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Assessment of deep levels in photorefractive materials by transient photoelectric methods

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Abstract. — Depending on their characteristics (energy, concentration, ...) localized imperfection levels, directly or indirectly, determine the properties of photorefractive materials. The aim of this paper is to present a summarized description of the principles of characterization techniques allowing the assessment of deep traps in high resistivity materials. Since this review paper addresses people working in the field of photorefractivity it will be necessary to first recall the characteristic parameters to be measured and to describe the underlying physical processes and their modelisation. The experiments which are basically of spectroscopic nature are subdivided in thermal and optical methods. They use as a tool the analysis of the current transient resulting respectively from the thermally or optically stimulated release of trapped carriers. The report will focus on PICTS (Photo Induced Current Transient Spectroscopy), a thermal method which so far allows the most complete trap characterization. A description of the principles of the experiments and of the different data processing modes will be given. Some important experimental aspects will also be discussed. A few representative results will be presented as an illustration.

1. Introduction.

For a better understanding of the complex processes occurring in photorefractive materials, a variety of research areas are involved including crystal growth and characterization, physics of the photorefractive effect and finally devices and applications. The objective is to tailor the relevant properties of a few materials to make them suitable for the fabrication of devices that are efficient and fast in appropriate spectral regions.

In this context, the identification of imperfections that affect, directly or indirectly, the photorefractive properties, is highly desirable. For a long time, a two level model including an absorption centre (donor) and a deep trap (acceptor) was admitted. However, since high energy pulsed lasers are used in photorefractivity, more than the two main species may be concerned, especially shallower levels [1, 2]. In many papers, the effects of traps are now considered. Therefore the characterization of the deep level spectrum could be very helpful both for the physics of the photorefractive effect and for adjusting the preparation conditions of crystals to optimize their photorefractive performance.

Since photorefractive materials are semi-insulators or insulators, the most powerful spectroscopic techniques that are currently employed for characterizing deep levels in semiconductors e.g. Hall effect, DLTS (Deep Transient Spectroscopy) and DLOS (Deep Level Optical Spectroscopy) lose their sensitivity [3]. More classical methods [4, 5] (Optical absorption, Photoconductivity, ESR (Electron Spin Resonance), photoluminescence, etc.), will of course provide useful information on specific imperfections. An interesting alternative is to make use, *via* an appropriate theoretical model, of the photorefractive effect itself to get some information on the participating defect species and on the transport parameters of photocarriers [6]. However, it would be desirable to dispose of more direct and more complete, DLTS and DLOS like, transient characterization techniques. Such possibilities actually exist, but they cannot be a simple copy of the original methods. Much more sophisticated data processings are required as well as carefully conducted experiments.

The aim of this review paper is to give a summarized comprehensive description of the principles of the methods that we developed, as well as of some important practical aspects. For more details, the reader may refer to several previously published papers [7-10]. Nevertheless, some particular points, which are evident only for deep level specialists, will be developed. As an illustration, a few representative results will be shown.

2. General theoretical background.

Before discussing the experimental methods, a review of the terminology and of the elementary processes concerning imperfection levels will be necessary.

2.1 CLASSIFICATION OF ENERGY LEVELS [3]. — Defect levels are labeled as absorption centres, photoconductivity centres, recombination centres, donor or acceptor levels, shallow or deep levels, electron or hole traps, etc. These denominations correspond in fact to different properties of the same defect species.

Carriers can be excited from levels in the gap to the conduction band (CB) or to the valence band (VB). This implies two possible electronic charges of the corresponding defects : 0 and + 1 (or + 1 and + 2) for donors ; 0 and - 1 (or - 1 and - 2) for acceptors. In this context, absorption centres in photorefractive sillenites can be considered as donors (Fig. 1).

The energy levels as a whole are usually classified in shallow and deep levels. This distinction is however somewhat arbitrary. In semiconductor physics [3] a shallow level is a

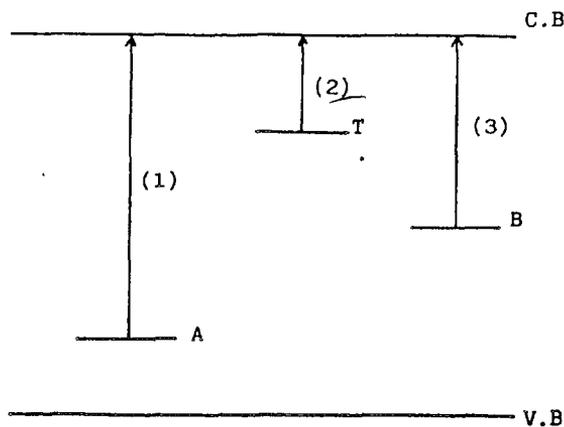


Fig. 1. — Energy level diagram showing three types of centres : (A) absorption centre, (T) shallow thermally active trap, (B) deep, optically active trap.

level that fits the simple hydrogenic model. Roughly speaking a level located at less than 0.1 eV below the CB or above the VB belongs to this category. All the others are considered as deep and will be concerned by the methods which will be described below.

In the field of photorefractive materials the distinction between the two types of levels is based on a different criterion. Are considered as deep traps those centres which are involved in the build up of a thermally stable holographic grating. They are usually labeled as « acceptors » (Fig. 1, B level). Shallow traps (Fig. 1, T level) on the other hand, are thermally linked to the CB. Under pulsed laser excitation, they may be responsible for transient gratings [1, 2].

Strictly speaking all the defects which introduce levels in the energy gap can act either as shallow or deep traps under suitable conditions e.g. respectively at high or low temperature. A better appellation would be thermally active or thermally inactive at the considered temperature of operation T_d . Indeed the demarcation energy E_d between the two behaviours can be roughly estimated using the semi-empirical relation $E_d = 24 kT_d$ [4]. This means that, at room temperature, levels separated from the CB or the VB by more than 0.7 eV can be considered as thermally inactive. Therefore this kind of centres are more likely encountered in large bandgap materials ($E_g > 1.5$ eV).

2.2 CAPTURE AND EMISSION PROCESSES AT A LEVEL. — A defect level exchanges charge carriers with the CB and VB under thermal and optical stimulations. Figure 2 depicts the capture and emission processes that can occur at e.g. a donor-type centre with electron energy E_t .

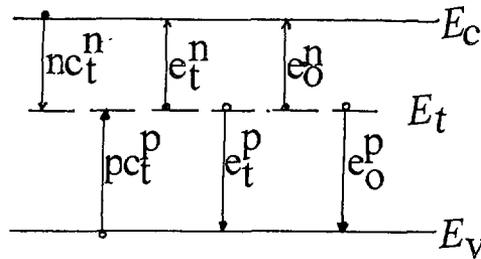


Fig. 2. — Emission and capture processes at a deep energy level E_t . Superscripts indicate whether the transition is by electron (n) or hole (p). Subscripts are respectively for thermal (t) or optical (o) process. The symbols are : e for an emission rate, c for a capture constant. n and p for the free carrier concentrations.

