EFFECT OF THE 2D PHONON SPECTRUM ON THE ELECTRIC CONDUCTIVITY AND THERMOPOWER OF TETRATHIOTETRACENE IODIDE CRYSTALS

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Abstract

Thermoelectric transport along the molecular chains of quasi-one-dimensional organic crystals of tetrathiotetracene iodide, TTT_2I_3, is studied in terms of a quasi-two dimensional (2*D*) model applying the linearized Boltzmann kinetic equation. Earlier, for simplicity, we have considered the lattice vibrations in a 1*D* approximation. In this paper, the full 2*D* spectrum for acoustic longitudinal phonons is taken into account and the effect of this consideration on the electric conductivity and thermopower (Seebeck coefficient) is studied. Numerical results and comparison with previous calculations are presented. It is shown that, if the 2*D* phonon spectrum is taken instead of the 1*D* one, the electric conductivity slightly increases and the thermopower decreases, although insignificantly.

1. Introduction

Theoretical and experimental investigations of new thermoelectric materials with increased thermoelectric figure of merit *ZT* continue to be an important and urgent problem of solid state physics. The preparation of these materials will promote the implementation of low-cost, pollution-free technologies of direct energy conversion for local power generators, local cooling systems, and infrared detectors.

The intensive research in the field of thermoelectricity started in the 1950s–1960s with the discovery of bulk thermoelectric materials, such as Bi_2Te_3, PbTe, and SiGe. Until the 1990s, the figure of merit was enhanced slowly until materials with $ZT \sim 1$ were obtained [1]. In the last two decades, because of the energetic crisis, a new intensification of researches in this field begun with the discovery of new kind of materials, such as compounds with a very complex lattice or the low-dimensional structures. The theoretical predictions [2] have led to the discovery of various compounds, such as the skutterudites [3, 4] and clathrates [5]. These materials have quite low thermal conductivity and high electric conductivity. A further development of the theory of low-dimensional systems [6] and the synthesis of new materials, such as structures with superlattices, quantum wires, or quantum dots, has led to a significant enhancement of figure of merit *ZT* up to 2.4 in Bi_2Te_3/Sb_2Te_3 superlattices [7] and 3.0 in PbTe/PbTeSe quantum dot superlattices [8]. At the same time, the implementation of these results requires the development of nanostructured, however, bulk thermoelectric materials [9]. From this point of view, nanostructured organic materials attract more and more attention of researchers. Thus, for poly (3,4-ethylenedioxythiophene) (PEDOT), a maximum *ZT* value of 0.42 has been achieved by minimizing the total dopant volume [10]. Very exciting is the recent observation of high carrier mobility on the order of 40 $cm^2\ V^{-1}\ s^{-1}$ in single-crystalline films of some organic

semiconductors [11]. Materials and structures with high mobilities are promising for thermoelectric applications.

It has been theoretically shown [12] that highly conducting quasi-one-dimensional organic crystals can be efficient thermoelectric materials. Due to their pronounced quasi-one dimensionality, TTT_2I_3 crystals are very good candidates for the purpose mentioned above [13]. This paper aims to highlight the influence of transversal component of acoustic phonon spectrum on electrical conductivity and thermopower of TTT_2I_3 organic crystals.

2. Theoretical Model

The crystal of TTT_2I_3 has an orthorhombic symmetry, the lattice constants are: a = 18.46, b = 4.97, and c = 18.35 Å [14]. The conducting direction b will be denoted as x direction and a as y direction. The TTT molecules are arranged in the x direction forming molecular chains. The iodine atoms lie in chains parallel to b direction [15]. Two molecules of TTT give one electron to an iodine atom. The iodine chains have very low electric conductivity; accordingly, the transport phenomena are related to TTT chains, where the electric conductivity is provided by majority carriers, i.e., holes. In the x direction, the overlapping of π- molecular orbitals lead to the formation of a narrow one-dimensional conduction band (the transfer energy is w_1 = 0.16 eV). This fact allows applying the electronic band transport model. In the y direction, the distance between the conducting chains is approximately two times larger than between molecules in the longitudinal direction. Consequently, the overlapping of Highest Occupied Molecular Orbitals (HOMO) is quite small; in this direction, the transport phenomena are of hopping type. The charge carriers perform phonon-assisted quantum transitions between the nearest molecules. Transfer energy w_2 in y direction was predicted to be in the range of $w_2 = d\ w_1 = 0.013\ w_1$. Coefficient d is estimated from experimental measurements of electric conductivity in transversal direction σ_{yy} and in longitudinal one σ_{xx}: $d = \sigma_{yy}/\sigma_{xx}$ [16]. The effect of the interchain interaction is small; however, it becomes observable if the crystal purity is increased [17].

