

## INFLUENCE OF SAMPLE HEATING MODE ON THERMALLY STIMULATED CURRENTS IN AMORPHOUS SOLIDS

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### INTRODUCTION

The electrical properties of disordered solids depend in an essential manner on the localized states in the energy gap. These states act as traps or recombination centres for the excess charge carriers. There were developed several experimental techniques for investigating the gap states in amorphous materials. One of them is the method of thermally stimulated currents (TSCs). It consists of the photogeneration of excess carriers in the sample at relatively low temperature and the subsequent sample heating, usually with a constant rate. The TSC course is determined by the kinetics of carrier trapping/detrapping and recombination. Particularly extensive TSC measurements were made in hydrogenated amorphous silicon (a-Si:H) [1 – 5], because of its technological importance.

The information extracted from the TSC measurements depends critically on the applicability of a theoretical model used for the interpretation. So far, the analyses of TSCs in disordered solids are usually based on the multiple-trapping (MT) model. A continuous trap distribution in the energy gap is presupposed and only the carrier transitions between extended and localised states are considered. Since the corresponding MT equations cannot be solved analytically, some approximations are necessary. In the most commonly used theory by Fritzsche and Ibaraki [1] and other authors [4, 6] the carrier retrapping was ignored or treated in approximate manner. In alternative theories the processes of carrier trapping/detrapping were described by simplified equations, corresponding either to strong non-equilibrium [7 – 9] or to quasi-equilibrium [10] distribution of trapped carriers. Since no assumptions about the rates of carrier capture, emission and recombination have been made (except for [7]), these approaches seem to be more adequate.

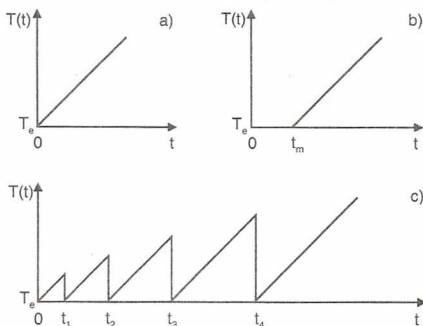
In the 'usual' TSC experiment the time of carrier photogeneration is relatively short and the sample temperature is linearly increased after the end of excitation (cf. Fig. 1 a). Sometimes, a more complex heating schemes are also used. Among others, these are:

delayed heating, when there is significant delay between carrier photogeneration and the onset of sample temperature increase (Fig. 1 b),

step heating, when the sample temperature is raised in steps to successively higher temperatures (Fig. 1 c).

Such experiments provide additional information about gap states and enable us to test the validity of TSC interpretation. As regards *a*-Si:H, Zhou and Elliott [5] have questioned the applicability of the theory by Fritzsche and Ibaraki [1], basing on results of their 'delayed TSC' experiments. Moreover, there exist some discrepancies between the TSC curves, obtained in the step heating experiment and calculated from the Fritzsche-Ibaraki theory. In the present work the theory [8] is extended to above-mentioned modes of sample heating. The predicted TSC features are compared with those established experimentally for *a*-Si:H. For readers' convenience, some formulae given in [8] are repeated in Appendix.

Figure 1. Time dependence of the sample temperature  $T(t)$  in the case of a) instantaneous heating, b) delayed heating, c) step heating of the sample



## ANALYTICAL RESULTS

In the paper [8] the processes of carrier capture and emission from the traps are described in terms of the function

$$\Phi(t) = C_t \int_{\varepsilon_1^0}^{\varepsilon_1} N_t(\varepsilon) \exp \left[ - \int_0^t \frac{dt'}{\tau_r(\varepsilon, t')} \right] d\varepsilon \quad (1)$$