The rate equation for the density n_t of trapped electrons is :

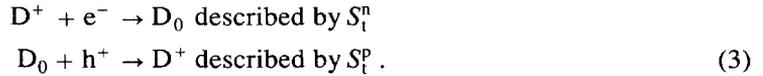
$$dn_t/dt = (nC_t^n + e_t^p + e_o^p)(N_t - n_t) - (pC_t^p + e_t^n + e_o^n) n_t \tag{1}$$

N_t is the total density of centres ; n and p are the free electron and hole densities. The term nC_t^n , where C_t^n is the electron capture coefficient, represents the rate of capture of free electrons by unoccupied levels (pC_t^p holds for holes) ; e_t^n and e_t^p are the thermal emission rates respectively of electrons from occupied neutral states to the CB and of holes from unoccupied (positively charged) states to the VB. In the same manner, e_o^n and e_o^p are the corresponding optical emission rates.

2.2.1 *Capture cross sections.* — The capture coefficient is the capture cross section S_t^n or S_t^p times the mean thermal velocity v :

$$C_t^n = S_t^n v \quad \text{for electrons and} \quad C_t^p = S_t^p v \quad \text{for holes .} \quad (2)$$

For a correct interpretation of experimental results, it is important to point out the exact signification of S_t^n and S_t^p . The capture processes which can occur at the considered donor type level are the following :



Because of the Coulomb attraction, S_t^n is larger (10^{-13} - 10^{-12} cm²) than S_t^p (10^{-16} - 10^{-14} cm²) which measures the weaker interaction between a hole and a neutral trap.

The capture cross section is determined by the potential variation in the neighbourhood of the centre [4]. Capture cross sections of Coulomb-attracting or neutral traps are only weakly temperature dependent. Coulomb-repelling centres on the contrary are characterized by a strong temperature dependence of their capture cross section :

$$S_t^n = S_\infty^n \exp(-E_b/kT) . \quad (4)$$

Such variation is observed when the capture occurs through multiphonon emission (3). E_b is found between 0.1 and 0.5 eV ; S_∞^n is of the order of 10^{-14} - 10^{-15} cm². This means that S_t^n can take values as low as 10^{-22} cm² at low temperature.

In conclusion, the capture cross section is an important parameter for a trap. Its value provides information about the electronic nature of the centre.

2.2.2 *Thermal emission rates.* — Equation (1) shows that capture is counterbalanced by thermal emission. The emission rates for electrons and holes are respectively :

$$e_t^n = S_t^n v N_c \exp[-(E_c - E_t)/kT] \quad (5)$$

$$e_t^p = S_t^p v N_v \exp[-(E_t - E_v)/kT] \quad (6)$$

N_c and N_v are the effective densities of states in the CB and VB.

It must be remembered that v varies as $T^{1/2}$ and N_c and N_v as $T^{3/2}$. Thus a temperature dependence T^2 must be taken into account. The ionization energies $(E_c - E_t)$ and $(E_t - E_v)$ vary as a function of T due to the usual linear temperature dependence of the bandgap :

$$(E_c - E_t)_T = (E_c - E_t)_{T=0} - \beta T . \quad (7)$$

Finally, if one also takes into account the thermal variation of the capture cross section, equation (5) can be rewritten :

$$e_t^n = S_t^n v N_c \exp(\beta/k) \exp[-(E_c - E_t)_0/kT - E_b/kT] . \quad (8)$$

Therefore, the ionization energies deduced from thermal emission rate measurements are not the true ones. Indeed, when plotting e_t^n/T^2 versus $1/kT$ one obtains $(E_c - E_t + E_b)$ instead of $(E_c - E_t)$ and $S_t^n \exp \beta/k$ instead of S_t^n .

2.2.3 *Optical emission rates.* — The optical emission rates in equation (1) are defined as follows :

$$e_0^n(h\nu) = S_0^n(h\nu) \Phi_0(h\nu) \quad (9)$$

$$e_0^p(h\nu) = S_0^p(h\nu) \Phi_0(h\nu) \quad (10)$$

$S_0^n(h\nu)$ and $S_0^p(h\nu)$ are the optical capture cross sections and $\Phi_0(h\nu)$ is the incident photon flux. Several theoretical models have been proposed for drawing up an analytic expression for $S_0(h\nu)$ best fitting the experimental measured spectral dependence and allowing the determination of the optical ionization energy [3]. It must be recalled that the optical ionization energy often differs from the thermal one, by the Franck-Condon shift (0.1 to 0.5 eV) which characterizes the magnitude of the lattice relaxation.

3. Basic principles of deep level transient spectroscopy.

3.1. GENERAL CASE. — If the experimental conditions (temperature, optical excitation) are kept constant, the trap occupancy takes an equilibrium value which can be related to the various variables in equation (1) by putting $dn_t/dt = 0$. If any of the variables, e.g. n , e_0^n , e_t^n via the temperature, is suddenly changed, the level is set out of equilibrium. Consequently, the trap occupancy will relax to the new stationary value fixed by the new value of the variable. The relaxation is in general not instantaneous, so, if n_t can be monitored by some means, a transient signal will be observed. The analysis of this transient is the key of deep level transient spectroscopy.

3.2 PRACTICAL CASES. — The problem cannot be solved in the general case where all the terms in equation (1) must be taken into account. Therefore, experimental conditions are achieved to allow using simpler forms of equation (1).

Since a trap has in general a dominant n or p behaviour, the case of an electron trapping level will be considered throughout. Equation (1) will take the simpler form :

$$dn_t/dt = (nC_t^n + e_0^n)(N_t - n_t) - (e_t^n + e_0^n) n_t. \quad (11)$$

3.2.1 *Deep level thermal spectroscopy.* — A further simplification is possible if there is no direct optical excitation of the level :

$$dn_t/dt = nS_t v(N_t - n_t) - e_t n_t. \quad (12)$$

(The superscript n for S_t and e_t is omitted.)

In this case, the trap occupancy is determined by n and by the thermal emission rate via the temperature. The free electron concentration can be fixed by factors independent of the level : dark conductivity, electrical injection, photoconductivity (produced by band to band transition).

In an insulator or semi-insulator, the dark concentration n_0 of electrons can be neglected at any temperature of the explored range (usually $T < 500$ K for sillenites). Thus, in darkness the trap is empty at these temperatures.

