronic properties. Generally speaking, these methods consist in first exciting a sample, for example, with electromagnetic radiation (photons or x rays), mechanical stress, or a high electric field. The remaining deformation at low temperature after cessation of excitation often resides in the displacement of charge carriers on defects or in atomic displacements (molecular electric dipoles for example).

Spontaneous relaxation of such an induced perturbation can result from the coupling of the localized site with the collective modes of vibration. Then, if the sample is heated, a thermally assisted relaxation can be observed. This phenomenon can manifest itself externally in various ways: transient conductivity, luminescence, transparency, electrical depolarization, and so on.¹

The observed signal, a function of time t , has roughly the form of a bell-shaped curve. In the case of a monotonic temperature rise this curve is a dynamic compromise between a characteristic

relaxation probability increasing with T and a decreasing density of available excited sites.

Whichever interpretation is chosen, the characteristic elements of such a graph (maximum value, temperature of the maximum, width, slopes, etc.) depend on the material, the initial excitation, and the function of temperature used. In order to simplify interpretation, a linear function $T(t) = \beta t + T_0$ is often chosen (β being the heating rate).

In this paper we shall look more closely at thermally stimulated conductivity (TSC) and luminescence (TSL). It is assumed that the remaining deformation consists essentially in the modification of charge-carrier distribution on the localized electronic levels located in the forbidden gap of a very resistive semiconductor (see Fig. 1).

It should first be remembered that the conventional methods of analysis using detailed-balance differential equations must be used with caution; they depend heavily on the simplified level model and on oversimplified elements introduced into the equations. In any case, they need to be carefully reexamined, *a posteriori*, in the light of the deductions.²

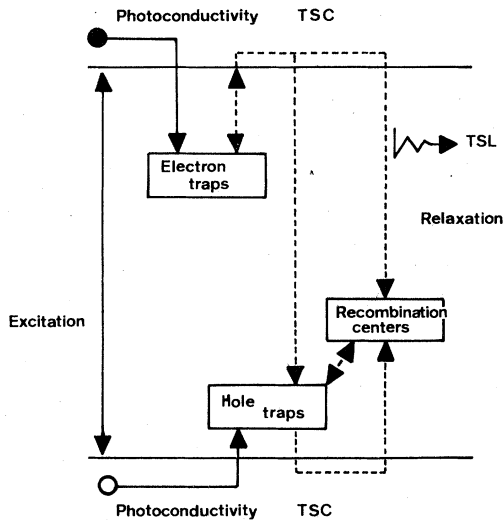


FIG. 1. Excitation-relaxation scheme for TSC and TSL.

Second, we shall show how a “functional” expression can fit with the fundamental mathematical nature of the general transient phenomenon and how explicit information can be deduced from this. We shall develop a new method of analysis from the underlying correlation between TSC and TSL.

Finally, we shall give an experimental example using ZnSe:Al monocrystals. It will be shown how it is possible to deduce, on the one hand, explicit and continuous information concerning the recombination cross section and, on the other hand, to evaluate directly the evolution of the filling of the recombination centers.

II. THEORY OF THERMALLY STIMULATED RELAXATION

Let us first recall the usual theoretical developments that start with the hypothesis of a simplified quantum scheme (Fig. 1). Trapped electrons (density n_t) on localized identical sites (density N_t) are thermally emitted into the conduction band (CB); after a drift in this band under the influence of an externally applied electrical field (assumed or checked to be homogeneous in the bulk) the free carriers are captured on hole-activated recombination centers (total density m).

Formal expressions for the current density J_{TSC} and emitted light J_{TSL} require a previous evaluation of the density n_c of carriers drifting in the CB, from the detailed balance equation

$$\frac{dn_c}{dt} = n_t \nu e^{-E_t/kT} - n_c(N_t - n_t)\sigma_t v_{\text{th}} - n_c m \sigma_r v_{\text{th}}, \quad (1)$$

where ν is the attempt-to-escape frequency of trapped electrons; E_t is the activation energy

related to the electron trap; σ_t, σ_r are the capture cross sections of the trap and recombination center (RC) for electrons in the CB at temperature T ; v_{th} is the mean thermal velocity for electrons in the CB at temperature T . In the simplest case of a linear heating of the sample, a universal solution of Eq. (1) cannot be expected but only local, restricted ones.

In the case of a first-order recombination (where m is constant), it can be deduced that

$$n_c = A' \exp\left(-\frac{E_t}{kT} - \frac{1}{\beta} \int_{T_0}^T B' e^{-E_t/kT'} dT'\right), \quad (2)$$

where A' and B' are constants unaffected by temperature. In expression (2) it must also be assumed that recapture is either negligible (Randall-Willkins³) or very active. (Hearing-Adams⁴).

In the case of a bimolecular recombination (m is affected by the recombination, and $m = n_t$) a similar calculation gives (Garlick-Gibson⁵)

$$n_c = A'' e^{-E_t/kT} \left(1 + \beta \int_{T_0}^T B'' e^{-E_t/kT'} dT'\right)^{-1}. \quad (3)$$

These estimates of n_c are therefore critically dependent on the kinetic model of population exchanges; n_c is then replaced in the macroscopic equations.

$$\begin{aligned} J_{\text{TSC}} &= e \mu \mathcal{E} n_c, \\ J_{\text{TSL}} &= A n_c / \tau_\lambda, \end{aligned} \quad (4)$$

where \mathcal{E} is the electric field, τ_λ is the lifetime relative to the radiative process, and A is a dimensional constant.

The determination of the characteristic parameters is based on outstanding features of the relaxation curves [for example, J_{TSC} if $\mu(T)$ is constant]. We can thus use the variation of the temperature of the maximum (Booth-Hoogenstraaten⁶), the variation of the maximum height with β (Boer *et al.*⁷ and Hearing-Adams⁴), the width at mid-height (Grossweiner⁸), the position of the inflexion points (Land⁹), or the low-temperature slope (Garlick Gibson⁵).

All of these factors are established in the case where the graph consists of a single, well-defined peak originating from only one type of trap. In general, the superposition of the components makes the use of a graph very risky. This way of demonstrating thermal stimulation (TS) is perfectly correct as long as it applies to a consistent model and satisfactorily checked approximations.

However, TS is often treated in the opposite manner as an investigation technique for little-known materials: the procedure starts from an experimental graph and moves towards a descriptive model. In this case most of the deductions are

irrelevant as long as all of the underlying hypotheses have not been verified. This difficult state, rarely encountered in literature, often leads to disagreements between the authors.¹⁰ Of all these methods the only accessible parameter is E_t . Others, such as densities N_t , attempt-to-escape frequency ν , or trapping cross sections, sometimes found in the literature, often require a complete reexamination.

Special credit must be given to Gobrecht and Hofmann for a very good method which they have perfected¹¹: it consists in increasing the temperature by successive cycles so that the traps are emptied one by one. This fractional emptying makes it to some extent possible to create a spectroscopy of the emitting traps by measuring the slopes on a logarithmic scale.

