

# Transport Properties of Nanostructured Organic Crystal of TTT(TCNQ)<sub>2</sub>

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**Abstract** – The numerical modeling of electrical conductivity and thermopower of TTT(TCNQ)<sub>2</sub> organic crystals is performed in order to investigate the prospect of using the mentioned crystals as thermoelectric material. The calculus is realized in the frame of three-dimensional (3D) physical model and the results are presented as function of Fermi energy for different degrees of the crystal purity. The influence of neighbor adjacent molecular chains on charge carrier transport is highlighted. The most effective methods to improve the thermoelectric efficiency are discussed.

**Index Terms** – Thermoelectric material, organic crystal, molecular chain, 3D physical model of TTT(TCNQ)<sub>2</sub>.

## I. INTRODUCTION

During the last two decades, an increasing interest was devoted to investigation and development of more efficient thermoelectric materials, which could be successfully implemented in different devices, such as local power generators, infrared detectors or cooling systems. Thermoelectric materials of organic type are very promising due to rather inexpensive and eco-friendly production technology. In these structures the properties of low-dimensional systems and those of multi-component systems are joined together. Consequently, the thermoelectric efficiency is increased due to the presence of more different and complicated internal interactions.

Important results were reported recently: in poly (3, 4-ethylenedioxy-thiophene) (PEDOT) and DMSO – treated PEDOT: PSS thermoelectric figure of merit,  $ZT$  achieves the values  $\sim 0.25$  and  $\sim 0.42$  [1, 2]. In mixed organic – inorganic compounds, such as hybrid material composed of polymer nanoparticles, carbon nanotubes and poly(vinyl chloride),  $ZT \sim 0.3$  [3]. In phenyl acetylene-capped silicon nano particles,  $ZT = 0.57$  at room temperature was measured [4]. Recently, mixed organic thermoelectric materials with high carrier mobility were reported. The enhancement of thermoelectric efficiency was realized by the method of doping control [5]. Earlier it was predicted theoretically that figure of merit of nanostructured organic materials may be increased up to  $ZT \sim 15$  [6] or even  $ZT \sim 20$  under some special conditions [7].

## II. DESCRIPTION OF THE PHYSICAL MODEL

The crystals of TTT(TCNQ)<sub>2</sub> are dark-violet needles of length 3 – 6 mm [8]. The internal structure of the complex consists of anion radical tetracyanoquinodimethan (TCNQ) coupled with cation radical tetrathiotetracene (TTT). The

molecules are arranged in stacks which proceed along one direction and form chains of TTT and TCNQ molecules. Further we consider a Cartesian system with  $x$  – axis lying in the direction of molecular chains. The overlap of High Occupied Molecular Orbitals (HOMO) of nearest molecules along the TCNQ chain is significant and the band-type transport mechanism takes place. In perpendicular directions the adjacent chains are spaced at  $\sim 0.6$  and  $1.9$  nm. Consequently, the overlap of  $\pi$  – orbital is insignificant and the charge transport is of hopping type. Below we consider thermoelectric phenomena along the  $x$  – direction with small corrections due to interchain interaction. Also, the scattering on impurities is taken into account.

The Hamiltonian of the crystal has the form:

$$H = \sum_{\mathbf{k}} E(\mathbf{k}) a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}} + \sum_{\mathbf{k}, \mathbf{q}} A(\mathbf{k}, \mathbf{q}) a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}+\mathbf{q}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^{\dagger}) + \left( I_i V_{0i} \sum_{j=1}^{N_i} e^{-iq_j r_i} + I_d V_{0d} e^{-E_0/k_B T} \sum_{j=1}^{N_d} e^{-iq_j r_j} \right) V^{-1} \sum_{\mathbf{k}, \mathbf{q}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}-\mathbf{q}}. \quad (1)$$

The first term describes the energy of conduction electrons, considering the tight-binding and nearest neighbor approximations:

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

here  $w_1$ ,  $w_2$  and  $w_3$  are transfer energies of the electron from given molecule to the nearest one (the indices 1, 2 and 3 indicate on the  $x$ ,  $y$  and  $z$  directions with corresponding lattice constants  $c$ ,  $b$ , and  $a$ );  $k_x$ ,  $k_y$ ,  $k_z$  are the projections of the quasi-wave vector  $\mathbf{k}$ .

