

EFFECT OF INTERCHAIN INTERACTION ON THE ELECTRICAL CONDUCTIVITY AND THERMOPOWER OF TTT_2I_3 CRYSTALS

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Abstract

Quasi one dimensional organic crystals of tetrathiotetracene-iodide TTT_2I_3 are promising materials for thermoelectric applications. A theoretical study of thermoelectric properties of these crystals was initially performed in terms of a one-dimensional (1D) model. In this paper, the effect of interaction between molecular chains on the electrical conductivity and thermopower (Seebeck coefficient) is investigated. For simplicity, a 2D model is applied. The criteria where the weak interaction between 1D molecular chains can be neglected are also determined.

1. Introduction

High energy needs of contemporary society constrain rational use of all energy resources. The abundance of thermal energy as a result of human activity or environmental factors, suggests the possibility to use even a part of this energy for human needs. For this purpose, thermoelectricity comes to propose advantageous solutions to convert thermal energy into electricity. The problem lies in the search of materials appropriate for these applications. It is required that these materials must have high thermoelectric efficiency in terms of exploitation and low cost in their synthesis. Ordinary thermoelectric materials have too low efficiency. Recently, attempts have been made to use nanostructured materials. Structures with quantum wells superlattices, quantum wires or quantum dots showed higher efficiency than ordinary materials. However, the preparation process is quite complicated and expensive. In recent years, investigations have been moving towards nanostructured organic materials, which promise to be more accessible and less expensive. It was theoretically demonstrated [1] that quasi-one-dimensional organic crystals may have very promising thermoelectric parameters. A large advantage of organic materials is that they can be synthesized by simple chemical methods. The thermal conductivity is much lower, which allows considerably reducing the parasitic thermal conductivity. In addition, organic materials are more flexible and lighter than inorganic ones.

Different types of organic compounds are investigated [2-7]. In [3] it was shown that thin layers of pentacene doped with iodine may be good candidates for various thermoelectric applications. This structure has a power factor $\sim 1.3 \cdot 10^{-5} \text{ W/mK}^2$. In bilayer structures composed of pentacene and an acceptor tetrafluoro-tetracyanoquinodimethane layers, as described in [4], the following values were measured for electrical conductivity: $\sigma = 43 \text{ S/m}$, Seebeck coefficient $S \sim 200 \mu\text{V/K}$ and power factor $P = \sigma S^2 \sim 2.0 \mu\text{W/mK}^2$.

In doped acetylene [5] at room temperature $ZT \sim 0.38$ was measured. To the best of our knowledge, the highest value of $ZT=0.57$ was obtained in phenylacetylene-capped silicon nanoparticles [6]. Another promising feature of these materials is the possibility to reduce the

Lorentz number as a violation of the Wiedemann-Franz law, a phenomenon predicted theoretically in one-dimensional organic crystals [7].

Theoretically, it was shown that TTT_2I_3 crystals are promising for thermoelectric applications [8, 9]. In really existing crystals, $ZT = 1.4$ is expected after the optimization of carrier concentration. Even higher values of ZT were predicted in purer crystals. However, these predictions were made in terms of 1D crystal model. This model can be accepted as first approximation. Now it is necessary to complete the 1D model and to determine the contribution of electron transitions from one chain to another on electrical transport phenomena along the molecular chains. This paper concerns to the two-dimensional model of TTT_2I_3 crystals.

2. Two-dimensional crystal model for TTT_2I_3

Tetrathiotetracene iodine molecular crystal has a needle-shaped structure. Its internal structure can be considered quasi-one-dimensional, because the distance between nearest molecules in \mathbf{b} direction taken as the x -axis is considerably smaller than in transversal y and z directions. The structure of this crystal is described in [9]. Crystals are formed of segregate tetrathiotetracene and iodine molecular chains. Iodine molecule receives one electron from two molecule of TTT which leads to creation of a hole on the TTT chain. Electrical conductivity of iodine chains is very low. Therefore, the transport phenomena in crystal are provided by TTT chains and carriers are holes. Although the molecular chains are packed into a 3D crystalline structure, the interaction between chains and its effect on transport phenomena is weak and can be neglected in the first approximation. This procedure is not applicable to the crystals with high level of purity, so as in this case the interchain interaction effects become more important than scattering on impurity.