The basic experimental sequence comprises two steps : optically induced filling of the levels, thermally stimulated emptying.

• At time $t = 0$, the sample is illuminated by bulk absorbed photons. While the light is on, a quasi-stationary density of free electrons is reached after a time τ , recombination lifetime.

which is assumed to be short compared to the capture time τ_c of electrons by the traps :

$$\tau_c \gg \tau \quad (13)$$

where

$$\tau_c = (S_t v N_t)^{-1} \quad (14)$$

This point will be discussed in section 4. Assuming weak absorption, the electron concentration is given by :

$$n = \alpha \Phi_0 \tau \quad (15)$$

where α is the absorption coefficient corresponding to all transitions generating free electrons. Finally, equation (12) takes the form :

$$dn_t/dt = -e_t n_t + \alpha \Phi_0 \tau (N_t - n_t) S_t v. \quad (16)$$

The solution to this equation is :

$$n_t(t) = [N_t / (1 + e_t/g_t)] [1 - \exp - (e_t + g_t) t] \quad (17)$$

where $g_t = \alpha \Phi_0 \tau S_t v$ is an effective filling rate.

Complete trap filling requires $g_t \gg e_t$ and a minimum illumination time $t_t = (g_t)^{-1}$. These conditions could not be achievable for relatively shallow traps at $T > T_d$ or for traps of small capture cross section. The time needed for a stationary trap occupancy strongly depends on S_t . Studying the filling of the level *versus* time may be a possibility to directly access the capture cross section and its temperature dependence.

• Thermally stimulated emission : basic physical model. — At time $t = t_t$, the light is abruptly interrupted. The free photoelectron concentration falls to zero within the recombination lifetime τ . Thus, at times $t > t_t + \tau$, equation (16) reduces to

$$dn_t/dt = -e_t n_t \quad (18)$$

the solution of which is :

$$n_t(t) = n_t(t_t) \exp[-e_t(t - t_t)]. \quad (19)$$

This expression contains all the characteristic parameters of the level : $(E_c - E_t)$ and S_t *via* the temperature dependence of e_t (Eq. (5)) and $n_t(t_t) = N_t$ if the trap is saturated. To determine these parameters, one therefore uses methods allowing the investigation of the temperature dependence of the decay of the trapped charge. In conclusion, it should be pointed out that the mathematical analysis will be based on an exponential time dependence of the trap occupancy, i.e. on a physical model which essentially neglects retrapping of emitted electrons. Note that this is the usual approximation in deep level spectroscopy [3] expressed by condition (13), and actually the fact in high resistivity materials (see Sect. 4).

3.2.2 Deep level optical spectroscopy. — A filled trap releases the charge carriers by thermal stimulation within a time $\tau_t = e_t^{-1}$

Below a certain temperature, the non-equilibrium state corresponding to the filled traps will exist for an indefinite time because the equilibrium can be reestablished only through the CB. This can in principle be achieved by direct optical stimulation of electron transitions from the trapping levels to the CB.

The preliminary condition, however, is that the threshold for the corresponding optical capture cross section $S_0^n(h\nu)$ is not rejected above the bandgap i.e. that the Franck-Condon

shift is not too large [3]. We further assume that retrapping can be neglected and that the functions $S_0^n(h\nu)$ (trap emptying) and $S_0^p(h\nu)$ (trap filling) do not overlap. Under these conditions, equation (11) reduces to :

$$dn_t/dt = -e_0^n n_t \quad (20)$$

the solution of which is :

$$n_t(t) = n_t(t_1) \exp[-e_0^n(t - t_1)] \quad (21)$$

The determination of the time constant e_0^n of the relaxation process as a function of the photon energy $h\nu$, at constant photon flux $\Phi_0(h\nu)$, will yield $S_0^n(h\nu)$ i.e. the so-called photoinduced absorption band of the trap.

It is obvious that equation (20) corresponds to an oversimplified physical model. Nevertheless, if the traps are completely filled with electrons by the preliminary illumination, the assumptions concerning retrapping and electron transitions from the VB, are at least valid at the beginning of the relaxation process. In this case, however, n_t does not decrease to zero but approaches, more likely, a practically constant value representing the quasi-equilibrium state of the crystal.

Conversely, if all centres are empty, their filling by direct optical excitation can be described by equation :

$$dn_t/dt = e_0^p(N_t - n_t) \quad (22)$$

This may be a possibility to assess $S_0^p(h\nu)$.

4. Discussion of some problems specific to high resistivity materials.

In the context of this paper, it was important to recall the physical meaning of the parameters which characterize a deep level. A complete characterization would normally imply the consideration of the two possible charge states. In practice, however, a deep level is linked thermally either to the CB or to the VB ; i.e. it acts as an electron or as a hole trap. A second category of levels acts as recombination centres : these capture holes, for example, and hold them until neutralization by subsequent capture of electrons.

The characterization of traps consists basically in measuring the thermal emission rate, as a function of temperature and, if possible, the optical emission rate *versus* photon energy, at low enough temperature. A fundamental condition in order to access the emission rates is that the relaxation processes be exponential. This implies several important assumptions :

- i) each trap species is associated with a discrete monoenergetic level [9] ;
- ii) retrapping of thermally or optically emitted carriers is neglected over the whole range of temperature ;
- iii) the centres are completely filled after the preliminary illumination.

Hypothesis (i) seems to be realized in photorefractive materials, since they are usually single crystals of good optical quality and chemical stability. So, the presence of a high degree of disorder is very unlikely.

Condition (ii) is naturally satisfied in large bandgap high resistivity materials : it simply means that the emitted electrons rapidly recombine with holes localized on recombination centres (since holes captured by traps are by definition released to the VB).

The total concentration N_t of a trap species is also an important information especially if one wants to study its evolution as a function of preparation conditions. Thus, condition (iii) is peremptory for this aim, but in fact not easy to achieve.

A number of points discussed above essentially apply to high resistivity and large bandgap materials. Usually they cannot be subjected to special purification processes. Consequently, there is every reason to assume that a large number of deep levels (crystalline defects, impurities) are present in the band-gap. Experimental studies indeed show that this is actually the case [10, 11]. The total concentration of these levels is considerably larger than the density of free photocarriers. In a compensated n-type material, as assumed here, the dark Fermi equilibrium level is located in the upper half, close to the middle of the bandgap. Photoelectrons are captured by empty levels above the Fermi level (of total density $\sum M_i$), photoholes by occupied levels below the Fermi level (of total density $\sum M_j$).