The longitudinal acoustic phonon frequency is:

$$\omega_{\mathbf{q}}^2 = \omega_1^2 \sin(q_x c/2) + \omega_2^2 \sin(q_y b/2) + \omega_3^2 \sin(q_z a/2), \quad (3)$$

where  $\omega_1$ ,  $\omega_2$  and  $\omega_3$  are limit frequencies and  $q_x$ ,  $q_y$ ,  $q_z$  are the projections of the quasi-wave vector  $\mathbf{q}$ . The condition of quasi-one dimensionality requires  $\omega_2$ ,  $\omega_3 \ll \omega_1$ . In this paper, the transversal terms in Eq.3 will be neglected in comparison with the longitudinal one, since their influence is very weak [9].

The electron-phonon interaction is described by the matrix element  $A(\mathbf{k}, \mathbf{q})$ . Two main interaction mechanisms are considered: of the deformation potential and of the polaron type. The coupling constant of the first mechanism is proportional to the derivative of transfer energies with respect

to intermolecular distances,  $w_1'$ ,  $w_2'$ ,  $w_3'$ . The second mechanism is similar to that of polaron – the polarization energy of molecules surrounding conduction electron fluctuates when the intermolecular distances are changing. The coupling constant is proportional to the mean polarisability of TCNQ molecule,  $\alpha_0$ . The ratio of amplitudes of the second mechanism to the first one is described by the parameter  $\gamma_n$ , where  $n = 1, 2, 3$ .

The last term in Eq.1 takes into account the scattering on randomly distributed, point-like and electric neutral impurity centers (with concentration  $n_{\text{imp}}$ ) and the scattering on thermally activated lattice defects (with concentration  $n_{\text{def}}$ ,  $E_0 = 0.034$  eV). The scattering processes are described at room temperature by the dimensionless parameter  $D_0$ :

$$D_0 = (n_i I_i^2 V_{0i}^2 + n_d I_d^2 V_{0d}^2 e^{-2E/k_0T}) \frac{M v_{s1}^2}{4c^3 a b w_1'^2 k_0 T} \quad (4)$$

Here  $I_i$  and  $I_d$  are the energy of interaction of electrons with an impurity and a defect within regions of volume  $V_{0i}$  and  $V_{0d}$ ,  $M$  is the mass of TCNQ molecule.

The expressions for electrical conductivity and thermopower in the  $x$  – direction are obtained by solving analytically the linearized kinetic equation of the Boltzmann type considering the scattering processes as elastic:

$$\sigma_{xx} = \sigma_0 R_0, \quad S_{xx} = (k_0/e)(2w_1/k_0T)R_1/R_0, \quad (5)$$

$$\sigma_0 = (e^2 v_{s1}^2 m |w_1'|^3 r) / [4\pi^3 \hbar abc (k_0T)^2 (w_1')^2]. \quad (6)$$

Here  $e$  is the elementary electric charge,  $v_{s1}$  – the sound velocity along the chains,  $r$  – the number of molecular chains passing through the elementary cell. The adimensional transport integrals  $R_n$  are defined in the form:

$$R_n = \iiint_{D=[-\pi,\pi]} dk_x dk_y dk_z \frac{|\sin^3(k_x c) \cdot [\varepsilon(\mathbf{k}) - (1 + d_2 + d_3)\varepsilon_F]^n n_k (1 - n_k)}{M_k}, \quad (7)$$

where  $\varepsilon(\mathbf{k}) = E(\mathbf{k})/2w_1$  is the dimensionless energy of the electron and  $\varepsilon_F = E_F/2w_1 = [1 - \cos(\mathbf{k}_F \mathbf{c})]$  is the dimensionless 1D Fermi energy. The parameters describing the ratio of transfer energies,  $d_2 = w_2/w_1 = w_2'/w_1' \ll 1$ ,  $d_3 = w_3/w_1 = w_3'/w_1' \ll 1$ , were calculated earlier for TTT<sub>2</sub>I<sub>3</sub> [10]. Because of similar crystalline structure of the crystals we have considered approximately the same values  $d_2$  and  $d_3$ .  $n_k$  is the Fermi distribution function for electrons with energy (Eq. 2) at room temperature.  $M_k$  is the dimensionless mass operator of bi-particle retarded Green function. The interaction with phonons and the scattering on impurities are included.