As in 1D case, we will use the approximations of tight binding electrons and nearest neighbors. Hamiltonian of the system has the form

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

The first term is the energy of free carriers (holes) in the periodic field of the lattice. The second term is the energy of acoustic longitudinal phonons and the last term describes the energy of interaction between holes and phonons. The energy of a hole is

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

where \mathbf{k} is two-dimensional wave vector with projections (k_x, k_y) , w_1 and w_2 are transfer energies of a carrier from one molecule to another along the chain (with lattice constant b) and in perpendicular direction (with a greater intermolecular distance $\sim 2b$). The condition of quasi-one-dimensionality requires $w_2 \ll w_1$. Due to this fact in perpendicular to chains direction the transport is of hopping-type. In (1) $a_{\mathbf{k}}^+$ ($a_{\mathbf{k}}$) are the creation (annihilation) operators of hole with the wave vector \mathbf{k} and energy $\varepsilon(\mathbf{k})$.

For acoustic longitudinal phonons, we will take

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

where ω_1 and ω_2 are the limit frequencies for oscillations in x and y directions. In (1) $b_{\mathbf{q}}^+$ ($b_{\mathbf{q}}$) are operators of creation (annihilation) of an acoustic phonon with two-dimensional wave vector \mathbf{q}

and frequency ω_q . Transversal phonons are not considered, because their contribution to the transport is negligible.

The matrix element $A(\mathbf{k}, \mathbf{q})$ takes into account two interaction mechanisms: the first is of polaron type and describes the fluctuations of polarization energy of molecules due to an additional carrier. Coupling constants of this mechanism of interaction is proportional to the polarizability of TTT molecule α_0 . The second interaction is of deformation potential type. Molecular vibrations generate the fluctuations of resonance integrals. Coupling constants are proportional to derivatives w_1' and w_2' of w_1 and w_2 with respect to intermolecular distances. Coulomb interaction between carriers is not considered, so as this interactions is significantly screened by polarization effects.

The square module of matrix element has the form

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

where N is the number of molecules in the basic region of the crystal, M is the mass of TTT molecule; γ_1 and γ_2 are parameters describing the ratio of amplitudes of the first interaction to the second ones:

$$\gamma_1 = 2e^2\alpha_0/b^5 w_1'; \gamma_2 = 2e^2\alpha_0/a^5 w_2' \quad (5)$$

Since w_1 and w_2 are positive, and w_1' , w_2' are negative, γ_1 and γ_2 will be also negative. So as the conduction band is not very large, the variation of wave vectors of phonons and holes will be considered in the entire Brillouin zone. Kinetic processes are also affected by scattering on impurities. They are considered neutral, point-like, and randomly distributed. In this case, the scattering on impurities is described by dimensionless parameter D_0 which is proportional to the concentration of impurity centers [10]:

$$D_0 = n_{im}^{2D} I^2 d_x^2 d_y^2 \frac{Mv_s^2}{4b^3 a w_1'^2 k_0 T} \quad (6)$$

where n_{im} is 2D concentration of impurities, I , d_x , d_y are effective height and widths of impurity potential in x and y directions, v_s is the velocity of sound along the chains.

3. Transport proprieties

Suppose that a weak electric field is applied along the molecular chains. In the linear approximation with respect to applied field the general expression for electrical conductivity tensor $\sigma_{\mu\nu}$ is

$$\text{Re } \sigma_{\mu\nu}(0) = \frac{i\pi e^2}{k_0 T V} \sum_{\mathbf{k}, \mathbf{k}', s} v_{\mu}(\mathbf{k}) v_{\nu}(\mathbf{k}') \langle\langle a_{\mathbf{k}}^+ a_{\mathbf{k}} / a_{\mathbf{k}}^+ a_{\mathbf{k}'} \rangle\rangle_{i\varepsilon} \quad (7)$$

where $\langle\langle a_{\mathbf{k}}^+ a_{\mathbf{k}} / a_{\mathbf{k}}^+ a_{\mathbf{k}'} \rangle\rangle_E$ is the Fourier transform of two-particle retarded Green function and $E = i\varepsilon$, $\varepsilon \rightarrow 0$, $v_{\mu}(\mathbf{k})$ is the projection of carrier velocity on μ axis.