Nevertheless, if the knowledge of n_c suffices for using J_{TSC} [where $\mu(T)$ is constant], it does however not suffice for interpreting thermoluminescence which, in addition, involves the parameter τ_λ . Initially, most authors assume that the measured radiative process related to a single recombination center constitutes the main recombination path (unity quantum yield); in a special case such as this, τ_λ can be identified with the recombination lifetime of the carriers. If in addition, the recombination center under consideration is not affected by other unexpected mechanisms such as hole emission or capture, then

$$J_{TSL} = -\frac{dm}{dt} \quad (5)$$

can be written.

This equation, as stated before, is a second definition of J_{TSL} independent of Eq. (4). Therefore

$$\int_{t_0}^{\infty} J_{TSL} dt = m(t_0) - m(\infty) \quad (6)$$

should be found at the end of the relaxation process. Certain more advanced models¹² include, however, the additional possibility of nonradiative filling of the recombination center.

The correlation between J_{TSC} and J_{TSL} , often found experimentally to exist simultaneously, makes a better study of the relaxation process possible. It will, however, be difficult to express it in the framework of the equations of the detailed balance since the recombination scheme enters into the initial hypotheses.

Chen was the first to attempt to interpret this correlation without using the equations of the detailed balance.¹³ Using Eqs. (4) and (5) he explains the difference observed between the maximum of J_{TSC} and that of J_{TSL} and also deduces from n_c the value of the quantity $\sigma_r \nu_{th}$. Similarly, Fields and Moran¹⁴ have made a correlated study of the two

phenomena also based on Eq. (5) but including a quantum yield factor. The lack of experimental success in these original investigations is probably due¹⁵ to the uncontrolled use of Eq. (5). Conventional studies of luminescence suggest, however, that recombination processes are very often more complex than Eq. (5) would seem to indicate. In Braunlich and Hagston's¹⁶ studies of thermoluminescence, this point concerning the outline of luminescent centers described by configurational coordinates or by a donor-acceptor structure was clearly made.

In short, it is our opinion that the results found in the literature which are deduced from TS data too often lack sufficient theoretical and experimental verification.² Furthermore the simultaneous presence of several manifestations of thermal relaxation is a fact which merits special attention.

In the following study we shall develop a new formalism capable of leading both to a precise knowledge of the material as well as to the evolution of the instantaneous relative density of activated radiative recombination centers (ARRC). We propose a convincing experimental illustration of these ideas based on experimentation with ZnSe:Al.

III. FUNCTIONAL APPROACH

The starting point for our deductions was suggested in a recent short note¹⁵; it is our aim here to take up this interpretation and develop it further. It is important to recall that thermal relaxation following an applied temperature program $T(t)$ corresponds to an irreversible transitory regime; the population densities of carriers on the various energy levels (localized sites and bands) follow, with time, a wholly optimized evolution. Such a spontaneous dynamic state is governed by a fundamental, underlying equilibrium principle analogous to the one which in mechanics leads to Maupertuis's principle or in optics to Fermat's principle.

The relationship between time t and the value X of the measured parameter is a "functional" one which can be expressed as $X = \psi\{T(t)\}$ using, for instance, Spataru's notations.¹⁷ This means that, generally speaking, the instant value of parameter X does not depend explicitly on t or T but on the total input function $T(t)$ defined from $t = -\infty$ (or $t = 0$) to the considered time t . This application of the function space onto the number space does not correspond to a conventional algebraic function but rather to a less known mathematical "functional."¹⁸ This simple observation makes it possible to consider the TSR globally without using the differential equations, thus avoiding the preliminary hypothesis of a precise quantum

scheme. At this point it is important to note that the functional expression refers to a universal meaning; instead of it, each applied stimulation $T(t)$ carries out a particular graph $X_{T(t)}(T)$ which is a conventional explicit function of T (or t); the meaning of the graph $X_{T(t)}(T)$ is not universal but restricted to the particular function $T(t)$. This differentiation is necessary when the derivatives are considered. To the extent of present knowledge it is impossible to get a formal, general expression of the derivatives of the functional $X\{T(t)\}$ either with respect to temperature or to time.¹⁹ Despite this fact, when dealing with the physical realizations [graphs $X_{T(t)}(T)$], the derivatives physically exist: temperature and time consist here of a single physical variable [through $T(t)$]. It is then meaningless to consider partial derivatives as long as T and t are not independent variables.¹⁹

Well-known mathematical developments in signal theory of linear systems through harmonic or impulsive analysis may be thought useful. However, there are sure to be experimental difficulties in thermal modulation or impulse. It must also be noted that the operation carried out on a sample by the input signal $T(t)$ is neither linear nor stationary.¹⁵

After these general remarks let us now emphasize the simultaneous occurrence of TSC and TSL. In the special case of TSC and TSL, the only requirements we need *a priori*, are that carriers of a given type ($n_c\{T(t)\}$) be emitted in a conduction band and recombine radiatively, and that optical signals measured be assigned to the same type of recombination transition throughout the entire evolution.

Generally speaking we can write [from Eq. (4)]

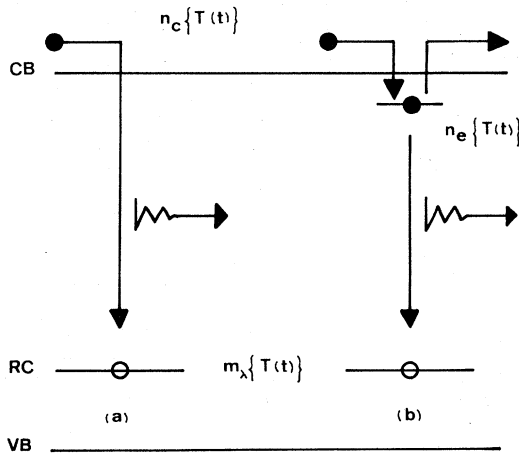


FIG. 2. (a) Free to bound, and (b) bound to bound transition types.

$$J_{\text{TSC}}\{T(t)\} = \mu(T)e\xi n_c\{T(t)\}, \quad (7)$$

$$J_{\text{TSL}}\{T(t)\} = An_c\{T(t)\}/\tau_\lambda\{T(t)\}. \quad (8)$$

A simple way of starting a development independent of $n_c\{T(t)\}$ is to use the correlation between TSC and TSL as it appears in the ratio

$$R\{T(t)\} = J_{\text{TSC}}/J_{\text{TSL}} = [e\mu(T)\xi/A]\tau_\lambda\{T(t)\}. \quad (9)$$

Thus we obtain an experimentally assemble parameter directly controlled by $\tau_\lambda\{T(t)\}$, a parameter conventionally included in the hypothesis. Accordingly, it is necessary to discuss $\tau_\lambda\{T(t)\}$. In the general case of a "free to bound" recombination, we will write

$$1/\tau_\lambda\{T(t)\} = v_{\text{th}}(T)\sigma_r(T)m_\lambda\{T(t)\} \quad (10)$$

and

$$R\{T(t)\} = \frac{e\xi}{A} \frac{\mu(T)}{v_{\text{th}}(T)\sigma_r(T)} \frac{1}{m_\lambda\{T(t)\}}, \quad (11)$$

where $m_\lambda\{T(t)\}$ stands for the density of the ARRC at time t , emitting the wavelength λ . More often $m_\lambda\{T(t)\}$ will be monotonically decreasing with time; nevertheless, the RC can be supplied²⁰ by a hole trap (sensitization phenomenon) thus causing $m_\lambda\{T(t)\}$ to vary in the opposite manner during thermoluminescent emission. When $m_\lambda\{T(t)\}$ is constant $R\{T(t)\}$ is thus found to be an explicit function $R(T)$ of temperature T , independent of the input signal $T(t)$.