It is very unlikely that the electron and hole lifetimes (τ_n and τ_p) are of the same order [5]. They can be expressed as :

$$\tau_n^{-1} = \sum \tau_i^{-1} \quad \text{and} \quad \tau_p^{-1} = \sum \tau_j^{-1} \quad (23)$$

($\tau_i^{-1} = C_i^n M_i$, $\tau_j^{-1} = C_j^p M_j$ where i is the number of an empty level and j the number of an occupied level).

Very often, one of these levels R dominates the recombination kinetics of photocarriers. (In n-type materials, R is usually a j centre). This means that its contribution to the sum $\sum \tau_i^{-1}$ is significantly larger than the total contribution of all others and at the same time than $\sum \tau_j^{-1}$. Consequently if photoexcitation produces band to band transitions, holes will be captured very quickly by the centres, in other words τ_n is expected to be much larger than τ_p . This is actually the case, in photorefractive crystals, for the absorption centres which also play the role of recombination centres.

It is easily seen that when the bandgap is large, or more generally at lower temperatures, the electrons and holes generated by « fundamental » excitation, simultaneously recombine at the R centres and are trapped respectively by the M_i and M_j levels. However, holes are much more likely to be accumulated at R levels whereas electrons, whose lifetime for capture by the R centres is long, are more likely to be trapped by the M_i centres. In conclusion, in a high resistivity material, one type of traps is usually active. However, if the concentration of R and the total concentration of M_i levels are of the same order, obviously the electron trapping will reduce the electron lifetime and, conversely, the hole lifetime will be increased.

The qualitative considerations presented in this section are of great importance for the remainder of the paper. We believe that the discussion could also be helpful for the interpretation of some particular observations in photorefractivity.

5. Photoinduced transient thermal spectroscopy.

5.1 EXPERIMENTAL TOOLS. — On the basis of the principles discussed above several experimental procedures can be used to have access to the main thermal parameters (i.e. those corresponding to the dominant n or p characters) and to the concentration of the centres acting as traps. They differ by the way the trapped charges are monitored, the excitation and stimulation conditions, the signal processing.

5.1.1 *Charge monitoring.* — For the investigation of traps in semiconductors, p-n or Schottky diodes are in general used. The trapped charges can then be monitored by capacitance measurements. Indeed, the capacitance of the space charge layer in a diode is directly proportional to the trapped charge [3].

Clearly in the case of high resistivity materials, this method cannot be applied. One can then have access to the trap occupancy changes by monitoring the free electrons released to the CB by thermal stimulation. In addition to equation (18) one has to take into account the rate

equation for the free electron density :

$$dn/dt = dn_t/dt - n/\tau . \quad (24)$$

We are here mainly interested in the decay of the trapped charge after preliminary illumination ($t > t_1$). Keeping in mind the assumption of negligible retrapping, the solution of (24) is straightforward

$$n(t) = G_1 \{ \exp[-e_1(t - t_1)] - \exp[-(t - t_1)/\tau] \} + n(t_1) \exp[-(t - t_1)/\tau] \quad (25)$$

$$G_1 = \frac{e_t}{\tau^{-1} - e_t} n_t(t_1) \approx \tau e_t n_t(t_1) . \quad (26)$$

In practice, the sample is provided with electrodes and inserted in a measuring circuit, allowing to apply an external field to the specimen and to collect the current.

The transient current $i(t)$ is related to $n(t)$ by :

$$i(t) = Aq\mu n(t) \quad (27)$$

where μ is the mobility of free electrons and A a constant amplification factor including geometrical parameters and the applied electrical field.

Actually, the experimental conditions are such that : $\tau^{-1} \gg e_t$ and $\tau^{-1} \gg (t - t_1)$.

Consequently (25) takes a simpler form and finally $i(t)$ is given by the expression :

$$i(t) = Aq\mu \tau n_t(0) \tau_i^{-1} \exp(-t/\tau_i) . \quad (28)$$

For sake of simplicity the origin of times is taken at $t = t_1$.

The preexponential factor of $i(t)$ depends on the thermal emission rate and on the transport parameter $\mu\tau$. Equation (28) is the basic equation of PICTS (PhotoInduced Current Transient Spectroscopy).

5.1.2 Excitation and stimulation procedures. — The principle of the procedures was already discussed in section 3. In PICTS, filling and emptying of the trap are monitored by recording the transient current as shown in figure 3. Excitation is best achieved by square light pulses. On the rise curve the two steps (FC, CD), discussed in section 3.2.1, are visible. On the decay, the initial rapid decrease (DE) corresponds to the recombination of the photoelectrons. The slower exponential decrease (EF) due to the thermal release of electrons contains informations concerning the trap.

The prime objective of the experiment is to determine the thermal emission rate as a function of temperature. Thus, the transient is recorded at every 2 K, while the temperature is swept up (or down) slowly. Later on, one extracts from the stored data the parameters of interest through proper signal processings.

5.1.3 Data treatment. — Since in a real material there are several trap species, whose contributions to the current may overlap, one has to resolve each transient into several components. This decomposition is performed through correlation techniques [3].

Figure 4 illustrates the principle of the treatment in the case of a single exponential charge transient with a temperature independent preexponential factor. The left-hand part of figure 4 shows how the shape of the transient changes when the temperature is progressively increased. The double gate procedure consists in sampling the decay at two times t_1 and t_2 and in plotting the difference $n_t(t_1) - n_t(t_2)$ as a function of temperature. It is clear that the function goes through a maximum at a temperature T_m . At this temperature, τ_t takes a value τ_m which can be