$$M_k = [1 + \gamma_1 \cos(k_x c)]^2 + \frac{d_2^2}{8 \sin^2(k_x c)} [1 + 2 \sin(k_y b)^2 + 2\gamma_2 \cos(k_y b) + \gamma_2^2] + \frac{d_3^2}{8 \sin^2(k_x c)} [1 + 2 \sin(k_z a)^2 + 2\gamma_3 \cos(k_z a) + \gamma_3^2] + D_0, \quad (8)$$

The partial compensation of both electron-phonon interaction mechanisms diminishes significantly the scattering of electrons and  $R_n$  manifests a pronounced maximum for a narrow interval of energetic states near  $\varepsilon_0 = (\gamma_1 + 1)/\gamma_1$ . The integration was performed numerically and the results are presented as function of dimensionless Fermi energy,  $\varepsilon_F$  for different values of the parameter,  $D_0$ .

### III. NUMERICAL RESULTS AND DISCUSSIONS

The numerical modeling was performed considering the following crystal parameters:  $c = 3.75$  Å,  $b = 12.97$  Å and  $a = 19.15$  Å,  $M = 3.72 \cdot 10^5 m_e$  ( $m_e$  is the electron rest mass),  $w_1 = 0.125$  eV,  $w_1' = 0.22$  eV Å<sup>-1</sup>,  $d_2 = 0.015$  and  $d_3 = 0.01$ ,  $v_{s1} = 2.8 \cdot 10^3$  m/s. The mean polarisability of TCNQ molecule is  $\alpha_0 = 9.5$  Å<sup>-3</sup> and this leads to  $\gamma_1 = 1.7$ .

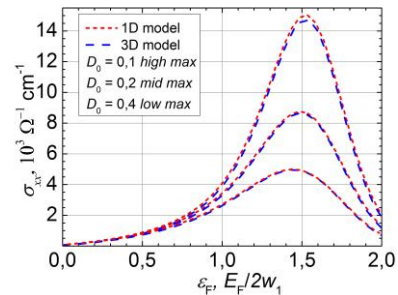


Fig. 1. Electrical conductivity as function of dimensionless Fermi energy for not very pure crystals.

In Fig.1 the electrical conductivity is presented as function of dimensionless Fermi energy,  $\varepsilon_F$  for crystals with low purity degree, i.e.  $D_0 = 0.4, 0.2, 0.1$ . We suppose that for TTT(TCNQ)<sub>2</sub> organic crystals synthesized at early stages corresponds approximately  $D_0 = 0.4$ .

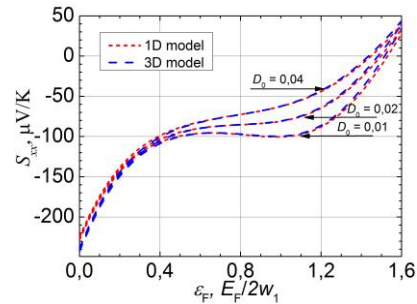


Fig. 2. Thermopower as function of dimensionless Fermi energy for not very pure crystals.

The stoichiometric concentration and the corresponding Fermi energy are  $n = 1.1 \cdot 10^{21}$  cm<sup>-3</sup> and  $\varepsilon_F = 0.35$ . The doping with donors will increase the electron concentration and this shifts the Fermi energy in the direction of the maximum. Consequently, if  $D_0$  is diminished up to 0.1 and  $n$  is increased twice, up to  $2.2 \cdot 10^{21}$  cm<sup>-3</sup> ( $\varepsilon_F \approx 1.04$ ) the electrical conductivity grows up to  $\sim 10$  times, from  $\sigma_{xx} \approx 0.4 \cdot 10^3$  Ω<sup>-1</sup> cm<sup>-1</sup> to  $4.4 \cdot 10^3$  Ω<sup>-1</sup> cm<sup>-1</sup>.

