THREE DIMENSIONAL MODELING OF KINETIC COEFFICIENTS OF TTT₂I₃ ORGANIC CRYSTALS.

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Abstract: Tetrathiotetracene-iodide organic crystal (TTT₂I₃) is a nanostructured bulk material with pronounced quasi-one-dimensionality and with more diverse and complicated interactions. Mainly, the thermoelectric properties are improved by the partial compensation of two electron-phonon interaction mechanisms and the relaxation time has a Lorentzian behavior as function of Fermi energy. Initial predictions were made in the frame of a more simplified one-dimensional (1D) physical model, when the relaxation time maximum was limited only by the scattering on impurities, neglecting the weak interaction between the nearest conductive chains. However, more detailed investigations have shown that for ultra-pure crystals the scattering on adjacent molecular chains becomes significant and should be considered. In this paper, a more realistic 3D physical model is presented. Also, the criteria of applicability of the simplified 1D model are estimated.

Keywords: Tetrathiotetracene-Iodide, Organic Crystals, Impurity, Quasi-one-dimensional, Molecular Chain, Interchain Interaction.

Introduction

In order to attain high thermoelectric figure of merit, it is needed to diminish the parasitic thermal conductivity and to increase the electrical conductivity and the thermopower of given material. In usually existing bulk materials, these kinetic coefficients are interconnected and the thermoelectric efficiency is low. The discovery of new nanostructured materials has made possible to attain new thermoelectric materials with improved figure of merit. In last years, remarkable results have been obtained in different compounds with complex crystalline structure. In materials like clathrates and skutterudites the atoms are loosely bonded, the thermal conductivity is low and $ZT \sim 1 \div 1.5$ at $T = 800 \div 1000$ K [1-3]. In *Zintl* compounds, the thermal conductivity is diminished due to the high fraction of low-velocity acoustical phonon modes [4]. Very promising results have been obtained in different low-dimensional systems, like superlattices, nanowires and quantum dots: in Bi_2Te_3/Sb_2Te_3 superlattices $ZT \sim 2.5$ and in superlattices with quantum dots PbTe/PbSe, $ZT \sim 3$ at 600 K have been measured [6, 7].

Recent investigations have shown that thermoelectric organic materials can successfully compete with the inorganic ones. Their diverse properties are well tunable through molecular chemistry and doping procedures. By minimizing the total dopant volume, in poly (3, 4-ethylenedioxythiophene) (PEDOT) a maximum ZT = 0.42 has been achieved in p-type [8, 9] and 0.20 in n-type [10] materials. Very promising thermoelectric properties are predicted theoretically for quasi-one-dimensional organic semiconductors [11]. In this connection, the crystals of TTT₂I₃ are very prospective for different thermoelectric applications [12, 13, 14].

Three-dimensional physical model

Tetrathiotetracene-iodide organic crystal is a nanostructured material, consisting of segregate donor TTT and acceptor iodine stacks. The charge transport is provided mainly through TTT molecular wires by the holes. The distance between nearest neighbor molecules along the chain (further considered as *x* - direction) is about 0.5 nm and the overlap of wave functions generates a narrow conduction band (0.64 eV). The adjacent molecular chains are spaced at ~ 1 *nm* one from other, so as in transversal directions (*y* and *z*) the transport phenomena is of hopping type: a process assisted by many phonons. Further, we'll consider the movement of charge carrier along the molecular wire and the scattering on adjacent chains and impurities. The Hamiltonian of the system has the form:

$$H = \sum_k E(\boldsymbol{k})a_k^+ a_k + \sum_q \hbar\omega_q b_q^+ b_q + \sum_{k,q} A(\boldsymbol{k},\boldsymbol{q})a_k^+ a_{k+q}(b_q + b_{-q}^+) + \left(I_i V_{0i}\sum_{l=1}^{N_i} e^{-iq r_l} + I_d V_{0d} e^{-E_0/k_0 T}\sum_{j=1}^{N_d} e^{-iq r_j}\right)V^{-1}\sum_{k,q} a_k^+ a_{k-q}. \tag{1}$$

The first two terms are describing the energy of holes and of longitudinal acoustic phonons:

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

where k_x, k_y, k_z are the projections of the quasi-wave vector $\boldsymbol{k}$, a, b, c – lattice constants, w_1, w_2 and w_3 are the transfer energies in the x, y, z directions. The tight binding approximation is considered.

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

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 $\boldsymbol{q}$, $\omega_2 \approx \omega_3$ $\omega_2 \ll \omega_1$.

The third term in (1) describes the hole-phonon interaction. The matrix element of this interaction has the form:

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

We consider two main interaction mechanisms: of the polaron type (the lattice vibrations causes the variation of the polarization energy of molecules surrounding the charge carrier) and of the deformation potential (the variation of transfer integrals with respect to the intermolecular distances). The ratios of amplitudes of the first to the second one are denoted by the parameters γ_1, γ_2 and γ_3.

The last term in (1) contains the carrier interaction with the randomly distributed, point-like and electric neutral impurities and the scattering on lattice defects, thermally activated ($E_a = 0.034$ eV).