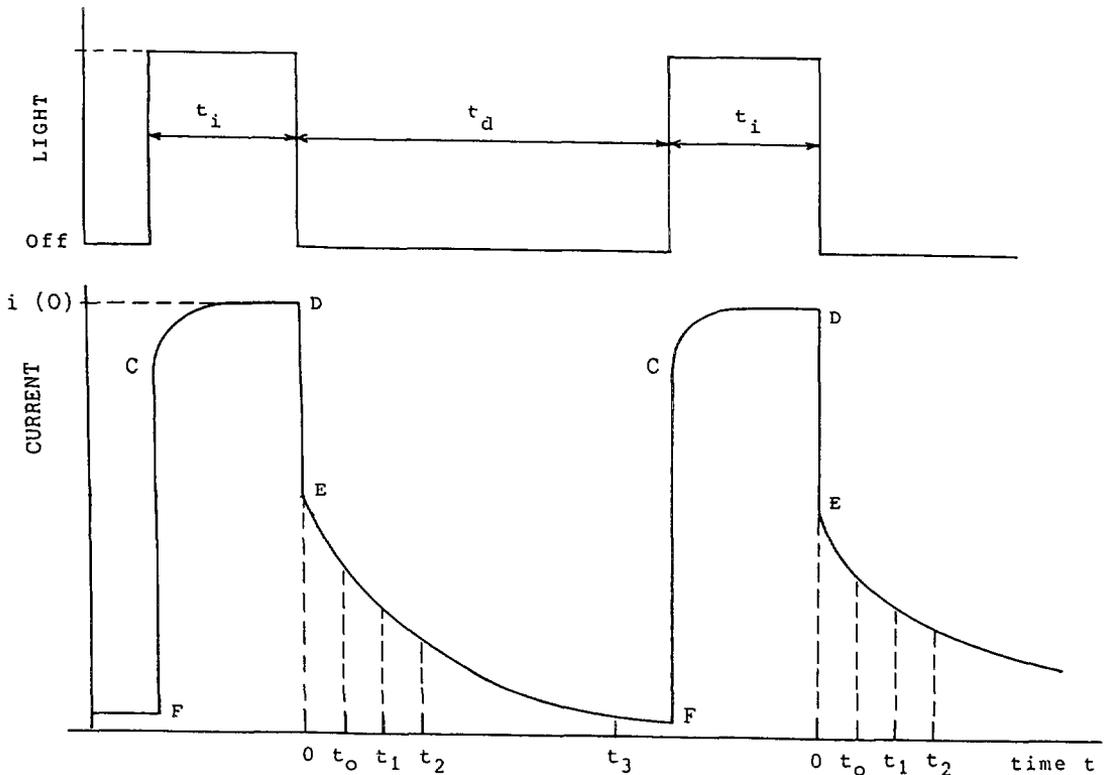


Fig. 3. — Current transient induced by a square light pulse. Both on the rise and decay curve the fast components (FC, DE) and slower components (CD, trap filling; EF, trap emptying) are shown. The origin of time is taken at the beginning of the decay; $i(0)$ is the saturation value of the photocurrent; t_0 , t_1 , t_2 , t_3 are fixed delay times; t_i and t_d are respectively the open and closed times.

related analytically to t_1 and t_2 , by searching the maximum of the double gate function :

$$f[\tau_t(T)] = \exp(-t_1/\tau_t) - \exp(-t_2/\tau_t) \quad (29)$$

yielding the solution :

$$\tau_m = (t_2 - t_1) / \ln(t_2/t_1). \quad (30)$$

The interesting point is, that for different values of (t_1, t_2) , different T_m will be produced. The plot of $\log(\tau_m T_m^2)$ versus T_m^{-1} (Arrhenius plot) will thus yield the trap parameters (Fig. 5) whereas the concentration can be deduced from the peak height, which, as can be easily checked, will be constant if the ratio t_2/t_1 is fixed.

Equation (30) shows that τ_m depends on t_1 only. T_m , on the contrary, depends on τ_m and on the trap parameters. This means, and this is the main advantage of the method, that for a given t_1 , the different trap species present in the material will be resolved in a series of peaks appearing at increasing T_m as the apparent thermal ionization energy increases. Finally the heights of the peaks may be a direct measure of the relative concentration.

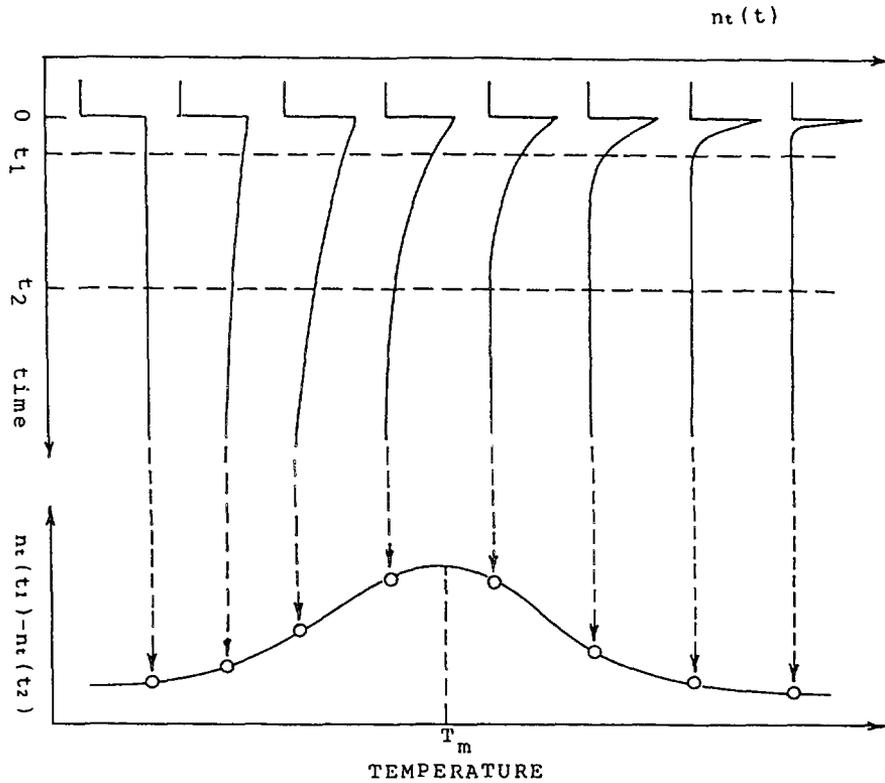


Fig. 4. — Illustration of the principle of data processing. Shape of the decay of the trapped charge $n_t(t)$ at various temperatures, and temperature dependence of the differential signal $n_t(t_1) - n_t(t_2)$.

5.2 THE PICTS TECHNIQUE.

5.2.1 Basic principles. — The PICTS technique represents a particular mode of photoinduced transient thermal spectroscopy. The principles of the experimental procedure have been discussed in the general frame. The basic experiment consists in recording the whole transient while the temperature is scanned (usually between 80-500 K).

To extract the parameters of the various trap species the following assumptions are made :

- i) the decay is considered as a sum of exponential functions, each one represented by an equation of the form (28) and corresponding to a discrete level ;
- ii) equation (28) is based on a simple physical two level model (trap + recombination centres) implying a majority carrier process, negligible retrapping and recombination lifetime unaffected by trapping (see Sect. 4).

5.2.2 Experimental details. — We now discuss some experimental aspects of PICTS. A platelet of the material, provided with metallic electrodes, in coplanar or in sandwich configuration, is fixed on a holder in the thermal exchange chamber of a variable temperature cryostat. The temperature of the sample must be controlled and measured very accurately. The main elements of the optical system are a stabilized high intensity conventional light source equipped with a moderately dispersive monochromator. The measuring circuit comprises a stable dc voltage source and a sensitive variable gain current amplifier whose output is fed to the data acquisition system.

