

## ON THE KINETICS OF THERMALLY STIMULATED CONDUCTIVITY

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A new kind of thermally stimulated conductivity peak corresponding to first order thermoluminescence is described. This peak is shifted to higher temperature as compared to the thermoluminescence one; the falloff half of the peak is relatively narrow. An empirical method for evaluating the activation energy is given.

The phenomena of thermoluminescence (TL) and thermally stimulated conductivity (TSC) [1] have usually been investigated in the past assuming that both obey the same laws [1,2]. Thus, for example, methods for computing the activation energies developed for TL peaks were freely used [1] for TSC peak analysis. The assumption beyond this, explicitly stated or implied, was that the lifetime for recombination of free carriers is constant.

This results in having the dependence of TL intensity on temperature  $I=I(T)$  proportional to the function of TSC,  $\sigma=\sigma(T)$ ,  $\sigma(T)=CI(T)$  where  $C$  is a constant (apart from a possible slight dependence of the mobility on temperature). Dussel and Bube [3] and Land [4] investigated the properties of TL and TSC peaks under rather general assumptions. Saunders [5] studied the case of TSC curves corresponding to second order TL peaks when the lifetime is not considered to be constant. This case was further investigated by Chen [6]. The present letter deals with the study of a TSC peak corresponding to a first order TL peak when the circumstances are such that one cannot assume a constant lifetime of the carriers. It will be shown that the TSC peak appears at a higher temperature than the corresponding TL peak and that it decreases relatively fast at temperatures above the maximum. An empirical method for evaluating the activation energy from the temperature of the peak and its shape will also be developed.

Halperin and Braner [7] used a set of three simultaneous differential equations for describing a single TL peak resulting from one active electron trap and one active hole recombination center. The parameters involved were  $E$  - the activation energy (eV),  $n$  - the concentration of

trapped electrons ( $\text{cm}^{-3}$ ),  $m$  - the concentration of holes in centers ( $\text{cm}^{-3}$ ),  $n_c$  - the concentration of electrons in the conduction band ( $\text{cm}^{-3}$ ),  $N$  - the concentration of traps ( $\text{cm}^{-3}$ ),  $s$  - the frequency factor ( $\text{sec}^{-1}$ ),  $A_m$ ,  $A_n$  - the probabilities for recombination and retrapping respectively ( $\text{cm}^3\text{sec}^{-1}$ ),  $k$  - the Boltzmann constant ( $\text{eV}/^\circ\text{K}$ ) and  $T$  the absolute temperature ( $^\circ\text{K}$ ). Assuming as usual [3,4,7] that  $n_c \ll n$  and  $\dot{n}_c \ll \dot{n}$ , they found that

$$I = \frac{-dm}{dt} = s \exp(-E/kT) \frac{nA_m m^2}{A_m m + A_n (N-n)}, \quad (1)$$

where  $I$  is the TL intensity. The assumption that only one trap and one recombination center are involved implies

$$n + c = m, \quad (2)$$

where  $c$  is a constant representing the net electrical charge in all the traps and centers which are not active in the temperature range dealt with;  $c$  can be positive, negative or zero depending on the concentrations of electrons and holes in non-active traps and centers. First order TL peaks are known to occur when recombination is dominant. In the present notation this would mean

$$A_m m^2 \gg A_n (N-n). \quad (3)$$

Since  $m$  and  $n$  are decreasing functions of time (temperature), this is a relation between functions rather than between parameters. A sufficient condition for the validity of relation (3) is  $A_m m_0 \gg A_n (N-n_0)$  which relates only constant parameters;  $n_0$  and  $m_0$  are the initial values of  $n$  and  $m$  respectively. Using the condition (3) together with  $\dot{n} = \dot{m}$ , a result of eq. (2), eq. (1) be-

$$I = -n = s n \exp(-E/kT). \quad (4)$$

The solution of eq. (4) is the well known first order function

$$I = sn_0 \exp\left(\frac{-E}{kT}\right) \exp\left[\frac{-s}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dT'\right], \quad (5)$$

where  $T_0$  is the initial temperature and  $\beta$  is the (constant) heating rate. The expression giving  $n = n(T)$  under these conditions is

$$n = n_0 \exp\left[\frac{-s}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dT'\right]. \quad (6)$$

From one of the basic equations of Halperin and Braner we have  $n_c = I/(A_m m)$  which by the use of eq. (2) may be written as  $n_c = I/[A_m(n+c)]$ . Substituting eqs. (5) and (6) in the above equation and writing  $\alpha = c/n_0$  we have

$$n_c = \frac{s}{A_m} \exp\left(\frac{-E}{kT}\right) / \left\{ 1 + \alpha \exp\left[\frac{s}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dT'\right] \right\}. \quad (7)$$

In cases where  $\alpha \gg 1$  ( $c \gg n_0$ ) eq. (7) reduces to an expression similar to that in eq. (5) (apart from the low temperatures where  $T \approx T_0$ ), which brings us back to the simple first order TSC peak. On the other hand,  $c \approx 0$  gives an exponentially increasing TSC (probably up to a certain temperature where one of the assumptions ceases to hold), a case which was discussed by Land [4]. The case of a negative  $c$  should be disregarded here. This condition means that  $n > m$  which leads to the conclusion that  $m$  would go to zero within the range of interest and this

