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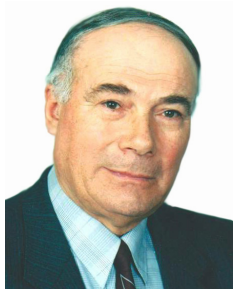
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ORGANIC THERMOELECTRIC MATERIALS: NEW OPPORTUNITIES

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The aim of the paper is to estimate the opportunities of organic materials for thermoelectric applications. Recently in molecular nanowires of conducting polymers the values of ZT ~ 15 were predicted. Still higher values of ZT have been predicted by us. However, these predictions were made in the frame of a strictly one-dimensional physical model. It is absolutely necessary to estimate the contribution of interchain interaction to these predictions. We present the results of thermoelectric properties modeling of tetrathiotetracene-iodide crystals, taking into account the interchain interaction. It is established that in crystals with not very high degree of purity this interaction can be neglected. However, in purer crystals it becomes important. The criteria when this interaction can be neglected, as well as the expected values of electrical conductivity, Seebeck coefficient and thermoelectric power factor limited by interchain interaction are determined.
Key words: thermoelectricity, electric conductivity, Seebeck coefficient, power factor, organic thermoelectric materials, tetrathiotetracene-iodide.

Introduction

Recent years have seen an increased number of publications devoted to investigation of thermoelectric opportunities of different organic materials. These materials have much more diverse and often unusual physical properties. As a rule, they have much lower thermal conductivity than the inorganic materials. It is expected that such materials will have much higher thermoelectric efficiency and will be less expensive in comparison with the known inorganic thermoelectric materials. Thus, exactly organic materials are good candidates for applications in the conversion of even a part of enormous low-grade waste heat into electrical energy.

From year to year the thermoelectric parameters of organic materials are improved. Now the highest measured value of the thermoelectric figure of merit at room temperature is $ZT = 0.57$ and was obtained in phenylacetylene-capped silicon nanoparticles [1]. The samples were prepared as pressed pellets. The measurements have shown very high value of Seebeck coefficient $S = 3228.8$ μV/K, modest electrical conductivity $\sigma = 18.1$ $\Omega^{-1} \cdot m^{-1}$, but low thermal conductivity $\kappa = 0.1$ W·m^{-1}·K^{-1}. This value of ZT is rather close to that of ordinary thermoelectric materials.

Many different organic materials are investigated in order to improve their thermoelectric properties. In [2] it was shown that the iodine-doped pentacene thin films can be potential candidates for good organic thermoelectric materials. In a bilayer structure composed of an intrinsic pentacene layer and an acceptor tetrafluoro-tetracyanoquinodimethane layer the value of the power factor $P = \sigma S^2 \sim 2.0$ μW/mK^2 was measured [3], when layer thickness was optimized. Doped acetylene with very high electrical conductivity of the order of 1.1×10^6 $\Omega^{-1} m^{-1}$, $S = 28$ μV/K and $\kappa = 0.7$ W·m^{-1}·K^{-1} has

demonstrated [4] $ZT = 0.38$ at room temperature. The problem is that this material is not stable, but this problem could be resolved in the future. In poly (3, 4-ethylenedioxythiophene) (PEDOT) the value of $ZT = 0.25$ was measured at room temperature with the parameters [5] $\sigma = 6700\ \Omega^{-1} \cdot m^{-1}$, $S = 220\ \mu V/K$, power factor $P = \sigma\ S^2 = 324\ \mu W \cdot m^{-1} \cdot K^{-2}$, $\kappa = 0.37\ W \cdot m^{-1} \cdot K^{-1}$, and the polymer is stable. It was also shown [6] that electrochemical doping, unlike chemical doping, allows better control of the oxidation level of polymer via tuning the electrode potential and measurement of the charging current, achieving in such a way improved thermoelectric properties.

The Japan Fujifilm Corp. announced in February 2013 about the development of a thermoelectric material (the site: greenoptimistic.com) using an organic polymer based on PEDOT with $ZT = 0.27$ and even higher. The material was elaborated in cooperation with Japan National Institute of Advanced Industrial Science and Technology. The advantages of this material are the low cost and that the converter module can be manufactured using printed technologies. A mini-review on the progress of poly (3, 4-ethylenedioxythiophene) (PEDOT)-based thermoelectric materials in recent years is presented in [7], where a $ZT \sim 1$ is predicted in this class of materials. In [8] both *n*-type and *p*-type organic thermoelectric materials have been developed with ZT values of 0.1 to 0.2 around 400 K. Thermoelectric module composed of 35 *n-p* couples was made which outputs a power of 2.8 $\mu W \cdot cm^{-2}$ (highest for organic thermal devices ever reported) under temperature difference of $\Delta T = 80$ K.

