

TRANSPORT COEFFICIENTS OF AMORPHOUS SEMICONDUCTORS BY QUASICLASSICAL APPROXIMATION

I. THERMOELECTRIC POWER

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In the presented paper a possible method for the calculation of transport coefficients of amorphous semiconductors is shown. The method employs the quasiclassical model of the electronic energy spectrum with randomly shifted bands. Thermoelectric power is analysed in detail. The results are confronted with experimental ones obtained with some single as well as multicomponent amorphous semiconductors.

ПОЛУКЛАССИЧЕСКАЯ ИНТЕРПРЕТАЦИЯ КОЭФФИЦИЕНТОВ ПЕРЕНОСА В АМОРФНЫХ ПОЛУПРОВОДНИКАХ

I. Термоэлектрическая сила

В предлагаемой работе показан возможный метод для вычисления коэффициентов переноса в аморфных полупроводниках. Используется полуклассическая модель энергетического спектра электронов с хаотически смещенными полосами. При этом термоэлектрическая сила анализируется подробно. Таким образом, полученные коэффициенты сравниваются с экспериментальными данными для некоторых простых и также мультикомпонентных аморфных полупроводников.

I. INTRODUCTION

It was shown that when calculating the density of states of an electron in a random potential, under certain circumstances the first and higher quantum-mechanical corrections can be neglected [1, 2]. This fact led to the elaboration of the quasiclassical model of randomly shifted bands [3]. The notions, notation, and illustration of the model are given in Fig. 1. The shift of energy band by a value of $\eta\xi$, denoted in the figure by a shifted edge of the conduction (valence) band: $E_c \rightarrow E'_c$, occurs with the probability

$$\frac{1}{\sqrt{2\pi}} \exp\left(-\frac{\xi^2}{2}\right). \quad (1)$$

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The averaging over random realizations of shifts yields the mean density of states $G(E)$, Fig. 1. The numerical calculation of the illustrated mean density of states is given in detail elsewhere [1, 2]. The parameter η (in Fig. 1 $\eta = 0.1$ eV), i.e. the dispersion of the random potential, represents in the quasiclassical model the only parameter characterizing the structural disorder. When calculating dc electrical conductivity [3] it was shown that for chalcogenide glasses and amorphous Si and Ge the values $\eta \in (0 \div 0.2$ eV) are reasonable.

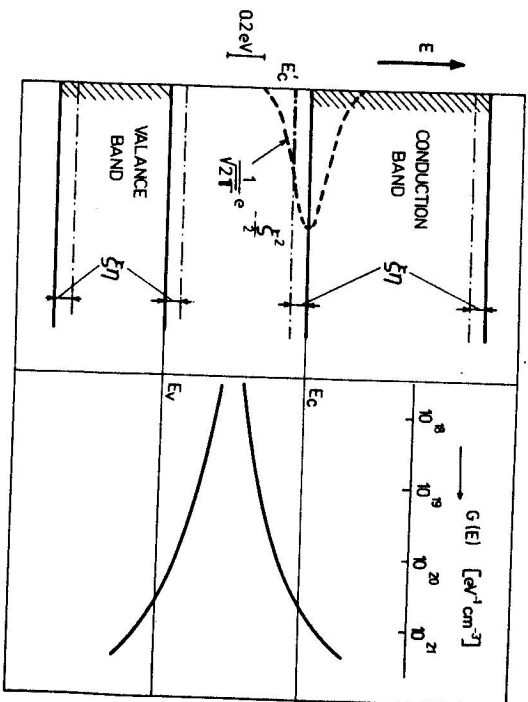


Fig. 1. Schematic illustration of the shifted bands model. The random shift $\xi\eta$, realized with the probability $1/\sqrt{2\pi} \exp(-\xi^2/2)$, is denoted by the shifted edge of the conduction (valence) band. The mean density of states, $G(E)$, is calculated for $\eta = 0.1$ eV.

II. TRANSPORT EQUATIONS

First we point out the fact that in the introduced quasiclassical model all states of an electron are delocalized, and their dynamics in external fields is like that of a Bloch electron. This conclusion is a starting point for the derivation of transport equations and transport coefficients.