Kinetic coefficients

The kinetic equation of Boltzmann type is solved analytically assuming the approximations of weak electric field and low temperature gradient. The scattering processes on phonons are considered elastic at room temperature [15].

The kinetic coefficients are expressed through the transport integrals in the form:

$$\begin{aligned} &\sigma_{xx} = \sigma_0 R_0 & &S_{xx} = (k_0/e)(2w_1/k_0 T)R_1/R_2 & &\kappa_{xx}^e = [4w_1^2\sigma_0/(e^2 T)](R_2 - R_1^2/R_0) \\ &P_{xx} = \sigma_{xx}S_{xx}^2 & &ZT = \sigma_{xx}S_{xx}^2 T/(\kappa_{xx}^L + \kappa_{xx}^e) & &L = (k_0^2/e^2)(k_0 T)^{-2}[R_2/R_0 - (R_1/R_0)^2] \end{aligned} \tag{5}$$

Where R_n are triple integrals and the variation of the quasi-wave vector $\boldsymbol{k}$ is considered over the whole Brillouin zone:

$$R_n = abc \int_0^{\pi/a} dk_x \int_0^{\pi/b} dk_y \int_0^{\pi/c} dk_z \sin^3(k_x b)n_{\boldsymbol{k}}(1-n_{\boldsymbol{k}}) \times \tag{6}$$

$$\frac{[\varepsilon - \varepsilon_F]^n}{(1-\gamma_1\cos(k_x b))^2 + \dfrac{1}{4\sin^2(k_x b)}\{d_1^2[1+\gamma_2^2+2\sin^2(k_y a)-2\gamma_2\cos(k_y a)] + d_2^2[1+\gamma_3^2+2\sin^2(k_z c)-2\gamma_3\cos(k_z c)]\} + G}$$

Here $\varepsilon = E(\boldsymbol{k})/2w_1$, $\varepsilon_F = E_F/2w_1$ are the energy of carriers and the Fermi energy in the unities of $2w_1$, $n_{\boldsymbol{k}}$ is the Fermi distribution function for carriers with energy (2), G is the parameter describing the scattering of carriers on impurity centers.

The coefficient σ_0 has the mean of electrical conductivity:

$$\sigma_0 = \frac{2e^2 w_1^3 v_{s1}^2 Mr}{\pi^3 abc\hbar(k_0 T)^2 w_1'^2} \tag{7}$$

Numerical modeling results

The calculations were made for crystals with different degrees of purity in the frame of both 1D and 3D models. The crystal parameters are: $M = 6.5\cdot10^5 m_e$ (m_e is the free electron mass), $a = 18.35$ Å, $b = 4.97$ Å, $c = 18.46$ Å, $v_{s1} = 1.5\cdot10^3$ m/s, $w_1 = 0.16$ eV, $w_1' = 0.26$ eVÅ^{-1} [12]. The parameters γ_2 and γ_3 are calculated from the relations $\gamma_2 = \gamma_1 b^5/(a^2 d)$ and $\gamma_3 = \gamma_1 b^5/(c^2 d)$. Here $\gamma_1 = 1.7$ was estimated using the mean polarisability value for TTT molecules, $\alpha_0 = 46$ Å^{-3}. The parameters $d_1 = w_2/w_1 =$ and $d_2 = w_3/w_1$ are estimated by comparing the numerical and experimental results for transversal electrical conductivity.

In Fig.1 the electrical conductivity as function of dimensionless Fermi energy is modeled for different values of the parameter $G = 0.3$ (which corresponds to crystals grown from solution), 0.1 (crystals growth from vapour phase) and 0.05 for somewhat purer TTT_2I_3 crystals.
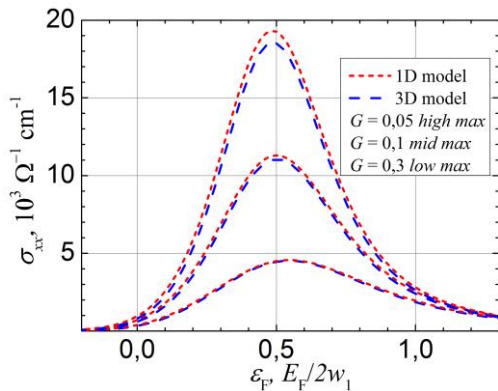

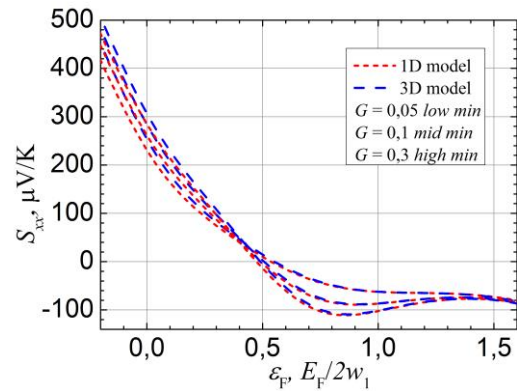Fig.1. Electrical conductivity of TTT_2I_3 crystal

Fig.2. Thermopower as function of ε_F.

