Modeling of Electronic Thermal Conductivity in Quasi-One-Dimensional Organic Crystals

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Abstract — **The electronic thermal conductivity is modeled in quasi-one-dimensional organic crystals with the parameters of TCNQ chains in the TTF-TCNQ crystals. Two more important electron-phonon interactions and the scattering on impurity are taken into account. The influence of interference of both electron-phonon interactions on electronic thermal conductivity is investigated. The dependences of electronic thermal conductivity on Fermi energy are analyzed for crystals with different degree of purity and different intensity of the interference. It is shown that the electronic thermal conductivity has a maximum, the position and the value of which strongly depend on crystal parameters.**

Index Terms — **electronic thermal conductivity, interference of electron-phonon interactions, quasi-one-dimensional organic crystals, relaxation time, Wiedemann-Franz law.**

I. INTRODUCTION

The electronic thermal conductivity is an important parameter of all materials, but especially of thermoelectric materials. The latter are used in thermoelectric converters which serve to convert directly the heat energy into an electrical current, and electrical current in cold. Presently, in spite of evident advantages of such thermal converters in comparison with the traditional ones, their large applications are limited by their low efficiency, which is caused by low efficiency of existing thermoelectric materials [1]. It is known that the thermoelectric opportunity of a given material is determined by its figure of merit ZT at operating temperature T, where $Z = \sigma S^2/\kappa$. Here σ is the electrical conductivity, S is the thermopower (Seebeck coefficient) and κ is the total thermal conductivity, $\kappa = \kappa^l + \kappa^e$, κ^l and κ^e being the lattice and electronic contributions to κ, respectively.

In the last years, the strategy to decrease κ in order to increase Z has been widely applied. For new bulk materials the idea of so-called phonon glass/electron crystal [2] was intensively developed [3-5].

Other approach in the decease of thermal conductivity is the preparation of thermoelectric materials in the form of low-dimensional structures [1]. A reduction of thermal conductivity is achieved in such structures due to phonon scattering at interfaces. Such structures offer also the possibility for engineering phonon transport via control of the phonon dispersion relation and phonon density of states [7], leading to the phonon group velocity reduction and corresponding decrease of thermal conductivity. A 100-fold reduction of thermal conductivity has been obtained in arrays of Si nanowires yielding $ZT = 0.6$ at room temperature [8] and $ZT \sim 1$ at 200 K [9].

Earlier, we have demonstrated [10-12] that in some highly conducting quasi-one-dimensional (Q1D) organic crystals it is possible to obtain increased values of the thermoelectric figure of merit ZT. This increase is determined by the interference of two more important electron-phonon interactions that leads to the increase of electrical conductivity and thermopower.

The aim of this paper is to study how the interference influences the electronic thermal conductivity. It is shown that the electronic thermal conductivity as a function of Fermi energy has a maximum the position and the value of which strongly depend on crystal parameters.

II. GENERAL CONSIDERATIONS

The main peculiarity of Q1D organic crystals is that they are formed of linear chains or stacks of molecules packed into a three dimensional crystalline structure. The distance between molecules along the chains is much less then between the chains. Accordingly, the conduction mechanism along the chains is band-like, whereas between the chains it is hopping-like. The latter creates a very small transversal conduction which is neglected.

The Hamiltonian of a Q1D organic crystal has been presented in [13]. It takes into account two main interactions of conducting electrons with acoustic phonons in the tight-binding and nearest-neighbors approximations. The first interaction is similar to that of deformation potential. The coupling constant of this mechanism is proportional to the derivative w' with respect to the intermolecular distance of the transfer energy w of the conduction electron between nearest molecules along the chains. The second interaction is similar to that of polaron, caused by induced polarization. The coupling constant in this case is proportional to the average polarizability α_0 of the molecule. The scattering of conduction electrons on impurities is also taken into account.

At room temperature the electron-phonon scattering can be considered elastic. Solving the Boltzmann kinetic equation as in [13], we obtain for electronic thermal conductivity the following expression

$$\kappa_e = (e^2 T)^{-1}[R_2 - (R_1)^2 / R_0] \, , \qquad (1)$$

where R_n are the transport integrals

$$R_n = -\frac{2e^2 az}{\pi\hbar^2 bc} \int_0^\Delta (E - E_F)^n [E(\Delta - E)]^{1/2} \tau(E) f_0' dE , \qquad (2)$$