The transport theory of crystalline semiconductors (e.g. [4]) yields the following relations for the vectors of current density and the thermal flux of electrons:

$$j_n = e \left[eK_{11}E + K_{11}\nabla E'_n + K_{21} \frac{\nabla T}{T} - K_{11}E'_n \frac{\nabla T}{T} \right] - \frac{e^2}{m_n} \left[eK_{12}E + K_{12}\nabla E'_n - K_{12}E'_n \frac{\nabla T}{T} + K_{22} \frac{\nabla T}{T} \right] \times B, \quad (2)$$

$$w_n = \left[-eK_{21}E - K_{21}\nabla E_{i_n} - K_{11}\frac{\nabla T}{T} + K_{21}E_{i_n}\frac{\nabla T}{T} \right] - \frac{e}{m_n} \left[-eK_{22}E - K_{22}E_{i_n} - K_{12}\frac{\nabla T}{T} + K_{22}E_{i_n}\frac{\nabla T}{T} \right] \times \mathbf{B},$$

where

$$K_n = -\frac{4}{3} \frac{1}{m_n} \int_0^\infty \epsilon^i \tau^i \frac{\partial f^{(0)}}{\partial \epsilon_i} \frac{g(\epsilon)}{1 + \left(\frac{e\tau}{m_n} B\right)^2} d\epsilon_i \quad (4)$$

$$f^{(0)} = \frac{1}{\exp\left(\frac{\epsilon - E_i'}{k_0 T}\right) + 1}, \quad g(\epsilon) = 2\pi \left(\frac{2m_n}{\hbar^2}\right)^{3/2} \epsilon^{1/2}, \quad (5)$$

$E_{i_n} = E_F - E_c + \eta\xi$ $i = n, p$

(The symbols have the usual meaning).

The relations (2) and (3) are valid for fixed bands. The energy of an electron in the conduction and the valence band, respectively, can be written as

$$E = E_c' + \frac{1}{2} \frac{(\hbar k)^2}{m_n} = E_c' + \epsilon_n \quad (6)$$

$$E = E_v' - \frac{1}{2} \frac{(\hbar k)^2}{m_p} = E_v' - \epsilon_p, \quad (7)$$

where $E_c' = E_c - \eta\xi$ and $E_v' = E_v - \eta\xi$ denote bands shift.

In the case of randomly shifted bands further averaging over the distribution function (1) is to be done. Then the relations (2, 3) become

$$i_n = e \left[e \langle K_{11n} \rangle E + \langle K_{11n} \rangle \nabla E_F + \gamma_{11n} \frac{\nabla T}{T} \right] - \quad (8)$$

$$- \frac{e^2}{m_n} \left[e \langle K_{12n} \rangle E + \langle K_{12n} \rangle \nabla E_F + \gamma_{12n} \frac{\nabla T}{T} \right] \times \mathbf{B}$$

$$w_n = - \left[e \langle K_{21n} \rangle E + \langle K_{21n} \rangle \nabla E_F + \gamma_{21n} \frac{\nabla T}{T} \right] + \quad (9)$$

$$+ \frac{e}{m_n} \left[e \langle K_{22n} \rangle E + \langle K_{22n} \rangle \nabla E_F + \gamma_{22n} \frac{\nabla T}{T} \right] \times \mathbf{B},$$

where

$$\langle K_{nm} \rangle = -\frac{4}{3} \frac{1}{m_n} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}\xi^2\right) \int_0^\infty \epsilon^i \tau^i \frac{\partial f^{(0)}}{\partial \epsilon} \frac{g(\epsilon)}{1 + \left(\frac{e\tau}{m_n} B\right)^2} d\epsilon d\xi \quad (10)$$

$$\gamma_{nm} = \frac{4}{3} \frac{1}{m_n} \frac{1}{\eta k_0 T} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \epsilon^i \tau^i \exp\left(-\frac{1}{2} \frac{(\epsilon - E_F + E_c - z)^2}{\eta^2}\right) \times \quad (11)$$

$$\times \frac{\exp\left(\frac{z}{k_0 T}\right)}{\left(1 + \exp\left(\frac{z}{k_0 T}\right)\right)^2} \frac{g(\epsilon)z}{1 + \left(\frac{e\tau}{m_n} B\right)^2} d\epsilon dz$$

$$f^{(0)} = \frac{1}{\exp\left(\frac{\epsilon - E_F + E_c - \eta\xi}{k_0 T}\right) + 1}. \quad (12)$$

