

Organic Nanostructured Material for Thermoelectric Sensors of Infrared Radiations

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Abstract—Thermoelectric sensors of infrared radiation are widely used in the detectors of IR radiations, in the systems of night vision, in the thermometers for contactless measurement of temperature including the human body one, in new thermal imaging systems. An important parameter that determines the possibility of a material to be used as sensitive element in the thermoelectric sensors is the thermoelectric power factor. Earlier we have shown that in the quasi-one-dimensional organic nanostructured crystals of tetrathiotetracene-iodide it is expected to obtain high values of the thermoelectric power factor. But this prediction was made on the base of a one dimensional crystal model. Now the power factor is modeled in a more complete physical model which takes into account the kinetic interaction between the molecular chains. It is obtained that this interaction can be neglected in not perfect crystals, but is important in very pure ones. The optimal values of the thermoelectric power factor are determined. The recommendations in order to obtain such values are elaborated.

Index Terms—organic nanostructured crystal, tetrathiotetracene-iodide, thermoelectric infrared detector, interchain interaction, thermoelectric power factor.

I. INTRODUCTION

In the last year it is observed an increased demand for the thermoelectric detectors of infrared (IR) radiation. Despite the photoelectric detectors which are sensitive in the spectral interval of wave lengths shorter than 1.5 μm , the thermoelectric detectors can collect and detect radiation from a very large spectral interval, including that of far IR wave lengths. Such detectors are widely used for detection of IR radiations, in the systems of night vision, in the thermometers for contactless measurement of temperature including that of the human body one, in new thermal imaging systems.

The main parameter that determine the possibility of a material to be used as sensitive element in the thermoelectric detectors of IR radiation is the thermoelectric power factor, $P = \sigma S^2$, where σ is the electrical conductivity and S is the thermopower (Seebeck coefficient). Higher the value of P is, the better this material is as sensitive element in the IR detectors. In the ordinary materials the simultaneous increase of electrical conductivity σ and of thermopower S is not possible, because the increase of σ usually leads to the decrease of S , and vice versa. New materials and structures with more complicated internal interactions are needed in order to overcome this contradiction.

High values of the thermoelectric power factor $P \sim 6.2 \cdot 6.6 \cdot 10^{-3} \text{ W/m.K}^2$ have been measured in n -PbTe/PbEuTe quantum wells at room temperature [1]. Even higher values of $P = 1.6 \cdot 10^{-2} \text{ W/m.K}^2$ have been measured in p -type PbTe/PbEuTe quantum wells [2]. We have calculated for (100) and (111) oriented n -PbTe/PbEuTe quantum wells $P_{100} = 1.75 \cdot 10^{-2} \text{ W/m.K}^2$ and $P_{111} = 1.1 \cdot 10^{-2} \text{ W/m.K}^2$, respectively [3] and $P \sim 2.5 \cdot 10^{-2} \text{ W/m.K}^2$ in p -type quantum structures [4]. These values are much higher than $P = 4 \cdot 10^{-3} \text{ W/m.K}^2$ which is obtained in widely

used thermoelectric material Bi_2Te_3 . However, the technology to product such quantum structures is rather complicated and expensive.

In the last years organic materials attract more and more attention as materials with more diverse and often unusual properties and which would be much less expensive in comparison with the inorganic ones. High values of the thermoelectric power factor have been already predicted in literature [5-7]. In [6] it was shown that in quasi-one-dimensional (Q1D) nanostructured crystals of tetrathiotetracene-iodide, TTT_2I_3 , the optimal value of $P = 1.53 \cdot 10^{-2} \text{ W/m.K}^2$ is expected. But this prediction was made on the base of a one dimensional crystal model.

The aim of this paper is the modeling of the electrical conductivity, thermopower and thermoelectric power factor in a more complete physical model which takes into account the possibility of charge carriers to pass from one molecular chain to another, i.e. the kinetic interaction between the molecular chains is considered. For simplicity a two-dimensional (2D) crystal model will be applied.