In Fig.2 the thermopower  $S_{xx}$  (Seebeck coefficient) is modeled as function of dimensionless Fermi energy.

For stoichiometric crystals  $S_{xx} = -115 \div -120 \mu\text{V/K}$ . If the concentration of electrons is increased up to 2 times,  $S_{xx} \approx -105, -110$  and  $-115 \mu\text{V/K}$  for  $D_0 = 0.4, 0.2$  and  $0.1$ , respectively.

After optimization of electron concentration, the maximum value of the electrical conductivity becomes closely linked to the parameter  $D_0$  and the manipulations with crystal purity and perfection is a keystone technique in order to improve thermoelectric efficiency.

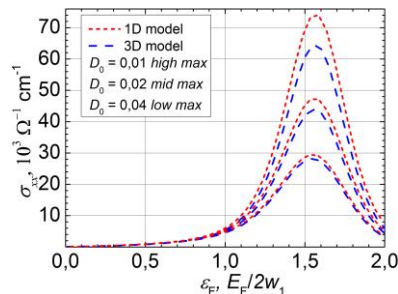


Fig. 3. Electrical conductivity as function of dimensionless Fermi energy for ultra-pure crystals.

If  $D_0$  is diminished from 0.1 to 0.01 (Fig.3.), the electrical conductivity grows in the 3D model up to  $6.6 \cdot 10^3 \Omega^{-1} \text{cm}^{-1}$ , when  $n = 2.2 \cdot 10^{21} \text{cm}^{-3}$ . But now the weak interchain interaction is manifested and the difference between the 1D ( $d_2 = d_3 = 0$ ) model and more complete 3D model ( $d_2 \approx d_3 \neq 0$ ) is observed.

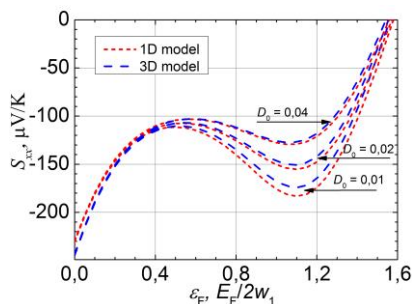


Fig. 4. Thermopower as function of dimensionless Fermi energy for ultra-pure crystals.

From Fig.4 it is seen that for stoichiometric crystals the Seebeck coefficient is less sensible to the crystal purity or interchain interaction. But by increasing the electron concentration twice and diminishing  $D_0$  up to 0.01, values of  $S_{xx} = -130, -150$  and  $-170 \mu\text{V/K}$  are obtained, very promising results.

#### IV. CONCLUSIONS

Transport properties (electrical conductivity and thermopower) of  $n$ -type organic crystals of TTT (TCNQ)<sub>2</sub> are modeled numerically in the frame of the three-dimensional (3D) physical model, taking into account the weak interaction

between adjacent molecular chains. It is shown that by increasing the degree of crystal perfection and by optimizing the electron concentration it is possible to improve significantly the transport properties of TTT(TCNQ)<sub>2</sub> crystals. It is demonstrated that for not very pure crystals with the stoichiometric electrical conductivity  $\sigma_{xx} < 0.5 \cdot 10^3 \Omega^{-1} \text{cm}^{-1}$  the weak interchain interaction is negligible and the simple one-dimensional (1D) model is applicable, while for ultra-pure crystal with higher  $\sigma_{xx}$  a more complete 3D model needs to be applied. The maximum values of  $\sigma_{xx} \approx 6.4 \cdot 10^4 \Omega^{-1} \text{cm}^{-1}$  and  $S_{xx} = -170 \mu\text{V/K}$  are predicted after optimization processes, very promising results.

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