

Modeling of the Thermoelectric Properties of Quasi-One-Dimensional Organic Semiconductors

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Abstract

Electrical conductivity σ , Seebeck coefficient S , electronic thermal conductivity κ^e and the thermoelectric figure of merit ZT are investigated theoretically in quasi-one-dimensional (Q1D) organic semiconductors that consist of linear conducting chains of molecules. Two main electron-phonon interaction mechanisms are considered simultaneously. It is shown that under certain conditions the interference between these interactions can occur. As a result, the relaxation time $\tau(E)$ as a function of carrier energy takes the form of a Lorentzian peak, which can be rather sharp. The increase of $\tau(E)$ leads to the increase of σ , and the strong dependence of $\tau(E)$ on E ensures, simultaneously, the growth of S , at relatively low values of thermal conductivity. Unusually high values of ZT are predicted in such Q1D organic semiconductors.

Introduction

From the general principles of solid state physics there is no upper limit for the thermoelectric figure of merit. Simply, the traditional methods for the search of materials with improved thermoelectric properties, formulated long time ago [1] have practically exhausted themselves [2]. Recently, this search has been extended significantly by the emergence of quantum confined structures: quasi-two-dimensional (Q2D), quasi-one-dimensional (Q1D) and quasi-zero-dimensional (quantum-dot) superlattice materials [3]. Theoretically, the possibility has been shown [4,5] to increase the thermoelectric figure of merit ZT (at room temperature T) of quantum well (QW) material in PbTe/PbEuTe QW structures, due to electron confinement, by 2.6 times in comparison with that of the best bulk value. The dimensional confinement leads also to an increase of the phonon scattering rate and, accordingly, to a strong drop of the in-plane lattice thermal conductivity [6]. The phonon engineering can give an important additional increase of ZT [7]. An improvement of thermoelectric properties of IV-VI based quantum well [8,9] and quantum dot [10] superlattice materials has been observed experimentally. A factor of seven enhancement of ZT relative to bulk Si has been measured for the Si/Ge superlattice [11]. A value of $ZT \sim 2.4$ has been observed [12] in p -type B_2Te_3/Sb_2Te_3 superlattice at room T . Certainly, in order to extend considerably the applications of thermoelectric devices it is necessary to obtain new materials with higher values of ZT . Therefore, it is of especial importance to search and investigate materials with more complicated electronic and phonon spectra, which would permit to overcome the restrictions on ZT increase, observed in conventional binary and ternary compounds. In this regard, the investigation of thermoelectric properties of new organic materials present

significant interest. Note that the possibility to achieve ZT enhancement in organic semiconductors has already been discussed in literature [13-15]. But only recently the progress in synthesis of organic materials made their proposed thermoelectric applications feasible.

In the present paper we show that in quasi-one-dimensional organic crystals it is possible to obtain values of ZT considerably higher than unity. It has been already demonstrated [16,17] that in such crystals it is possible to achieve an extremely high carrier mobility or electrical conductivity.

Description of Quasi-One-Dimensional Crystals

From the structural point of view the highly conducting Q1D organic crystals are formed of linear chains of molecules that are packed into a 3D crystalline structure. The distance between the molecules along the chains is considerably less than in transversal direction. Accordingly, the overlap of electronic wave functions along the chains is significant, whereas between the chains it is very small. The carriers are moving mainly along the separate chains and jump from one chain to another rarely. The ion-radical salts of tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) type, complexes with a charge transfer, crystal polymers belong to the Q1D class of crystals [18].

Usually, in Q1D systems there are different phase transitions, characterized by respective critical parameter, for example the temperature. However, it is known that for temperatures higher than the maximum phase transition temperature, in order to study the transport phenomena, it is possible to neglect in the first approximation the weak interaction between the chains. Then we obtain a simpler 1D crystal model [16,17]. It is important to note, that the considered here model takes into account simultaneously two electron-phonon interaction mechanisms. The first is determined by the variation of the transfer energy W (or transfer integral) for an electron from one molecule to the neighboring one, caused by the lattice acoustic vibrations. This interaction is similar to that of the deformation potential and was already used to describe the electrical transport in Q1D crystals of TTF-TCNQ type [19]. The coupling constant of this mechanism is proportional to the derivative W' of W with respect to the intermolecular distance. The second interaction mechanism is connected with the variation, due to the same intermolecular vibrations, of the polarization energy of molecules surrounding the conduction electron. This mechanism is similar to that of the continuum polaron model, only here the question is about induced polarization. The coupling constant of this mechanism is proportional to the mean polarizability α_0 of the molecule. This mechanism has been considered in literature as well [20,21], but only in

particular cases. It is very important to consider both these interactions together, because under certain values of crystal parameters the interference between them becomes possible [16].

