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Thermoluminescence and continuous distributions of traps

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A recent proposal of Simmons and co-workers for the analysis of high-field thermally stimulated currents is extended to the case of thermoluminescence, with significant advantages for the study of continuous distributions of traps in bulk samples. The effect of the temperature smearing of the occupation function is also evaluated, and a short discussion of the method is given, especially in view of its application to the study of localized states distributions in disordered semiconductors.

The use of thermally stimulated phenomena for studying the localized levels in disordered semiconductors is hampered by the fact that one actually deals with continuous distribution of states, whereas the various methods to analyze these phenomena have been set up on discrete trap models.[1] Recently Simmons and co-workers[2–5] have presented a series of papers with some interesting suggestions for the study of continuous distributions of traps, by means of high-field isothermal and thermally stimulated currents; in their approach, however, one has to reach conditions in which there is neither retrapping, nor recombination of the free carriers. Experimentally this is achieved by applying to the samples high electric fields, which sweep the carriers away, before they can recombine or be retrapped. Consequently, the method they suggest is limited to *p-n* junctions, metal-oxide-semiconductor interfaces, and insulating or semiconducting thin films. This limitation is unfortunate, since, in view of the present interest in the properties of disordered semiconductors, a knowledge of the distribution of the localized states within the gap of bulk samples would be very interesting. We have been recently working on the thermoluminescence of disordered crystals, and think that the work of Simmons *et al.* can be profitably discussed in relation to some of our results (a full account of which will be published soon[6]). In particular, in this comment, we will show that the use of thermoluminescence can effectively remove the limitation discussed above, and we will shortly discuss the possibility of getting, in this way, an approximate evaluation of the localized states distribution.

From the viewpoint of our discussion, the relevant difference between thermally stimulated currents (TSC), and thermally stimulated luminescence, or thermoluminescence (TL), is the following: In TSC the "channels" open to the free carriers, once released from the traps, are (a) collection at the electrodes, (b) recombination, and (c) retrapping. The analysis of a TSC experiment is straightforward only if channels (b) and (c) can be neglected, since in this case the current is proportional to the rate of release of the carriers; Simmons *et al.*[3–5] obtain this condition by means of a high electric field. In TL, on the other hand, channel (a) does not exist, channel (b) is just the one exploited in the experiment, and channel (c), which determines the kinetics of the process, can be accounted for. It can also be shown that the "two-carriers" kinetics effects, which must be considered to account more correctly for the amphoteric character of the trap levels,[2] can, in the analysis of TL, be included directly in the traditional "one-carrier" models by readjusting some of the parameters of the models themselves.[6]

In what follows, we will consider only electron trapping centers, but the arguments can easily be adapted to the dual case of hole trapping. The lifetime of the released electrons is in general so small, that one usually assumes, in the traditional models of TL,[7]

$$\frac{dn}{dt} \ll \frac{dm}{dt} , \tag{1}$$

where n and m are the electron concentrations in the conduction band and in the traps, respectively. Assumption (1) has recently been criticized by Kelly *et al.*,[8] but the work itself of these authors shows that, at least in the case of TL, the use of (1) gives rise to appreciable discrepancies only for low values of m ($m < 10^{15}$ cm^{-3}). As a consequence of (1), the intensity I_{TL} of the TL emission, as a function of the temperature T, is given by

$$I_{\mathrm{TL}}(T) = -\eta(T)\frac{dm(T)}{dT} , \tag{2}$$

where $\eta(T)$ is the temperature-dependent efficiency for radiative recombination. If the temperature is raised as a linear function of the time,

$$T = T_0 + \rho t\,, \tag{3}$$

where T_0 is the initial temperature and ρ (°K/sec) is the heating rate, relation (2) becomes

$$I_{\mathrm{TL}}(T) = -\eta(T)\rho\frac{dm(T)}{dT}\,. \tag{4}$$

In our generalization of the traditional discrete trap models to the continuous case,[6] one has a trap distribution $M(E)$, whose occupancy $m(E)$ is described by a distribution function $f(E)$:

$$m(E) = M(E)f(E)\,. \tag{5}$$

Consequently, the total number of trapped electrons at any instant is given by

$$Q(t) = \int_0^{E_g} M(E)f(E,t)\,dE\,, \tag{6}$$

where E_g is the energy gap.