(cf. Appendix, Eq. (A1)). The meaning of the notations being used is:  $t$  and  $\varepsilon$  - the time and energy variables;  $C_t$  - the carrier capture coefficient,  $N_t(\varepsilon)$  - the trap density per energy unit;  $\varepsilon_1^0$  and  $\varepsilon_1$  - the limits of trap distribution.  $\tau_r(\varepsilon, t)$  is the mean carrier dwell time in the trap of depth  $\varepsilon$  at the sample temperature  $T(t)$ ,

$$\tau_r(\varepsilon, t) = \frac{1}{\nu_0} \exp\left[\frac{\varepsilon}{kT(t)}\right], \quad (2)$$

with  $\nu_0$  the frequency factor and  $k$  the Boltzmann constant. In general case the frequency factor may be a function of temperature and/or trap depth. The temperature-independent frequency factor relates to the charged empty traps, which attract the carriers of opposite sign by Coulombic forces. The function  $\Phi(t)dt$  is the probability that the free carrier is captured in a time interval  $(0, dt)$  and remains in the trap until a time  $t$ . In the following, for the purpose of exemplary calculations, an exponential distribution of trapping states in the energy gap is assumed,

$$N_t(\varepsilon) = \frac{N_{\text{tot}}}{kT_c} \exp\left(-\frac{\varepsilon - \varepsilon_t^0}{kT_c}\right), \quad \varepsilon_t = \infty. \quad (3)$$

where  $N_{\text{tot}}$  is the total density of traps and  $T_c$  is the characteristic temperature, which determines the decay rate of trap density.

An important quantity in the approximate description of TSCs is the demarcation level  $\varepsilon_0(t)$ , defined by the implicit equation

$$\int_0^t \frac{dt'}{\tau_r[\varepsilon_0(t'), t']} \approx 1. \quad (4)$$

The demarcation level separates the shallower states ( $\varepsilon < \varepsilon_0(t)$ ), which reached equilibrium occupancy, and the deeper ones ( $\varepsilon > \varepsilon_0(t)$ ), characterised by non-equilibrium population. In the case of 'instantaneous' carrier generation and linear sample heating,  $T(t) = T_e + \beta t$  ( $T_e$  - the initial temperature,  $\beta$  - the heating rate), as well as  $\nu_0 = \text{const}$ , the demarcation energy is given by

$$\varepsilon_0(t) \approx k[c'T(t) - T'], \quad (5)$$

with

$$c' = 0.967 \ln(\nu_0/\beta) + 3.7,$$

$$T' = 180\text{K},$$

where  $\nu_0/\beta$  is expressed in  $\text{K}^{-1}$ . Since the exponential function in the integrand of Eq. (1) has a similar course as the unit step function,  $H[\varepsilon - \varepsilon_0(t)]$ , the function  $\Phi(t)$  can be approximated by

$$\Phi(t) \approx C_t \int_{\varepsilon_0(t)}^{\varepsilon_t} N_t(\varepsilon) d\varepsilon, \quad \varepsilon_t^0 < \varepsilon_0(t) < \varepsilon_t. \quad (6)$$

Considering more complex heating schemes one has to notice, that the formula (1) is valid for arbitrary time dependence of the sample temperature. In any case, the TSC may be computed from the equations given in Appendix and the Eq. (1). This can be done only numerically. Nevertheless, the influence of sample heating regime on the TSCs can be established in a simple way.

Let us assume that, following fast photogeneration of the carriers at  $t \approx 0$ , the sample is heated and cooled in an arbitrary manner and after

some time  $t_m$  the sample temperature reaches its initial value  $T_0$ . Then, the sample is heated with a constant rate  $\beta$ . In this case the formula (1) takes the form of

$$\Phi(t) = C_t \int_{\varepsilon_0}^{\varepsilon_i} N_t(\varepsilon) \exp\left[-\int_0^{t_m} \frac{dt'}{\tau_r(\varepsilon, t')}\right] \exp\left[-\int_{t_m}^t \frac{dt'}{\tau_r(\varepsilon, t')}\right] d\varepsilon. \quad (7)$$

It is seen that both the first and the second exponential factors in the integrand can be approximated by the unit step functions,  $H(\varepsilon - \varepsilon_m)$  and  $H[\varepsilon - \varepsilon_0(t)]$ , respectively. Here,  $\varepsilon_m$  is the demarcation energy at  $t = t_m$ , determined implicitly by the Eq. (4), i.e.,

$$\int_0^{t_m} \frac{dt}{\tau_r(\varepsilon_m, t)} \approx 1, \quad (8)$$

whereas  $\varepsilon_0(t)$  is the demarcation energy for  $t > t_m$ , given by the approximate Eq. (5). Provided that  $\varepsilon_m \geq \varepsilon_1^0$ , the resulting formulae for the function  $\Phi(t)$  have the form of

$$\Phi(t) \approx C_t \int_{\varepsilon_m}^{\varepsilon_i} N_t(\varepsilon) d\varepsilon, \quad \varepsilon_0(t) \leq \varepsilon_m, \quad (9a)$$

$$\Phi(t) \approx C_t \int_{\varepsilon_0(t)}^{\varepsilon_i} N_t(\varepsilon) d\varepsilon, \quad \varepsilon_m < \varepsilon_0(t) < \varepsilon_1. \quad (9b)$$