The Hamiltonian of the crystal takes into account the adiabatic, tight-binding, and the nearest-neighbors approximations:

$$H = \sum_{\boldsymbol{k}} \varepsilon(\boldsymbol{k}) a_{\boldsymbol{k}}^{+} a_{\boldsymbol{k}} + \sum_{\boldsymbol{q}} \hbar\omega_{\boldsymbol{q}} b_{\boldsymbol{q}}^{+} b_{\boldsymbol{q}} + \sum_{\boldsymbol{k},\boldsymbol{q}} A(\boldsymbol{k},\boldsymbol{q}) a_{\boldsymbol{k}}^{+} a_{\boldsymbol{k}+\boldsymbol{q}} (b_{\boldsymbol{q}} + b_{-\boldsymbol{q}}^{+}) \ . \tag{1}$$

The first term is the operator of energy of carriers in the periodic field of the crystalline lattice. The energy of electrons in the frame of 2D model has the form:

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

where w_1 and w_2 are the transfer energies in the x and y directions.

The second term in (1) describes the energy of the longitudinal acoustic phonons

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

where ω_1 and ω_2 are limit frequencies in the x and y directions, (q_x, q_y) are the projections of the 2D quasi-wave vector $\boldsymbol{q}$, $\omega_2 << \omega_1$.

The electron-phonon interaction is described by the third term in (1). It takes into account two electron-phonon interaction mechanisms: the first one results from the variation of the polarization energy of molecules surrounding the conduction hole; the second one is due to the

variation of the transfer energies. The square of the matrix element $A(\boldsymbol{k},\boldsymbol{q})$ of electron-phonon interaction is

$$\begin{aligned}\left|A(\boldsymbol{k},\boldsymbol{q})\right|^2 = 2\hbar/(NM\omega_{\boldsymbol{q}})\{w_1'^2[\sin(k_x b)-\sin(k_x-q_x,b)+\gamma_1\sin(q_x b)]^2 + \\ w_2'^2[\sin(k_y a)-\sin(k_y-q_y,a)+\gamma_2\sin(q_y a)]^2\}\end{aligned} \quad (4)$$

Here, $M = 6.5\cdot10^5\, m_e$ (where m_e is free electron mass) is the mass of TTT_2I_3 molecule, N is the total number of molecules in the basic region of the crystal, w_1' and w_2' are the derivatives of the transfer energies with respect to the intermolecular distances, γ_1 and γ_2 are parameters describing the ratio of amplitudes of polaron-type interaction to the deformation potential one in the x and y directions. From the Kubo formulas for electric conductivity [18], we have

$$\mathrm{Re}\,\sigma_{xx}(0) = \frac{i\pi e^2}{k_0 TV}\sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{s}} v_x(\boldsymbol{k})v_x(\boldsymbol{k}) << a_{\boldsymbol{k}}^+ a_{\boldsymbol{k}} \mid a_{\boldsymbol{k}'}^+ a_{\boldsymbol{k}'} >>_{i\varepsilon}, \quad (5)$$

where $v_x(\boldsymbol{k})$ is the projection of carrier velocity on x direction and $<< a_{\boldsymbol{k}}^+ a_{\boldsymbol{k}} \left| a_{\boldsymbol{k}'}^+ a_{\boldsymbol{k}'} >>_{i\varepsilon}\right.$ is the Fourier transform of the two-particle retarded Green function. In this connection, the mass operator for the Green function was defined as follows [19]:

$$M_x(\boldsymbol{k}) = \sum_{\boldsymbol{k}'} W(\boldsymbol{k},\boldsymbol{k}')[1 - v_x(\mathrm{k}_x')/v_x(\mathrm{k}_x)] \quad (6)$$

where $W(\boldsymbol{k},\boldsymbol{k}')$ is the probability of carrier scattering on acoustic phonons [1]:

$$W(\boldsymbol{k},\boldsymbol{k}') = 4\pi k_0 T\left|A(\boldsymbol{k}+\boldsymbol{q},\boldsymbol{q})\right|^2 \delta[\varepsilon(k_x+q_x)-\varepsilon(k_x)]/\hbar^2\omega_{\mathrm{q}}. \quad (7)$$