Here e is the electron charge, T is the temperature, Δ is the conducting band width, $\Delta = 4w$, E is the carrier energy, $0 \le E \le \Delta$, E_F is the Fermi energy, a, b and c are the lattice constants, z is the number of chains through the transversal section of the unit cell, $f_0'(E)$ is the derivative of Fermi distribution function with respect to E, and $\tau(E)$ is the relaxation time

$$\tau(E) = \frac{\hbar M v_s^2 w [E(\Delta - E)]^{1/2}}{2a^2 k_0 T w'^2 \gamma^2 [(E - E_0^{s,p})^2 + 4w^2 \gamma^{-2} D]} , \qquad (3)$$

where M is the mass of molecule, v_s is the sound velocity along the chains, k_0 is the Boltzmann constant, γ is the ratio of amplitudes of above mentioned electron-phonon interactions $\gamma = 2e^2 \alpha_0 /(a^5 |w'|)$, $E_0^{s,p} = 2w(\gamma \pm 1/\gamma)$ is the resonance energy (for s- and p-type bands, respectively), which corresponds to the maximum of $\tau(E)$. The dimensionless parameter D in Eq. (3) describes the scattering of carriers on impurities, considered neutral and point-like

$$D = n_{im} I^2 d^2 M v_s^2 /\left(4a^3 k_0 T w'^2\right) \qquad (4)$$

where n_{im} is the linear concentration of impurity, I and d are the effective height and width of impurity potential. So as D is proportional to n_{im}, it can be made much less than unity, if the crystal purity is sufficiently high.

II. RESULTS AND DISCUSSION

At the beginning we will consider the case when only the first electron-phonon interaction is included, i.e. $\gamma = 0$ and $D = 0$. Then for nondegenerate gas of carriers the transport integrals R_0, R_1 and R_2 can be calculated analytically. The exact expressions are rather complicated. But keeping only the terms with the smallest power of $(k_0 T/2w) \square 1$, we obtain

$$\kappa^e = 2(k_0^2 / e^2) T\sigma , \qquad (5)$$

where σ is the electrical conductivity in the same approximation

$$\sigma = \frac{e^2 n M v_s^2 w}{(2\pi)^{1/2} \hbar w'^2} \left(\frac{2w}{k_0 T}\right)^{1/2} , \qquad (6)$$

where n is the bulk concentration of carriers. It results from (5) the Wiedemann-Franz law: the Lorentz number L takes the usual value for scattering of nondegenerate carriers on acoustic phonons, $L = \kappa^e/\sigma T = 2(k_0/e)^2$.

For strongly degenerate gas one can apply the known calculation method of integrals with the derivative of Fermi function. We then obtain

$$\kappa^e = (\pi^2 / 3)(k_0 / e)^2 T\sigma(E_F) , \qquad (7)$$

where $\sigma(E_F)$ is the electrical conductivity in the approximation $f_0'(E) \cong -\delta(E - E_F)$

$$\sigma(E_F) = \frac{e^2 n M v_s^2 E_F (\Delta - E_F)}{4\pi\hbar w'^2 k_0 T} . \qquad (8)$$

Note that for the calculation of κ^e this approximation of $f_0'(E)$ is not sufficient, so as it gives $\kappa^e = 0$. In this case all carriers have the same energy and therefore they can not transport heat. It also results from (6) the Wiedemann-Franz law: $\kappa^e = (\pi^2/3) (k_0/e)^2$ as it is expected for strongly degenerate carriers.

In general case, when $\gamma \ne 0$, the numerical calculation is necessary. The expression (1) has been modeled as a function of dimensionless Fermi energy $\varepsilon_F = E_F / 2w$ for different values of parameters γ and D. The crystals with the parameters of TCNQ chains in the tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) crystals with the parameters: $M = 3.7 \times 10^5 m_e$ (m_e is the mass of free electron), $w = 0.125$ eV, $w' = 0.2$ eV $^{-1}$, $v_s = 2 \times 10^5$ cm/s, $z = 2$, $a = 12.3$, $b = 3.82$, $c = 18.47$. The parameter γ is unknown in quasi-one-dimensional organic crystals because the polarizability of molecule in crystal is unknown. Therefore we have modeled κ^e as a function of dimensionless Fermi energy ε_F for an interval of γ from 0 up to 3. Higher values of γ requires too large values of molecule polarizability. The parameter D is proportional to impurity concentration and can be made much less than unity in rather pure crystals. We have chosen three easier achievable values $D = 0.1$, 0.05 and 0.01. The interval of Fermi energy variation is from $\varepsilon_F = -0.5$ ($E_F = -6k_0 T_0$, $T_0 = 300$ K) up to 2.5. The value $\varepsilon_F = 1$ corresponds to half filled band and strongly degenerate gas of electrons.