In the initial time interval, when  $\varepsilon_0(t) \leq \varepsilon_m$ , the function  $\Phi(t)$  does not depend on time. This indicates that the carrier release from the traps does not occur and the TSC is almost equal to zero. In the following time region, when  $\varepsilon_0(t) > \varepsilon_m$ , the function  $\Phi(t)$  is given by the same formula as in the case of instantaneous sample heating (Eq. (6)). Therefore, the TSC course in this time interval is independent of the sample heating regime up to the moment  $t_m$ .

The above considerations imply that for  $\varepsilon_0(t) \approx \varepsilon_m$  a sudden increase of TSC should take place. According to the formulae (A4) – (A6), given in Appendix, the TSC fulfills then the approximate relationship

$$I(t) \propto -\frac{d\Phi(t)}{dt} \quad (10)$$

(the time dependence of  $\Phi(t)$  is much weaker and can be ignored). The derivative of  $\Phi(t)$  may be estimated as follows. Differentiating the Eq. (7), replacing the first exponential factor in the integrand by the unit step function  $H(\varepsilon - \varepsilon_m)$  and setting in the second factor  $t = t_m$  yields

$$-\frac{d\Phi(t)}{dt} \approx C_t \int_{\varepsilon_m}^{\varepsilon_i} \frac{N_t(\varepsilon)}{\tau_r(\varepsilon, t)} d\varepsilon \approx C_t N_t(\varepsilon_m) \int_{\varepsilon_m}^{\varepsilon_i} \frac{d\varepsilon}{\tau_r(\varepsilon, t)}. \quad (11)$$

The last approximate formula is obtained under assumption that  $N_t(\varepsilon)$  varies with energy much slower than  $\tau_r(\varepsilon, t)$ . Calculating the last integral and assuming that  $\varepsilon_1 - \varepsilon_m \gg kT(t)$  one gets the formula

$$-\frac{d\Phi(t)}{dt} \approx C_t N_t(\varepsilon_m) \nu_0 kT(t) \exp\left[-\frac{\varepsilon_m}{kT(t)}\right]. \quad (12)$$

As follows from Eqs. (10) and (12), the initial rise of TSC has, in the first approximation, thermally activated character,

$$I(t) \propto \exp\left[-\frac{\varepsilon_m}{kT(t)}\right], \quad (13)$$

where the activation energy  $\varepsilon_m$  is determined by the Eq. (8). A similar formula for the initial increase of TSC was obtained in [7], but the authors do not considered the influence of experimental conditions on the activation energy.

For both heating schemes, mentioned in the Introduction, the activation energy  $\varepsilon_m$  of the TSC rise can be easily calculated. We shall consider at first the 'delayed' sample heating (Fig. 1b), when

$$T(t) = T_e, \quad t < t_m, \quad (14a)$$

$$T(t) = T_e + \beta(t - t_m), \quad t \geq t_m. \quad (14b)$$

Since the sample temperature is constant prior the onset of linear heating, from the Eq. (8) one gets the formula

$$\varepsilon_m \approx kT_e \ln(1.8v_0 t_m) \quad (15)$$

(the correction factor 1.8 was introduced in [11]). Thus, the activation energy increases with the temperature  $T_e$  of sample excitation and the delay time  $t_m$ .

