

TTT₂I₃ organic crystals: 3D modeling of thermoelectric properties

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Abstract — It was demonstrated theoretically, that organic crystals of TTT₂I₃ (tetrathiotetracene-iodide) are very prospective thermoelectric materials. The internal structure is strongly quasi-one-dimensional and the thermoelectric transport takes place mainly along the molecular chains of TTT. Numerical results, obtained initially in the frame of the simplified one-dimensional (1D) physical model are very promising. In the 1D model, the weak interaction between the conductive TTT molecular chains is neglected. In order to define more precisely the criteria of applicability of the 1D model, the more complete 3D physical model was elaborated. It is shown that for crystals with rather low degree of purity the scattering on impurities and defects predominates on the scattering on nearest neighbor chains and the 1D model is applicable. For ultra-pure crystals, the interchain interaction becomes important and the transport phenomena should be generalized for the 3D case. Also, it is shown that for diminished carrier concentration and rather pure crystals, the thermoelectric figure of merit may achieve rather high values.

Index Terms — molecular chain, tetrathiotetracene iodide, thermoelectric materials, three-dimensional crystal model, thermoelectric figure of merit.

I. INTRODUCTION

In the context of rapid development of technology and industry, the energy requirements of the humanity are growing rapidly. At present most of the required energy is obtained from coal, oil, nuclear energy and other sources. But a big part of this energy is lost as low level heat. The recuperation and the saving of even a part of this lost thermal energy is an important and urgent problem. In this area, the thermoelectric devices, destined to transform directly the heat into electrical energy, are very attractive. The search and investigation of new more efficient and cheaper materials for such devices is an important problem of solid state physics. The recent investigations on nanostructured organic thermoelectric materials have shown that they are very prospective for the mentioned above aim. Such materials join together the peculiarities of low-dimensional systems and of multi-component materials with more diverse and complicated interactions. The main requirement is a big thermoelectric figure of merit, ZT . It increases when the electrical conductivity and thermopower are increased and the thermal conductivity and the Lorenz number are diminished. This phenomenon represents the violation of the Wiedemann-Franz law, and was predicted earlier for quasi-one-dimensional organic crystals [1]. In recent years, the investigations of different organic, inorganic and mixed compounds have given very good results. Poly (3,4-ethylenedioxythiophene) (PEDOT) doped by poly (styrenesulphonate) (PSS) is promising as an organic-based thermoelectric material due to its stability in air and very high electrical conductivity (measured over $3 \cdot 10^3 \Omega^{-1} \text{cm}^{-1}$). The maximum $ZT = 0.42$ has been achieved by minimizing the total dopant volume in p – type and $ZT = 0.2$ in n – type materials [2-4]. Mixed nanostructures, as

phenyl acetylene-capped silicon nanoparticles, have been shown values of $ZT = 0.57$ at room temperature [5].

Tetrathiotetracene-iodide organic crystals (TTT₂I₃) are very promising thermoelectric materials. Values of $ZT \sim 20$ have been predicted in highly conducting organic crystals, if the purity is sufficiently high [6], assuring huge carrier mobility. However, these predictions were made in the frame of somewhat simplified strictly one-dimensional crystal model, where the movement of the charge carriers is considered only along the conductive molecular chains. Further, in the 2D model [7] it was demonstrated that for crystals with high degree of purity, the weak interchain interaction becomes important and needs to be considered. In this paper, the numerical modeling for electronic thermal conductivity, figure of merit and Lorenz number is generalized for the three-dimensional case (3D). The criteria of applicability of the 1D model are also determined.

II. 3D PHYSICAL MODEL: THEORETICAL NOTES

Tetracene organic molecules (TTT) are arranged in linear chains spaced at approx. 1 nm one from other. In combination with iodine, a CT-complex (charge-transfer complex) is obtained: two TTT molecules give one electron to iodine chain and the charge transport is provided mainly by the holes, since the electrical conductivity of iodine chains is very low. A brief description of crystal structure is presented in [7, 8]. The atoms in molecule are bonded with covalent forces, which are much stronger than the interaction between adjacent molecules. For thermoelectric applications we assume that the electric fields and temperature gradients are weak, so the molecular energetic levels are not excited and the molecules may be considered point-like. In the direction along the molecular chains (further considered as x direction), the overlap of π -orbitals

generates a narrow conduction band with the width of 0.64 eV. In the transversal directions (y and z) the carriers transfer energies are quite small ($w_2 \approx w_3 = 0.0024$ eV). Two charge transport mechanisms are considered: of the band-type in the x direction and of the hopping type in the y and z directions.

