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# Thermally Stimulated Carrier Transport Due to Stepwise Sample Heating

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**Summary:** The article concerns non-isothermal dispersive carrier transport in an insulating solid with traps. The approximate solutions of transport equations derived previously are extended to the case of stepwise sample heating. The specific features of thermally stimulated currents (TSCs) can be attributed to non-linear dependence of the demarcation level on temperature. In particular, the initial TSC rise has a thermally activated character where activation energy equals to the demarcation energy at the end of previous heating cycle. The accuracy of the formulae describing TSCs is verified by Monte Carlo calculations for Gaussian trap distribution.

**Keywords:** amorphous solids; dispersive charge transport; Monte Carlo simulation; multiple-trapping model; thermally stimulated currents

## Introduction

A characteristic feature of amorphous materials, both inorganic and organic, is a continuous distribution of localised states throughout the energy gap. The excess carrier transport in these materials has frequently dispersive character, due to carrier multiple trapping (MT) or hopping[1]. One of the important tools in determining the energy distribution of localised states in high-resistivity amorphous solids is the measurement of thermally stimulated currents (TSCs). Two kinds of the experiments can be distinguished: (1) The sample with sandwich electrodes is initially excited by strongly absorbed light. TSC is then related to one–sign carrier transport through the sample and to carrier neutralization on the collecting electrode ('TSC drift peak'). (2) The sample having coplanar electrodes is illuminated by weakly absorbed light. TSC is then determined by carrier trapping/detrapping or hopping kinetics as well as by carrier recombination ('TSC recombination peak'). So far, a majority of theoretical analyses of TSCs in amorphous solids, concerning both transport[2-4,6] and recombination peaks[5-8], are based on the MT model. According by, the carriers move in the allowed band, being temporarily captured by the localised states (traps) in the energy gap.

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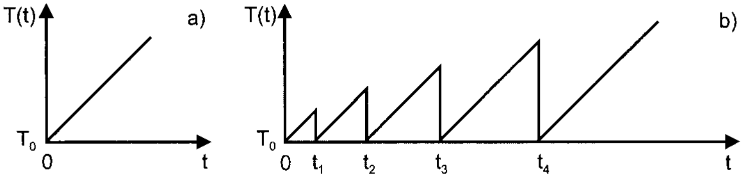

Figure 1. Time dependence of the sample temperature $T(t)$ in the case of linear heating (a) and stepwise heating (b).

One of the advantages of the TSC technique is the possibility of applying various heating schemes. In particular, apart from the most commonly used linear sample heating (Figure 1a), the stepwise heating of the sample (Figure 1b) is also frequently utilised. The TSC measurements using complex heating schemes would provide additional information about gap states and make it possible to test the validity of TSC interpretation. So far, only few theoretical works have appeared concerning the TSC recombination peaks due to stepwise sample heating[5,9]. In the present paper, the results obtained in [3,4], concerning the TSC drift peaks and linear heating scheme, are extended to the stepwise heating regime. The corresponding TSC measurements were performed, e.g., in poly(*N*-vinylcarbazole)[10].

## General formulae

According to refs.[3,4], in the case of strongly dispersive MT transport of carriers, the TSC transport peak is expressed by the approximate formula

$$I(t) = I_0 \frac{\mathrm{d}}{\mathrm{d}t}\left\{\frac{1-\exp[-\tau_0\Phi(t)]}{\Phi(t)}\right\}, \tag{1}$$

where the function

$$\Phi(t) = C_t \int_{\varepsilon_0(t)}^{\varepsilon_t} N_t(\varepsilon)\mathrm{d}\varepsilon, \tag{2}$$

Here, $t$ and $\varepsilon$ are the time and energy variables ($\varepsilon$ is measured from the edge of allowed band), $\tau_0 = d/\mu_0 E$ is the free-carrier time-of-flight ($d$ – sample thickness, $\mu_0$ – free carrier mobility, $E$ – electric field strength), $I_0 = Q_0/\tau_0$, where $Q_0$ is the total charge released from the traps, $C_t$ is the carrier capture coefficient, $N_t(\varepsilon)$ is the trap density per energy unit, $\varepsilon_0(t)$ is the demarcation energy defined below and $\varepsilon_t$ is the upper limit of trap distribution. The function $\Phi(t)$ determines the probability that the carrier, being free at $t$ = 0 is captured in a time unit and stays in the trap until time $t$. The demarcation level $\varepsilon_0(t)$ is given implicitly by

$$\int_0^t \frac{\mathrm{d}t'}{\tau_r\left[\varepsilon_0(t),t'\right]} \approx 1, \tag{3}$$

where

$$\tau_r(\varepsilon,t) = \frac{1}{\nu_0}\exp\left[\frac{\varepsilon}{kT(t)}\right] \tag{4}$$