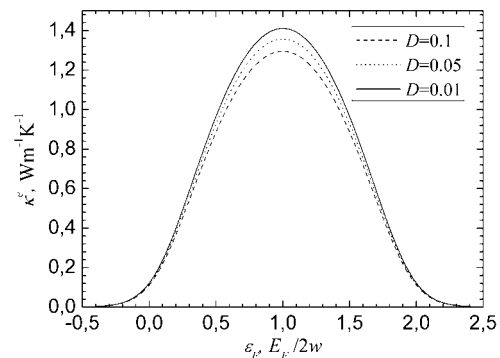In the Fig.1 the results for $\gamma = 0$, when only the first

Fig. 1. The electronic thermal conductivity κ^e as a function of Fermi energy ε_F for $\gamma = 0$.

electron-phonon interaction is involved, are presented. It is seen that κ^e has a maximum at $\varepsilon_F = 1$ and weakly depends on D. But even in maximum the values of κ^e are not high.
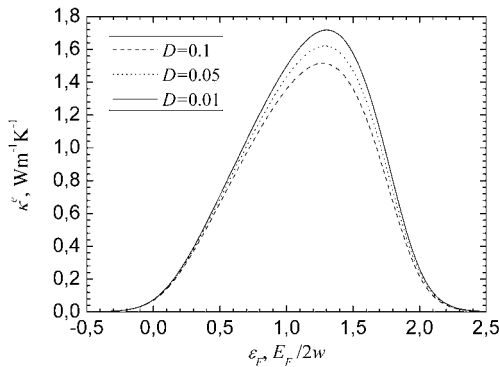

Fig.2. The electronic thermal conductivity κ^e as a function of Fermi energy ε_F for $\gamma = 0$.

In the Fig.2 the case when $\gamma = 0.5$ is shown. κ^e is somewhat increased, but remains small. The maximum is a little displaced to higher value of ε_F. The resonance energy is yet in the forbidden band ($E_0 = 3\Delta/2$) and the interference only slightly manifests itself. The energetic distance between E_0 and ε_F is still large and the thermal excitation of carriers on the states near E_0 is negligible. In the Fig.3 the results for $\gamma = 1$ are presented. Now the
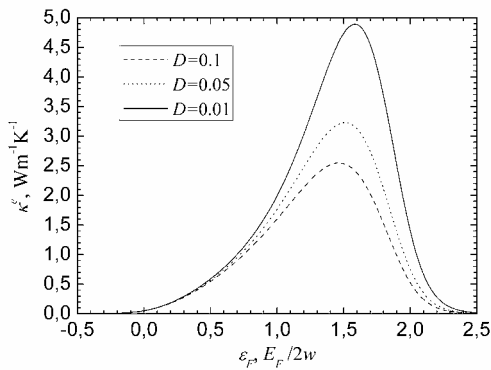

Fig.3. The electronic thermal conductivity κ^e as a function of Fermi energy ε_F for $\gamma = 1$.

resonance energy E_0 is exactly at the top of the conduction band, $E_0 = \Delta$, and the Lorentzian from (3) begins to manifest itself more intensively. As a result, the maximum of κ^e is considerably increased and is displaced to some higher values of $\varepsilon_F \sim 1.5$ - 1.6. The dependence of κ^e on parameter D, i.e. on crystal purity became more pronounced, because the contribution of Lorentzian from (3) became more important.

When $\gamma = 1.5$ (Fig.4), the maximum of κ^e achieves in the purest crystals very high values of the order of 8.5 W/m×K,

which is more than five times larger then in the best bulk thermoelectric material Bi_2Te_3 at room temperature. But now the maximum is displaced to lower values of ε_F, because the resonance energy is already into the conduction band, $E_0 = 0.83\,\Delta$. Even in crystals with lower purity ($D = 0.1$) the maximum of κ^e is still ~ 3.5 W/m×K, a rather high value. In the same time, at $\varepsilon_F \sim 0.5$, typical for TCNQ chains in TTF-TCNQ crystals, the values of κ^e are of the
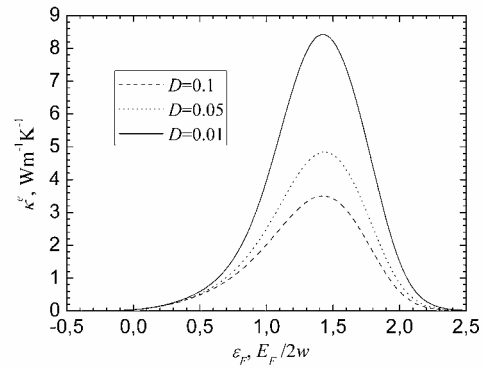

Fig.4. The electronic thermal conductivity κ^e as a function of Fermi energy ε_F for $\gamma = 1.5$.

order of 0.8 W/m×K, two times lower then in Bi_2Te_3.