II. THERMOELECTRIC POWER FACTOR

The physical model for TTT_2I_3 has been briefly described in [8]. The crystals are formed of segregate linear chains of TTT and iodine. But only TTT chains are electrically conductive and the carriers are holes. Due to such molecular structure the crystals have needle like form with the length of 3 -10 mm and thickness $\sim 60 \mu\text{m}$. Such crystals were grown from solution [9], from gas phase [10] and by gas transport reactions [11]. The electrical conductivity σ is very sensitive to the crystal perfection and therefore varies in rather large interval. In the most perfect crystals grown by gas transport reactions the values of $\sigma \sim 10^4 \Omega^{-1}\text{cm}^{-1}$ have been measured.

In order to describe the charge transport the tight

binding and nearest neighbors approximations are applied. The energy of hole with the 2D quasi-wave vector \mathbf{k} with projections (k_x, k_y) is measured from the upper margin of the conduction band and has the form

$$\varepsilon(\mathbf{k}) = -2w_1[1 - \cos(k_x b)] - 2w_2[1 - \cos(k_y a)], \quad (1)$$

where w_1 and w_2 are the carrier transfer energies between the nearest molecules along and between the chains, b and a are lattice constants along and in transversal direction to the chains. The conducting chains are directed along \mathbf{b} which is taken as the axis x . Axis y is perpendicular to x .

The frequency ω_q of the acoustic longitudinal phonon with the 2D quasi-wave vector \mathbf{q} and projections (q_x, q_y) is taken in the form

$$\omega_q^2 = \omega_1^2 \sin^2(q_x b / 2) + \omega_2^2 \sin^2(q_y a / 2), \quad (2)$$

where ω_1 and ω_2 are the limit frequencies in the x and y directions. The conditions of the crystal quasi-one-dimensionality impose that $w_2 \ll w_1$, and $\omega_2 \ll \omega_1$.

Two the most important interactions of charge carriers with longitudinal acoustic phonons are taken into consideration. The first interaction is similar to that of polaron, but determined by induced polarization of molecules surrounding the conduction hole. The coupling constant is proportional to the mean polarizability α_0 of TTT molecule. In Q1D crystals the molecules are big and the polarizability is also big. Therefore, the fluctuation of the polarization energy due to the lattice vibrations must be taken into consideration.

The second interaction is similar to that of deformation potential. The coupling constants are proportional to the derivatives w'_1 and w'_2 with respect to the intermolecular distance of the energies w_1 and w_2 of a carrier transfer between the nearest molecules along and between the chains. Until our publications only this interaction was taken into account.

The scattering of carriers on impurities is also taken into account and is described by the dimensionless parameter D_0 which is proportional to the carrier concentration, and may be made very small, if the crystal purity is sufficiently high.

The linearized kinetic equation for nonequilibrium distribution function of carriers has been deduced. In the energy conservation law for the scattering process it was neglected the phonon energy, because at room temperature the latter is much less than the carrier energy. It was neglected also the carrier kinetic energy in transversal direction with respect to the longitudinal one, due to the relation $w_2 \ll w_1$. In this case the kinetic equation can be solved analytically. The electrical conductivity along the chains σ_{xx} , noted also by σ , and the thermopower S have been expressed through the transport integrals [8]. As a result, for the thermoelectric power factor we obtain

$$P = \sigma S^2, \text{ where } \sigma = \sigma_0 R_0, S = (k_0/e)(2w_1/k_0 T)R_1/R_0. \quad (3)$$

Here k_0 is the Boltzmann constant, e is the hole charge

$$\sigma_0 = 2e^2 M v_{s1}^2 w_1^3 / (\pi^2 \hbar a b c (k_0 T)^2 w_1'^2),$$

R_n are the transport integrals

$$R_n = \int_0^2 d\varepsilon \int_0^\pi d\eta (\varepsilon - \varepsilon_F)^n \varepsilon (2 - \varepsilon) n_{\varepsilon, \eta} (1 - n_{\varepsilon, \eta}) \times$$

$$[\gamma_1^2 (\varepsilon - \varepsilon_0)^2 + \frac{w_2'^2}{2\varepsilon(2 - \varepsilon)w_1'^2} (1 + \gamma_2^2 + 2 \sin^2 \eta -$$