Let us consider now the step heating of the sample (Fig. 1c). For the  $i$ -th heating cycle the sample temperature is given by

$$T(t) = T_e + \beta(t - t_{i-1}), \quad t_{i-1} \leq t < t_i, \quad (16)$$

where  $t_0 = 0$ . For simplicity, the time of sample cooling after each heating cycle is ignored. One can prove that this is acceptable when the cooling rate  $\beta$  is sufficiently large, say  $\beta/\beta \geq 10$ . According to the Eq. (8), the activation energy  $\varepsilon_m$  of TSC increase in the  $(m+1)$ -th heating cycle is then given by the implicit equation

$$\sum_{i=1}^m \int_{t_{i-1}}^{t_i} \frac{dt}{\tau_r(\varepsilon_m, t)} \approx 1. \quad (17)$$

Provided that the maximum sample temperatures in the sequential cycles increase remarkably, in the above sum only the  $m$ -th term is of significance. One then gets the equation

$$\int_{t_{m-1}}^{t_m} \frac{dt}{\tau_r(\varepsilon_m, t)} \approx 1. \quad (18)$$

Since the sample temperature increases linearly in the time interval  $t_{m-1} \leq t < t_m$ , the energy  $\varepsilon_m$  is given by the formula

$$\varepsilon_m \approx k(c^* T_m - T^*), \quad (19)$$

which follows from the Eqs. (8) and (5). Here

$$T_m = T_e + \beta(t_m - t_{m-1}) \quad (20)$$

is the maximum sample temperature reached in the  $m$ -th heating cycle. The activation energy  $\varepsilon_m$  of TSC rise depends now linearly on the maximum temperature  $T_m$ .

It is worth noting that the influence of sample heating mode on the TSCs can be described in alternate, mathematically equivalent, way. In such a description the function  $\Phi(t)$  is given by the Eq. (6), in which the demarcation level  $\varepsilon_0(t)$  is determined by the Eq. (4) over the whole time interval. The above-discussed features of TSCs are then related with non-linear time dependence of the demarcation energy. This approach has been reported in [12] and will be presented in detail elsewhere.

## NUMERICAL RESULTS AND DISCUSSION

In order to verify the correctness and the accuracy of derived formulae we performed the numerical calculations of TSCs, corresponding to delayed and step heating of the sample. The numerical method was similar to that described in [9,10]. The calculations were made for the exponential distribution of traps (3) and both the cases of monomolecular and bimolecular carrier recombination (cf. Appendix, Eqs. (A2) – (A3)). In the following figures, the TSC curves computed analytically and numerically (marked respectively by lines and points) are compared.

Fig. 2 a, b presents the TSC curves in semi-logarithmic scale, computed for delayed sample heating and, respectively, for monomolecular and bimolecular carrier recombination. The individual curves correspond to different temperatures  $T_e$  of sample excitation. Despite some discrepancies between the analytical and numerical results due to approximations involved in the theory, the general features of TSCs remain the same. The initial part of TSC curve depends on the excitation temperature  $T_e$  and the initial slopes of separate curves increase with  $T_e$ . The following TSC course is independent of the temperature  $T_e$  and the TSC curves overlap in this temperature region. These TSC features are in qualitative agreement with the experimental results by Zhou and Elliott [5] in *a*-Si:H.

One should to note that the Fritzsche-Ibaraki theory [1] predicts somewhat different dependence of TSC on the initial temperature  $T_e$ . Namely, the initial part of the TSC curve should shift parallelly towards higher temperatures with increasing  $T_e$ .



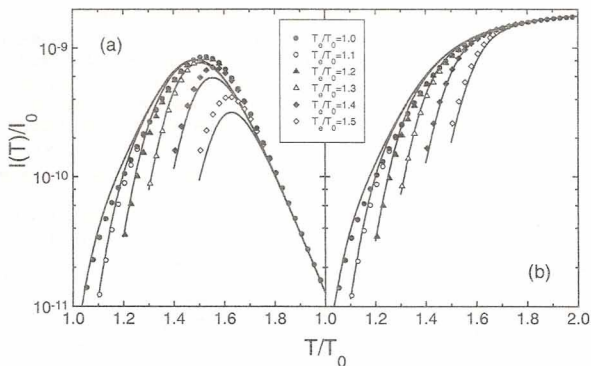


Figure 2. TSC curves, corresponding to the delayed heating and the monomolecular (a) and bimolecular (b) carrier recombination, for several temperatures of sample excitation. The parameters:  $\tau_{tv}0 = 103$ ,  $\tau_{Rv}0 = 3 \times 10^5$  (a),  $CRn0/v0 = 5 \times 10^{-6}$  (b),  $T_c/T_0 = 3$ ,  $\epsilon t_0/kT_0 = 30$ ,  $\tau_{mv}0 = 3 \times 10^{14}$ ,  $\beta/v_0T_0 = 10-15$ ,  $T_0 = 100$  K