A similar approach yields the following expressions for the vectors of current density and the thermal flux of holes:

$$i_p = e \left[e \langle K_{11p} \rangle E - \langle K_{11p} \rangle \nabla E_F - \gamma_{11p} \frac{\nabla T}{T} \right] + \quad (13)$$

$$+ \frac{e^2}{m_p} \left[e \langle K_{12p} \rangle E - \langle K_{12p} \rangle \nabla E_F - \gamma_{12p} \frac{\nabla T}{T} \right] \times \mathbf{B}$$

$$w_p = \left[e \langle K_{21p} \rangle E - \langle K_{21p} \rangle \nabla E_F - \gamma_{21p} \frac{\nabla T}{T} \right] + \quad (14)$$

$$+ \frac{e}{m_p} \left[e \langle K_{22p} \rangle E - \langle K_{22p} \rangle \nabla E_F - \gamma_{22p} \frac{\nabla T}{T} \right] \times \mathbf{B}$$

where

$$\langle K_{np} \rangle = -\frac{4}{3} \frac{1}{m_p} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}\xi^2\right) \int_0^\infty \epsilon^i \tau^i \frac{\partial f^{(0)}}{\partial \epsilon} \frac{g(\epsilon)}{1 + \left(\frac{e\tau}{m_p} B\right)^2} d\epsilon d\xi \quad (15)$$

$$\gamma_{np} = \frac{4}{3} \frac{1}{m_p} \frac{1}{\eta k_0 T} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \epsilon^i \tau^i \exp\left(-\frac{1}{2} \frac{(\epsilon + E_F - E_v - z)^2}{\eta^2}\right) \times \quad (16)$$

$$\times \frac{\exp\left(\frac{z}{k_0 T}\right)}{\left(1 + \exp\left(\frac{z}{k_0 T}\right)\right)^2} \frac{g(\epsilon)z}{1 + \left(\frac{e\tau}{m_p} B\right)^2} d\epsilon dz$$

$$f^{(0)} = \frac{1}{\exp\left(\frac{\epsilon + E_F - E_v + \eta\xi}{k_0 T}\right) + 1}. \quad (17)$$

The relations (8, 9, 13, 14) are useful for the calculations of transport parameters in the case of pure electrical phenomena ($\nabla E_F = 0$, $\nabla T = 0$, $\mathbf{B} = 0$), thermoelectric phenomena ($\mathbf{B} = 0$), and galvanomagnetic phenomena. The electric conductivity

was studied in our paper [3]: in the following chapter we shall pay attention to thermoelectric phenomena.

II. THERMOPOWER

A formula for thermopower (the Seebeck coefficient) can be obtained from the expression for current density (8, 13) by putting $B = 0$. When adding equations (8) and (13) under the condition $i = i_p + i_n = 0$ a simple manipulation yields

$$\alpha = \frac{\gamma_{11p} - \gamma_{11n}}{eT((K_{11n}) + (K_{11p}))} \quad (18)$$

We shall assume that the relation constant can be written as $\tau = \tau_0 e^p$, for scattering on charged centres $\tau_c = \tau_0 e^{3/2}$, for scattering on phonons $\tau_F = \tau_0 e^{p-1/2}$.

An analytical treatment for thermopower in the whole temperature range is impossible. In the limiting cases, i.e. both in regions of high and low temperatures, the following asymptotic expressions can be found:

a) high temperature region (using the Boltzmann statistics)

$$\alpha = \frac{\eta^2}{ek_0 T^2} \frac{b-1}{b+1} + \frac{1}{eT} \frac{(E_F - E_c) - b(E_c - E_F)}{b+1} + \frac{k_0}{e} \left(p + \frac{5}{2} \right) \frac{1-b}{1+b}, \quad (19)$$

where

$$b = \frac{\tau_{0n} M_p}{\tau_{0p} M_n}$$

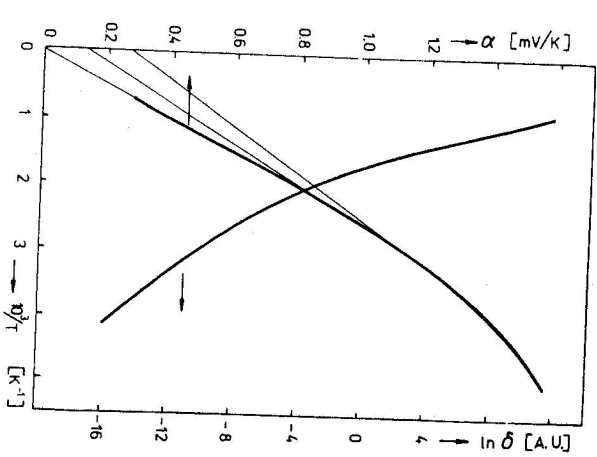


Fig. 2. Temperature dependence of electric dc conductivity and thermopower for $\eta = 0.06$ eV in the case of the dominance of holes. Extrapolating $\alpha(1/T \rightarrow 0)$ one can obtain various values for β/k_0 , which are dependent on the choice of the interval of temperature where the extrapolation was performed.