If, on the contrary (Fig. 2), the radiative transition originates from an excited state physically associated with the RC ("bound to bound" transition), the density $n_e\{T(t)\}$ of the active centers should be linked to the density $n_c\{T(t)\}$. Three cases can be expected:

(a) All of the active levels are always full:

$$n_e\{T(t)\} = m_\lambda\{T(t)\},$$

thus thermoluminescence is controlled by the characteristic lifetime τ_λ of the center. This is identical to a phosphorescence, independent of thermal evolution.

(b) Density n_e is proportional to $n_c\{T(t)\}$ through a coefficient $\gamma(T)$:

$$n_e\{T(t)\} = \gamma(T)n_c\{T(t)\},$$

$$J_{\text{TSL}} = (1/\tau_\lambda)\gamma(T)n_e\{T(t)\},$$

and

$$R\{T(t)\} = \mu(T)/\gamma(T).$$

R is an explicit function of T independent of $T(t)$ and of excitation.

(c) Density n_e is functionally linked to n_c :

$$n_e\{T(t)\} = \gamma\{T(t)\}n_c\{T(t)\},$$

with

$$\gamma\{T(t)\} = g(T)m_\lambda\{T(t)\},$$

where $g(T)$ represents the coupling between the conduction band and the luminescent center, assuming pseudoequilibrium has been established. It follows that

$$R\{T(t)\} = \frac{e\xi}{A} \frac{\mu(T)}{g(T)} \frac{1}{m_\lambda\{T(t)\}}. \quad (12)$$

This last equation is structurally similar to Eq. (11). A typical function $g(T) \sim e^{-E_e/kT}$ should be often suggested, due to the immediate vicinity of CB to the excited level.

In order to further the analysis of $R\{T(t)\}$ without being tied to a level scheme, it is necessary to look for methods which allow us to separate the functional part of $R\{T(t)\}$ from its explicit part. Fractional emptying is a common analysis method for TSC and TSL: thermal evolution is cycled in such a way that the thermodynamic process can be considered as reversible for some temperature zones of the cycles; that is to say, carrier ex-

change rates between localized levels (traps or RC) and the bands are low enough not to affect the instant density of filling of these levels; nevertheless, these rates are high enough for external measurements (conductivity and luminescence) to be available. Such a situation can be used to analyse $R\{T(t)\}$ as we shall demonstrate.

$R\{T(t)\}$ can be expressed as a logarithm to show separately a constant, an explicit function and a functional of T :

$$\ln R\{T(t)\} = \ln e\xi/A + \ln f(T) - \ln m_\lambda\{T(t)\}, \quad (13)$$

with

$$f(T) = \mu(T)/\sigma_r(T)v_{th}(T).$$

In the special case of fractional emptying, and as a result of the reversibility of the process in the low part of each temperature cycle, $n_c\{T(t)\}$ behaves locally as an explicit function of T , and $m\{T(t)\}$ as a constant. It can be seen on the graphs that J_{TSC} , J_{TSL} , and R "retrace" when the temperature is decreased and increased [see Fig. 3(a)].

These curves correspond for $R\{T(t)\}$ to the formula (13) in which $m_\lambda\{T(t)\}$ takes a constant value but changes with each cycle: they thus differ by a constant in relation to each other.

We can thus reconstruct $\ln f(T)$ (in arbitrary units and on a logarithmic scale) by superposing parts of these curves as shown in Fig. 3(c).

At this point, it is necessary to check experimentally the uniqueness of the explicit function $f(T)$; this can be carried out by varying the thermal program, the electrical bias, and the initial excitation.

It is thus possible to conceive of two kinds of use. The first is to interpret $f(T)$ in order to find $\mu(T)$ or $\sigma_r(T)$. The second is to use the final graphic determination of $f(T)$ to find the amount of filling of the RC, $m_\lambda\{T(t)\}$, in another experiment (for example, a linear single-shot sweep). In the latter case, the expression of the functional $m_\lambda\{T(t)\}$ can be directly deduced from the difference between $\ln R\{T(t)\}$ and $\ln f(T)$. The common constant [Eq. (11)] $[\ln e\xi/A - \ln m_\lambda(T_0)]$ is eliminated in bringing $R\{T(t)\}$ and $f(T)$ to coincide at the point of departure (Fig. 4). $m_\lambda\{T(t)\}/m_\lambda(T_0)$ can then be plotted on a linear graph and eventually be used to find

$$-\frac{d}{dt} \left(\frac{m_\lambda\{T(t)\}}{m_\lambda\{T_0\}} \right),$$

$T(t)$ being a known function.

The problem of recombination transition can thus be approached independently by a study of both the conduction band J_{TSL} and the recombination center $-(dm/dt)\lambda$. In particular we shall be able to verify if radiative transition is the only

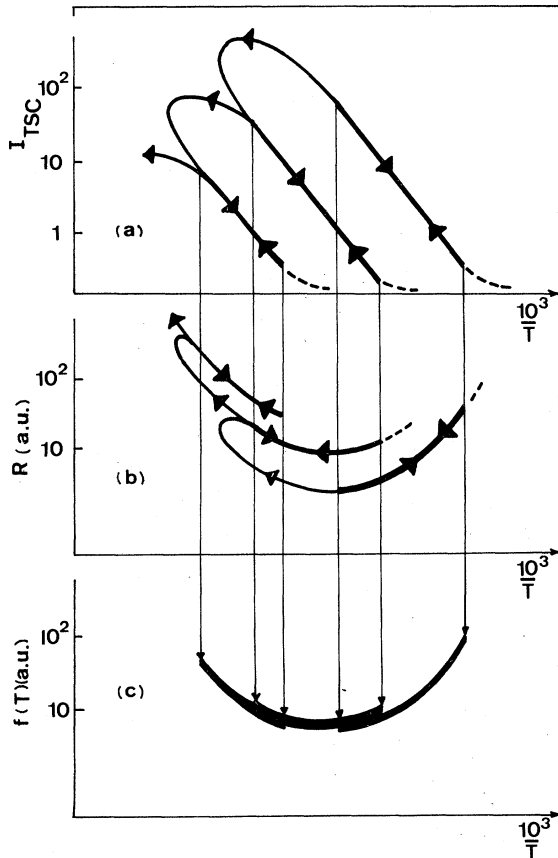


FIG. 3. (a) Schematic behavior of I_{TSC} , I_{TSL} , (b) $R = I_{TSC}/I_{TSL}$, and (c) the explicit function $f(T)$ graphically deduced.