The function $f(E,t)$, unless the cross section σ of the traps is strongly dependent on E, can be assumed to have the following general features: it goes to zero for very low values of E (when thermal ionization empties all the traps), and to a maximum value P for very high energies (when thermal ionization is ineffective). [Note that P includes the two-carriers kinetics effects; see, e.g., Ref. 2, formula (20)]. In the transition region, which is usually some kT wide (k is the Boltzmann constant), we can characterize the distribution by the "effective level" ϵ^*, at which the derivative has its maximum value. [This derivative is a generalization of the function $P(E,T)$, shown in Ref. 5, Fig. 1].

In the continuous case, in analogy with (2), I_{TL} is again proportional to the rate of effective release of trapped electrons from the trap system, independently of the kinetics[6]; that is

$$I_{\mathrm{TL}}(T) = -\eta(T)\frac{d}{dt}Q(T)\,. \tag{7}$$

On taking (3) into account one has

$$I_{\mathrm{TL}}(T) = -\eta(T)\rho\int_0^{E_g} M(E)\frac{d}{dT}f(E,T)\,dE\,, \tag{8}$$

where $f(E,T)$ is the distribution function of the system at the temperature T. The peaked shape of $df(E,T)/dT$ is related to the fact that the traps positioned around ϵ^* are those which, at a given instant, contribute most of the emission at the corresponding T.

Let us now first assume that

$$f(E,T) = P\Theta(E-\epsilon^*(T))\,, \tag{9}$$

where Θ is the step function (which is equal to 1 for $E \gg \epsilon^*$, and is zero for $E < \epsilon^*$). The only temperature dependence of $f(E,T)$, in this approximation, is included in the temperature dependence of ϵ^*; as T increases, ϵ^* also increases, i.e., the "filling" level moves away from the bottom of the conduction band. Taking the properties of the Θ function into account, one has from (8) and (9)

$$I_{TL}(T) = \eta(T)\rho P\frac{d\epsilon^*}{dT}M(\epsilon^*(T)) \tag{10}$$

The meaning of (10) is very clear: The TL curve $I_{TL}(T)$ reflects the trap distribution, being proportional at any temperature T, to the value of $M(E)$ at the corresponding ϵ^*. This result is independent of the kinetics of the recombination process, and is analogous to that obtained by Simmons *et al.*[5] for the high-field TSC in first-order kinetics. A relevant limit of this result lies in the fact that the actual width of df/dE, and its temperature dependence, are completely neglected. Anyway, its "validity" improves the larger the intrinsic "width" of the trap distribution, since the TL peak has a finite width (of the order of some kT) even for a discrete trap level.

In order to take the temperature-dependent width of df/dE into account, let us now assume that $f(E,T)$ is given by a Fermi function

$$f(E,T) = \frac{P}{1+\exp\{[\epsilon^*(T)-E]/kT\}}\,. \tag{11}$$

Rigorously, $f(E,T)$ is never a Fermi function during the thermal evolution of the system, but it is actually assumed to be so in quasiequilibrium conditions in many real cases.[9] Anyway, for our purpose, the Fermi function includes the temperature effects in a realistic way. Substitution of (11) into (8) gives now

$$I_{\mathrm{TL}}(T) = \eta(T)\rho P\int_0^{E_g} M(E)\left(\frac{d\epsilon^*}{dT} + \frac{E-\epsilon^*}{T}\right)\frac{df}{dE}\,dE\,, \tag{12}$$

which, using well-known properties of the Fermi function,[10] becomes

$$I_{\mathrm{TL}}(T) \cong \eta(T)\rho P\left[M(\epsilon^*)\frac{d\epsilon^*}{dT} + \frac{\pi^2}{3}k^2T\left.\frac{\partial M}{\partial E}\right|_{E=\epsilon^*} + \frac{\pi^2}{6}(kT)^2\frac{d\epsilon^*}{dT}\left.\frac{\partial^2 M}{\partial E^2}\right|_{E=\epsilon^*} + \cdots\right]. \tag{13}$$