Several works about inorganic-organic TE composites have been reported [9-14]. However, the obtained values of ZT are still very low. Different theoretical models were presented for the description of thermoelectric transport in organic materials [15-18]. In molecular nanowires of conducting polymers the values of $ZT \sim 15$ at room temperature were predicted [18]. It is important that in this paper the charge and energy transport was described in the hopping model which is applied in the case of strong electron-phonon interaction and usually yields smaller conductivity than the band model. It is also predicted that the largest power factor can reach 500 $\mu W/cmK^2$ for PEDOT: PSS molecular chain, which is much larger than that for inorganic nanowires.

Still higher values of $ZT \sim 20$ were predicted by us [19-21] in highly conducting quasi-one dimensional (Q1D) charge transfer organic crystals. However, the above predictions were made in the frame of a strictly one dimensional physical model. Even if from the experimental data it is known that the interaction between molecular chains in Q1D crystals is weak, it is absolutely necessary to estimate the contribution of this interaction to the charge and heat transport.

The aim of present paper is to carry out a more detailed modeling of thermoelectric properties of tetrathiotetracene-iodide, TTT_2I_3 Q1D crystals, taking into account the interchain interaction. The results of paper [22] will be also verified in the frame of this more complete physical model. For simplicity the 2D crystal model is applied. It is established that in crystals with a low degree of purity this interaction can be neglected, because impurity scattering already limits carrier mobility. However, in purer crystals which allow higher values of ZT, this interaction becomes important. The criteria when this interaction can be neglected are determined. The expected values of electrical conductivity, the Seebeck coefficient and thermoelectric power factor limited by interchain interaction are also determined.

2. Two-dimensional crystal model for *TTT₂I₃*

The quasi-one-dimensional organic crystals of tetrathiotetracene-iodide, TTT_2I_3, are formed of segregate chains or stacks of planar molecules of tetrathiotetracene TTT, and iodine ions. This compound is of mixed-valence: two molecules of TTT give one electron to the iodine chain which is formed from I_3^- ions. Only TTT chains are electrically conductive and the carriers are holes. The

crystals admit nonstoichiometric composition of the form $TTT_2I_{3\pm\delta}$ with the surplus or deficiency of iodine. So as the iodine plays the role of acceptor, the hole concentration depends on the iodine content and may be higher or lower than stoichiometric concentration $n = 1.2 \times 10^{21}$ cm^{-3}. It is very important because in thermoelectric materials it is usually necessary to optimize carrier concentration in order to achieve maximum efficiency.

The crystals are named quasi-one-dimensional because the carriers are moving mainly along the conducting molecular chains and rarely jump from one chain to another. As a result, the electrical conductivity along the *TTT* chains is approximately by three orders of magnitude higher than in transversal to chains directions. The transport mechanism along the chains is of band type, whereas in the transversal direction is of hopping type. Due to this fact, earlier [23-25] we neglected the latest mechanism and considered a strictly one-dimensional crystal model. In other words, we neglected the possibility for a carrier to pass form one to another conducting chain. This approximation has permitted us to investigate the thermoelectric properties of these crystals in a simpler physical model. Now we will take into account this possibility, in order to determine how this new interaction will modify the previously estimated values of thermoelectric efficiency.

For simplicity we will consider two-dimensional crystal model. The charge and energy transport are described in the tight binding and nearest neighbors approximations. The energy of hole with the 2D quasi-wave vector **k** and projections (k_x, k_y) is of the form

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

The energy is measured form the upper margin of the conduction band, 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 axis x is directed along **b**, and y is in perpendicular direction. The condition of crystal quasi-one-dimensionality means that $w_2 \ll w_1$. The frequency of longitudinal acoustic phonons is given below

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

where 2D quasi-wave vector **q** has the projections (q_x, q_y), and ω_1 and ω_2 are the limit frequencies in the x and y directions, $\omega_2 \ll \omega_1$.

The two most important hole-phonon interactions considered earlier are completed by taking into account the interchain hopping of carriers. The first interaction is similar to that of deformation potential. The second interaction is similar to that of polaron, but is determined by induced polarization of molecules surrounding the conduction hole. The square of matrix element module of total interaction is of the form

$$\begin{aligned}|A(\mathbf{k},\mathbf{q})|^2 = 2\hbar / (NM\omega_q)\{w_1'^2[\sin(k_x b) - \sin((k_x - q_x)b) + \gamma_1 \sin(q_x b)]^2 + \\ + w_2'^2[\sin(k_y a) - \sin((k_y - q_y)a) + \gamma_2 \sin(q_y a)]^2\}\end{aligned} \tag{3}$$