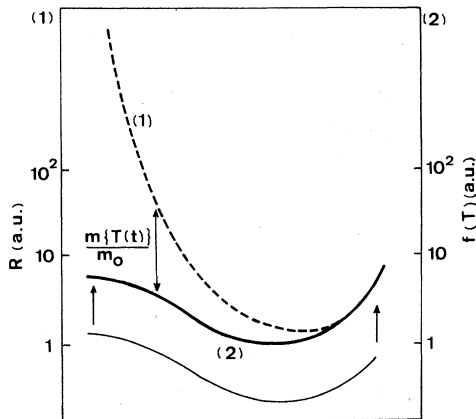


FIG. 4. $f(T)$ (from fractional emptying), is subtracted from a $R\{T(t)\}$ single-shot plot.

way of filling the recombination center. ZnSe:Al monocrystals have been used experimentally to test the validity of these deductions.

IV. EXPERIMENT

The theoretical considerations described above have been tested in several experiments. It is, in fact, relatively common to simultaneously show TSC and TSL emissions. The execution of a fractional emptying, however, requires quite strong signal levels. Of the materials tested (ZnSe, LiF, ZnS, SnO₂, AgBr) we have chosen ZnSe monocrystals to demonstrate this method of investigation. This choice is justified because of the presence of signals of sufficient amplitude and because of the fact that the transitions follow a simple scheme which can be checked directly by isothermal measurements. Samples were obtained from Centre National d'Etude de Télécommunications: they consist of ZnSe monocrystals grown from va-

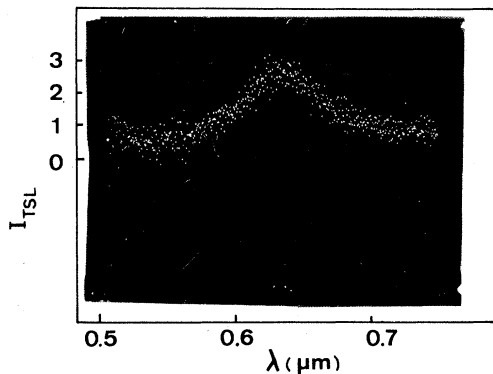


FIG. 5. TSL spectrum.

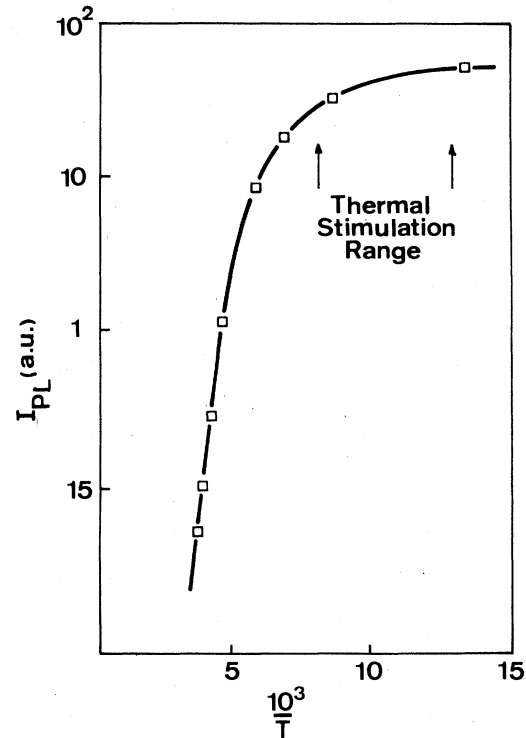


FIG. 6. Photoluminescence as a function of temperature (quantum yield).

por phase and annealed under Se atmosphere. Their resistivity is particularly high ($10^{12} \Omega \text{ cm}$ at room temperature). The silver-paste electrical connections have been checked to be ohmic for the range of currents used. The electrical field was probed to be homogeneous in the bulk.

Conductivity varies with an activation energy of 0.62 eV for the temperature range involved. It was not possible to measure the Hall effect, but all of the studies in the literature report constant electron mobility.^{21,22}

Preliminary measurements of luminescence and photoconductivity were also made on our samples. Luminescence was detected by means of a PAR optical multichannel analyzer placed at the outlet of a Jobin-Yvon monochromator, from which the output slit has been removed.²³ The emission which was measured at room temperature consists of a single, rather wide peak, centered on $\lambda = 0.615 \mu\text{m}$. This peak moves slightly towards the shorter wavelengths at the temperature of liquid nitrogen, without its form being affected. The spectrum of TSL integrated on a complete temperature sweep is represented in Fig. 5.

It is reasonable to presume that the radiative process remains the same between 77 and 300 °K. Under constant stimulation, the evolution of the

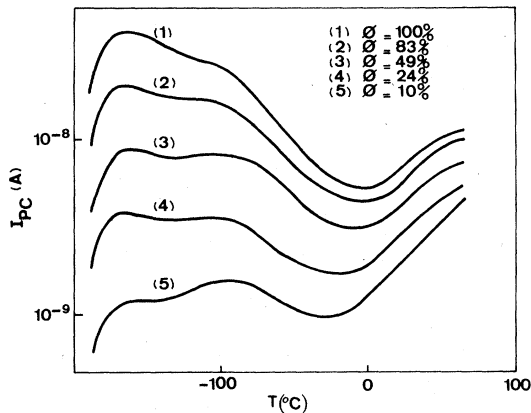


FIG. 7. Photoconductivity for various illumination levels.

radiative quantum yield $\eta(T)$ of the luminescent center is seen in Fig. 6.

Photoconductivity J_{PC} has also been measured (Fig. 7) as a function of temperature and at different illumination levels. We note the experimental relationship $J_{PC} \sim \phi^n$, where the exponent n varies with T (Fig. 8). This behavior is typical of a continuous thermal quenching (CTQ) process²⁴ between two hole centers of classes I and II.²⁰

As soon as the temperature rises above 77 °K, the probability of hole emission from recombination center I to the valence band (VB) increases. The hole trap emits and there is a tendency for the recombination path to establish itself through the class-II center (Fig. 9) whose time constant is faster. We shall see how thermal stimulation confirms this observation.