Along the x - direction:

$$\sigma_{xx}(0) = \frac{\pi e^2}{k_0 T V} \sum_{\mathbf{k}, s} v_x(\mathbf{k}) G_{\mathbf{k}}^x, \quad (8)$$

where

$$G_{\mathbf{k}}^x = i \sum_{\mathbf{k}'} v_v(\mathbf{k}') \ll a_{\mathbf{k}}^+ a_{\mathbf{k}} | a_{\mathbf{k}'}^+ a_{\mathbf{k}'} \gg_{i\varepsilon} \quad (9)$$

The equation for $G_{\mathbf{k}}^x$ takes the form of Boltzmann kinetic equation:

$$\frac{1}{\pi} n_{\mathbf{k}} (1 - n_{\mathbf{k}}) = \sum_{\mathbf{q}} (W_{\mathbf{k}, \mathbf{k}+\mathbf{q}} G_{\mathbf{k}+\mathbf{q}}^x - W_{\mathbf{k}+\mathbf{q}, \mathbf{k}} G_{\mathbf{k}}^x) \quad (10)$$

where $n_{\mathbf{k}}$ is the equilibrium distribution function of carriers with the energy $\varepsilon(\mathbf{k})$, $G_{\mathbf{k}}^x$ has the sense of deviation from equilibrium state and $W_{\mathbf{k}, \mathbf{k}+\mathbf{q}}$ is the probability of a carrier scattering on acoustic phonons

$$W_{\mathbf{k}, \mathbf{k}+\mathbf{q}} = 2\pi \hbar^{-1} |A(\mathbf{k} + \mathbf{q}, \mathbf{q})|^2 \{ (1 + N_{\mathbf{q}} - n_{\mathbf{k}+\mathbf{q}}) \delta[\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}) + \hbar\omega_{\mathbf{q}}] + (N_{\mathbf{q}} + n_{\mathbf{k}-\mathbf{q}}) \delta[\varepsilon(\mathbf{k} + \mathbf{q}) - \varepsilon(\mathbf{k}) - \hbar\omega_{\mathbf{q}}] \} \quad (11)$$

Here, the matrix element is defined in (4). $N_{\mathbf{q}}$ is the equilibrium distribution function of phonons with the energy $\hbar\omega_{\mathbf{q}}$. At room temperature, we can consider scattering processes as elastic [10]. We may also replace $1 + 2N_{\mathbf{q}} \approx 2k_0 T / \hbar\omega_{\mathbf{q}} \gg 1$. The expression in the δ functions from (11) contains also the carrier energy in direction perpendicular to the chains. We may neglect this term too, taking into account the relation $w_2 \ll w_1$. Under these conditions, kinetic equation (10) can be solved exactly and the relaxation time $\tau(\mathbf{k})$ may be introduced as

$$\tau(k_x, k_y)^{-1} = 2 \sum_{q_x, q_y} W_{\mathbf{k}+\mathbf{q}, \mathbf{k}}. \quad (12)$$

Finally, we obtain for σ_{xx} the expression

$$\sigma_{xx} = \frac{e^2 r}{2\pi^2 c k_0 T} \int_{-\pi/b}^{\pi/b} dk_x \int_{-\pi/a}^{\pi/a} n_{\mathbf{k}} (1 - n_{\mathbf{k}}) v_x^2(k_x) \tau(k_x, k_y) dk_y, \quad (13)$$

where e is carrier charge, c is the lattice constant in the direction perpendicular to x , y , and r is the number of chains through the transversal section of unite cell, $v_x(k_x) = \hbar^{-1} (\partial\varepsilon(\mathbf{k}) / \partial k_x)$ is the carrier velocity. In order to compare with 1D case we will introduce a new variable $\varepsilon = 1 - \cos(k_x b)$. In variables ε and k_y the expression for relaxation time takes the form

$$\tau(\varepsilon, k_y) = \frac{v_{s1}^2 w_1 M \hbar}{a^2 k_0 T w_1^2} \cdot \frac{\varepsilon(2-\varepsilon)}{\gamma_1^2 (\varepsilon - \varepsilon_0)^2 + \frac{w_2^2}{w_1^2} \cdot \frac{1}{2\varepsilon(2-\varepsilon)} (1 + 2\sin^2(k_y a) - 2\gamma_2 \cos^2(k_y a) + \gamma_2^2) + D_0}, \quad (14)$$

where ε is the dimensionless kinetic energy of the hole along chains in unities of $2w_1$, and $\varepsilon_0 = (\gamma_1 - 1) / \gamma_1$ is the dimensionless resonance energy. We have also changed the signs of γ_1 and γ_2 ; hereinafter, they are positive.