b) low temperature region

$$\alpha = \frac{k_0 x^2}{3\eta e} \cdot T \cdot F \quad (20)$$

The function F (see [11]) is not dependent upon T .

In the case of ordered systems, i.e. $\eta = 0$, the expression (19) converts into the well-known formula for crystalline semiconductors. For the low temperature range α is proportional to T and, according to the third thermodynamic law, α approaches to zero if $T \rightarrow 0$. However, the expressions (19), (20) give only an incomplete information about the temperature dependence of thermopower. A more complete picture is provided by a numerical approach.

The obtained results for the case of the dominance of holes with $\eta = 0.06$ eV are shown in Fig. 2. Here, the calculated conductivity values are given, too. At higher temperatures the thermopower is nearly proportional to $1/T$. Also the curve $\ln \sigma$ versus $1/T$ at higher temperatures yields nearly a line with a slope corresponding to the activation energy $\Delta E = E_c - E_v$. At lower temperatures a moderate deviation from the linear dependence can be seen. The experimental results obtained with chalcogenide glasses are often interpreted by the one-carrier formula [5, 6]:

$$\alpha = \frac{k_0}{e} \left(\frac{E_F - E_v}{k_0 T} + A \right), \quad (21)$$

where A is a constant, for which the value $A = 1$ has often been proposed [7, 8]. Assuming the temperature dependence of $E_F - E_v$ to be of the form $E_F - E_v =$

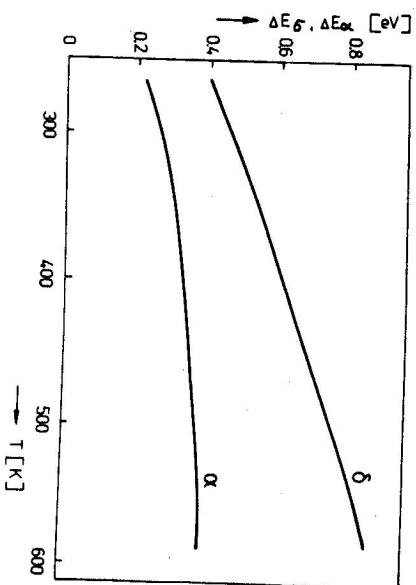


Fig. 3. Temperature dependence of activation energies obtained from temperature dependences of $\sigma(T)$ and $\alpha(T)$ (the case from Fig. 2).

$\Delta E_a - \beta T$, the value of β can be determined from thermopower measurements as it is obvious from the following relation:

$$\alpha = \frac{k_0}{e} \left(\frac{\Delta E_a}{k_0 T} \frac{\beta}{\beta + 1} \right). \quad (22)$$