A. Experimental setup

The sample is held on a beryllium oxide platelet and placed in a vacuum-tight minicryostat. This miniaturized apparatus permits very easy temperature evolution; a few cubic centimeters of liquid nitrogen are enough for stabilization at 77 °K. A 10-W heating coil allows temperature increase with linear heating rate ($\beta \approx 0.1$ °K/sec) according

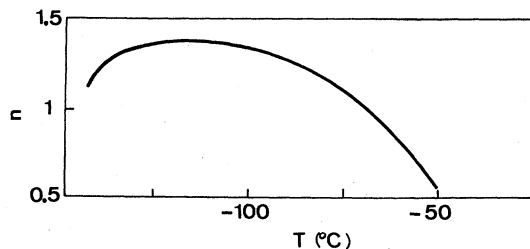


FIG. 8. Flux power dependence of photocurrent with temperature ($J_{PC} \sim \phi^n$).

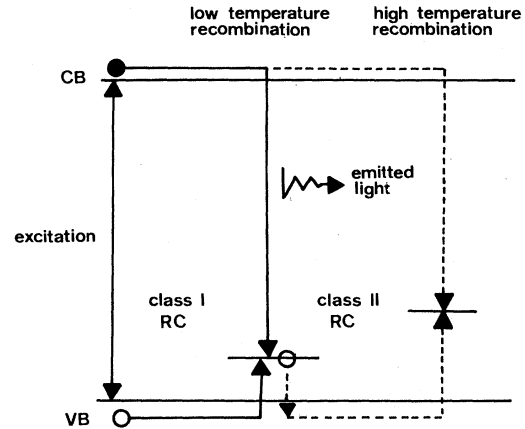


FIG. 9. Continuous thermal quenching mechanism of photoconductivity.

to a fixed program. Stabilization of the speed β after starting is achieved within 10 deg.

The block diagram of the experimental set up is sketched in Fig. 10. Thermoluminescence is read globally with an EM1 6256B photomultiplier and an HP 7563 A logarithmic converter. The TSC current is measured with a Keithley 413 logarithmic ammeter. The ratio $R = J_{TSC}/J_{TSL}$ is given directly by a differential amplifier. The three parameters J_{TSC} , J_{TSL} , and R are simultaneously recorded on the y inputs of three xy recorders driven in x by an analogical system which linearizes the thermocouple voltage (it is possible to display T or $1/T$). The $5 \times 4 \times 0.5$ mm samples are electrically polarized at 1.5 V and illuminated with a wavelength $\lambda = 0.490$ μ m.

B. Results

Figures 11 and 12 shows the results obtained by fractional emptying for simultaneous TSC and TSL.²⁵ We note the satisfactory exponential behavior at low temperatures. For TSC the activation energies develop between 0.15 and 0.33 eV. The conventional explanation for this would be the spreading of the trap levels on an energy band or a single trap, the attempt-to-escape frequency of which being temperature dependent. In TSL, activation energies are appreciably different: 0.2–0.37 eV. This difference can be attributed to the varying lifetime of the carriers $\tau_\lambda(T)$. The integration of TSL to the entire evolution leads us to think that the total number of radiative transitions observed is in the region of 10^{14} cm^{-3} . The density of the RC should therefore be larger than this number. Using conventional methods of analysis it is scarcely possible to carry these conclusions any further.

Let us examine the "functional" use of the numer-

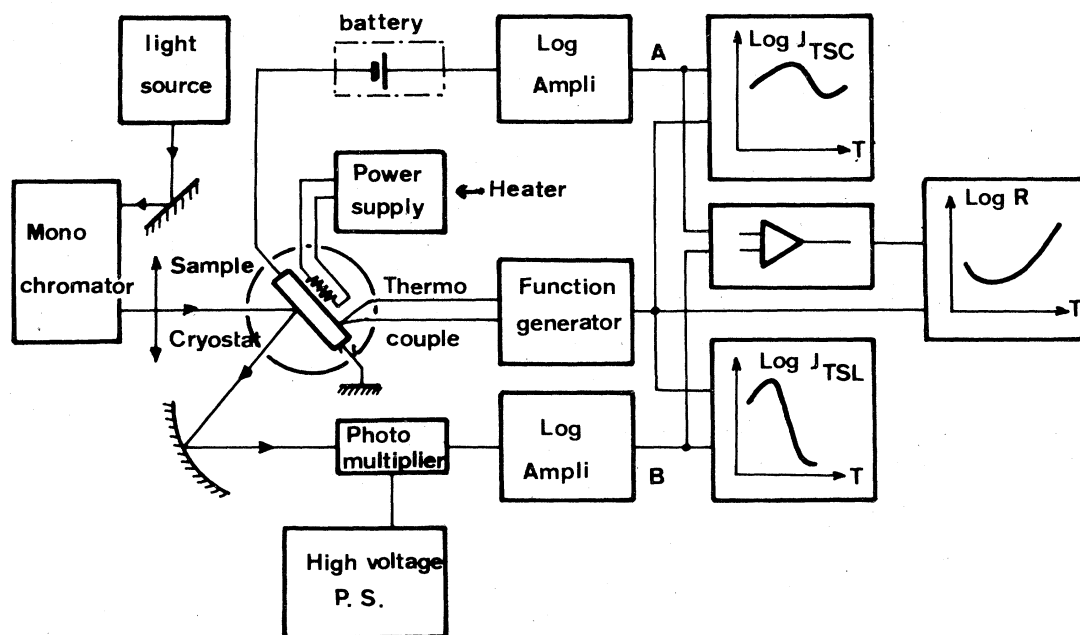


FIG. 10. Experimental setup.