Using the band scheme in the tight-binding and nearest-neighbors approximations, the matrix element $A(k, q)$ of the electron-phonon interaction can be written in the form

$$A(k, q) = 2i\hbar^{1/2}W'(2NM\omega_q)^{-1/2} \times [\sin ka - \sin(k - q, a) + \gamma \sin qa], \quad (1)$$

$$\gamma = 2e^2\alpha_0/a^5W', \quad (2)$$

where the first two terms in Eq.(1) represent the matrix element of the first interaction mechanism, and the third term, respectively, that of the second mechanism mentioned above. The parameter γ has the meaning of the ratio of amplitudes of these two mechanisms, e is the electron charge, M is the mass of the molecule, N is the number of molecules in the basic region of the chain, a is the lattice constant along the chains. The dispersion law of conduction electrons is given by the usual expression $\varepsilon(k) = 2W(1 - \cos ka)$, where k is the projection along the chains of the electron wave vector. The sign of W is chosen so that $W > 0$ for the band of s -type, and $W < 0$ for the p -type one. The dispersion law for longitudinal acoustic phonons has the standard form $\omega_q = 2v_s a^{-1} |\sin qa/2|$, where v_s is the sound velocity along the chains, q is the projection along the chains of the phonon wave vector.

Thermoelectric Transport

We are interested in the study of thermoelectric transport at temperatures T close to room temperature. At such T the scattering processes can be considered elastic. The mentioned interference of electron-phonon interactions may be disturbed by the scattering of carriers on impurities or by other scattering mechanisms. The latter will be neglected as less important. But the impurities will be taken into account and considered for simplicity neutral, randomly distributed and point-like (δ -function similar). In this case the Boltzmann kinetic equation is solved exactly, confirming the existence of the relaxation time. It is convenient to present the relaxation time $\tau_{s,p}(E)$ as a function of the carrier energy for s - and p -type bands respectively

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

$$D^2 = n_{im} I^2 d^2 M v_s^2 / (4a^3 k_0 T W'^2) = D_0^2 T_0 / T. \quad (4)$$

Here $\Delta = 4W$ is the conduction band width, $0 \leq E \leq \Delta$, $E_0^{s,p} = 2W(\gamma \pm 1)/\gamma$ is the resonance energy, k_0 is the Boltzmann constant, $T_0 = 300\text{K}$, D is a parameter, which takes into account the impurity scattering, n_{im} is the linear impurity concentration, I and d characterize the effective height and width of the impurity potential, and the phonon distribution function has been replaced by its high T limit.

If $\gamma = 0$ and $D = 0$, i.e. only the first interaction mechanism is included, the expression which results from (3) coincides with the formula (2.38) of Ref. [19]. But if $\gamma \geq 1$, $\tau_{s,p}(E)$ as a function of energy E takes the form of a Lorentzian centered in the conduction band at $E = E_0^{s,p}$. If additionally $D \ll 1$, i.e. the impurity scattering is very weak, the Lorentzian becomes rather sharp. This means that the energy states around $E_0^{s,p}$ are characterized by very long relaxation time and reduced scattering rate. The carriers in these states will have increased mobility.

Already from expression (3) for $\tau_{s,p}(E)$ it is seen that the crystals with such parameters will have improved thermoelectric properties. Increased values of $\tau_{s,p}(E)$ will ensure high value of σ , and a sharp dependence of $\tau_{s,p}(E)$ on E will lead simultaneously to the growth of the thermopower S .

By using the Eq.(3) for $\tau_{s,p}(E)$ it is possible to write the expressions for σ , S and κ^e in integral form. Here we will consider only the non-degenerate case when the calculations are simpler. We obtain

$$\sigma = R_0; \quad S = R_1/eTR_0; \quad \kappa^e = (R_2 - R_1^2/R_0)/e^2T, \quad (5)$$

where

$$R_n = \frac{1}{k_0 T} \int_0^\Delta (E - E_F)^n \sigma(E) \exp\left(\frac{E_F - E}{k_0 T}\right) dE, \quad (6)$$

$$\sigma(E) = e^2 v^2(E) \tau(E) \rho(E), \quad (7)$$

with $\tau_s(E)$ and $\tau_p(E)$ for s - or p -type bands, respectively. Here E_F is the Fermi energy, which will be considered of the order of $(-3k_0 T_0)$, $v^2(E) = \hbar^{-2} a^2 E(\Delta - E)$ is the square of the carrier velocity as a function of energy E , $\rho(E) = (2r/\pi a) [E(\Delta - E)]^{-1/2}$ is the density of states per unit volume and energy, and r is the number of chains on 1 cm^2 of the transversal section of the crystal. The integrals in σ , S and κ^e can be calculated in analytical form, but the respective expressions are very cumbersome and cannot be presented here.