The Hamiltonian of the system was described in [7, 9] for the 2D model. Now it has the form:

$$H = \sum_k E(k) a_k^+ a_k + \sum_q \hbar \omega_q b_q^+ b_q + \sum_{k,q} A(k,q) a_k^+ a_{k+q} (b_q + b_{-q}^+) + \sum_{n,j} IV_0 a_j^+ a_j \delta(r_n - r_j) \quad (1)$$

The tight binding electrons and the nearest neighbors' approximations are considered. The energy of holes in the 3D case, measured from the top of the conduction band is:

$$E(\mathbf{k}) = -2w_1[1 - \cos(k_x b)] - 2w_2[1 - \cos(k_y a)] - 2w_3[1 - \cos(k_z c)] \quad (2)$$

where k_x, k_y, k_z are the projections of quasi-wave vector \mathbf{k} , w_1, w_2, w_3 are the transfer energies of holes. a, b and c are the lattice constants.

There are 3 branches of phonon dispersion, one is for longitudinal and two other are for bend vibrations. The latest are neglected because they give small contribution. The frequency of longitudinal acoustic phonons is

$$\omega_q^2 = \omega_1^2 \sin^2(q_x b/2) + \omega_2^2 \sin^2(q_y a/2) + \omega_3^2 \sin^2(q_z c/2) \quad (3)$$

where ω_1, ω_2 and ω_3 are limit frequencies in the x, y and z directions, (q_x, q_y, q_z) are the projections of the quasi-wave vector \mathbf{q} , $\omega_2 \approx \omega_3 \ll \omega_1$.

There are two main hole-phonon interaction mechanisms, considered in the matrix element $A(\mathbf{k}, \mathbf{q})$ from (1). The first mechanism is of the deformation potential type, determined by the variation of transfer energy with respect to the intermolecular distance and the second is similar to that of polaron, with coupling constant of interaction proportional to the mean polarisability of the molecules, α_0 .

$$|A(\mathbf{k}, \mathbf{q})|^2 = 2\hbar/(NM\omega_q) \times \{w_1'^2 [\sin(k_x b) - \sin(k_x - q_x, b) + \gamma_1 \sin(q_x b)]^2 + w_2'^2 [\sin(k_y a) - \sin(k_y - q_y, a) + \gamma_2 \sin(q_y a)]^2 + w_3'^2 [\sin(k_z c) - \sin(k_z - q_z, c) + \gamma_3 \sin(q_z c)]^2\} \quad (4)$$

here w_1', w_2', w_3' are the derivatives of transfer energies (2) with respect to intermolecular distances, M is the mass of TTT molecule.

The ratio of amplitudes of polaron-type interaction to the deformation potential one in the x, y and z directions are described by the parameters γ_1, γ_2 and γ_3 :

$$\gamma_1 = 2e^2 \alpha_0 / (b^5 w_1'), \quad \gamma_2 = 2e^2 \alpha_0 / (a^5 w_2'), \quad \gamma_3 = 2e^2 \alpha_0 / (c^5 w_3') \quad (5)$$

The last term in (1) describes the scattering of charge carriers on point-like, electric neutral and randomly distributed impurity centers; I is the energy of hole-impurity interaction and V_0 is the volume of interaction region. The summation is provided on all the impurity

centers in the base region of the crystal.

III. TRANSPORT MECHANISMS

The kinetic equation is linearized and solved analytically assuming the condition of weak electric field and low temperature gradient. At room temperature, the scattering processes are considered elastic, since $\hbar\omega_q \ll k_0 T_0$. The probability of carrier scattering is

$$W(\mathbf{k}, \mathbf{k}') = 2\pi k_0 T / (\hbar^2 \omega_q |A(\mathbf{k} + \mathbf{q}, \mathbf{q})|^2) \times \delta[\varepsilon(k_x + q_x) - \varepsilon(k_x)] \quad (6)$$

It was neglected in the law of energy conservation during the carrier scattering the contributions of terms containing w_2 and w_3 in comparison with the kinetic energy along the chain, $w_2, w_3 \ll w_1$.