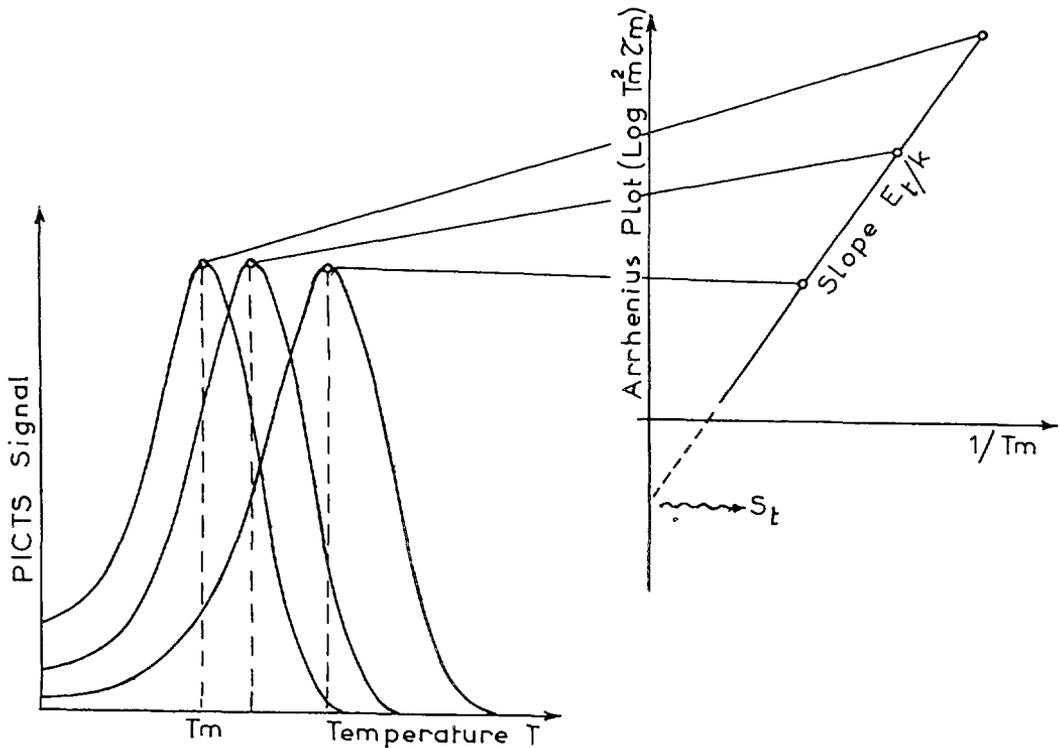


Fig. 5. — Illustration of the principle of data processing. Shift of the maximum for different values of t_1 at constant ratio t_2/t_1 , and corresponding Arrhenius plot allowing the determination of the parameters (E_t , S_t) of the trap.

Practice has shown that the most powerful and flexible set up is a computer based system [8, 9]. A computer operated electronic shutter allows an independent choice of t_1 and t_d (Fig. 2) for complete filling and emptying of the traps. Data acquisition offers also various possibilities : different sampling modes, single shots, averaged transients, etc.

5.2.3 Data processing methods. — Following the basic method of section 5.1.3, the idea is to separate the time dependent and thermal (i.e. the stimulating thermal energy) variations of the transient. The complication is that the factors in the preexponential term are temperature dependent. So, the transport parameter $\mu \tau$ varies usually strongly and formally in an unknown manner, with temperature but not necessarily over the whole temperature range. Finally, on account of the problem of trap saturation, $n_t(0)$ is likely also to depend on T . Consequently, the double-gate method is not directly applicable.

This led to introduce two original data processing methods :

- the so-called « four-gate » (FG) processing for the determination of the trap parameters :
- the so-called « normalized double-gate » (NDG) method which is less liable for the determination of the parameters, but is mainly used for the evaluation of the concentrations.

These methods were largely analysed in previous publications [7-10] from a theoretical point of view and evaluated for practical applications. So, we just focus on the principles and on some important aspects.

5.2.4 *The four-gate technique.* — The decay is sampled at four times t_0 , t_1 , t_2 and t_3 (Fig. 2). The ratio

$$Y[\tau_i(T)] = [i(t_1) - i(t_2)]/[i(t_0) - i(t_3)] \quad (31)$$

when plotted as a function of T , yields the so-called four-gate-PICTS spectrum.

$$Y(T) \text{ takes a symmetrical peak shape if } t_0 < t_1 < t_2 \text{ and } t_3 > 10 t_0. \quad (32)$$

Then, $i(t_3)$ can be neglected in equation (31). Experimentally $i(t_3)$ represents the baseline of the transient; this justifies its formal presence. It is easily seen that finally an expression similar to equation (29) is obtained, except that t_1 and t_2 are replaced respectively by $t_1 - t_0$ and $t_2 - t_0$, as well as in the condition for a maximum (30). Hence the main conclusions drawn in section 5.1.3 still apply.

Usually, t_1/t_0 and t_2/t_0 are kept constant whereas t_0 is varied. The trap species appear if their emissions do not interfere with those of energetically nearby levels, as a series of well separated peaks. However, since the FG processing eliminates the preexponential factor in equation (28) the peak amplitude depends only on the ratios t_1/t_0 and t_2/t_0 whereas τ_m and T_m vary with t_0 . Thus the ideal FG spectrum should consist of a series of well contrasted peaks, having all the same theoretical predicted height.

The FG procedure presents a number of advantages. Computer simulations on a single level model show that a peak shifting *versus* t_0 keeps a constant predicted amplitude. When this is experimentally observed, it constitutes a clear proof of validity of the postulated physical model. Deviations from the exponential relaxation model result in a reduced peak height. On the contrary, if the peak height varies with t_0 , one may conclude that the current transient is no more strictly exponential due to the time dependence of the transport parameter $\mu\tau$. Several factors were found to be responsible for a reduction of the predicted peak height: retrapping of emitted carriers, time dependent transport parameter, enlarged energy level, interference with nearby levels, external factors such as background noise, signal distortion... Actually, computer simulations showed that it should be possible to apply a correction to the Arrhenius plot which can be estimated from the difference between the actual and theoretical peak heights. However, it should be pointed out that the spectrum is insensitive to the magnitude of the applied electrical field (up to at least 500 V/cm).

In practice, the experimental conditions are adjusted to optimize the contrast of the spectrum and to approach the predicted peak heights. At first, external distortion factors are minimized. This is a usual instrumental or noise problem when very small currents (down to 10^{-10} – 10^{-11} A) are measured. Significant improvements are achieved by adjusting the level of illumination and its duration t_i . In general, two temperature scanning experiments are carried out, one at low excitation level for subsequent FG data processing, and a second one at high excitation level for subsequent NDG processing to evaluate the trap concentrations.