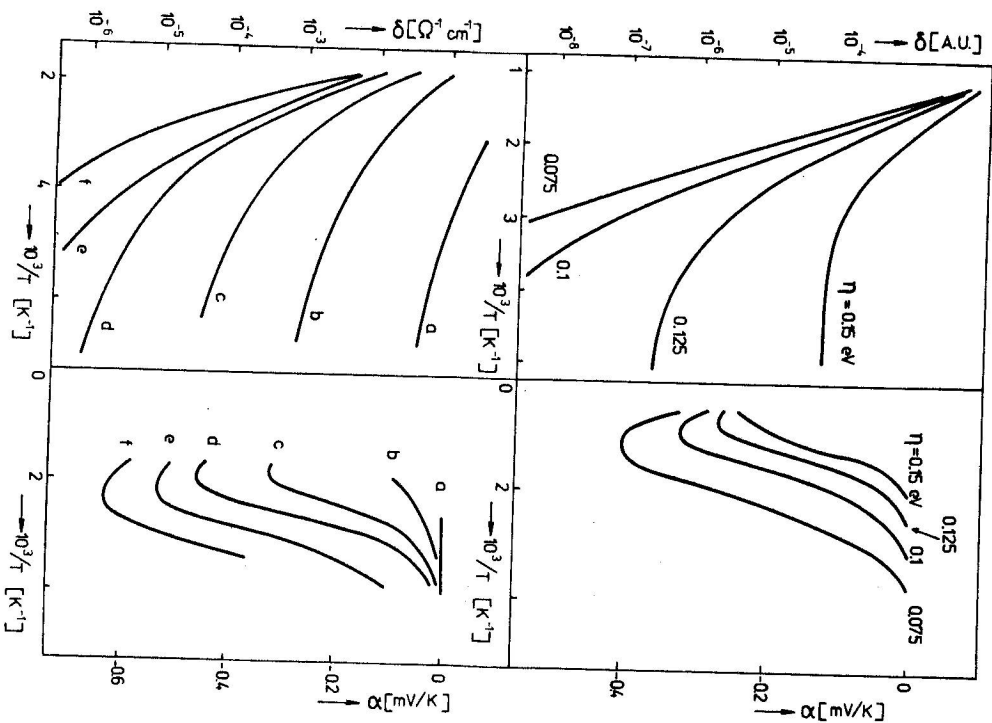


Fig. 4. Temperature dependence $\alpha(T)$ calculated from (18) and $\sigma(T)$ (for the detailed calculation see (3)) for various values of η . In the case of scattering on charged centres the value $m_n/m_p = 0.3$ was used. For qualitative comparison the experimental data for different annealing states (a—f) of am. Ge samples [10] are presented, too (at the bottom of the figure).

The obtained curves (Fig. 2) are analysed with regard to the formula (22). The activation energy ΔE_a obtained as $d\alpha/d(1/T)$ is shown in Fig. 3 together with the activation energy for conductivity $\Delta E_\sigma = d(\ln \sigma)/d(1/T)$ as a function of temperature. In the whole temperature region $\Delta E_\sigma > \Delta E_a$ is valid. This inequality is well known from the experimental experience. By extrapolation of the dependence $\alpha(1/T)$ for $1/T \rightarrow 0$ the value of β is obtained. As schematically shown in Fig. 2, the determination of β is denoted on the choice of the temperature interval where the extrapolation is made. This situation has an analogue in the experimental praxis, where for various reasons (high material resistivity, melting point, glass transition temperature) the temperature range where α can be measured is limited, so the determination of the value by extrapolation may lead to false results.

In Fig. 4 (top) the results of calculation of thermopower and conductivity for various values of the parameter η are given. The calculation was performed for scattering on charged centres. The transport involves both electrons and holes, the ratio between their effective mass being chosen as $m_n/m_p = 0.3$. In Fig. 5 the calculated temperature dependences of conductivity and thermopower with the same parameters are shown for the case of scattering on phonons. The results exhibit an approximately linear dependence of $\alpha(1/T)$ on $1/T$ at higher temperatures and other character of the dependence at lower temperatures. Such a shape of

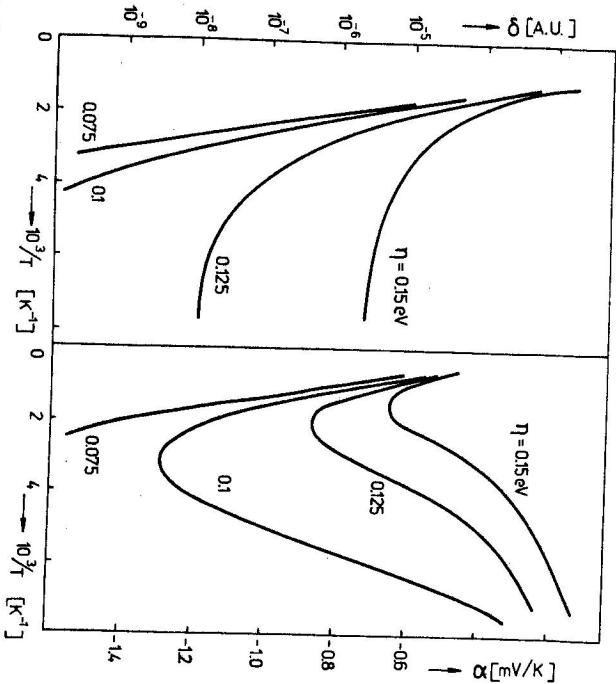


Fig. 5. The calculated (expression (18)) temperature dependence of $\sigma(T)$ and $\alpha(T)$ for the same values as in Fig. 4 in the case of scattering on phonons.

dependence is typical for amorphous Ge, GaSb, InSb [10] and amorphous Si [11, 12]. Fig. 6 involves further results for the case of a broader gap ($\Delta E = 0.4$ eV). The change of the character of $\alpha(T)$ in the low temperature region is explained by the transport through localized states [13]. Let us note that within the frame of our model the measurements $\alpha(T)$ may be interpreted in the whole temperature range without introducing any additional transport mechanism.