Here, we have considered the scattering processes to be elastic near room temperature and have neglected the y - component of carrier energy in the δ-function being much less than longitudinal component. Limit acoustical frequency ω_2 in the y direction in $\omega_{\mathbf{q}}$ is not neglected.
Thus, for electric conductivity, we have the following expression:

$$\sigma_{xx}(0) = \frac{4e^2 w_1^2 b^2}{k_0 TV\hbar^2}\sum_{\boldsymbol{k}} \sin^2(k_x b) n_{\boldsymbol{k}}(1-n_{\boldsymbol{k}})/M_x(\boldsymbol{k}), \quad (8)$$

where $n_{\boldsymbol{k}}$ is the Fermi-Dirac distribution function for carriers with energy (2) and $\boldsymbol{k} = (k_x, k_y, k_z, s)$, s are the electron spin projections. If the 1D approximation is used for $\omega_{\mathbf{q}}$, the integrals in (6) can be calculated analytically. Now this is not possible and expression (6) is calculated numerically.
The expressions for the electric conductivity and Seebeck coefficient have the previous forms [20]:

$$\begin{aligned}&\sigma_{xx} = \sigma_0 R_0,\ S_{xx} = (k_0/e)(2w_1/k_0 T)R_1/R_0 \\ &\sigma_0 = \frac{16e^2 w_1^3 v_{s1}^2 Mr}{\pi(k_0 T)^2\hbar\, abc\, w_1'^2}\end{aligned} \quad (9)$$

only the bi-dimensional transport integrals R_1 and R_2 become much more complicated:

$$\begin{aligned}R_n = \int_0^{\pi} d\eta \int_0^{\pi} d\xi \left|\sin^3(\eta)\right| n_{\boldsymbol{k}}(1-n_{\boldsymbol{k}})\times 1/\int_{-\pi}^{\pi} d\lambda\{4\sin^2(\eta)[1-\gamma_1\cos(\eta)]^2 + \\ d^2[\sin(\xi)-\sin(\xi-\lambda)-\gamma_2\sin(\lambda)]^2\}/[\sin^2(\eta)+\nu^2\sin^2(\lambda/2)]+8\pi D_0\end{aligned} \quad (10)$$

Here, d is the ratio w_2'/w_1' and $\nu^2 = (\omega_1/\omega_2)^2 = (a^2 v_{s2}^2)/(b^2 v_{s1}^2)$, r is the number of molecular chains through the transversal section of the elementary cell, v_{s1} is the sound velocity along the

chains. D_0 is the parameter describing the scattering of carriers on impurity centers. The impurities are considered to be point-like, randomly distributed, and electrically neutral [20]:

$$D_0 = n_{im}^{2D} I^2 d_x^2 d_y^2 \frac{M v_s^2}{4b^3 a w_1'^2 k_0 T}, \quad (11)$$

where n_{im}^{2D} is the 2*D* carrier concentration, *I* is the height and d_x, d_y are the width of the impurity potential.

3. Results and Discussion

The numerical results for the electric conductivity and thermopower of organic TTT_2I_3 crystals are presented in Figs. 1–4. The sound velocity and the derivative of transfer energy along the *x* direction are $v_{s1} = 1.5 \cdot 10^3$ m/s, $w_1' = 0.26$ eV^{-1} [21], $r = 4$, $\gamma_1 = 1.7$ and $\gamma_2 = 32\ \gamma_1\ a^5/(b^5 d)$. The sound velocity in the *y* direction is taken as $v_{s2} = v_{s1}/3$ and this leads to $v^2 = 0.008$.

Figure 1 shows the absolute deviations $\sigma_{xx}(\omega_{2D}) - \sigma_{xx}(\omega_{1D})$ for the electric conductivity as a function of the Fermi energy in units of $2w_1$, where physical models with ω_{2D} and ω_{1D} are applied, respectively. Crystals with a not high degree of purity are considered ($D_0 \rho 0.1$), $D_0 = 0.1$ corresponds to the TTT_2I_3 crystals grown by the gas phase method [22] with $\sigma \sim 10^4\ \Omega^{-1}\ cm^{-1}$.

The result is that the electric conductivity slightly increases—on the order of $10^{-2}\ \Omega^{-1}\ cm^{-1}$.

