

THERMOELECTRIC PROPERTIES OF NANOSTRUCTURED TETRATHIOTETRACENE IODIDE CRYSTALS WITH HIGH DEGREE OF PERFECTION

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Abstract: Nanostructured Tetrathiotetracene Iodide Crystals (TTT_2I_3) are very promising materials for thermoelectric applications, as it was predicted earlier. Initially, we have considered a more simplified one-dimensional (1D) physical model. For transport along conductive chains in crystals with rather low purity, the effect of interaction of carriers with the nearest chains is negligible in comparison with the scattering on impurities. For ultra-pure crystals, the effect of impurities on charge transport along a molecular chain becomes rather small, and the effect of interchain interaction stands out. In order to verify these conclusions, a two-dimensional (2D) model is elaborated which explicitly takes into account the weak interaction of carriers with the nearest conductive chains.

Keywords: Tetrathiotetracene-Iodide, Organic Crystals, Impurity, Quasi-one-dimensional, Interchain Interaction, Thermoelectric figure of merit.

1. Introduction

The most acute problems of the humanity are the deficiency of energy and the environmental preservation. The statistic shows that a big percentage of required global energy is wasted as low-level heat and the recovery of even a part of this widespread available energy is a very promising perspective in its economy. Contemporary thermoelectric devices based on inorganic structures, are very expensive technologically and not very friendly with environment to be applied in this purpose. Organic thermoelectric devices, using low-cost, readily available, renewable and sustainable organic materials will open new perspectives. The investigations of these materials show very promising results and the reported thermoelectric figure of merit of different nanostructured organic systems increases from one year to another.

As example, in poly (3, 4-ethylenedioxy-thiophene) (PEDOT) a value of $ZT = 0.25$ has been measured [1] and $ZT = 0.42$ at room temperature was obtained [2] in PEDOT: PSS. It is predicted that in this class of materials $ZT = 1$ can be achieved [3]. The highest thermoelectric figure of merit reported from direct measurements is $ZT = 0.57$ for phenylacetylene-capped silicon nanoparticles [4]. This value is rather close to $ZT \sim 1$, which is characteristic for the best inorganic bulk TE material Bi_2Te_3 near room temperature.

Highly conducting quasi-one-dimensional (Q1D) organic crystals are very promising for TE applications, as they combine the advantages of multi component systems with that of low dimensional one. Theoretically, it was shown that TTT_2I_3 crystals have prospect thermoelectric applications [5, 6].

2. Physical 2D model of the crystal

The structure of Q1D organic crystals of tetrathiotetracene – iodide (TTT_2I_3) is briefly described in [7]. The crystals have needle shape and consist of segregate stacks or chains of planar TTT molecules and I_3^- ions. Only TTT chains are conductive, due to large overlap of TTT π -orbitals along the chains. The overlap of orbitals between neighboring TTT chains is very small. Therefore, the conduction mechanism along TTT chains is band-like and between the chains this mechanism is of hopping type. Respectively, the electrical conductivity along the molecular chains is almost by three orders of magnitude higher than in the transversal direction.

Due to this fact, earlier [7-8] the possibility for a carrier to pass from one conducting chain to another was neglected and the transport was considered in a 1D conduction band. Now it will be estimated the effect of interchain interaction and the restrictions on thermoelectric efficiency that this interaction involves. The tetrathiotetracene iodide crystals admit non-stoichiometric compound of the form $TTT_2I_{3\pm\delta}$. This property allows improving ZT figure of merit by varying iodine concentration.

The Hamiltonian of the system has the form:

$$H = \sum_{\mathbf{k}} \varepsilon(\mathbf{k}) a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}} + \sum_{\mathbf{k}, \mathbf{q}} [A(\mathbf{k}, \mathbf{q}) a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}-\mathbf{q}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^{\dagger})] \quad (1)$$

where $\varepsilon(\mathbf{k})$ is the energy of carrier with the 2D quasi-wave vector, $\omega_{\mathbf{q}}$ is the frequency of longitudinal acoustic phonons, $A(\mathbf{k}, \mathbf{q})$ is the matrix element describing hole-phonon interaction. The last is introduced by two main mechanisms: the deformation of lattice potential, due to the variation of transfer energies and the induced polarization of molecules surrounding the conducting hole.

The two interaction mechanism mentioned above interferes, and under special condition, they may compensate each other. In this case, the hole scattering probability is reduced for certain states in the conduction band. This leads to an increase of relaxation time, until it attains maximum and, consequently the thermoelectric coefficients increase too. In the earlier approximation (1D), the maximums were limited only by the impurity scattering of carriers. Recently, it was demonstrated the additionally limitation of maximum due to the hole interaction with neighboring molecular chains [10, 12].