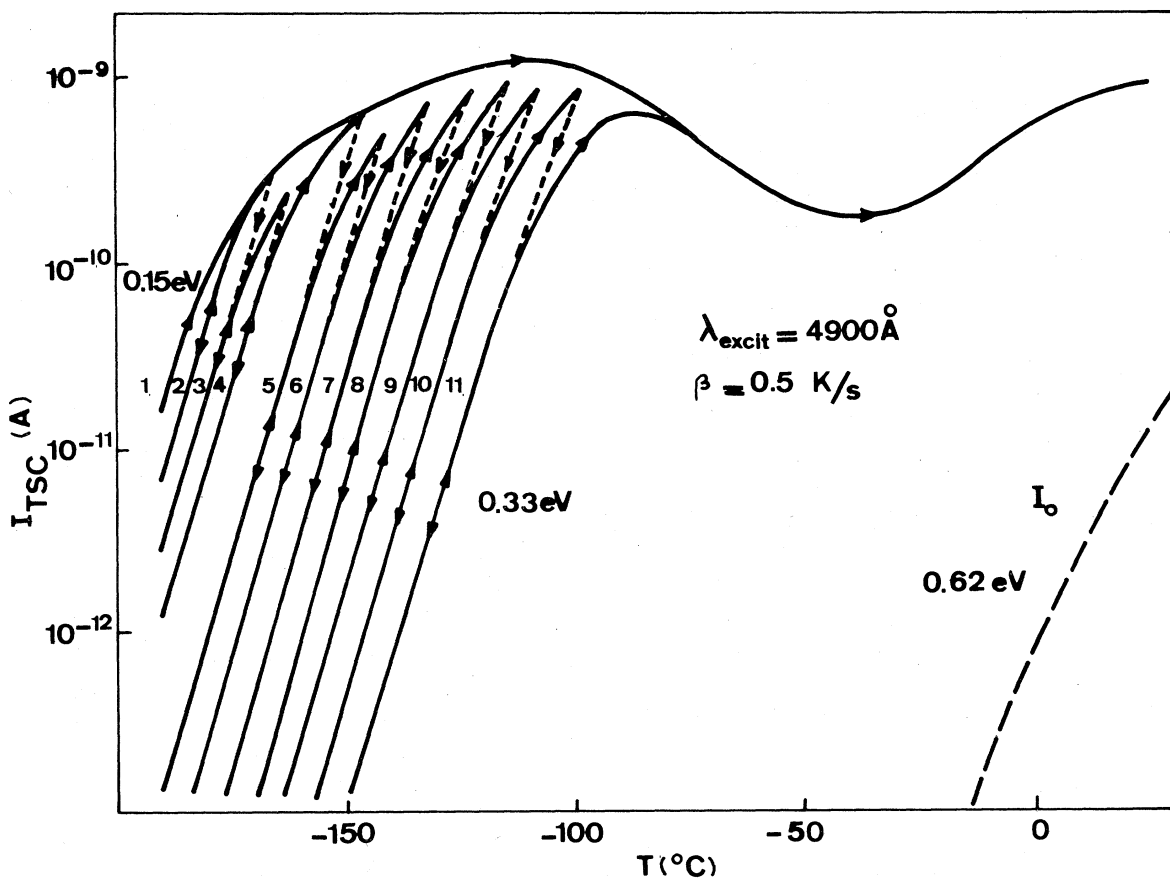


FIG. 11. Thermally stimulated conductivity-fractional emptying.

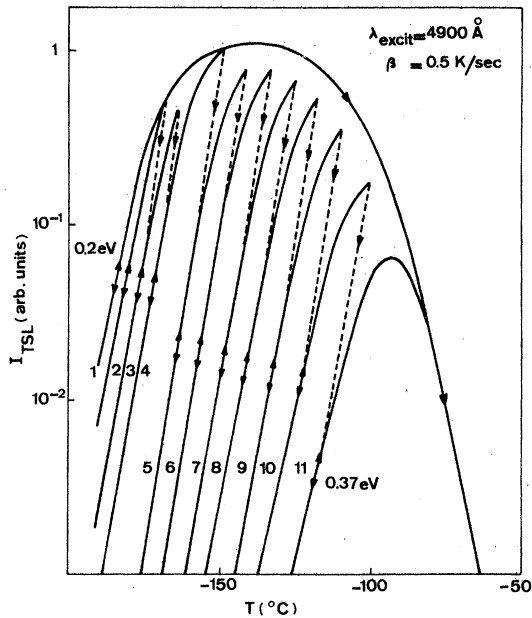


FIG. 12. Thermoluminescence fractional emptying.

ical data: Fig. 13 represents the recording of $R\{T(t)\}$ in two stages of experiments. The first is a succession of fractional emptyings; the second (envelope curve) corresponds to a single-shot operation of a linear sweep $\beta = 0.5^\circ/\text{sec}$. We note for each cycle that a part of a curve where the back and forth parts overlap. This section is quite wide for the first cycles, then shortens with tem-

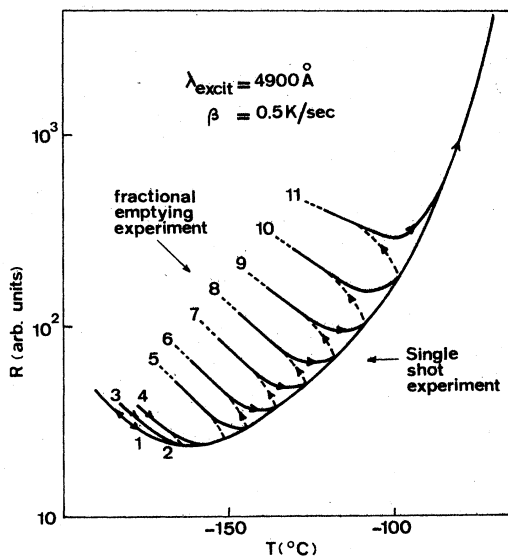


FIG. 13. Plots of R corresponding to the fractional and a single-shot experiment.

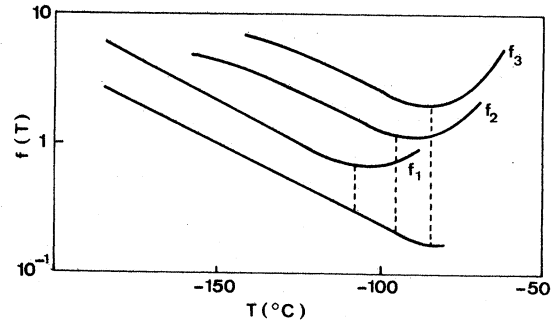


FIG. 14. Graphical determinations of $f(T)$.

perature rise. Each cycle ends by dotted lines which correspond to the regions where the measurement of R becomes uncertain (level too weak for TSC or TSL). This must be verified cycle by cycle with reference to the individual recordings of TSC and TSL. The quality of the graphic use of the data thus depends on the correct definition of these curves elements limited on the one hand by the detection level and on the other by the non-reversible kinetics of the phenomenon. As seen above, the function $f(T) = \mu(T)/\sigma_r(T)v_{th}(T)$ will be reconstructed on a logarithmic scale by making parts of the curve coincide by superposing them. Figure 14 shows three representations of $f(T)$ which each correspond to different heating rates. We can see that it is possible, to a certain extent, to displace the determination zone of $f(T)$ by varying the conditions for evolution.

It must also be stressed that the validity of these representations is not linked to the linearity of temperature rise. It was thus possible, with no further difficulties, to determine $f(T)$ from 77°K

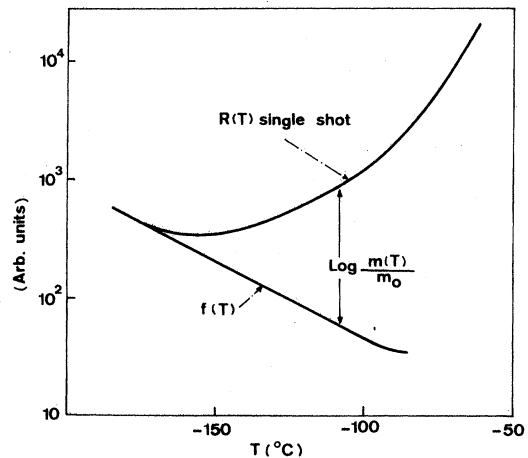


FIG. 15. Graphical determination of $\ln[m(T)/m_0]$.