Here N is the number of molecules in the basic region of the crystal, M is the mass of *TTT* molecule, w_1' and w_2' are the derivatives with respect to the intermolecular distance of the energies w_1 and w_2. In Eq. 3, the terms which depend on k_x and k_y describe the first interaction, and the terms which depend only on q_x and q_y describe the second interaction. The parameters γ_1 and γ_2 have the meaning of the ratios of amplitudes of second interaction to the first one along and in transversal direction to the chains

$$\gamma_1 = 2e^2\alpha_0 / (b^5 w_1'), \quad \gamma_2 = 2e^2\alpha_0 / (a^5 w_2') \tag{4}$$

where e is the carrier charge and α_0 is the average polarizability of *TTT* molecule. Note that so as w_1 and w_2 are positive and exponentially decrease with the increase of intermolecular distance, w_1' and w_2' will be negative, and γ_1 and γ_2 will be likewise negative.

Since the conduction band is not very large and the Debye temperature is relatively low, the variation of wave vectors **k** and **q** should be taken over the entire Brillouin zones for holes and phonons: $-\pi/b \leq k_x \leq \pi/b$, $-\pi/a \leq k_y \leq \pi/a$, $-\pi/b \leq q_x \leq \pi/b$, $-\pi/a \leq q_y \leq \pi/a$.

The impurity scattering of holes is also taken into account. The impurities are considered point like and neutral. In this case the impurity scattering rate is described by the dimensionless parameter D_0 which is proportional to impurity concentration and can be made very small, if the crystal purity is rather high.

3. Charge and energy transport

We will consider that a weak electrical field and temperature gradient are applied along the chains. In this case the kinetic equation for nonequilibrium distribution function can be linearized and it takes the form of the Boltzmann equation. Near room temperature we can neglect in the scattering process of a hole from the state **k** to **k** ± **q** the phonon energy and the transversal kinetic energy of the hole, because these energies are much less than the kinetic energy of the hole along the chains. Then the kinetic equation is solved analytically and the notion of relaxation time can be introduced as in 1D case. But now the relaxation time is a function of k_x and k_y

$$\tau(k_x, k_y) = \frac{\hbar M v_{s1}^2 w_1 |\sin(k_x b)|}{4 b^2 k_0 T w_1'^2 [(1 - \gamma_1 \cos(k_x b))^2 + D_0 + w_2'^2 (1 + \gamma_2^2 + 2\sin^2(k_y a) - 2\gamma_2 \cos(k_y a)) / (2 w_1'^2 \sin^2(k_x b))]}. \tag{5}$$

In deriving Eq. 5 the term proportional to $(b v_{s2} / a v_{s1})^2$ which comes from the phonon dispersion law and is much less than unity was neglected, where v_{s1} is the sound velocity along the chains and v_{s2} is the sound velocity in the direction perpendicular to chains, k_0 is the Boltzmann constant. Also, in Eq. 5 we have replaced the phonon distribution function N_q by its high temperature limit $N_q \cong k_0 T / \hbar \omega_q \gg 1$, so as near room temperature T_0 we have $\hbar \omega_q \ll k_0 T_0$. We have also changed the signs of γ_1 and γ_2. From here and further γ_1 and γ_2 are positive.

If in Eq. 5 the interchain interaction is neglected, i.e. if we put $w_2 = 0$, $w_2' = 0$, and $\gamma_2 = 0$, the previous results which correspond to 1D model are obtained. It is seen that the relaxation time has a maximum for values of k_x close to those for which the first term in the denominator of (5) is equal to zero. It means that for these values of k_x in the conducting band the two hole-phonon interactions mentioned above strongly compensate each other. In 1D case the height of relaxation time maximum is limited by parameter D_0, i.e. by the carrier scattering on impurity. Since the improvement of the thermoelectric properties is determined by the height of the relaxation time, it was recommended to increase the crystal purity in order to diminish D_0 and increase the maximum of relaxation time as much as possible. In 2D model the height of maximum is also limited by the interchain interaction. Now we have to determine the values of parameters, when the last interaction becomes more important. In this case the further purification of crystal in order to diminish D_0 will not improve the thermoelectric properties, because the interchain interaction already limits the height of relaxation time.

With the help of (5), the electrical conductivity along *TTT* chains σ_{xx}, the thermopower (Seebeck coefficient) S_{xx} and the power factor P_{xx} can be expressed through the transport integrals as follows

$$\sigma_{xx} = \sigma_0 R_0, \ \ S_{xx} = \left(k_0 / e\right)\left(2w_1 / k_0 T\right) R_1 / R_0, \ \ P_{xx} = \sigma_{xx} S_{xx}^2, \tag{6}$$

where
$$\sigma_0 = (2e^2 M v_{s1}^2 w_1^3 r) / (\pi^2 \hbar abc(k_0 T)^2 w_1'^2), \tag{7}$$

r is the number of chains through the transversal section of the unit cell and R_n are the dimensionless transport integrals

$$R_n = \int_0^2 d\varepsilon \int_0^\pi \frac{(\varepsilon - \varepsilon_F)^n \varepsilon (2 - \varepsilon) n_{\varepsilon,\eta} (1 - n_{\varepsilon,\eta}) d\eta}{\gamma_1^2 (\varepsilon - \varepsilon_0)^2 + D_0 + w_2'^2 (1 + \gamma_2^2 + 2\sin^2 \eta - 2\gamma_2 \cos \eta) / (2w_1'^2 \varepsilon (2 - \varepsilon))}. \tag{8}$$