The final spectrum will still show differences in the peak heights which reflect the degree of interference between the different levels. This is not a drawback specific to the method, but a shortcoming of most of the semi-insulating materials that we have so far characterized, due to the large number of defects or contaminants in the crystals. Up to ten levels were currently detected within an energy range of 0.2-1 eV. Indeed the FG method has both much higher spectral resolution and sensitivity (minimum detectable trap concentration) compared to the NDG procedure or to DLTS. These qualities are due to the fact that, within the frame of this method, the species all have the same weight in the spectrum, independently of their concentrations. As a consequence, better Arrhenius plots are obtained allowing a more accurate evaluation of the trap parameters. Concerning photorefractive materials, it is usually enough to be able to recognize the various types of centres through their signatures. For

example, the Arrhenius plot is a characteristic signature of a level, giving E_t and S_t . An alternative manner to identify a given trap species in the spectrum is to take the temperature T_m corresponding to a fixed t_0 as the signature.

In conclusion, the FG technique can be a powerful trap characterization tool provided that the experiments be carefully conducted. It even makes possible a fine analysis of the trap relaxation processes.

5.2.5 The normalized double-gate technique. — This procedure aims at taking into account the temperature dependence of $\mu\tau$ in equation (28) without eliminating the initial trap occupancy $n_t(0)$. This can be simply achieved by normalizing the transient $i(t)$ by the saturation value $i(0)$ of the photocurrent which is given by :

$$i(0) = A\mu\tau\alpha\Phi_0. \quad (33)$$

The normalized transient takes the form :

$$i_N(t) = (N_t/\alpha\Phi_0)\tau_t^{-1}\exp(-t/\tau_t). \quad (34)$$

The point is now that the temperature dependence of α must be taken into account. This can be done in an indirect manner. It is well known that the spectral response of photoconductivity shows in general a maximum near the absorption edge [4]. This maximum is determined by the relative magnitudes of surface and volume recombination lifetimes of photocarriers. It occurs for the wavelength $\lambda = \lambda_{\max}$ corresponding to an absorption coefficient $\alpha_{\max} = 1/d$ where d is the sample thickness i.e. to $(1 - 1/e) = 0.63$ of the incident radiation. Tuning the monochromator to achieve maximum photoresponse, while scanning the temperature, allows to perform the measurement at a fairly constant photogeneration rate $\alpha_{\max}\Phi_0 = \Phi_0/d$.

Now the NDG procedure can be applied to $i_N(t)$. The condition for the maximum is :

$$(t_2 - t_1)/\tau_m = \text{Log} [(t_2 - \tau_m)/(t_1 - \tau_m)]. \quad (35)$$

The peak height can be related to N_t by expression :

$$h = N_t \frac{d}{\Phi_0} \frac{1}{\tau_m} \frac{t_2 - t_1}{t_2 - \tau_m} \exp(-t_1/\tau_m). \quad (36)$$

In principle, a complete characterization of a trap should be possible. However, practice has shown that the performances of this method are rather poor for two main reasons : small spectral resolution and difficulty to achieve complete filling of the traps in the whole temperature range where the emission of a species is measurable. Nevertheless, the method allows to evaluate the trap concentrations.

5.2.6 Experimental results. — We performed PICTS measurements on photorefractive materials ($\text{Bi}_{12}\text{GeO}_{20}$ = BGO, CdTe : V) (10, 11) and on several others including binary, ternary and amorphous compounds.

Concerning BGO and CdTe, discrete levels spectra were obtained. The FG spectra present the general characteristics predicted by the theoretical analysis. As an illustration, the behaviour of a particular peak in the spectrum of BGO, as a function of t_0 is shown in figure 6.

As a rule, the potential great sensitivity and high spectral resolution expected for the FG spectrum, by means of computer simulations are clearly demonstrated by the results represented in figures 7 and 8. The detection sensitivity is 10^{12} cm^{-3} .

A general impression seems to emerge from the investigation of several materials : as long as the same starting materials are used for the synthesis and the overall preparation conditions

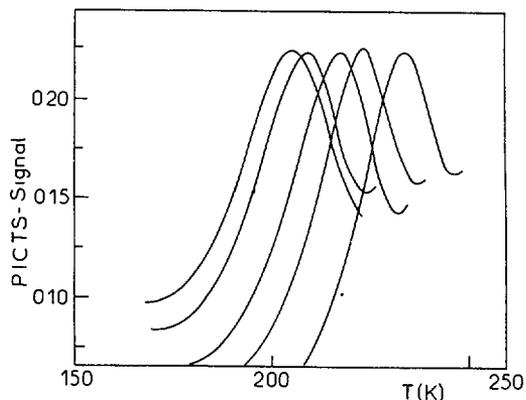


Fig. 6. — Shift of a particular peak in the four-gate spectrum of BGO for different values of t_0 at constant ratios t_1/t_0 and t_2/t_0 .

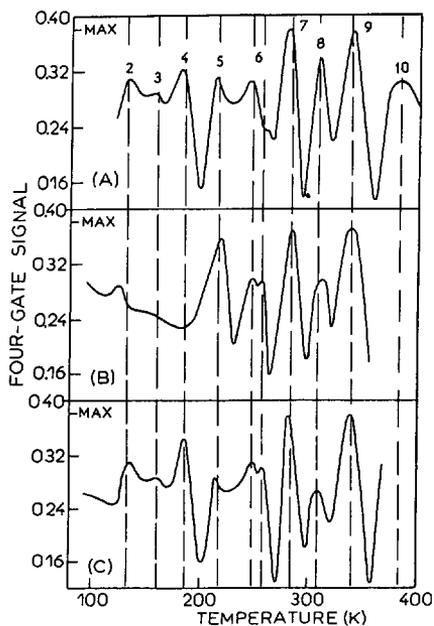


Fig. 7. — Four-gate spectra for three different BGO samples for the same value of t_0 at constant ratios t_1/t_0 and t_2/t_0 . The theoretical peak height (single trap model) is indicated by the mark MAX.

are kept constant, the same spectrum is obtained with different samples (Fig. 7). This latter can thus be considered as characteristic of the material and be taken as a reference. The concentration of the trap species may of course vary from specimen to specimen. On the other hand intentional doping may result in the observation of new peaks in the FG spectra and in changes in the concentration of some levels.