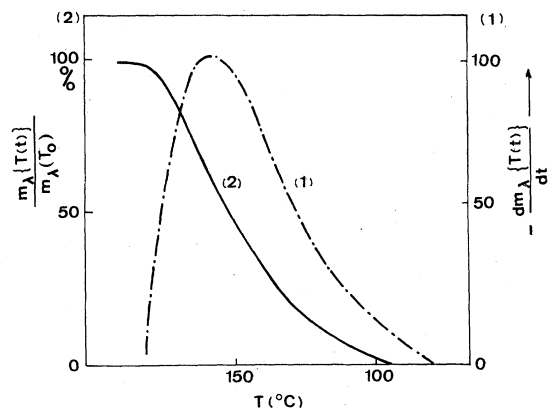


FIG. 16. Linear scale transfer for $m(T)$ and deduced derivative.

up to 220 °K (cf. Fig. 14). The experiment shows that the determination of $f(T)$ is a lot more precise than previously thought. It can also be inferred from these experiments that $f(T)$ has a single value for the temperature range involved. Thus, based on the knowledge of $f(T)$, it is possible to deduce the evolution of $m_\lambda\{T(t)\}$ in any other sweep operation and especially a linear one.

Figure 15 shows such a recording a $R\{T(t)\}$ connected to $f(T)$. From this follows the evolution of $m_\lambda(T)$ (Fig. 16) as well as $dm_\lambda(T)/dt$, its derivative.²⁶

C. Discussion

Let us first consider the meaning of $f(T)$. Taking into account what we know from the theoretical

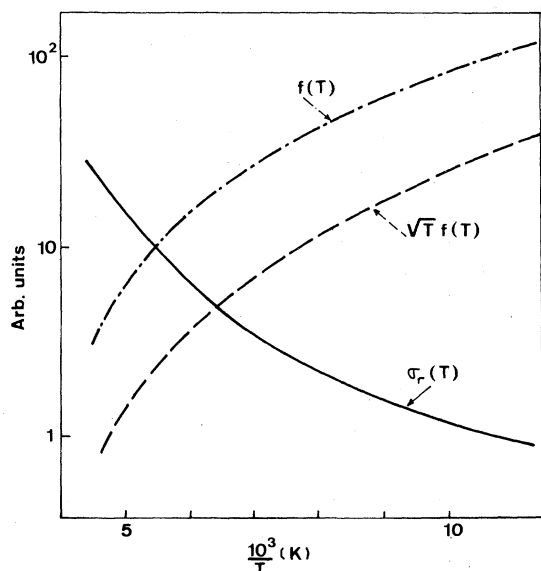


FIG. 17. Temperature dependence of $\sigma_r(T)$.

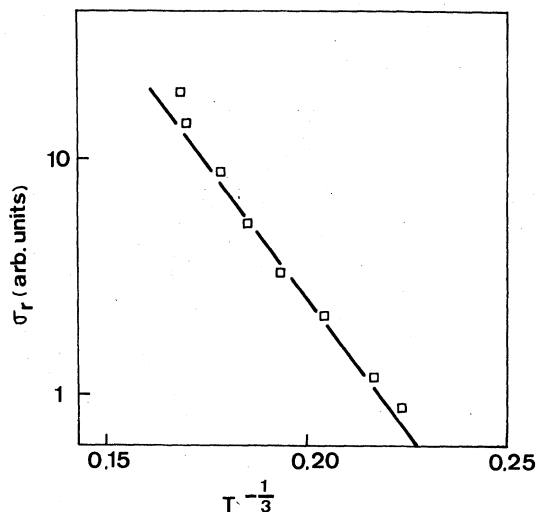


FIG. 18. Linear dependence of $\ln\sigma_r$ vs $T^{-1/3}$.

development, the existence of the increasing function $f(T)$ can only be explained by a "free-to-bound" transition starting from the conduction band:

$$f(T) \sim \mu(T)/\sigma_r(T)v_{th}(T).$$

In the present case of ZnSe:Al, for the temperature range in question and where $\mu(T)$ is constant, we can deduce $\sigma_r(T)$. Its variation is shown in Fig. 17:

$$\sigma_r(T) \sim [f(T)T^{1/2}]^{-1}.$$

The dependence of $\sigma_r(T)$ on temperature can be satisfactorily explained by the repulsive nature (Coulomb's law) of the trapping center. For this, Bube's²⁷ well-known analysis can be used: capture can intervene either by a Boltzmann limitation of electrons having energy superior to that of the potential barrier height E_B , or by a tunnel effect. In the first case, $\sigma(T) = S_0 e^{-E_B/kT}$ is found. In the second case, Boltzmann's formula should be considered in the light of barrier transparency and adjusted to the most efficient energy level (see Ref. 27). Thus

$$\sigma(T) = S_0 e^{-3(\alpha/2)^{2/3}/kT} (kT)^{-1/3},$$

where

$$\alpha = 2\pi^2 e^2 / h\epsilon_r (2m_e)^{1/2} \approx 3 \text{ eV}^{-1},$$

with $\epsilon_r = 8$. We can therefore express $\sigma(T)$ as $\sigma(T) = S_0 e^{-\theta T^{-1/3}}$, with the theoretical value of $\theta \approx 90 \text{ K}^3$. As seen in Fig. 18, $\ln\sigma_r(T)$ does in fact vary linearly with $T^{-1/3}$ over the entire range of $f(T)$. The slope $\theta = 65 \text{ K}^3$ deduced from the graph corresponds quite satisfactorily with the theoretical value. This type of repulsive recombination center is quite frequently observed in electroluminescent materials.

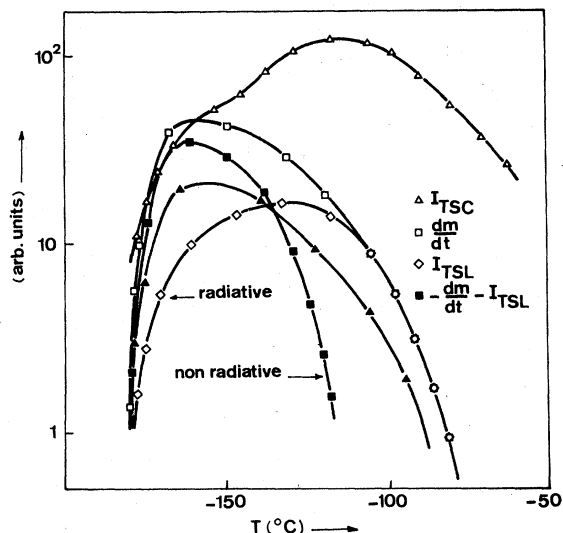


FIG. 19. Thermally stimulated transients.