For $\gamma = 2$ (Fig.5) the maximums of electronic thermal conductivity are slightly decreased and are displaced to still lower value of ε_F with respect to previous case. Now almost whole Lorentzian from the relaxation time is placed into the conduction band, so as the resonance energy $E_0 = 0.75\,\Delta$. One could expect that the maximum of κ^e will further increase. However, as it is seen from (3), when $\gamma > 1$, the relaxation time decreases with the increase of γ, and for $\gamma \square 1$ a dependence of relaxation time and of electronic
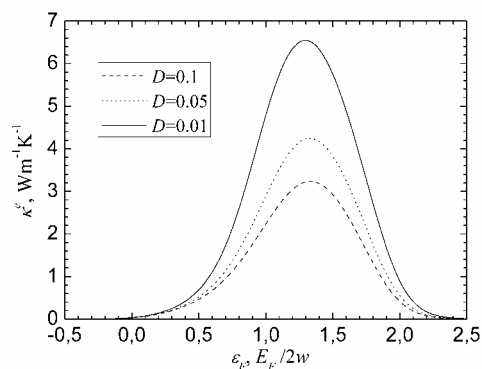

Fig.5. The electronic thermal conductivity κ^e as a function of Fermi energy ε_F for $\gamma = 2$.

thermal conductivity $\sim \gamma^{-2}$ is expected.

Really, when γ is increased up to 2.5 (Fig.6) the maximums of electronic thermal conductivity are some more decreased and are displaced to lower value of Fermi

energy. For $\varepsilon_F \sim 0.5$, typical for TCNQ chains in TTF-TCNQ crystals, the values of κ^e remain small, but now depend more strongly on the parameter D, which determines the crystal perfection.

Fig. 7 confirms such behavior of the electronic thermal conductivity. The maximums of κ^e are additionally
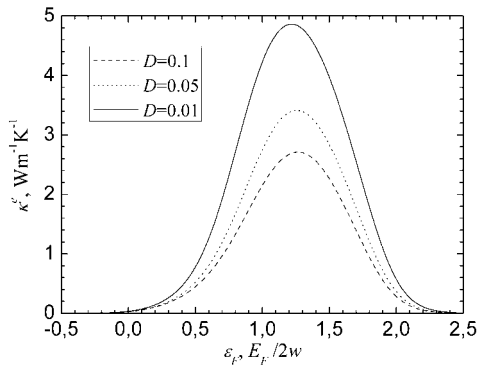

Fig.6. The electronic thermal conductivity κ^e as a function of Fermi energy ε_F for $\gamma = 2.5$.

diminished and are displaced to lower value of Fermi energy.

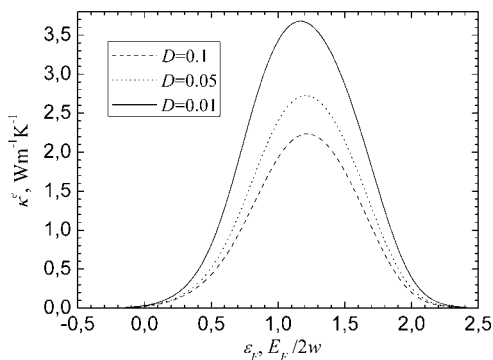Thus, by varying the parameters γ and D one can change

Fig.7. The electronic thermal conductivity κ^e as a function of Fermi energy ε_F for $\gamma = 3$.

the electronic thermal conductivity κ^e in a large interval. For the range of dimensionless Fermi energy of the order of 0.5 − 0.7 the electronic thermal conductivity receives not very high values. It is favorable for thermoelectric applications of such crystals. As it was shown in [14, 15] for other Q1D organic crystals of tetrathiotetracene–iodide, TTT_2I_3, the interference of above mentioned electron-phonon interactions has a less strong influence on the electronic thermal conductivity than on electrical conductivity.

III. CONCLUSIONS

The electronic thermal conductivity has been modeled in quasi-one-dimensional organic crystals with the parameters of TCNQ chains in the tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) crystals. Two more important electron-phonon interactions and the scattering on impurities are taken into account. The first interaction is similar to that of deformation potential and the second is similar to that of polaron, caused by induced polarization. Earlier it was shown that under certain conditions between these interactions the interference can take place. The interference leads to considerable mutual compensation of both interactions for a strip of sates in the conduction band and to relaxation time which has the form of Lorentzian as a function of carrier energy. The crystal model is characterized by two main parameters: γ which is the ratio of amplitudes of both electron-phonon interactions, and D which describes the scattering on impurities. The position of Lorentzian in the conduction band depends on parameter γ and the height – on parameter D. The electronic thermal conductivity has been calculated as function of dimensionless Fermi energy ε_F for different values of parameters γ and D. It is shown that the electronic thermal conductivity has a maximum the position and the value of which strongly depend on parameters γ and D.

By varying the parameters γ and D one can change the electronic thermal conductivity κ^e in a large interval. For the range of dimensionless Fermi energy of the order of 0.5 − 0.7, typical for TCNQ chains in TTF-TCNQ crystals, the electronic thermal conductivity receives not very high values. It is favorable for thermoelectric applications of such crystals.

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