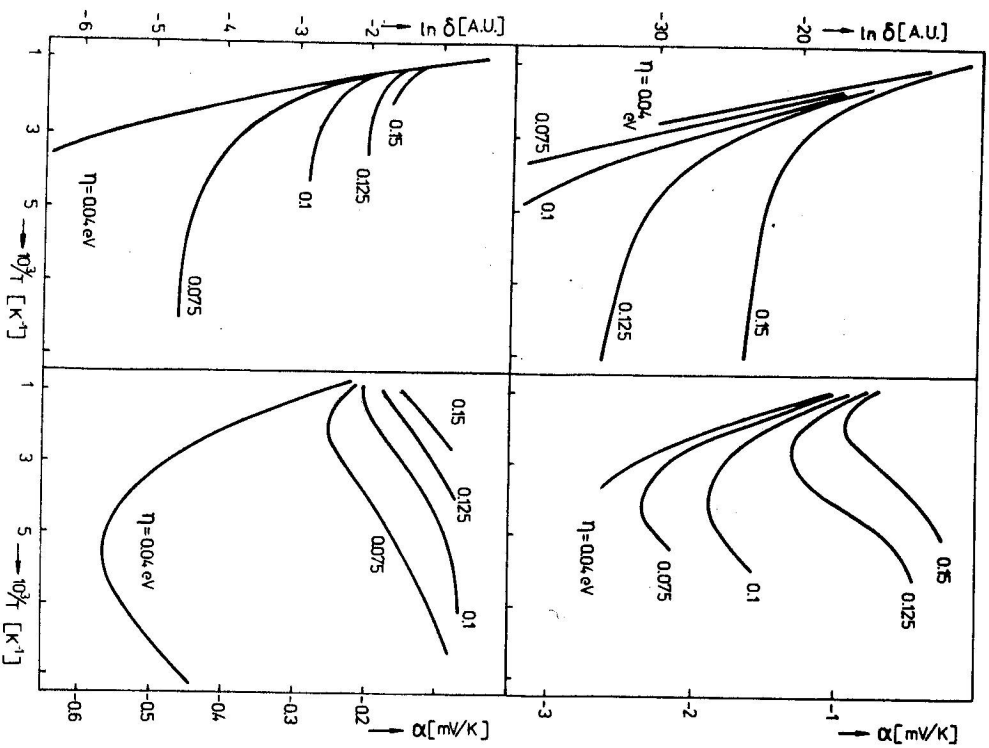


Fig. 6. The calculated temperature dependence of $\sigma(T)$, $\alpha(T)$ for a narrow band semiconductor (bottom of the figure — $\Delta E = 0.4$ eV) and for a wide band semiconductor (top — $\Delta E = 2$ eV).

It is known that annealing strongly influences the measured dependences of both $\alpha(T)$ and dc conductivity. Some typical experimental results are shown in Fig. 4 (bottom) [10]. It is reasonable to assume that annealing decreases the degree of disorder ($\eta \rightarrow 0$). When comparing the experiment and calculation of Fig. 4 in this light a good qualitative agreement is found. Concluding we note that the calculations were done always for one transport mechanism only ($p = -1/2$ or $p = 3/2$). However, the case of mixed scattering corresponds to physical reality, scattering on phonons being dominant at higher temperatures and scattering on charged centres being dominant at lower temperatures. A simultaneous account of both scattering types would probably influence the position of the peak.

III. CONCLUSION

The simple model of randomly shifted bands can describe not only the basic features of dc conductivity [3] but also those of thermopower, namely a) experimentally observed inequality $\Delta E_\sigma > \Delta E_\alpha$ b) influence of annealing c) the basic character of the $\alpha(T)$ dependence in a wide temperature range.

It should be noted, however, that an explanation of extremely high negative values of $(A - \beta/k_0)$ [5] and of thermopower anomalies at low temperatures (e.g. in amorphous Ge [14]) is beyond the scope of this simple model.

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