The study of the variation of $m\{T\}$ also leads to a better understanding of the recombination mechanism. If thermoluminescent emission is the only contribution to RC filling, then $J_{\text{TSL}} = -dm_{\lambda}/dt$, and the two independently obtained experimental curves, J_{TSL} and $-dm_{\lambda}/dt$, should be identical to [Eq. (4)] to a multiplicative factor. That is, it should be possible to superpose them onto a logarithmic diagram of arbitrary units. In reality, however, it is possible for deviations from this simple scheme to occur. The first results from the radiative luminescent yield, $\eta(T)$ of the transition. The second results from the possible exchange of holes between RC and VB. In the case at hand it can be seen (Fig. 6) that the luminescent yield, $\eta(T)$ is constant for the temperature range involved. Furthermore it can be noted (Fig. 19) that J_{TSL} can only be brought to coincide with $-dm_{\lambda}/dt$ (transposed from Fig. 16) on the high-temperature side. The difference between the two

curves (dotted curve) should thus correspond to thermal hole emission from RC and VB. This conclusion is in perfect agreement with the observation of continuous thermal quenching in photoconductivity (Fig. 9). The activation energy of the phenomenon $E_h = 0.4$ eV is also in accordance with the extinction of luminescence.

V. CONCLUSION

The new approach to thermally stimulated processes which we have suggested leads to a series of conclusions. The study of TSL may lead to something other than the spectroscopy of trap activation energies. It is important not to trust *a priori* in a scheme or in a system of differential equations resulting from the detailed balance. A functional expression makes practical conclusions possible. The expression of thermoluminescence cannot be based *a priori* on $-dm_{\lambda}/dt = J_{\text{TSL}}$.^{15,28} All the experimental cases which we have encountered demonstrate the existence of complex exchange phenomena with the RC during radiative emission.

We have proposed a new method for handling experimental data to be used when it is possible to carry out a simultaneous fractional TSC and TSL. In the case of ZnSe:Al monocrystals this study has demonstrated that the cross section of the RC behaves according to a tunnel effect model through a Coulomb-type barrier. This study also shows that the RC does in fact take part in a CTQ mechanism by emitting holes towards the VB. The agreement of these preliminary conclusions leads us to believe that the "functional" approach to TSP merits further exploration.

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¹R. Chen, J. Mater. Sci. **11**, 1521 (1976).

²P. Kelly and P. Braunlich, Phys. Rev. B **1**, 1887 (1970); **1**, 1596 (1970); P. Kelly, M. J. Laubitz, and P. Braunlich, *ibid.* **4**, 1960 (1971).

³J. T. Randall and M. H. F. Wilkins, Proc. R. Soc. A **184**, 366 (1945).

⁴R. R. Hearing and E. N. Adams, Phys. Rev. **117**, 451 (1960).

⁵G. F. J. Garlick and A. F. Gibson, Proc. R. Soc. Lond. **60**, 574 (1948).

⁶A. H. Booth, Can. J. Chem. **32**, 214 (54); Hoogenstra-

ten, Philips Res. Rep. **13**, 515 (1958); see also A. Bohum, Czech. J. Phys. **4**, 91 (1954).

⁷K. W. Boer, S. Oberlander, and J. Voigt, Ann. Phys. (Leipzig) **7**, 130 (1958); Z. Naturforsch. A **13**, 544 (1958).

⁸L. J. Grossweiner, J. Appl. Phys. **24**, 1306 (1953); C. G. Lusich, Dok. Akad. Nauk. SSSR **101**, 641 (1955).

⁹P. L. Land, J. Phys. Chem. Solids **30**, 1693 (1969).

¹⁰H. J. Dittfeld and J. Voigt, Phys. Status Solidi **3**, 1941 (1963); K. H. Nicholas and J. Woods, Br. J. Appl. Phys. **15**, 783 (1964); R. H. Bube, G. A. Dussel, C. Ho,

and L. D. Miller, J. Appl. Phys. **37**, 2 (1966).

¹¹H. Gobrecht and D. Hofmann, J. Phys. Chem. Solids

- 27, 509 (1966).
- ¹²P. Braunlich, in *Thermoluminescence of Geological Materials*, edited by D. J. McDougall (Academic, New York, 1968).
- ¹³R. Chen, *J. Appl. Phys.* **42**, 5899 (1971).
- ¹⁴D. E. Fields and P. R. Moran, *Phys. Rev. B* **9**, 1836 (1974).
- ¹⁵J. P. Fillard and J. Gaslot, *Phys. Status Solidi A* **32**, K85 (1975); J. Gaslot and J. P. Fillard, *J. Appl. Phys.* (to be published).
- ¹⁶P. Braunlich and A. Scharmann, *Z. Phys.* **177**, 320 (1964); W. E. Hagston, *J. Phys. C* **6**, 784 (1973).
- ¹⁷A. Spataru, *Théorie de la Transmission de L'information* (Masson, Paris, 1970).
- ¹⁸A. Kolmogorov and S. Fomine, *Elements de la Théorie des Fonctions et de L'Analyse Fonctionnelle* (MIR, Moscow, 1974).
- ¹⁹B. K. P. Scaife, *J. Phys. D* **7**, L68 (1974); and **8**, L72 (1975); J. Van Turnhout, *ibid.* **8**, L68 (1975); B. Gross, *ibid.* **8**, L 127 (1975).
- ²⁰R. H. Bube, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1967).
- ²¹F. F. Morehead, IBM Res. Rep. RC 1505 (1965) (unpublished).
- ²²G. B. Stringfellow and R.H. Bube, *Phys. Rev.* **171**, 903 (1968).
- ²³J. P. Fillard, M. de Murcia, J. Gaslot, and Sovanhan Chor, *J. Phys. E* **8**, 993 (1975).
- ²⁴A. Rose, *Photoconduction* (Dunod, Paris, 1966).
- ²⁵The authors wish to acknowledge the skill and care exhibited by D. Sovanhan Chor in performing some of the measurements.
- ²⁶Here one can choose either the notation $m(T)$ or $m(t)$ because they both refer to a particular graph of the universal functional $m\{T(t)\}$.
- ²⁷R. H. Bube, *J. Appl. Phys.* **37**, 121 (1966).
- ²⁸Thermally Stimulated Processes, International Workshop (La Grande Motte, 1976) (American Elsevier, New York, to be published).

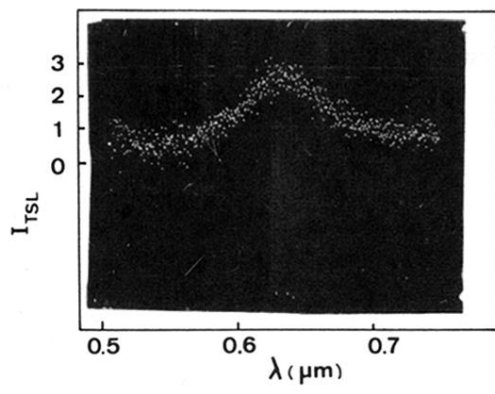


FIG. 5. TSL spectrum.