Here, in order to obtain an expression for transport integrals (and also for relaxation time) closer to previous 1D case, we have introduced instead of k_x a new variable $\varepsilon = (1 - \cos(k_x b))$, where ε has the meaning of dimensionless kinetic energy of a hole along chains measured from the bottom of conduction band in units of $2w$ and $\varepsilon_0 = (\gamma_1 - 1)/\gamma_1$ has the meaning of resonance energy (in the same units) which corresponds to relaxation time maximum. Also, instead of k_y a dimensionless projection $\eta = k_y a$ was introduced, and $n_{\varepsilon,\eta}$ is the Fermi distribution function in the variables ε and η. If in Eq. 8 we put $w_2' = 0$, and $\gamma_2 = 0$, the previous results which correspond to 1D model are obtained.

Thermoelectric properties

Unfortunately, the thermoelectric properties can be investigated only numerically. Expressions (6) – (8) have been calculated for quasi-one-dimensional organic crystals of TTT_2I_3 with different degrees of purity. The crystal parameters are: $M = 6.5 \times 10^5 m_e$ (m_e is the mass of free electron), $a = 18.35$ Å, $b = 4.96$ Å, $c = 18.46$ Å, $v_{s1} = 1.5 \times 10^3$ m/s, $w_1 = 0.16$ eV, $w_1' = 0.26$ eVÅ^{-1}, $r = 4$. The parameters w_2 and w_2' were estimated in Ref. 26, $w_2 = 1.44 \times 10^{-3}$ eV and $w_2' = 2.34 \times 10^{-3}$ eVÅ^{-1}. The value of polarizability α_0 in TTT_2I_3 can be estimated approximately comparing with the known polarizabilities of other molecules of the same type. We have taken $\alpha_0 = 45$ Å^3, to which corresponds $\gamma = 1.7$, as in [22]. For γ_2 it follows that $\gamma_2 = \gamma_1 (a^5 w_1')/(b^5 w_2') = 3.47 \gamma_1$, i.e. $\gamma_2 = 5.9$.

For the parameter D_0 we will choose three values: 0.3 that corresponds to crystals grown by gas phase method [27] with $\sigma \sim 3500$ Ω^{-1}·cm^{-1}; 0.1 that corresponds to crystals grown by gas phase method in [28] with $\sigma \sim 10^4$ Ω^{-1}·cm^{-1} and 0.05 which corresponds to purer crystals with somewhat higher $\sigma \sim 1.7 \times 10^4$ Ω^{-1}cm^{-1}.

In Fig. 1 the dependences of electrical conductivity along chains σ_{xx} on the Fermi energy in units of $2w_1$ are presented for these values of D_0. In stoichiometric crystals of TTT_2I_3 the hole concentration is $n = 1.2 \times 10^{21}$ cm^{-3}, to which corresponds $\varepsilon_F \sim 0.37$. From Fig. 1 it is seen that the values of σ_{xx} calculated in more complete 2D model practically coincide with those calculated in 1D approximation for the entire interval of the Fermi energy variation. This means that for stoichiometric crystals, the more so for those with a lower carrier concentration needed for the improvement of thermoelectric properties, but with the same degree of purity, it is sufficient to apply the simpler 1D approximation.

In Fig. 2 the dependences of thermopower (Seebeck coefficient) S_{xx} on the Fermi energy at room temperature are presented. It is seen that for crystals with considered degree of purity the interchain interaction has even lower effect on thermopower than on σ_{xx}: the curves for 1D and 2D models coincide. This also means that, due to an additional factor $(\varepsilon - \varepsilon_F)$ in the numerator of integrand in (8), the value of relaxation time maximum has a lower effect on the thermopower than on the electrical conductivity. In Fig. 3 the dependences of the thermoelectric power factor P_{xx} on the