is the mean carrier dwell-time in the trap ($\nu_0$ – frequency factor, $k$ – Boltzmann constant, $T(t)$ – sample temperature). The level $\varepsilon_0(t)$ separates the shallower states which reached yet the equilibrium occupancy and the deeper states, characterised by non-equilibrium carrier distribution. In the case of linear sample heating,

$$T(t) = T_0 + \beta t \tag{5}$$

($T_0$ – initial temperature, $\beta$ - heating rate), the demarcation energy varies linearly with temperature,

$$\varepsilon_0(t) \approx k[c^* T(t) - T^*], \tag{6}$$

with $c^* = 0.967\ln(45.9\ \mathrm{K}\cdot\nu_0/\beta)$ and $T^* = 180$ K (the ratio $\nu_0/\beta$ is expressed in $\mathrm{K}^{-1}$). However, the formulae (1)–(3) are valid for arbitrary time dependence of sample temperature and can be adopted to other heating schemes.

## Stepwise heating regime - analytical results

In the case of stepwise sample heating,

$$T(t) = T_0 + \beta(t - t_{i-1}), \quad t_{i-1} \le t < t_i, \tag{7}$$

Eq. (3) for the $(m+1)$-th heating cycle can be rewritten as:

$$\sum_{i=1}^{m}\int_{t_{i-1}}^{t_i} \frac{\mathrm{d}t'}{\tau_r\left[\varepsilon_0(t),t'\right]} + \int_{t_m}^{t} \frac{\mathrm{d}t'}{\tau_r\left[\varepsilon_0(t),t'\right]} \approx 1. \tag{8}$$

For simplicity, the time of sample cooling after each heating cycle is ignored. Provided that the maximum sample temperature in sequential cycles increases remarkably, only the $m$-th and $(m+1)$-th terms are of significance in the above sum. Let us denote by $T_m = T(t_m)$ the maximum temperature reached in the $m$-th cycle. If the time $t$ exceeeds only slightly $t_m$, such that $T(t) < T_m$, the last term may also be omitted. Then, $\varepsilon_0(t) \approx \varepsilon_m$, where $\varepsilon_m$ is the demarcation energy at the end of previous heating cycle, given by

$$\varepsilon_m \approx k\left(c^* T_m - T^*\right). \tag{9}$$

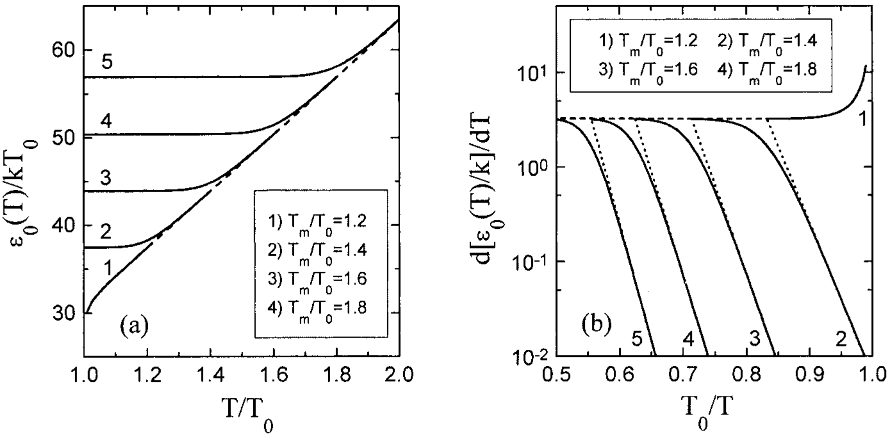

Figure 2. Normalised plots of the demarcation energy $\varepsilon_0(T)$ (a) and its derivative (b) calculated from Eq. (8) for linear (dashed lines) and stepwise (solid lines) sample heating. The derivative of $\varepsilon_0(T)$ computed from Eq. (10) is marked by dotted lines. The numbers on plots refer to sequential heating cycles. The value of $\beta/T_0\nu_0 = 10^{-15}$.

For larger values of $t$, when $T(t) > T_m$, the last term in Eq. (8) is dominant and the demarcation energy is determined by Eq. (6), independently of the sample heating regime up to the moment $t_m$ (cf. Figure 2a).

We shall consider now the function $\mathrm{d}\varepsilon_0(t)/\mathrm{d}t$, which determines the 'velocity' of the demarcation level movement in the energy gap. Making use of Eq. (8) and the differentiation rule for implicit function, one gets, after some approximations

$$\frac{\mathrm{d}\varepsilon_0(t)}{\mathrm{d}t} \approx \frac{\beta\varepsilon_m}{T_m}\exp\left[\frac{\varepsilon_m}{kT_m} - \frac{\varepsilon_m}{kT(t)}\right]. \tag{10}$$

Therefore, the increase in $\mathrm{d}\varepsilon_0(t)/\mathrm{d}t$ at $t \approx t_m$ has a thermally activated character (see Figure 2b).