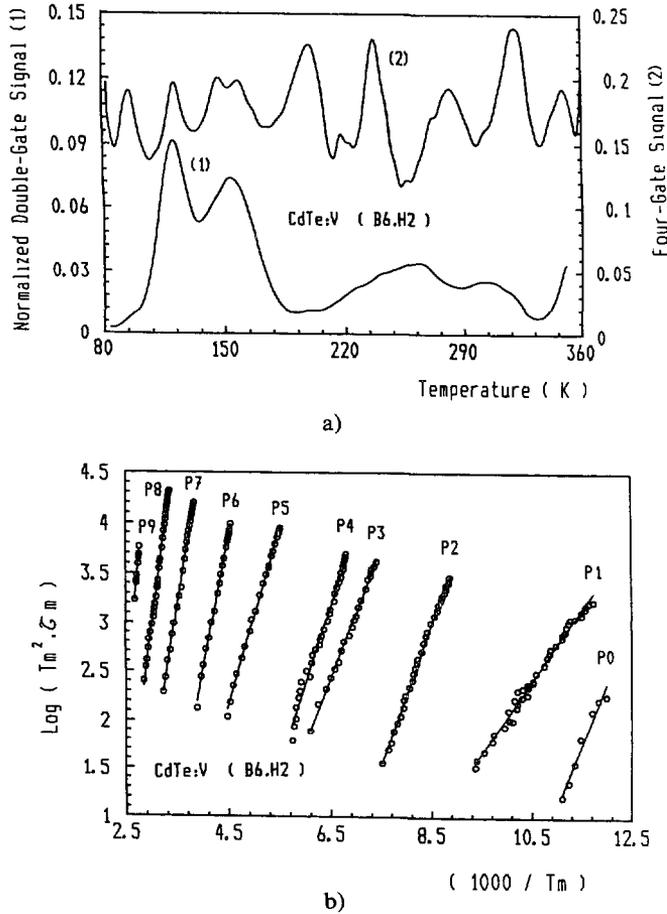


Fig. 8. — Typical normalized double gate (curve 1) and four-gate (curve 2) spectrum for CdTe:V (a) and corresponding Arrhenius plots (b).

Concluding remarks.

6.1 GENERAL CONCLUSION. — Noticing the importance of deep levels in photorefractive effects and devices, the aim of this paper was to discuss the problem of their characterization in high resistivity materials. To understand the used experimental procedures, it was necessary to first define the characteristic parameters to be measured and to describe the underlying physical processes and their modelisation. Indeed, literature on these topics which should be specifically devoted to insulators or semi-insulators, is still rather scarce. On the other hand, until recently, no satisfactory measuring technique was available for the investigation of deep levels in high resistivity materials. The PICTS technique represents a first important step in this direction. Indeed, it allows to probe the whole trap spectrum in semi-insulators whose bandgap does not exceed 2 eV. In fact, the Fermi level being located in the vicinity of the middle of the gap, majority carrier traps lying in the corresponding half of the forbidden band are more likely concerned. However, part of the minority carrier traps should in principle also be detectable in the other half of the forbidden bandgap, but there is not possibility to identify them, in so far as, by the four gate PICTS method. In the case of bandgaps larger than 2 eV, like BGO with $E_g = 3.25$ eV, trap levels deeper than 1 eV should be detectable by optical methods [12].

6.2 FURTHER IMPROVEMENTS OF THE PICTS TECHNIQUE. — Clearly here some further improvements of the experimental procedure are needed. This could be possible by providing the sample with electrodes in the sandwich configuration, the incident light beam being in the same direction than the applied electric field. Bulk absorbed optical excitation, through the semi-transparent front contact, generates free electrons and holes which are both moving, but in opposite directions. The drift of the carriers is stopped either by trapping or recombination. A strongly absorbed light pulse, on the contrary, generates free electron-hole pairs in a thin surface layer. Depending on the direction of the field either electrons or holes are drawn towards the rear collecting electrode. This allows to measure the transit time which is related to the drift mobility of the majority carriers. Part of the carriers may of course be captured by traps and released with some delay by thermal stimulation. This also provides the possibility of determining the sign of the detected traps. We already have developed such a measuring technique which combines drift mobility and trap emission measurements [13].

6.3 DEEP LEVEL OPTICAL SPECTROSCOPY. — In principle, any trapping level should become optically active as soon as it has been filled, provided that the temperature is kept below the corresponding T_d and that the electronic state is weakly coupled with phonons (Sect. 3.3.2).

If these conditions are satisfied and if the trap concentration is high enough, the corresponding absorption spectrum (photoinduced absorption [12]) can be measured unless it cannot be resolved with respect to the background spectrum. In the same manner one can measure the photoinduced photoconductivity spectral responses of traps.

Although these steady-state methods are still frequently used to get some overall information on the traps, they present two important drawbacks. Overlapping photoinduced bands can hardly be resolved. On the other hand the probe beam may disturb the trapped electron or hole populations [12].

Transient methods will in principle be more efficient for the characterization of traps. In section 3.3.9 we sketched such a procedure, based on equations (21) and (22) which should be similar to those of PICTS.

The best way to monitor the trapped charge should of course be to measure the time dependent absorption coefficient $\alpha_0(h\nu) = n_1(t) S_0^n(h\nu)$.

Usually the photoinduced absorption is weak, so the transmitted photon flux $\Phi_1(h\nu, t)$ can be approximated by expression :

$$\Phi_1(h\nu, t) = \Phi_0(h\nu) [1 - \alpha_0^n(h\nu)] . \quad (37)$$

The transmission rate will be :

$$T(h\nu, t) = 1 - \alpha_0^n(h\nu, t) . \quad (38)$$

According to equations (22) and (38) the monochromatic probe beam induces an exponentially increasing transmission rate. In principle, it should be possible to determine the concentration N_t and the spectral dependence of the optical capture cross section.

An alternative, probably more sensitive, method consists in monitoring the trapped charge by current measurements (12). The expression for the current transient is the same as equation (30) in which τ_t^{-1} has simply to be replaced by $e_0^n(h\nu)$.

Although optically stimulated emission transients are basically the same as the thermally stimulated ones, they cannot, however, be handled in the same manner i.e. by FG and NDG treatments since e_0^n does not strongly vary with $h\nu$ [3], whereas τ_t^{-1} depends exponentially on $1/T$. The only possibility to determine e_0^n and N_t will be to fit the experimental decay to an exponential. Moreover in the case of strongly overlapping photoinduced bands fitting the

transient to a multiexponential will be rather tedious. However, following the methodology used in D.L.O.S. (Deep Level Optical Spectroscopy) capacitance measurements on III-V semiconductors [3], experimental procedures can be imagined likely to enhance or to reduce the weight of one or of several bands and, hence, to simplify the treatment.

Work aimed to develop optical transient techniques are in progress.

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