Fermi energy E_F are presented. It is seen that the curves for 1D and 2D models are very close to each other. For $\varepsilon_F = 0.2$ the value of P_{xx} is $\sim 1.4 \times 10^{-2}$ W/m·K^2, or 3.5 times higher than in Bi_2Te_3.
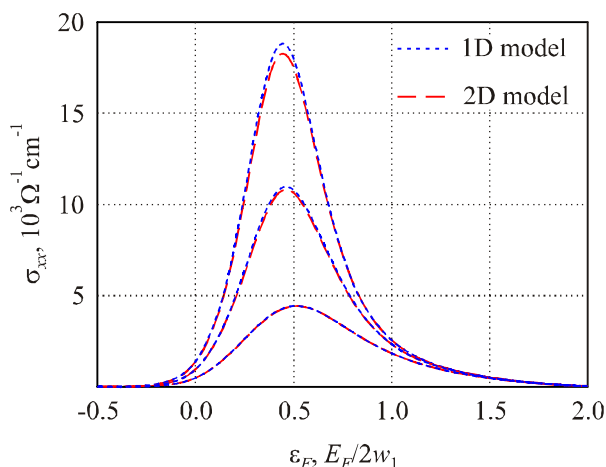

Fig. 1. Electrical conductivity along chains as a function of E_F for $\gamma = 1.7$: lower, middle and upper curves are for $D_0 = 0.3$, 0.1 and 0.05, respectively.

In order to determine when the interchain interaction becomes important, let's consider still more pure crystals of TTT_2I_3 with lower values of parameter D_0: 0.04, 0.03 and 0.02. To these values of D_0 and stoichiometric carrier concentration correspond $\sigma_{xx} \sim 2 \times 10^4$ Ω^{-1}·cm^{-1}, 2.5×10^4 Ω^{-1}·cm^{-1} and 3.2×10^4 Ω^{-1} cm^{-1}, respectively. Crystals of TTT_2I_3 with such a high degree of purity and, respectively, with such a high conductivity have not been synthesized yet, but it is possible in the future.
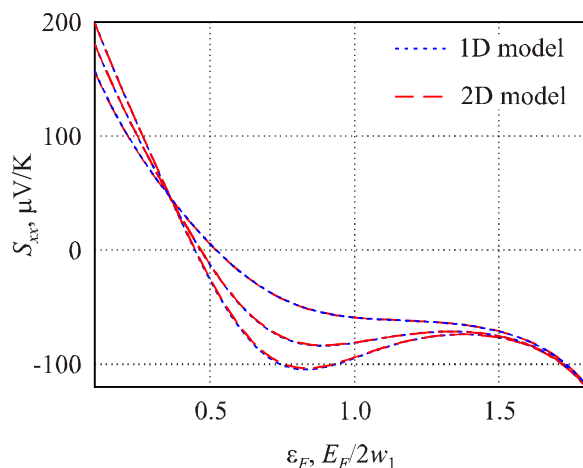

Fig. 2. Thermopower S_{xx} as a function of E_F: lower, middle and upper curves are for $D_0 = 0.05$, 0.1 and 0.3, respectively.
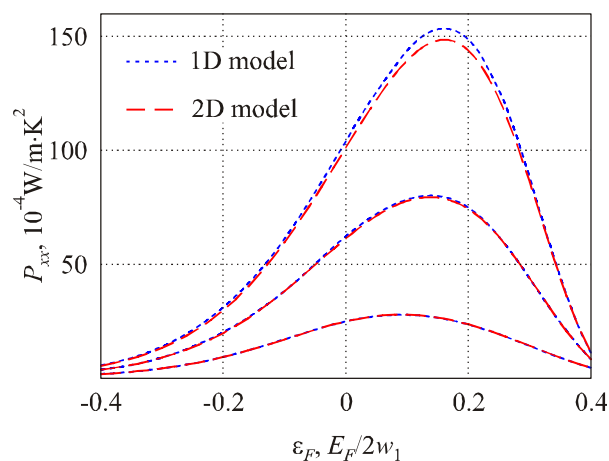
Fig. 3. Thermoelectric power factor as a function of E_F: lower, middle and upper curves are for $D_0 = 0.3$, 0.1 and 0.05, respectively.

In Fig. 4 the dependences of electrical conductivity along chains σ_{xx} on the Fermi energy are presented for these lower values of D_0. It is seen that now the deviations between 2D and 1D models are more significant, especially in the case of the purest crystals with $D_0 = 0.02$, when for stoichiometric crystals the value of conductivity in 2D model is by 10 % lower than in 1D one. But for crystals with ε_F around 0.2, needed in order to increase the power factor, the curves for 2D and 1D models practically coincide.
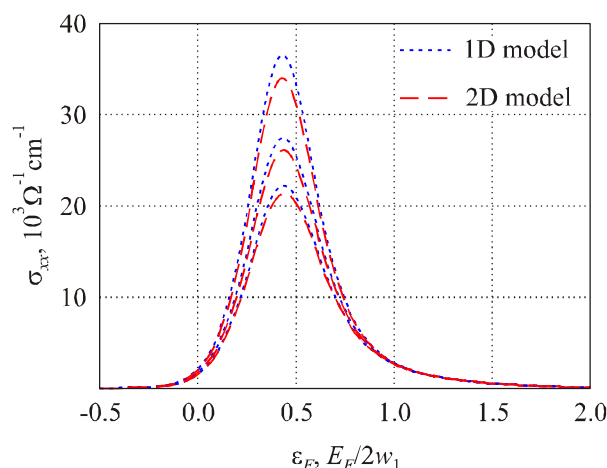
Fig. 4. Electrical conductivity along chains as a function of E_F: lower, middle and upper curves are for $D_0 = 0.04$, 0.03 and 0.02, respectively.