The dispersion equations of free carriers in the periodic field of the lattice and that of phonons have the form:

$$\varepsilon(\mathbf{k}) = 2w_1 \cos(k_x b) + 2w_2 \cos(k_y a) \quad (2)$$

$$\omega_{\mathbf{q}}^2 = \omega_1^2 \sin^2(q_x b/2) + \omega_2^2 \sin^2(q_y a/2) \quad (3)$$

here we have introduced the bi-dimensionality for both dispersion equations. w_1 and w_2 are the transfer energies (or resonance integrals) of a hole between the nearest neighbor molecules along and between the chains, $w_2 \ll w_1$ as a consequence of the quasi-one-dimensionality of the system under study; ω_1 and ω_2 are the limit frequencies in the x and y directions, $\omega_2 \ll \omega_1$. The impurity parameter D_0 is described by the equation [11]

$$D_0 = n_{im}^{2D} I^2 d_x^2 d_y^2 \frac{M v_s^2}{4b^3 a w_1^2 k_0 T} \quad (4)$$

where n_{im} represent the 2D concentration on impurities, I , d_x , d_y are the effective height and widths of the impurity potential in x and y direction, v_s is the velocity of sound along the chains. The parameters γ_1 and γ_2 are the relative amplitudes of the second interaction with respect to the first one along the x and y directions, respectively.

3. Numerical Results

Numerical calculations of thermoelectric coefficients for the TTT_2I_3 crystals are presented below. Crystal parameters are: $M = 6.5 \cdot 10^5 m_e$ (where m_e is free electron mass), $a = 18.46 \text{ \AA}$, $b = 4.97 \text{ \AA}$, $c = 18.35 \text{ \AA}$, $v_{s1} = 1.5 \cdot 10^3 \text{ m/s}$, $w_1 = 0.16 \text{ eV}$, $w_1' = 0.26 \text{ eV \AA}^{-1}$, $r = 4$, [7]. From experimental measurements, the conductivity in the transversal direction is by three orders of magnitude smaller than in the longitudinal direction, $\sigma_{yy}/\sigma_{xx} \sim 10^{-3}$. This result is used to estimate the parameters $w_2 = 1.44 \cdot 10^{-3} \text{ eV}$ and $w_2' = 0.01 \cdot w_1'$ [9]. For the polarizability of the TTT molecule we have taken $\alpha_0 = 42 \text{ \AA}^3$ [10]. This value corresponds to the parameters $\gamma_1 = 1.6$ and $\gamma_2 = \gamma_1 b^5 / (a^5 d) = 5$.

Electrical conductivity along the molecular chains as function of dimensionless Fermi energy is presented in Fig.1. The small displacement between maximums in the direction of lower ε_F is explained by the small increase of the Fermi energy, for the same hole concentration, due to the interaction with neighbouring chains. For impurity parameter $D_0 > 0.02$, the 1D model is applicable. For values of D_0 smaller than the mentioned above, the interaction between chains becomes significantly.

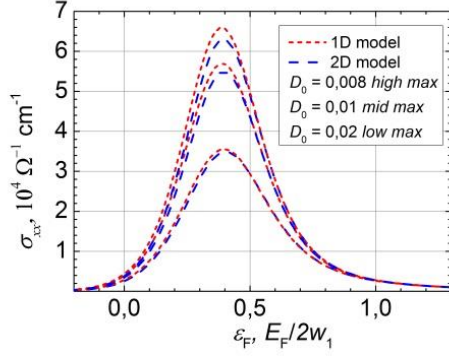


Fig.1. Electrical conductivity as function of dimensionless Fermi energy $\varepsilon_F = E_F / 2w_1$ for different D_0 .

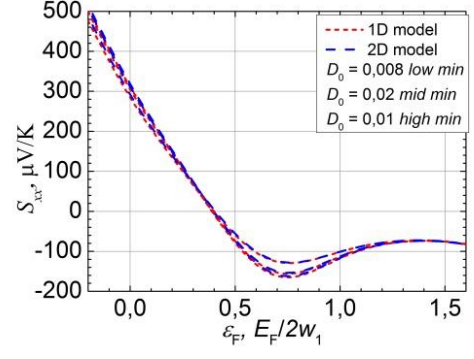


Fig.2. Seebeck coefficient S_{xx} as function of dimensionless Fermi energy $\varepsilon_F = E_F / 2w_1$ for different D_0 .

In Fig.2, the thermoelectric power as function of dimensionless Fermi energy for different impurity parameter at room temperature is considered. Seebeck coefficient is less influenced by the small interchain interaction, in comparison with electrical conductivity. In the positive region S_{xx} takes rather high values and the charge transport is provided by holes. At ε_F that corresponds to maximum of sigma, S_{xx} takes value zero.

For $\varepsilon_F \sim 0.33$, when $D_0 = 0.008, 0.01, 0.02$, Seebeck coefficient has practically the same values for both 1D and 2D models: $S_{xx} = 69 \mu\text{V/K}$ for 1D model and $74 \mu\text{V/K}$ for 2D one. When D_0 increases, the differences between models are smaller. Thus, for Seebeck coefficient 1D model is applicable also for crystals with high degree of purity.

In Figs.3, 4, the power factor and electronic thermal conductivity for TTT_2I_3 crystals along the molecular wire are presented for $T = 300 \text{ K}$.