In the first approximation, where the interaction of molecular chains is neglected, the relaxation time achieves a maximum value corresponding to the energy $E_0 = 2w_1\varepsilon_0$ in the conducting band, when $\gamma_1 > 1$. Around this energy region, the both interaction mechanisms described by the matrix element $|A(\mathbf{k} + \mathbf{q}, \mathbf{q})|^2$ interfere and compensate each other, the peak of relaxation time being limited only by impurities (parameter D_0). In 2D model, this maximum is limited also by the effects of interaction between the molecular chains.

Let us define the transport integrals R_n :

$$R_n = \frac{2e^2 M v_{s1}^2 z w_1^3 (2w_1)^n}{\pi^2 abc (k_0 T)^2 w_1^2 \hbar} \int_0^\pi d\varepsilon \int_0^\pi d\eta \frac{\varepsilon(2-\varepsilon)}{\gamma_1^2 (\varepsilon - \varepsilon_0)^2 + \frac{w_2^2}{w_1^2} \cdot \frac{1}{2\varepsilon(2-\varepsilon)} (1 + 2\sin^2(\eta) - 2\gamma_2 \cos^2(\eta) + \gamma_2^2) + D_0} \times \frac{(\varepsilon - \varepsilon_F)^n}{\{\exp[(w_1(\varepsilon - \varepsilon_F) + w_2 \cos(\eta))/k_0 T] + \exp[-(w_1(\varepsilon - \varepsilon_F) + w_2 \cos(\eta))/k_0 T]\}^2} \quad (15)$$

where we have introduced a dimensionless variable for the wave vector $k_y a = \eta$.

The electrical conductivity σ and the thermopower S along the chains are expressed through transport integrals in the form

$$\sigma = R_0, \quad S = R_1 / eTR_0 \quad (16)$$

Unfortunately, the transport integrals R_n can be calculated only numerically.

4. Results and discussion

In this part of paper, we present the results of numerical calculations for electrical conductivity σ and Seebeck coefficient S along chains, for different values of parameter D_0 . Also the 2D model will be compared with the 1D model. The parameters of TTT_2I_3 crystal are: $M = 6.5 \cdot 10^5 m_e$ (where m_e is free electron mass), $a = 18.46 \text{ \AA}$, $b = 4.97 \text{ \AA}$, $c = 18.35 \text{ \AA}$, $v_{s1} = 1.5 \cdot 10^3 \text{ m/s}$, $w_1 = 0.16 \text{ eV}$, $w_1' = 0.26 \text{ eV \AA}^{-1}$, $r = 4$, [11]. It is known from experiments that the conductivity in the transversal direction is by three orders of magnitude smaller than in the longitudinal direction, $\sigma_x/\sigma_y \sim 10^3$. This result is used to estimate the parameters $w_2 = 1.44 \cdot 10^{-3} \text{ eV}$ and $w_2' = 0.009 w_1'$ [12]. So as the transfer energy for a carrier between molecular chains w_2 takes a very small value, the transport mechanism in the transversal direction is of hopping type. For the polarizability of the TTT molecule, we took $\alpha_0 = 48 \text{ \AA}$ [12]. This value corresponds to the parameters $\gamma_1 = 1.8$ and $\gamma_2 = \gamma_1 a^5 w_1' / b^5 w_2' = 3.47 \gamma_1 = 6.25$.

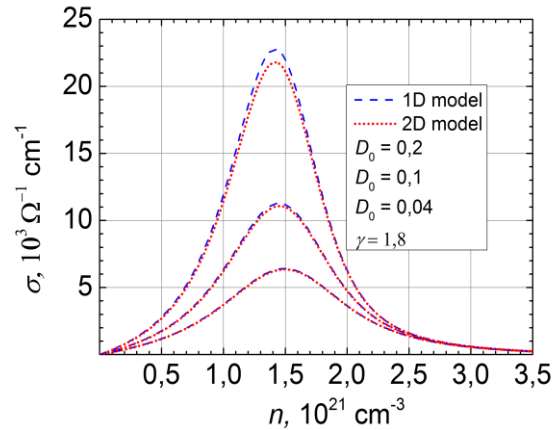


Fig.1. Electrical conductivity σ as function of carriers concentration for some values of D_0 .