The relaxation time of carriers is expressed through the probability of scattering as:

$$\tau(\mathbf{k})^{-1} = 2 \sum_q W_{\mathbf{k}+\mathbf{q}, \mathbf{k}} \quad (7)$$

The summation may be replaced with the integral. Two parameters are introduced: $d_1 = w_2/w_1 = w_2'/w_1'$ and $d_2 = w_3/w_1 = w_3'/w_1'$:

$$\tau(\varepsilon, k_y, k_z) = \frac{\hbar M v_{s1}^2 w_1}{a^2 w_1'^2 k_0 T} (2\varepsilon - \varepsilon^2)^{1.5} / \{\gamma_1^2 (\varepsilon - \varepsilon_0)^2 + d_1^2 [1 + 2\sin^2(k_y b) - 2\gamma_2 \cos(k_y b) + \gamma_2^2] / 2 + d_2^2 [1 + 2\sin^2(k_z c) - 2\gamma_3 \cos(k_z c) + \gamma_3^2] / 2 + D_0\} \quad (8)$$

here v_{s1} is the sound velocity along the chains and $\varepsilon = E(k_x)/2w_1$ is the energy of hole moving along the x-direction.

The expression (8) has a maximum for states near $\varepsilon = \varepsilon_0 = (\gamma_1 - 1) / \gamma_1$. This phenomenon occurs mainly in organic compounds. The molecules have relatively high mean polarisability, revealing a hole-phonon interaction mechanism of polaron type, which interferes with the mechanism of deformation potential type. For a narrow range of energy states, this compensation is quite pronounced, a very promising feature which enables the possibility to improve the thermoelectric properties of the material. In the case of the simplified 1D physical model, the high of the relaxation time maximum is limited only by the scattering on impurities (the parameter D_0). In the 3D case the weak interchain interaction is included also (the terms with d_1 and d_2) and the last has the maximal contribution when $k_y = k_z = \pm \pi$ (fig.1- dashed lines).

The electrical conductivity (σ_{xx}), thermopower (S_{xx}) and the power factor (P_{xx}) of TTT₂I₃ crystals were calculated numerically earlier [10, 11]. In this paper, the electronic thermal conductivity (κ_{xx}^e), thermoelectric figure of merit (ZT) and Lorenz number (L) are modeled for different crystal purity parameter:

$$\kappa_{xx}^e = [4w_1^2 \sigma_0 / (e^2 T)] (R_2 - R_1^2 / R_0) \quad (9)$$

$$(ZT)_{xx} = \sigma_{xx} S_{xx}^2 T / (\kappa_{xx}^L + \kappa_{xx}^e) \quad (10)$$

$$L = \frac{k_0^2}{e^2} \frac{1}{(k_0 T)^2} \left[\frac{R_2}{R_0} - \left(\frac{R_1}{R_0} \right)^2 \right] \quad (11)$$

here $\sigma_0 = 2.78 \cdot 10^3 \Omega^{-1} \text{cm}^{-1}$.

Transport integrals R_n are calculated numerically. So as the conduction band is not very large, the variation of electron and phonon wave vectors on the whole Brillouin zone is considered:

$$R_n = abc \int_0^{\pi/a} dk_x \int_0^{\pi/b} dk_y \int_0^{\pi/c} dk_z \sin^3(k_x b) n_k (1 - n_k) \times$$

$$[\varepsilon + d_1(1 - \cos(k_y a)) + d_2(1 - \cos(k_z c)) -$$

$$(1 + d_1 + d_2)\varepsilon_F]^n / \{[(1 - \gamma_1 \cos(k_x b))^2 +$$

$$\frac{1}{4\sin^2(k_x b)} \{d_1^2[1 + \gamma_2^2 + 2\sin^2(k_y a) - 2\gamma_2 \cos(k_y a)] +$$

$$d_2^2[1 + \gamma_3^2 + 2\sin^2(k_z c) - 2\gamma_3 \cos(k_z c)]\} + D_0]\}$$

here n_k is the Fermi distribution function, $\varepsilon_F = E_F/2w_1$ is the Fermi energy for the 1D case in the unities of $2w_1$. Lattice thermal conductivity $\kappa_{xx}^L = 0.6 \text{ mW/cm}\cdot\text{K}$. The transfer energies w_2 and w_3 are evaluated by comparing the numerical results of electrical conductivity in transversal directions with the experimental ones.

For this purpose the Hamiltonian of the system was written in the representation of localized states at TTT molecules, instead of Bloch representation, used for describing the transport phenomena in the longitudinal direction. In transversal directions, the energy of carriers is much smaller than the hole-phonon interaction energy. The canonical transformation Lang-Firsov was applied to consider the main part on hole-phonon interaction in the zero approximation. The same canonical transformation applied for the operator of density of the electrical current revealed that in transversal directions carriers become small polarons, the transport mechanism becomes of hopping type and the electrical conductivity – thermally activated.