$$- 2\gamma_2 \cos \eta) + D_0]^{-1}, \quad (4)$$

$$\varepsilon_0 = (\gamma_1 - 1) / \gamma_1, \quad (5)$$

$$\gamma_1 = \frac{2e^2 \alpha_0}{b^5 w_1'}, \gamma_2 = \frac{2e^2 \alpha_0}{a^5 w_2'}, \quad (6)$$

and M is the mass of TTT molecule, v_{s1} is the sound velocity along the chains, a, b, c are the lattice constants, $n_{\varepsilon, \eta}$ is the Fermi distribution function in the variables ε and η , $\varepsilon_F = E_F / 2w_1$ is the Fermi energy in the approximation, when the second term in (1) is neglected. The dimensionless parameter D_0 describes the carriers scattering on impurities considered neutral and point like. It is proportional to impurity concentration and can be made very small, if the impurity concentration is sufficiently small. We will consider the crystals with low, middle and high degree of purity and have chosen $D_0 = 0.2, 0.1, 0.05$, respectively, as in [6].

From (4) it is seen that the expression under integral (or the relaxation time) may have a maximum at $\varepsilon = \varepsilon_0$, when $0 < \varepsilon_0 < 2$, and the other terms in square bracket are small. This means that the above mentioned hole-phonon interactions strongly compensate each other for values of ε close to ε_0 . In the 1D approximation the value of this maximum was limited only by the value of the parameter D_0 , or by the intensity of impurity scattering. Now this maximum is limited also by the strength of interchain interaction. Therefore, it is necessary to investigate, when the interchain interaction can be neglected, and when it becomes important.

III. RESULTS AND DISCUSSIONS

The electrical conductivity σ , the thermopower S and the thermoelectric power factor P along the chains have been calculated numerically after (3) – (6). The crystal parameters are the same as in Ref. 8: $M = 6.5 \times 10^5 m_e$ (m_e is the mass of the free electron), $a = 18.35 \text{ \AA}$, $b = 4.96 \text{ \AA}$, $c = 18.46 \text{ \AA}$, $v_{s1} = 1.5 \times 10^3 \text{ m/s}$, $w_1 = 0.16 \text{ eV}$, $w_1' = 0.26 \text{ eV \AA}^{-1}$, $w_2 = 1.44 \times 10^{-3} \text{ eV}$, $w_2' = 2.34 \times 10^{-3} \text{ eV \AA}^{-1}$, $r = 4$.

The parameter γ_1 was taken equals to 1.6 as in [6], that corresponds to $\alpha_0 = 42 \text{ \AA}^3$. For comparison, in anthracene $\alpha_0 = 25 \text{ \AA}^3$, but TTT molecule is bigger and α_0 must be bigger too. From (6) it results that $\gamma_2 = 3.47 \gamma_1$.

In Fig. 1 the results of σ calculations are presented. It is seen that the lower and middle curves practically coincide. Only the maximums of upper curves a little differ, $\sigma_{1D} = 18.1 \cdot 10^3 \Omega^{-1} \text{cm}^{-1}$, but $\sigma_{2D} = 17.5 \cdot 10^3 \Omega^{-1} \text{cm}^{-1}$.

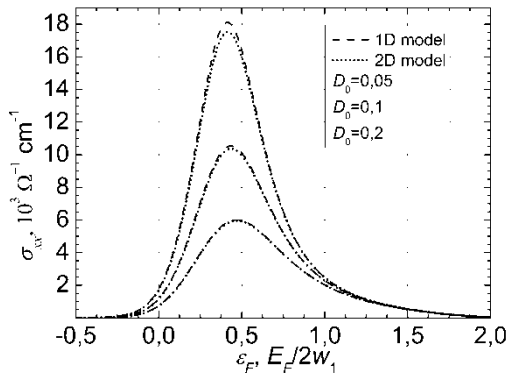


Fig.1. Electrical conductivity as a function of ϵ_F for $\gamma = 1.6$: upper, middle and lower curves are for $D_0 = 0.05, 0.1$ and 0.2 , respectively.

Thus, for crystals of considered degree of purity the interchain interaction very little influences the values of electrical conductivity and can be neglected. Of cause, for much purer crystals this interaction will change σ significantly.