Figure 1 shows the dependence of electrical conductivity on carrier concentration for crystals with different degrees of purity. The results for 1D model and 2D model are denoted by dashed and dotted lines, respectively. For stoichiometric crystals, the Fermi level is located at $k_x = \pi/4b$ in the Brillouin zone and the corresponding concentration $n \approx 1.2 \cdot 10^{21} \text{cm}^{-3}$. The electrical conductivity for this concentration is: $\sigma(1D) = 19 \cdot 10^3 \Omega^{-1} \text{cm}^{-1}$, $\sigma(2D) = 18 \cdot 10^3 \Omega^{-1} \text{cm}^{-1}$, for $D_0 = 0.04$; $\sigma(1D) = 9.3 \cdot 10^3 \Omega^{-1} \text{cm}^{-1}$, $\sigma(2D) = 9.1 \cdot 10^3 \Omega^{-1} \text{cm}^{-1}$ for $D_0 = 0.1$ and $\sigma(2D) = \sigma(1D) = 5.2 \cdot 10^3 \Omega^{-1} \text{cm}^{-1}$ for $D_0 = 0.2$. The parameter $D_0 = 0.1$ corresponds to TTT_2I_3 crystals grown from gas phase in [13]. The decrease in conductivity after the maximum with a further increase in hole concentration is explained by the fact that, for these concentrations, the role in electrical conductivity is played by electrons and their concentration is diminished with the filling of conduction band with holes. It is also observed that the curves for 1D and 2D models nearly coincide for all concentrations, except a narrow interval near the maximum for $D_0 = 0.04$. For less concentration we are interested, the 1D model describes well enough the electrical conductivity.

It is evident that, for small degrees of purity of crystals, 1D and 2D models give almost the same results over the entire range of concentrations. For purer crystals with $D_0 < 0.04$ and electrical conductivity higher than $2.5 \cdot 10^4 \Omega^{-1} \text{cm}^{-1}$, it is necessary to take into account the effect of the interaction between molecular chains, because this effect will give a significant contribution.

Figure 2 shows the dependences of thermopower (Seebeck coefficient) S on carrier concentration at room temperature for different impurity parameters D_0 . For stoichiometric crystals

($n = 1.2 \cdot 10^{21} \text{cm}^{-3}$) we obtained the following theoretical values for the thermopower: $S(1D) = 55 \mu\text{V/K}$ and $S(2D) = 54 \mu\text{V/K}$ for $D_0 = 0.2$; $S(1D) = 59 \mu\text{V/K}$ and $S(2D) = 57 \mu\text{V/K}$ for $D_0 = 0.1$; $S(1D) = 65 \mu\text{V/K}$ and $S(2D) = 64 \mu\text{V/K}$ for $D_0 = 0.04$.

These values are in the range of those obtained experimentally in [14, 15]. It can be seen that, for p region, Seebeck coefficient can take quite large values, especially for crystals with high purity. In addition, it is evident that, for stoichiometric concentration, the differences between 1D and 2D model are negligible. This means that the height of relaxation time maximum has a lower effect on S than on σ . It is expected that the differences between 1D and 2D models for S will be less pronounced than for σ even in crystals with higher degree of purity.

5. Conclusions

TTT_2I_3 crystals are very promising materials for thermoelectric applications. Initial calculations of transport parameters of these crystals were performed in terms of a 1D model, where the interaction between molecular chains was neglected. This paper presents the results of numerical calculations for electrical conductivity σ and Seebeck coefficient S along chains in the case where this interaction is taken into account. A spatial crystalline structure is modeled as two-dimensional layers packaged into a 3D crystal. The transport is described in tight binding

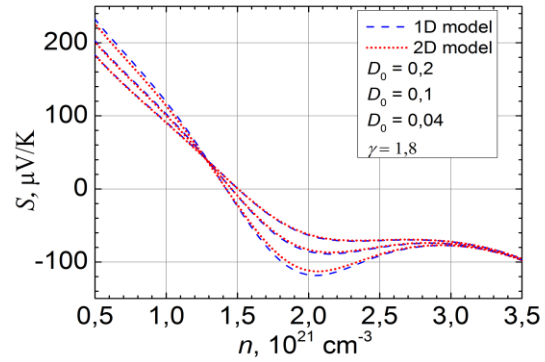


Fig.2. Seebeck coefficient, S as function of carriers concentration for some values of D_0 .

electrons and the nearest neighbor approximations. Two electron-phonon interaction mechanisms are considered: one of polaron type and the other of deformation potential type. Scattering on impurities is also taken into account and described by dimensionless parameter D_0 . It is demonstrated that the 1D model can be applied for large degrees of crystal purity that were previously achieved in experiments. For the crystals with higher purity and electrical conductivity higher than $\sim 2.5 \cdot 10^4 \Omega^{-1} \text{cm}^{-1}$, the interchain interaction must be taken into account.

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