In (12) the D_0 parameter depends on the concentration of impurities and defects which can be considered in stationary state at room temperature, T_0 :

$$D_0 = n_{im}^{3D} I^2 V_0^2 \frac{M v_s^2}{4b^3 a c w_1'^2 k_0 T_0} \quad (13)$$

here n_{im}^{3D} is the concentration of impurity, k_0 is the Boltzmann constant.

IV. NUMERICAL RESULTS AND DISCUSSIONS

Numerical calculations are performed after (9) – (12) using the following crystal parameters: $M = 6.5 \cdot 10^5 m_e$ (m_e is the mass of the free electron), $a = 18.35 \text{ \AA}$, $b = 4.96 \text{ \AA}$, $c = 18.46 \text{ \AA}$, $w_1 = 0.16 \text{ eV}$, $w_1' = 0.26 \text{ eV}\cdot\text{\AA}^{-1}$, $v_{s1} = 1.5 \cdot 10^3 \text{ m/s}$, $E_F = 0.12 \text{ eV}$. The values w_2 and w_3 are the same because the respective lattice constants (a and c) are very close. This leads to $d_1 = d_2 = 0.015$. The mean polarisability of TTT molecules, $\alpha_0 = 46 \text{ \AA}^{-3}$ and $\gamma_1 = 1.7$ [12]. The parameters $\gamma_2 = \gamma_1 b^5 / (a^5 d)$ and $\gamma_3 = \gamma_1 b^5 / (c^5 d)$.

In Fig.1 the relaxation time of holes as function of dimensionless kinetic energy ε in the x – direction is

presented. The diminishing of impurity and lattice defects scattering (i.e. the improvement of crystal purity) provides a rapid growth of the relaxation time maximum. In the same time, this procedure reveals the weak interchain interaction, which becomes significant for ultra-pure crystals.

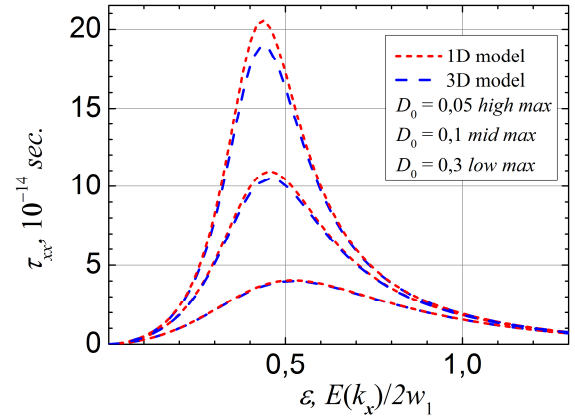


Fig.1. Relaxation time of carrier as function of ε for $D_0 = 0.3, 0.1, 0.05$ at room temperature.

In Fig.2 the dependences of the electronic thermal conductivity κ_{xx}^e on dimensionless Fermi energy ε_F are presented. The interchain interaction has a negligible effect even for purest crystals. For stoichiometric concentrations ($n = 1.2 \cdot 10^{21} \text{ cm}^{-3}$ or $\varepsilon_F = 0.33$), $\kappa_{xx}^e = 1.5, 3$ and 4.3 W/mK when $D_0 = 0.3, 0.1, 0.05$ respectively. It is observed that the further diminution of ε_F leads to the decrease of κ_{xx}^e and, consequently, ZT is increased.

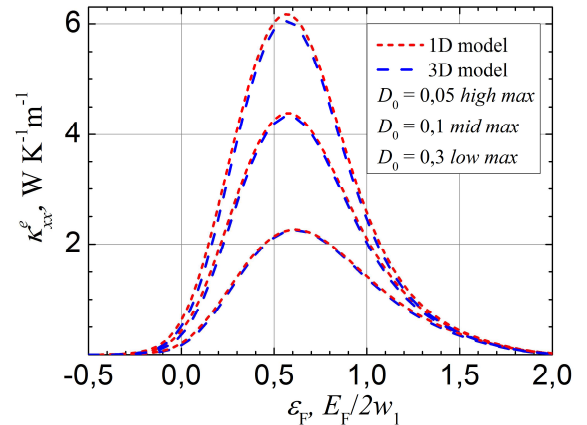


Fig.2. Electronic thermal conductivity as function of ε_F for $D_0 = 0.3, 0.1, 0.05$ at room temperature