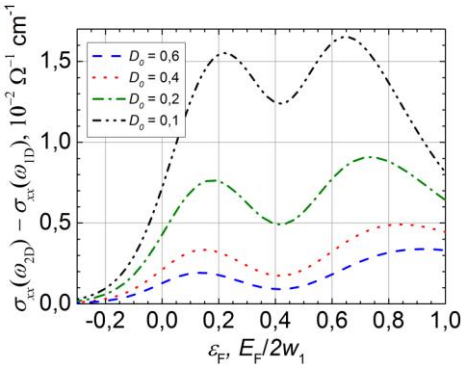

Fig. 1. Absolute deviation of the electric conductivity for crystals with a not high degree of purity.

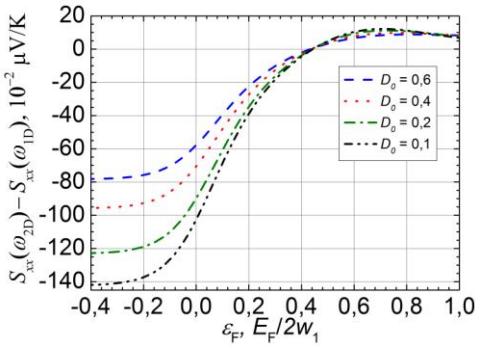

Fig. 2. Absolute deviation of the Seebeck coefficient for crystals with a not high degree of purity.

Figure 2 shows analogical dependences for the absolute deviations of Seebeck coefficient. Now $S_{xx}(\omega_{2D})$ is slightly diminished with respect to $S_{xx}(\omega_{1D})$; for higher concentrations, it hardly changed at all. These estimations allow us to use the previous simpler model where the phonon energy is approximated in the 1*D* case.

Figure 3 and 4 shows the same dependences for crystals with a higher degree of purity, $D_0\ \beta\ 0.1$. Now the absolute deviations of the electric conductivity become more significant. The deviations of the thermopower are almost the same as for crystals with a lower purity.

Thus, the full 2*D* spectrum for acoustic longitudinal phonons has hardly any effect on the electric conductivity and Seebeck coefficient with respect to a simpler 1*D* phonon spectrum due to pronounced quasi-one-dimensional properties of TTT_2I_3 crystals; however, the calculations with the 1*D* phonon spectrum are simpler and take much less time.

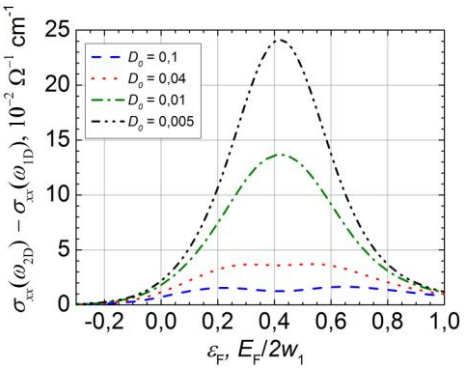

Fig. 3. Absolute deviation of the electric conductivity for crystals with a high degree of purity.

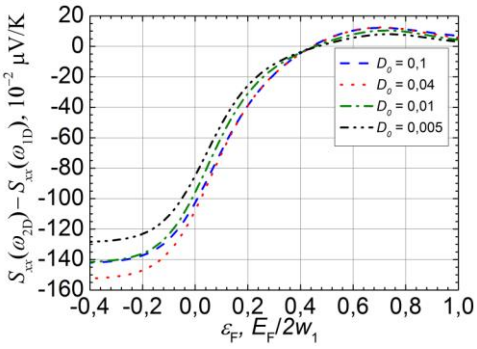

Fig. 4. Absolute deviation of the Seebeck coefficient for crystals with a high degree of purity.

4. Conclusions

Transport coefficients (electrical conductivity and Seebeck coefficient) are calculated for organic quasi-one-dimensional crystals of tetrathiotetracene iodide, TTT_2I_3, with different degrees of purity determined by parameter D_0. In the 2*D* crystal model considered in previous papers, a simpler 1*D* phonon spectrum was applied. Now this model was completed by taking into account the full 2*D* spectrum for acoustic longitudinal phonons. It is found that the full 2*D* spectrum for acoustic longitudinal phonons has negligible effect on the electric conductivity and Seebeck coefficient with respect to a simpler 1*D* phonon spectrum due to pronounced quasi-one-dimensional properties of TTT_2I_3 crystals. As a result, we can conclude that, for the modeling of electric conductivity and Seebeck coefficient of TTT_2I_3 crystals, it is possible to apply the simpler 1*D* phonon spectrum. This considerably reduces the time of calculus.

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