In Fig. 2 thermopower (S_{xx}) as function of dimensionless Fermi energy at room temperature is presented. For p-type crystals, S_{xx} takes positive values. The diminution of carrier concentration provides a rapid growth of S_{xx}. The interchain interaction has a negligible effect.
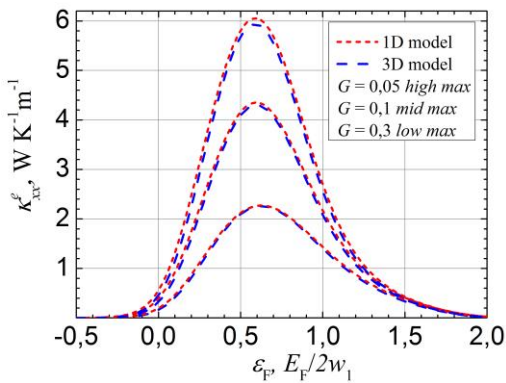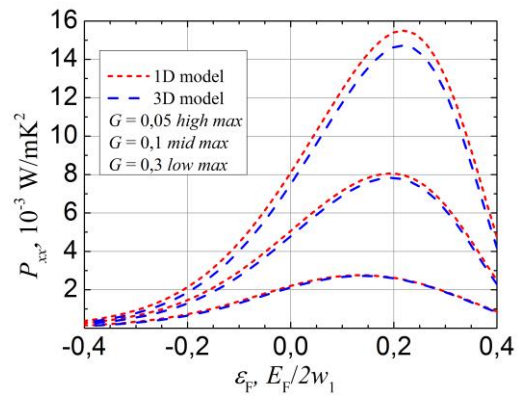

Fig.3. Electronic thermal conductivity

Fig.4. Power factor as function of dimensionless Fermi energy

Thermal conductivity of carriers is also less sensitive to interchain interaction (Fig.3). The maximum is a little displaced to higher values of ε_F in comparison with the maximum of σ_{xx}. This phenomenon denotes the violation of the Wiedemann-Franz law and the diminution of carrier concentration will provide a more rapid diminution of the parasitic thermal conductivity.

The power factor (Fig.4) for stoichiometric crystals ($\varepsilon_F = 0.33$ or $n = 1.2 \cdot 10^{21}$ cm^{-3}) grows significantly when the crystal purity is improved. The difference between the 3D and 1D models becomes more significant.

From Fig.5 it is seen that the thermoelectric figure of merit for stoichiometric crystals is low ($\sim 0.2, 0.3, 0.5$) but after optimisation of carrier concentration it grows at least by three times. In such a way, after purification and diminution of the concentration of iodine, TTT_2I_3 crystals may be fairly good materials for different thermoelectric devices. The diminution of the Lorenz number in a large interval of E_F is also favorable for the increase of ZT. More realistic 3D model needs to be applied for crystals with $ZT > 3.5$, while for less pure crystals the 1D model describes very well the thermoelectric properties.

Conclusions

The kinetic coefficients of the quasi-one-dimensional organic crystal of TTT_2I_3 of p – type are modeled in the frame of a three-dimensional physical model. The scattering of charge carriers on impurities and neighboring molecular chains is considered. Three values of crystal purity parameter are considered and it was demonstrated that for ultra-pure crystals with $\sigma_{xx} > 3 \cdot 10^4$ Ω^{-1}cm^{-1} or $ZT > 3.5$ the weak interchain interaction becomes significant and should be considered. It was established that the improvement of crystal purity and the optimisation of carrier concentration will provide very good materials for different thermoelectric applications.
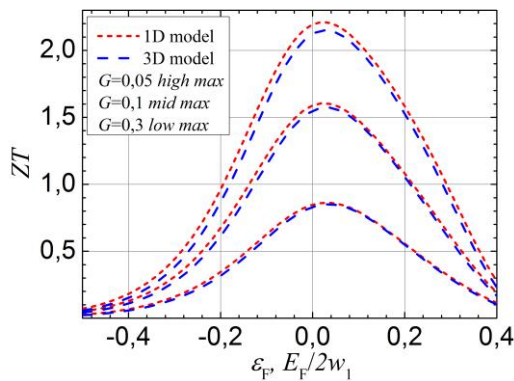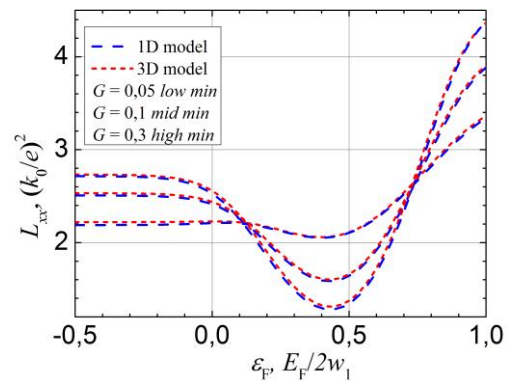
Fig.5. Thermoelectric figure of merit ZT

Fig.6. Lorenz number.

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