The dependences of ZT on ε_F are presented in Fig.3. The results of calculations made in the 1D model are denoted by red dotted lines and those made in the 3D model – by blue dashed lines. For purest crystals (the curves with the highest maximum) the difference is slightly increased but the 1D approximation is still applicable. For stoichiometric crystals obtained from vapour phase ($D_0 = 0.1$), the figure of merit ZT has small values. Basing on the fact that TTT_2I_3 crystal admits nonstoichiometric compounds, the improvement of ZT may be achieved by varying the concentration of acceptors (iodine). In such a way, the diminution of iodine concentration of 1.5 times (from $\varepsilon_F = 0.33$ to 0.18) leads to a relative increase of $ZT(\varepsilon_F = 0.33) /$

$ZT(\varepsilon_F = 0.18)$ up to 3.1 times for crystals with $D_0 = 0.3$. When the crystal purity is increasing, this ratio is growing up to 3.4 for $D_0 = 0.05$. Further improvement of crystal purity tends to diminish the mentioned above ratio, because of the growth of interchain scattering probability.

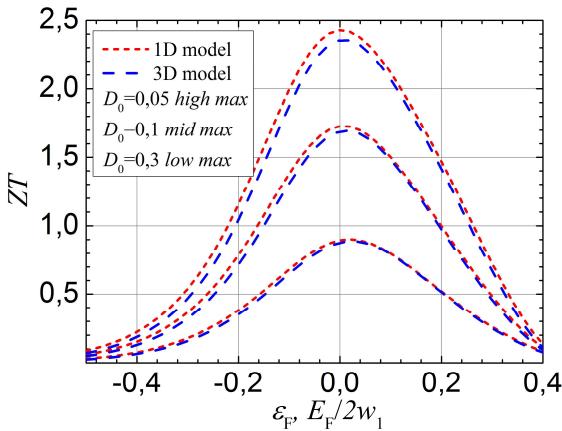


Fig.3. Thermoelectric figure of merit $(ZT)_{xx}$.

Lorenz number L_{xx} (Fig.4) is considerably diminished in a large interval of carrier concentration important for thermoelectric applications. This fact leads to a significant growth of ZT . The interchain interaction has a negligible effect. For $n = 0.8 \cdot 10^{21} \text{ cm}^{-3}$ $L_{xx} = 2, 1.9$ and 1.7 in units of $(k_0/e)^2$ in comparison with the value $L_{xx} = 3.3 (k_0/e)^2$ which is observed in metals and in usual degenerated semiconductors.

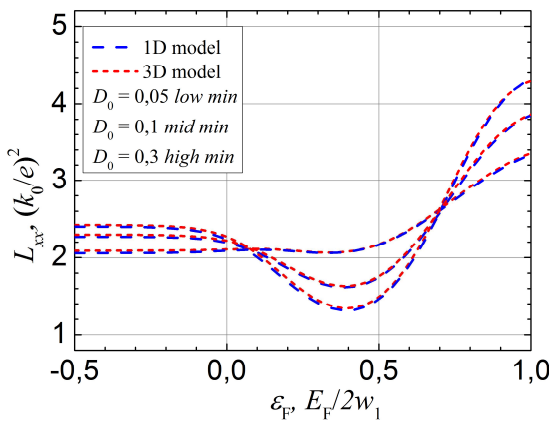


Fig.4. Lorenz number L_{xx} .

V. CONCLUSION

Thermoelectric properties (electronic thermal conductivity, thermoelectric figure of merit and the Lorenz number) are calculated numerically in the frame of more realistic 3D physical model for crystals of TTT_2I_3 with different degrees of purity. The restrictions of applicability of the 1D model are revealed. It is shown that for crystals growth from gaseous phase ($D_0 = 0.1$), the 1D approximation is applicable. For rather pure crystals with electrical conductivity $\sigma_{xx} > 3 \cdot 10^4 \Omega^{-1}\text{cm}^{-1}$, the interchain interaction becomes significant and the 3D model is need to be applied. Due to the property of TTT_2I_3 crystal to admit nonstoichiometric compounds, the diminution of

Fermi energy ε_F down to 0.2 will provide an increase of ZT up to 1.0, and for $\varepsilon_F = 0.1$ up to 1.5 in crystals obtained earlier experimentally by gaseous phase method. Even higher values of ZT are predicted in purer crystals.

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