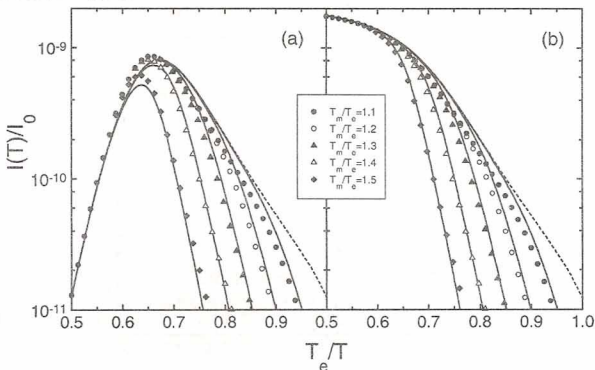


Figure 3. TSC curves, corresponding to the step heating and the monomolecular (a) and bimolecular (b) carrier recombination, for several heating cycles.  $T_c/T_e = 3$ ,  $\epsilon t_0/kT_e = 30$ ,  $\beta/v_0T_e = 10-15$ ,  $T_e = 100$  K; other calculation parameters are the same as in Fig. 2. The dashed line refers to the first heating cycle with delay time  $\tau_{mv}0 = 5 \times 10^{13}$

This was the reason why Zhou and Elliott questioned the applicability of the theory [1] in the case of  $\alpha$ -Si:H. The differences between the results

of both theories are due to another simplifying assumptions. As already mentioned, the Fritzsche-Ibaraki theory ignores the carrier retrapping. However, from the theory developed in [8,9] it follows that in the initial temperature region the rates of carrier capture and release are approximately equal and the carrier retrapping cannot be neglected.

Fig. 3 a, b shows the TSC curves in semi-logarithmic scale, calculated for several cycles of step heating of the sample and for monomolecular and bimolecular carrier recombination, respectively. The curves are identified by the maximum temperature  $T_m$ , reached in the previous heating cycle. The TSC courses are similar to those corresponding to delayed sample heating. However, in order to show the thermally activated character of the initial TSC rise, the currents are plotted here versus  $T_e/T$ . It is seen that the initial parts of the TSC curves computed both analytically and numerically are approximately linear and that their slopes increase with increasing temperature  $T_m$ . Such a behaviour was established experimentally for *a*-Si:H by Valentin *et al* [3] and Fritzsche and Ibaraki [1].

According to the Eq. (19), the activation energy  $\varepsilon_m$  of initial TSC rise should depend linearly on the maximum temperature  $T_m$  of preceding heating cycle. This can be verified for the experimental results given in [1, 3]. The corresponding plot, shown in Fig. 4, is in fact approximately linear. The value of the frequency factor calculated

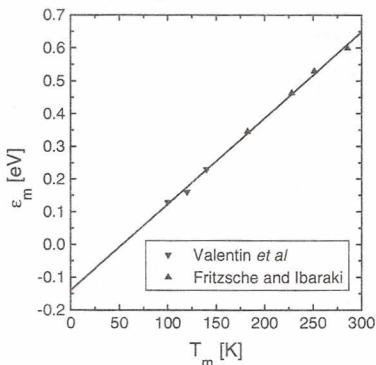


Figure 4. Dependence of the demarcation energy  $\varepsilon_m$  on the maximum temperature  $T_m$  of preceding heating cycle, determined from the TSC curves obtained in the step heating measurements in *a*-Si:H [1, 3]. The points refer to experimental results, the solid line is determined by the least-squares method

from the slope of straight line in the plot (cf. Eqs. (19) and (5)), equals to  $\nu_0 = 7 \times 10^{11} \text{ s}^{-1}$ , which seems to be quite reasonable. It should bear



in mind that the measurements in [1] and [3] were performed on different samples and with different heating rates. However, the coefficient  $\dot{c}$  in the Eq. (19) is the slowly varying, logarithmic function of the ratio  $\nu_0/\beta$ . Since the values of frequency factors for both samples are expected to be of the same order of magnitude and the ratio of sample heating rates in [1] and [3] do not exceeded 30 (in [3] only the range of heating rates was specified), the possible differences in the values of  $\dot{c}$  and  $\varepsilon_m$  could not be larger than 6%.