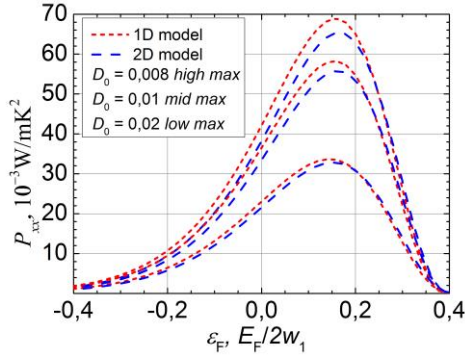


Fig.3. Power factor P_{xx} , as function of dimensionless Fermi energy $\varepsilon_F = E_F / 2w_1$ for different D_0 .

For power factor, the differences between 2D and 1D model are more pronounced. For stoichiometric concentrations, and low impurity scattering ($D_0 = 0.008, 0.01, \text{ and } 0.02$), the power factor achieves the following values in the frame of 1D and 2D models respectively: $P_{xx} = (13 \text{ and } 14.8, 11 \text{ and } 12.8, 6.8 \text{ and } 7.8) \cdot 10^{-3} \text{ W/mK}^2$. Experimentally obtained values for power factor for different bismuth telluride Bi_2Te_3 compounds varies in the range: $P = 32.6 \div 55.3 \cdot 10^{-4} \text{ W/mK}^2$ [12]. From Fig.3 it is seen that maximum values for power factor are ~ 5 times higher (when $D_0 = 0.02$) and more than 16 times higher for quite pure crystals ($D_0 = 0.008$) that values mentioned above [12] for Bi_2Te_3 . Thermal conductivity is, on the contrary, less influenced by interchain interaction, even for rather pure crystals. The κ_{xx}^e maximums are slightly displaced in comparison with maximums for σ_{xx} . This situation leads to

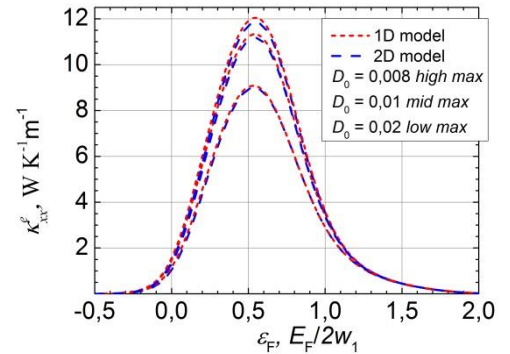


Fig.4. Electronic thermal conductivity, κ_{xx}^e as function of dimensionless Fermi energy $\varepsilon_F = E_F / 2w_1$ for different D_0 .

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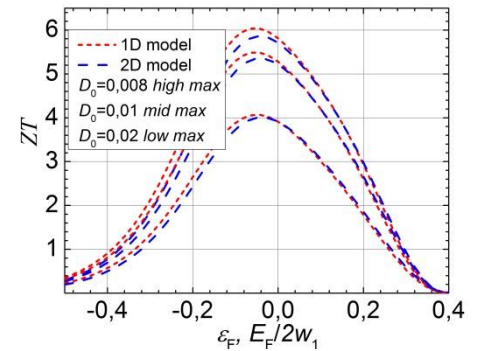


Fig.5. Thermoelectric figure of merit, ZT as function of dimensionless Fermi energy $\varepsilon_F = E_F / 2w_1$ for different D_0 .

the violation of the Wiedemann-Franz law in TTT_2I_3 crystals [13] and is favorable for the improvement of thermoelectric properties.

In Fig.5, the thermoelectric figure of merit ZT as function of dimensionless Fermi energy is presented. The charge transport is provided by holes. A small displacement of maximums, for 2D model versus 1D model, in the direction of higher ε_F is noticed. In stoichiometric crystals ($\varepsilon_F = 0.33$), ZT is very small – less than 0.2. In order to increase ZT it is necessary to decrease the Fermi energy, i.e. to diminish the carrier concentration. This diminution of Fermi energy is possible because TTT_2I_3 admits non-stoichiometric compounds with surplus and deficiency of iodine. It is seen that a diminution of Fermi energy even by 1.5 times leads to very promising results: for $\varepsilon_F \sim 0.2$, $ZT = 1.8, 2.6$ and 3 for $D_0 = 0.02, 0.01$ and 0.008 , respectively. In addition to the others thermoelectric coefficient, the largest contribution to the increase of ZT comes from the high values of the power factor (Fig. 3).

4. Conclusions

The bi-dimensional physical model for TTT_2I_3 crystals, which takes into account the weak interchain interaction and its influence on the transport coefficients, is presented. Also, the effect of scattering on impurities and defects is considered through the parameter D_0 . It is demonstrated that for D_0 higher than 0.02, the effect of interaction of carriers with the neighboring one-dimensional (1D) conductive chains may be neglect while for rather pure crystals this interaction becomes significantly. It was noted a small displacement between maximums of thermoelectric coefficients in 1D and 2D models due to the increase of Fermi energy when the influence of neighboring conductive chain is considered. Very promising results for thermoelectric applications are predicted.

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