On the basis of the above results, the main features of TSCs for the stepwise heating regime can be easily established. From Eqs. (1) and (2) it follows that in the initial time region, $t \approx t_m$, the approximate relationship

$$I(t) \propto \frac{\mathrm{d}\varepsilon_0(t)}{\mathrm{d}t} \tag{11}$$

holds, which implies that

$$I(t) \propto \exp\left[-\frac{\varepsilon_m}{kT(t)}\right]. \tag{12}$$

Thus, the initial rise of TSC has also a thermally activated character. It should be recalled that, according to Eq. (9), the activation energy $\varepsilon_m$ is a linear function of the maximum temperature $T_m$ reached in the former heating cycle. Since the coefficient $c^*$ in Eq. (9) depends on the frequency factor $\nu_0$, the value of $\nu_0$ can be simply determined from the measured dependence of $\varepsilon_m$ on $T_m$. For longer times the demarcation energy and, in consequence, the TSC intensity are independent of the sample heating regime until the time $t_m$. This implies that the TSC curve, obtained at linear sample heating, constitutes an envelope for the TSC peaks, registered during individual stepwise heating cycles. Such a behaviour was established experimentally for poly(*N*-vinylcarbazole)[10].

## Stepwise heating regime - numerical results

In order to check the accuracy of the derived formulae, we performed the numerical simulation of TSCs corresponding to linear and stepwise heating of the sample by the Monte Carlo method similar to that used in [4]. The calculations were made for the Gaussian distribution of traps,

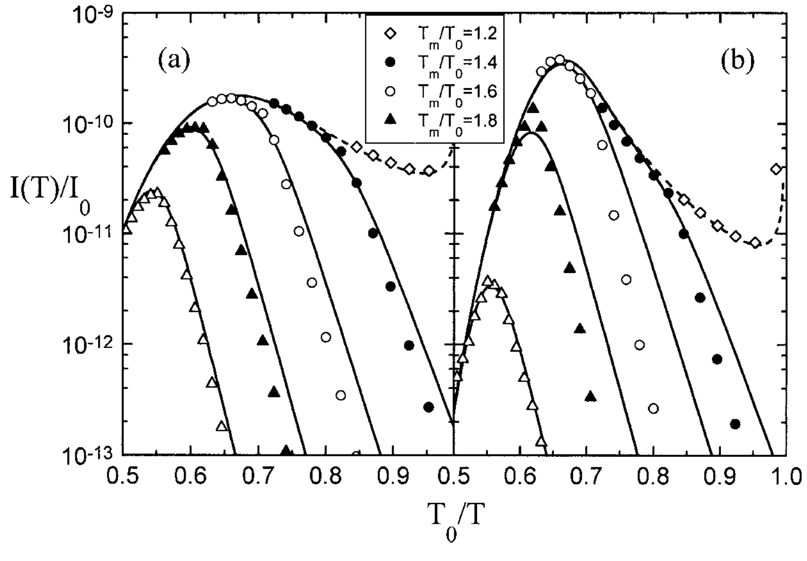

Figure 3. Normalised TSC curves for Gaussian trap distribution of Eq. (13), corresponding to linear (dashed lines) and stepwise (solid lines and points) sample heating. The legend shows maximum temperatures, reached in sequential heating cycles. The calculation parameters: $C_t N_{tot}/\nu_0 = 2.5 \cdot 10^{-4}$ (a), $2.0 \cdot 10^{-3}$ (b); $\tau_0 \nu_0 = 10^5$; $T_c/T_0 = 15$ (a), 10 (b); $\varepsilon_{tm}/kT_0 = 30$; $\beta/T_0\nu_0 = 10^{-15}$.

$$N_t(\varepsilon)=\frac{N_{\text{tot}}}{\sqrt{\pi}kT_c}\exp\left[-\left(\frac{\varepsilon-\varepsilon_{tm}}{kT_c}\right)^2\right], \tag{13}$$

and two different values of the characteristic temperature $T_c$.

In Figure 3 the TSC curves computed from the Eqs. (1), (2) and (8) and obtained numerically (marked respectively by lines and points) are compared. All the TSC features, established in the former section, can be found. In particular, the initial slopes of separate TSC curves increase with the temperature $T_m$. The initial rise of TSCs computed numerically is somewhat faster than of those calculated from approximate formulae. The discrepancies diminish with increasing heating cycle number and with increasing characteristic temperature $T_c$. The latter feature follows from the fact that the given formulae show a good accuracy for strongly dispersive transport, i.e. for trap distributions slowly varying with energy.

## Conclusion

On the basis of the MT model, the analytical description of TSC drift peaks for stepwise sample heating as well as the corresponding Monte Carlo results have been given. It has been established that the initial TSC rise in the course of individual heating cycle has a thermally activated character. The activation energy approximately equals the demarcation energy for trapped charge carriers at the onset of heating cycle. The subsequent TSC course is independent of the mode of previous sample heating. Analogous TSC features should occur for some other heating modes, e.g. for 'delayed' sample heating, when a significant delay between the carrier photogeneration and the onset of temperature increase exists.

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