In Fig. 5 the dependences of thermopower S_{xx} on the Fermi energy are presented. As it was expected, in this case the deviations between 2D and 1D models are still smaller than for σ_{xx}, the dotted and dashed curves practically coincide, especially in the interval of ε_F between 0.2 and 0.4. This is an additional confirmation that the height of relaxation time maximum has a lower effect on S_{xx} than on σ_{xx}. In this case for the calculation of thermopower S_{xx} it is sufficient to apply the simpler 1D model.
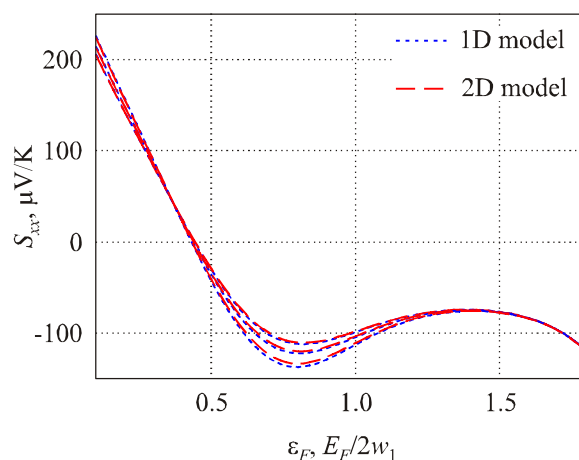

Fig. 5. Thermopower S_{xx} as a function of E_F: lower, middle and upper curves are for $D_0 = 0.02$, 0.03 and 0.04. respectively.

The dependences of the thermoelectric power factor P_{xx} on the Fermi energy are presented in Fig. 6. Now, the deviations between 2D and 1D models, accumulated from σ_{xx} and S_{xx}, have been increased, but to a little degree. So, even in the purest crystals with $D_0 = 0.02$ the maximum value of P_{xx} is lower in 2D case only by 10 %. Taking into account that the modeling error is also $\sim$ 10 %, we can conclude that for all crystals with degrees of purity considered here the simpler 1D physical model is applicable and previously predicted results for the improvement of the thermoelectric properties of TTT_2I_3 crystals are valid. Thus, in earlier synthesized crystals with $\sigma_{xx} \sim 10^4 \, \Omega^{-1} \cdot cm^{-1}$ [28] it is expected to obtain after optimization of carrier concentration a value of $P_{xx} \sim 8 \times 10^{-3}$ W/m·K^2 (see Fig. 3, the line with $D_0 = 0.1$), or twice higher than in Bi_2Te_3. In the purest crystals with $\sigma_{xx} \sim 3.2 \times 10^4 \, \Omega^{-1} \cdot cm^{-1}$ for stoichiometric compounds, the maximum value of P_{xx} is expected to be $\sim 3.2 \times 10^{-2}$ W/m·K^2 (see Fig. 6, the line with

$D_0 = 0.02$), or 8 times higher than in Bi_2Te_3. To this value of P_{xx} correspond $\sigma_{xx} = 9 \times 10^3 \, \Omega^{-1} \cdot cm^{-1}$ and $S_{xx} = 190 \, \mu V/K$. It is very good predicted result. Of course, for crystals with still higher degree of purity the interchain interaction must be taken into account.
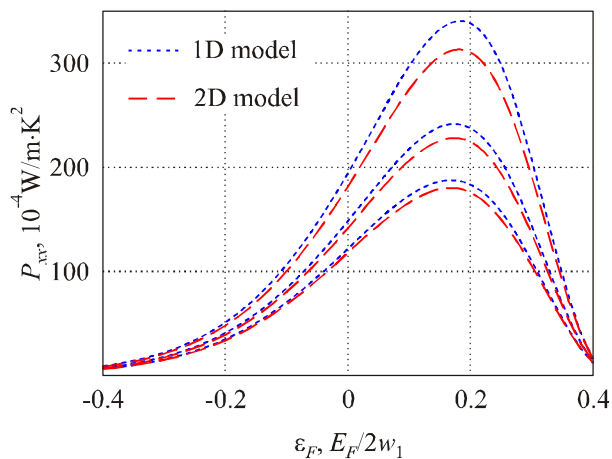

Fig. 6. Thermoelectric power factor as a function of E_F: lower, middle and upper curves are for $D_0 = 0.04$, 0.03 and 0.02, respectively.