One point remains, however, unclear. It is seen from Fig. 4 that the value of energy  $\varepsilon_m$ , extrapolated to the temperature  $T = 0$ , equals to  $\varepsilon_{m0} \approx -0.14$  eV whereas its theoretical value, according to (19) and (5), is equal to  $\varepsilon_{m0} = -kT^* \approx -0.015$  eV. Possible explanation of this discrepancy is the approximate character of the theory. As can be recognized from Fig. 3, the initial, linear portions of TSC curves calculated from the approximate formulae have somewhat larger slopes than those computed numerically. Hence, the values of energy  $\varepsilon_m$ , determined from the experimental data on the basis of Eq. (13), are lowered. The resulting deviations of demarcation energy depend both on the trap distribution as well as on the carrier recombination kinetics and are difficult to estimate. Alternative explanation is the relatively strong dependence of frequency factor in a-Si:H on the temperature and/or the trap depth, when the formulae (5) and (19) do not apply. For example if the traps are electrically neutral when empty, the frequency factor is quadratic function of the temperature,  $\nu(T) = \nu_0(T/T_e)^2$ . The expression for the demarcation energy has then the form (5), with the coefficients  $\dot{c} = 0.974 \ln(\nu_0/\beta T_e^2) + 16.6$  and  $T^* = 700$  K [13]. In this case the theoretical value of  $\varepsilon_{m0} = -kT^* \approx -0.06$  eV, which is much closer to that determined from Fig. 4.

## CONCLUSIONS

In this paper we have studied the influence of sample heating regime on the TSCs in disordered solids, characterised by a continuous distribution of trapping states. Two cases have been considered in detail: delayed heating and step heating. It has been established that the initial TSC rise, during the sample heating with a constant rate, has a thermally activated character. The activation energy equals to the demarcation energy for trapped charge carriers at the onset of corresponding heating cycle. The subsequent TSC course is independent of the mode of previous sample heating. The analytical results have been verified by numerical calculations of TSCs performed for the exponential distribution of traps and the cases of both monomolecular and bimolecular carrier recombination. The above-described TSC features are consistent with those established

experimentally in a-Si:H. This proves the validity and the usefulness of demarcation energy concept in the description of TSCs in this material.

## APPENDIX

The basic set of equations, used in [8] for the description of TSCs, consists of the approximate equation for the carrier trapping/detrapping kinetics [11, 13],

$$\frac{d}{dt} \left[ \frac{n_t(t)}{\Phi(t)} \right] \approx n(t), \quad (A1)$$

with the function  $\Phi(t)$  determined by the Eq. (1), as well as of the equation describing the monomolecular,

$$\frac{d}{dt} [n(t) + n_t(t)] = -\frac{n(t)}{\tau_R}, \quad (A2)$$

or bimolecular,

$$\frac{d}{dt} [n(t) + n_t(t)] = -C_R n(t)[n(t) + n_t(t)], \quad (A3)$$

carrier recombination. Here,  $n(t)$  and  $n_t(t)$  are the free and trapped carrier densities,  $\tau_R$  is the mean carrier recombination time and  $C_R$  is the recombination coefficient.

The approximate solutions of Eqs. (A1) and (A2) as well as of Eqs. (A1) and (A3) have, respectively, the form of

$$n(t) = \frac{n_0}{[\Phi(t) + 1/\tau_R]^2} \left[ -\frac{d\Phi(t)}{dt} \right] \quad (A4)$$

and

$$n(t) = \frac{n_t(t)}{\Phi(t)[\Phi(t) + C_R n_t(t)]} \left[ -\frac{d\Phi(t)}{dt} \right] \quad (A5)$$

with  $n_t(t)$  given implicitly by

$$\ln[n_t(t)/n_0] = -C_R n_t(t)/\Phi(t) \quad (A6)$$

( $n_0$  is the generated carrier density). The TSC intensity is proportional to free carrier density,

$$I(t) = en(t)\mu_0 ES \quad (A7)$$

( $e$  is the elementary charge,  $\mu_0$  is the free carrier mobility,  $E$  is the electric field strength and  $S$  - the sample cross-section area, perpendicular to the carrier flow direction). In Figs. 2 - 3 the TSC intensity is normalized to  $I_0 = en_0\mu_0 ES$ .

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