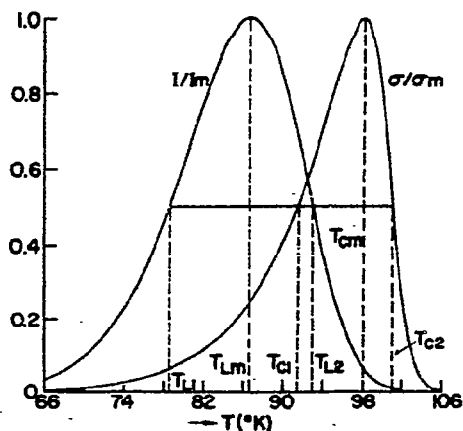


Fig. 1. Normalized calculated curves of TL ( $I/I_m$ ) and TSC ( $\sigma/\sigma_m$ ) for  $E=0.1$  eV,  $s=10^5 \text{sec}^{-1}$ ,  $A_m=10^{-5} \text{cm}^3 \text{sec}^{-1}$  and  $\alpha=10^{-3}$ .  $T_{Lm}$ ,  $T_{L1}$  and  $T_{L2}$  are the maximum and half intensity temperatures on the TL curve;  $T_{Cm}$ ,  $T_{C1}$  and  $T_{C2}$ , on the TSC curve.

would contradict (3) which is essential.

The remaining cases, those for which  $c$  is of the order of magnitude of or smaller than  $n_0$ , constitute an important new possibility of a TSC peak.

Fig. 1 shows a normalized curve of  $\sigma/\sigma_m$  versus temperature as computed from eq. (7) where  $E=0.1$  eV,  $A_m=10^{-5} \text{cm}^3 \text{sec}^{-1}$ ;  $s=10^5 \text{sec}^{-1}$ ,  $\beta=1 \text{OK sec}^{-1}$  and  $\alpha=10^{-3}$ . For comparison, the normalized curve  $I/I_m$  versus  $T$  for the same conditions is given. The TSC peak is seen to be shifted to higher temperatures as compared to the corresponding TL peak, a phenomenon which was already noticed under different circumstances [5]. The amount of this shift increases with decreasing values of  $\alpha$ . Another feature of this TSC peak is that the falloff range is relatively narrow indicating a very fast decrease of  $\sigma$  at temperatures above the maximum  $T_{Cm}$ . Let us denote by  $T_{C1}$  and  $T_{C2}$  the two temperatures at which the intensity attains half the maximum intensity and use the symbols [7]  $\tau = T_{Cm} - T_{C1}$ ,  $\delta = T_{C2} - T_{Cm}$  and  $\omega = T_{C2} - T_{C1}$  and the "geometrical factor"  $\mu_g = \delta/\omega$  [7]. Typical values of  $\mu_g$  for first order TL peaks were found [8] to be  $\approx 0.42$  and for second order peaks  $\approx 0.52$ . For TSC peaks reported by Saunders [5],  $\mu_g$  was found [6] to be around 0.8. For the curve given in fig. 1,  $\mu_g$  is 0.3 and smaller values were found for smaller  $\alpha$ 's.

Further values of  $T_{Cm}$ ,  $\tau$ ,  $\delta$ ,  $\omega$  and  $\mu_g$  have been calculated by computer for various given values of  $\alpha$ . These calculations have been repeated for various values of  $s$  between  $10^5$  and  $10^{13} \text{sec}^{-1}$  and of  $E$  between 0.1 and 2.0 eV, ranges which cover most of the experimentally observed glow curves.

Table 1 gives as an example values of  $T_{Cm}$  and  $\mu_g$  for  $\alpha$ 's between  $10^2$  and  $10^{-4}$ . A similar dependence of  $\mu_g$  on  $\alpha$  was found for various values of  $E$  and  $s$ . It has also been found that for all the cases,  $\mu_g kT_{Cm}^2/\tau$  was approximately proportional to the given value of  $E$ . Thus, an empirical equation for calculating the activation energy may be given by

$$E_c = 3\mu_g kT_{Cm}^2. \quad (8)$$

Values of  $E_c$  are given in the last column of table 1 and are seen to be too high by up to 15%. For the other extreme cases, where  $s \approx 10^{13} \text{sec}^{-1}$ , the values of  $E_c$  are found to be slightly below the given value of  $E$ . For all the  $E$ 's and  $s$ 's examined,  $E_c$  was correct to 15% or better.

It is to be noted that the well-known "initial rise" method [9] for evaluating the activation energies,

Table 1.

Values of  $T_{cm}$ ,  $\mu g$  and  $E_c = 3 \mu g k T_{cm}^2 / \tau$  for  $\alpha$ 's between  $10^2$  and  $10^{-4}$  for  $E = 0.1$  eV,  $s = 10^5 \text{sec}^{-1}$  and  $A_m = 10^{-5} \text{cm}^3 \text{sec}^{-1}$ . The corresponding value of  $T_{Lm}$  is  $86.7^\circ \text{K}$

$\alpha$	$T_{cm} (^{\circ}\text{K})$	$\mu g$	$E_c$ (eV)
$10^2$	86.8	0.436	0.104
$10^1$	87.0	0.434	0.105
$10^0$	88.3	0.419	0.107
$10^{-1}$	91.7	0.379	0.113
$10^{-2}$	95.3	0.335	0.115
$10^{-3}$	98.2	0.297	0.111
$10^{-4}$	100.5	0.267	0.105

which is known to be correct for most glow curves, should hold true for this case as well. This would, however, be subject to the same restrictions reducing the accuracy of the calculated activation energies by the initial rise method for all low intensity glow peaks.

TSC peaks corresponding to first order TL peaks have been investigated. The general feature of these peaks is that they appear at higher

temperature than the accompanying TL peaks and decrease very sharply at the higher temperature range. The analysis of the shape of this TSC peak brought about an approximate empirical formula for calculating the activation energy. This formula has been checked by computational methods.

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