Conclusions

The investigations of new organic materials for thermoelectric applications published in the last two years are analyzed. Organic materials attract the increasing attention of investigators. These materials are expected to have higher efficiency and to be less expensive than the known inorganic ones. The highest measured value of the thermoelectric figure of merit ZT at room temperature is $ZT = 0.57$ and was obtained in phenylacetylene-capped silicon nanoparticles. This value of ZT is rather close to that of ordinary thermoelectric materials. In poly (3, 4-ethylenedioxythiophene) (PEDOT) the value of $ZT = 0.25$ has been measured with the parameters [5] $\sigma = 6700 \, \Omega^{-1} \cdot m^{-1}$, $S = 220 \, \mu V/K$, power factor $P = \sigma \cdot S^2 = 324 \, \mu W \cdot m^{-1} \cdot K^{-2}$, thermal conductivity $\kappa = 0.37 \, W \cdot m^{-1} \cdot K^{-1}$, and the polymer is stable. $ZT \sim 1$ is predicted in this class of materials [7]. Several works on inorganic-organic TE composites have been reported, however, the obtained values of ZT are still very low. Different theoretical models were also presented. It is interesting that in molecular nanowires of conducting polymers the values of $ZT \sim 15$ at room temperature were predicted [18] in spite of hopping conduction mechanism. Earlier we have predicted in quasi-one-dimensional organic crystals even higher values of ZT at room temperature. However, this and above predictions were made in the frame of a strictly one-dimensional crystal model. In the present paper, we have taken into account the possibility for a carrier to pass from one molecular chain to another in the frame of a two-dimensional physical model. The crystals of tetrathiotetracene-iodide, TTT_2I_3 are considered. It is shown that in crystals with not very high degree of purity this additional interaction can be neglected, because impurity scattering already limits carrier mobility. The predicted parameters in this case are: $\sigma_{xx} = 9 \times 10^3 \, \Omega^{-1} \cdot cm^{-1}$, $S_{xx} = 190 \, \mu V/K$ and $P_{xx} = 3.2 \times 10^{-2} \, W/m \cdot K^2$, or 8 times higher than in Bi_2Te_3. For TTT_2I_3 it is possible to neglect the interchain interaction and to apply 1D approximation for stoichiometric crystals with electrical conductivity along the chains up to $\sigma_{xx} \sim 4 \times 10^4 \, \Omega^{-1} \cdot cm^{-1}$ or a little higher. However, in purer crystals with higher values of σ_{xx}, the interchain interaction becomes important.

References

1. S.P. Ashby, J. Garcia-Canadas, G. Min, and Y. Chao, Measurement of Thermoelectric Properties of Phenylacetylene-Capped Silicon Nanoparticles and Their Potential in Fabrication of Thermoelectric Materials, *JEM*, DOI: 10.1007/s11664-012-2297-x (2012).

2. K. Hayashi, T. Shinano, Y. Miyazaki and T. Kajitani, Fabrication of Iodine-Doped Pentacene Thin Films for Organic Thermoelectric Devices, *J. Appl. Phys*. **109**, 023712, 2011.

3. K. Harada, M. Sumino, C. Adachi, S. Tanaka and K. Miyazaki, Improved Thermoelectric Performance of Organic Thin-Film Elements Utilizing a Bilayer Structure of Pentacene and 2, 3, 5, 6-tetrafluoro-7, 7, 8, 8-tetracyanoquinodimethane (F4-TCNQ), *Appl. Phys. Lett*. **96**, 253304, 2010.

4. Y. Xuan, et al., Thermoelectric properties of Conducting Polymers: The Case of Poly (3-hexylthiophene), *Phys. Rev*. **B 82,** 115454, 2010.

5. O. Bubnova, et al., Optimization of the Thermoelectric Figure of Merit in the Conducting Polymer Poly (3,4-Ethylenedioxythiophene), *Nature Materials* **10**, 429, 2011. DOI: 10.1038/NMAT3012.

6. O. Bubnova, M. Berggren, and X. Crispin, Tuning the Thermoelectric Properties of Conducting Polymers in an Electrochemical Transistor, *J. Am. Chem. Soc*. **134,** 16456 (2012).

7. R. Yue and L. Xu, Poly (3, 4-ethylenedioxythiophene) as Promising Organic Thermoelectric Materials: A Mini-Review, *Synt. Met*. **162**, 912 (2012).

8. Y. Sun et al., Organic Thermoelectric Materials and Devices Based on *p*- and *n*-type Poly (metal 1, 1, 2, 2-ethenetetrathiolate)s, *Adv. Mater*. **24**, 932 (2012).