In Fig. 2 the dependences of the thermopower S are presented. It is seen that the interchain interaction has still less influence on thermopower, than on σ . For crystals with considered degree of purity the curves for 1D and 2D

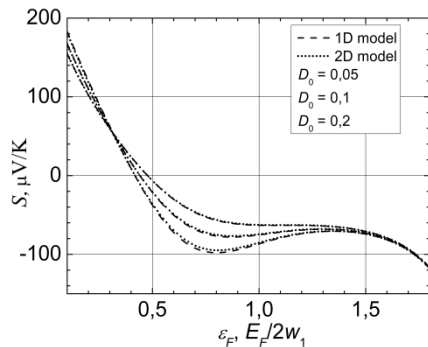


Fig.2. Thermopower S as a function of ϵ_F for $\gamma = 1.6$: lower, middle and upper curves are for $D_0 = 0.05, 0.1$ and 0.2 , respectively.

models practically coincide. This means that due to an additional factor $(\epsilon - \epsilon_F)$ in the numerator of (4), the maximum of relaxation times influences the thermopower in a less extent than σ . For values of ϵ_F between 0.1 and 0.2, when the maximum of the thermoelectric power factor is expected, the interchain interaction even less changes the values of S , calculated in the 1D model. In this case we may use for optimization process the simpler 1D crystal model.

The dependences of the thermoelectric power factor P

on dimensionless Fermi energy ϵ_F are presented in the Fig. 3. Even if dependences of P have accumulated more accurate calculations of σ and S in the 2D model, the curves practically coincide for less pure crystals with $D_0 = 0.2$ and 0.1 . Only in the purest crystals with $D_0 = 0.05$ it

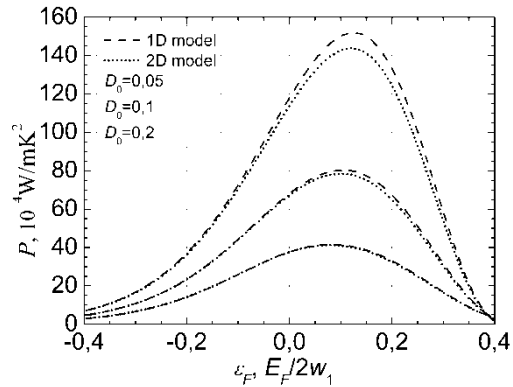


Fig.3. Thermoelectric power factor as a function of ϵ_F for $\gamma = 1.6$: upper, middle and lower curves are for $D_0 = 0.05, 0.1$ and 0.2 , respectively.

is observed a small decrease of P in the region of the maximum. Therefore, it becomes important to investigate P for still more pure crystals. Accordingly, we have modeled σ , S and P for crystals with $D_0 = 0.4, 0.2$ and 0.1 .

The dependence of electrical conductivity σ on Fermi energy ϵ_F in these more perfect crystals are presented in the Fig. 4. It is seen that the values of σ have increased both in 1D and in 2D models. It was expected. But now in the purest crystals with $D_0 = 0.01$ the maximum of σ in the 2D model is by 11% lower than in 1D case, and for

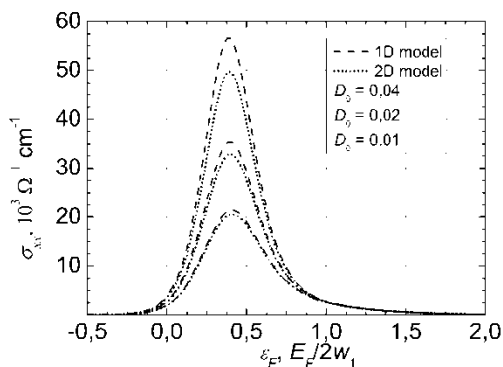


Fig.4. Electrical conductivity as a function of ϵ_F for $\gamma = 1.6$: upper, middle and lower curves are for $D_0 = 0.01, 0.02$ and 0.04 , respectively.

these values of ϵ_F the interchain interaction becomes important. In the same time, for values of ϵ_F between 0.1 and 0.2 which are the most important in our case, the differences between calculated values in 1D and 2D models are much less.