This result shows clearly the "distortion" caused by the temperature dependence of $f(E,T)$ on the simple result (10). The first term on the right-hand side (r.h.s.) is the same as in (10). The second term is always small in comparison with the third one, which increases quadratically with T. If the trap distribution $M(E)$ is sufficiently smooth, as it tends to be in disordered systems, its derivatives are small. In this case the third term is also small (a few percent) in comparison with the first one at realistic values of T. However, when the distribution of traps is exponential

$$M(E) = M_0 e^{-\delta E} , \tag{14}$$

the ratio between the third and the first term in the r.h.s. is given by $1.22\times 10^{-8}\delta^2 T^2$, and, for a "slope" of 150 meV/decade, corresponding to $\delta = 15.35$ eV^{-1} (a typical value for the amorphous semiconductors), this ratio ranges from 1.76×10^{-2} at 80 °K, to 6.18×10^{-2} at 150 °K, to 24.73×10^{-2} at 300 °K. The temperature corrections must therefore be taken into account when studying the trap distributions near the energy-band edges, where exponential distributions are likely to occur.

So far we have considered the distribution of localized states versus a temperature scale. If one wants to get $m(E)$ vs E, it is necessary to know the relationship between ϵ^* and T. This presents some difficulties, since the exact dependence of ϵ^* on T varies with the details of the model, and involves parameters which are not known *a priori*, and which are not easily obtained experimentally. The problem is somewhat simplified by assuming that ϵ^* depends linearly on kT over a limited temperature range, with the coefficient of proportionality logarithmically (i.e., not strongly) dependent on the escape frequency s of the electrons from the traps. (s is related to σ by $s = \sigma N_c v$, where N_c is the effective density of states in the conduction band and v is the thermal velocity of the free carriers.) This problem has recently been considered by Simmons *et al.*[3,5] and independently, but on similar lines, also by us.[11] Moreover, in a previous work,[12] we have also tried to obtain information on this relationship, at least at the beginning of the heating process, using the method of the initial rise.[13] This approach, of course, holds rigorously only for discrete trap levels. However, when applied to the continuous case, it gives an error which, in physically meaningful situations, is always less than 30%.[6] An alternative way is to use the experimental procedures discussed by Bube *et al.*[14] under the hypothesis of quasiequilibrium.

In order to show the usefulness and the limitations of the procedure described above, we report in Table I the results of a numerical analysis, performed for an exponential distribution of states (14), in first- and second-order kinetics for a meaningful set of values of δ and s, where s has been assumed to be independent on E. Starting from a given distribution, the TL curves have been calculated numerically, and then treated according to (10). (Details of the procedure are given in Ref. 6.) As one can see, the use of (10) systematically enhances the value of the slope found with respect to the starting one, in agreement with the predictions of (13). The discrepancy, however, is always less than 15%.

TABLE I. Values of the "slopes," in meV/decade, obtained by analyzing according to (10), the TL emission curves calculated numerically for the values of δ and s shown in the entries. The upper and lower values, for any set of entries, refer to first- and second-order kinetics, respectively.

δ	s (sec^{-1})					
(meV/decade)	10^7	10^8	10^9	10^{10}	10^{11}	10^{12}
100			106	106		
			117	109		
150	159	158	158	158	158	158
	164	166	164	164	163	163
200			209	209		
			216	217		
300	319	319	314	314	317	317
	338	329	321	319	324	325

The idea of using thermally stimulated phenomena in the study of some controversial problems about disordered systems, in particular in the study of the localized states in the gap, seems very tempting. One must be careful, however, since at very high densities of states, as one is likely to find near the band edges, other processes (donor-acceptor transitions,[15] tunnel recombination,[16] etc.) which do not involve the thermal escape from the traps to the conduction band, might become very important. These processes of course, are not taken into account in the classical models of the thermally stimulated phenomena.

In conclusion, we have shown that the approach of Simmons *et al.*[5] can be advantageously applied also to the analysis of the TL due to continuous distribution of traps, extending significantly the range of the physical systems which can be investigated. We have also taken into account in a realistic way the temperature smearing of the distribution function, allowing one to correct the simple results obtained by a straightforward application of (10). A limitation of the approach lies in a possible strong dependence of σ on E, which could invalidate the above analysis. A method which seems to be rather insensitive to this dependence, and which is in principle more correct, though experimentally more complicated, is discussed elsewhere.[6]

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