9. Y.Y. Wang, K.F. Cai, J.L. Yin, B.J. An, Y. Du, and X. Yao, In Situ Fabrication and Thermoelectric Properties of *PbTe*-polyaniline Composite Nanostructures, *J. Nanopart Res*. **13**, 533 (2011).

10. W.Q. Ao, L. Wang, J.Q. Li, F. Pan, and C.N. Wu, Synthesis and Characterization of Polythiophene/Bi_2Te_3 Nanocomposite Thermoelectric Material, *J. Electron. Mat*. **40**, 9(2011).

11. N. Toshima, N. Jiravanichanun, and H. Marutani, Organic Thermoelectric Materials Composed of Conducting Polymers and Metal Particles. *J. Electron. Mat*. **41**, 6 (2012).

12. Y. Wang, K. Cai, and X. Yao, Facile Fabrication and Thermoelectric Properties of *PbTe*-Modified Poly (3, 4-ethylenedioxythiophene) Nanotubes, *ACS Appl. Mater. Interfaces* **3**, 1163 (2011).

13. J. Carrete, N. Mingo, G. Tian, H. Agren, A. Baev, and P.N. Prasad, Thermoelectric Properties of Hybrid Organic-Inorganic Superlattices, *The Journal of Physical Chemistry C*, **116** (20), 10881 (2012).

14. C. Yu, K. Choi, L. Yin, and J.C. Grunlan, Light-Weight Flexible Carbon Nanotube Based Organic Composites with Large Thermoelectric Power Factors, *ACS Nano*, **5** (10), 7885 (2011).

15. G. Kim and K.P. Pipe, Thermoelectric Model to Characterize Carrier Transport in Organic Semiconductors, *Phys. Rev. B* **86**, 085208 (2012).

16. D.S. Dudis, J.D. Ferguson, M. Check, J.E. Schmidt, E.R. Kemp, T. Robbins, J.A. Shumaker, G. Chen, H.A. Seibel, Multidimensional Nanoscopic Approaches to New Thermoelectric Materials, *Proc. SPIE* 76830S (2010).

17. J. Chen, D. Wang, Z. Shuai, First-Principles Predictions of Thermoelectric Figure of Merit for Organic Materials: Deformation Potential Approximation, *J. Chem. Theory Comput*. **8** (9), 3338 (2012).

18. Y. Wang, J. Zhou, and R. Yang, Thermoelectric Properties of Molecular Nanowires, *J. Phys. Chem. C* **115**, 24418 (2011).

19. Casian, Z. Dashevsky, H. Scherrer, V. Dusciac, and R. Dusciac, *Proc. of 22nd Intern. Conf. on Thermoel.,* La Grande-Motte, France (IEEE, Piscataway, NJ, 2004), p. 330-335.A. Casian, in:

Thermoelectric Handbook, Macro to Nano, Ed. by D.M. Rowe, CRC Press, 2006, Chap.36.

20. Casian, Prospects of the Thermoelectricity Based on Organic Materials, *J. Thermoelectricity* **3**, 45-50 (2007).

21. A.I. Casian, B.M. Gorelov, and I.V. Dubrovin, State of the Art and Prospects of Thermoelectricity on Organic Materials, *J. Thermoelectricity* **3**, 7-16 (2012).

22. Casian, V. Dusciac and Iu. Coropceanu, Huge Carrier Mobilities Expected in Quasi-One-Dimensional Organic Crystals. *Phys. Rev.* **B 66**, 165404 (2002).

23. Casian, V. Dusciac, and V. Nicic, Thermoelectric Opportunities of Quasi-One-Dimensional Organic Crystals of Tetrathiotetracene-Iodide, *J. Thermoelectricity* **2**, 33-39 (2009).

24. Casian, J. Stockholm, V. Dusciac, and V. Nicik, Low-Dimensional Organic Crystal Tetrathiotetracene-Iodide as Thermoelectric Material: Reality and Prospects, *J. Nanoelectronics and Optoelectronics* **4**, 95-100 (2009).

25. Casian, I. Sanduleac, Effect of Interchain Interaction on Electrical Conductivity in Quasi-One-Dimensional Organic Crystals of Tetrathiotetracene-Iodide, *J. Nanoelectronics and Optoelectronics* **7**, 706-711 (2012).

26. I.C. Isset, Magnetic Susceptibility, Electrical Resistivity and Thermoelectric Power Measurements of Bis(tetrahtiotetracene)-Triiodide, *Phys. Rev.* **18**, 439 (1978)

27. Hilti and C.W. Mayer, Electrical Properties of the Organic Metallic Compound bis (Tetrathiotetracene)-Triiodide, $(TTT)_2I_3$, *Helvetica Chimica Acta* **61** (40), 501 (1978).

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