The dependencies of the thermopower S on ϵ_F for these more perfect crystals are presented in the Fig. 5. It is seen that for some intervals of ϵ_F , due to the interchain

interaction, calculated values of S for 2D model were diminished in comparison with the 1D model. In other intervals S remains practically unchanged. In order to demonstrate such behavior of the thermopower we have

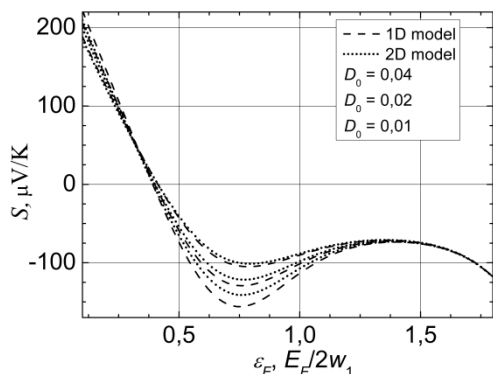


Fig.5. Thermopower S as a function of E_F for $\gamma = 1.6$: lower, middle and upper curves are for $D_0 = 0.01, 0.02$ and 0.04 , respectively.

presented in Fig. 6 the dependencies of S in a narrower interval of ϵ_F . Really, the diminution of S in this interval of ϵ_F is very small. Nevertheless, in the purest crystal with $D_0 = 0.01$ the diminution of S must be taken into account. At $\epsilon_F \sim 0.4$ the sign of S is changed. This means that carriers with opposite sign (electrons) are excited.

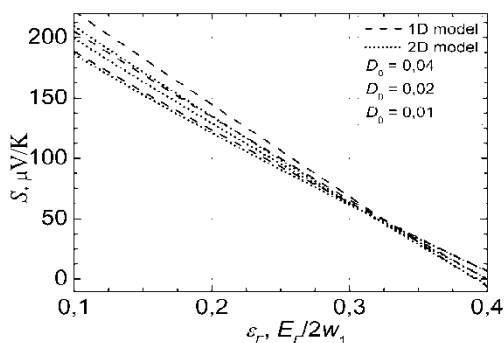


Fig.6. Dependencies of the thermopower S as in Fig.5, but now upper, middle and lower curves are for $D_0 = 0.01, 0.02$ and 0.04 , respectively.

In Fig.7 the dependencies of the power factor P on ϵ_F for purer crystals are presented. The values of P have increased considerably. Now the maximum value of P is $580 \cdot 10^{-4} \mu\text{Wm}^{-1}\text{K}^{-2}$ in 1D model and $450 \cdot 10^{-4} \mu\text{Wm}^{-1}\text{K}^{-2}$ in 2D model. The interchain interaction becomes more important because P is diminished by 22.4%. For $\epsilon_F = 0.2$ the values of P are $550 \cdot 10^{-4} \mu\text{Wm}^{-1}\text{K}^{-2}$ and $420 \cdot 10^{-4} \mu\text{Wm}^{-1}\text{K}^{-2}$, respectively. Even so, these calculated values of P in more realistic 2D model are 10 times higher than measured value in Bi_2Te_3 , an inorganic widely used commercial material. But the maximums of P are placed at lower values of Fermi energy than those that

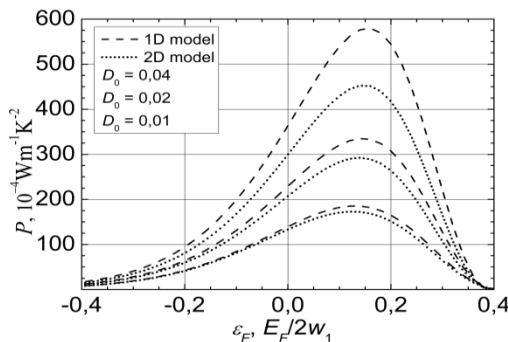


Fig.7. Thermoelectric power factor as a function of ϵ_F for $\gamma = 1.6$: upper, middle and lower curves are for $D_0 = 0.01, 0.02$ and 0.04 , respectively.

correspond to ordinary crystals. At ϵ_F a little less than 0.4 which correspond to stoichiometric crystals the power factor is very small. In order to increase P it needs to diminish the carrier concentration, i.e. to diminish the content of iodine which have the role of acceptors. This is possible because nonstoichiometric crystals of the type $\text{TTT}_2\text{I}_{3-\delta}$, where δ is the deviation of stoichiometry, are allowed.

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