At the same time it is interesting to consider the situation when the Lorentzian in $\tau(E)$ is very sharp, i.e. $\gamma > 1$ and $D \ll 1$. In this case the integrals R_0 , R_1 and R_2 can be calculated approximately by decomposing the Lorentzian in series on D .

For the calculation of σ it is sufficient to take only the first term from the decomposition, which corresponds to the replacement of the Lorentzian by delta function, and we obtain

$$\sigma_{s,p} \cong \sigma_0 \frac{\pi(\gamma^2 - 1)}{2\gamma^3 D_0 (1 - k_0 T_0 / 2W)} \left(\frac{2W}{k_0 T}\right)^2 \exp\left(-\frac{E_0^{s,p}}{k_0 T}\right), \quad (8)$$

where σ_0 is the approximated conductivity, determined by only the first interaction mechanism ($\gamma = 0$, $D_0 = 0$) at $T_0 = 300 \text{ K}$,

$$\sigma_0 = e^2 n M v_s^2 W^{3/2} [1 - k_0 T_0 / (2W)] / [\pi^{1/2} \hbar W'^2 (k_0 T_0)^{1/2}], \quad (9)$$

and n is the 3D carrier concentration. It is seen that if only $E_0^{s,p}$ is not very much greater than $k_0 T_0$, then $\sigma_{s,p} > \sigma_0$, so as D_0 is in the denominator and $D_0 / (\gamma^2 - 1) \ll 1$. Thus, the inclusion of the second interaction does not diminish $\sigma_{s,p}$, but increases it, due to above mentioned mutual compensation of interaction mechanisms. The growth of $\sigma_{s,p}$ is determined by the carriers that populate through thermal activation the range of states near $E_0^{s,p}$ with high mobility.

For the calculation of $S_{s,p}$ it is necessary to take two terms in the decomposition of the Lorentzian after D_0 , and we find

$$S_{s,p} = (k_0 / e) [(E_0^{s,p} - E_F) / k_0 T + (\sim D_0)]. \quad (10)$$

In thermoelectric applications the first term in (10) must be as great as possible, and the second term, which is proportional to D_0 , may be neglected. The value of $S_{s,p}$ directly depends on the difference $(E_0^{s,p} - E_F)$, and may easily achieve $\pm(400 \div 600) \mu\text{V}/\text{K}$. If $E_0^{s,p} > E_F$, the sign of $S_{s,p}$ coincides with that of the majority carriers. If $E_0^{s,p} < E_F$, the excitation of carriers lower than E_F means the creation of opposite sign carriers, and the sign of $S_{s,p}$ is opposite.

For $\kappa_{s,p}^e$ it is necessary to take at least two terms in the decomposition of the Lorentzian, and we obtain

$$\kappa^e = 4\sigma_0 W^2 T_0^{1/2} / (e^2 \gamma^2 T^{3/2}), \quad (11)$$

where σ_0 is defined by (9). It is seen that κ^e does not depend on the band type, therefore the indexes s - and p - were omitted. As κ^e is proportional to $W^{7/2}$, its value grows rapidly with the increase of W (or band width). Therefore, we will choose for calculations a crystal with a not large band width. Let's take a crystal with the parameters close to those of TTF p -type chains in the TTF-TCNQ crystal [19]: $M = 3.7 \times 10^5 m_e$, $W = 0.075 \text{ eV}$, $W' = 0.02 \text{ eV \AA}^{-1}$, $v_s = 2 \times 10^5 \text{ cm/s}$, $r = 2/bc$ (2 chains through the bc section of the elementary cell), $a = 12.3 \text{ \AA}$, $b = 3.82 \text{ \AA}$, $c = 18.47 \text{ \AA}$ (\vec{b} is the direction of chains). If we shall put $E_F = -3k_0 T_0$, it corresponds to the hole concentration $n = 3.83 \times 10^{19} \text{ cm}^{-3}$ and $\sigma_0 = 11.7 \Omega^{-1} \text{ cm}^{-1}$. For $\gamma = 1.5$ the formula (11) gives $\kappa^e = 0.39 \text{ mW/cmK}$, a rather low value of κ^e . With the increase of γ , κ^e will continue to decrease as γ^{-2} .

Now the expression for $(ZT)_{s,p}$ can be written as

$$(ZT)_{s,p} = \frac{2\pi\sigma_0(\gamma^2 - 1)W^2(E_0^{s,p} - E_F)^2}{e^2(\kappa^L + \kappa^e)\gamma^3 T D_0 (k_0 T)^2 (1 - k_0 T_0 / 2W)} e^{-E_0^{s,p} / k_0 T}, \quad (12)$$

where κ^L is the lattice thermal conductivity and κ^e is determined by (11). The thermal conductivity of TTF-TCNQ crystals at 300K has been determined experimentally [22], being equal to 10 mW/cmK and dominated by the phonon part. If we shall take this value for κ^L and the above

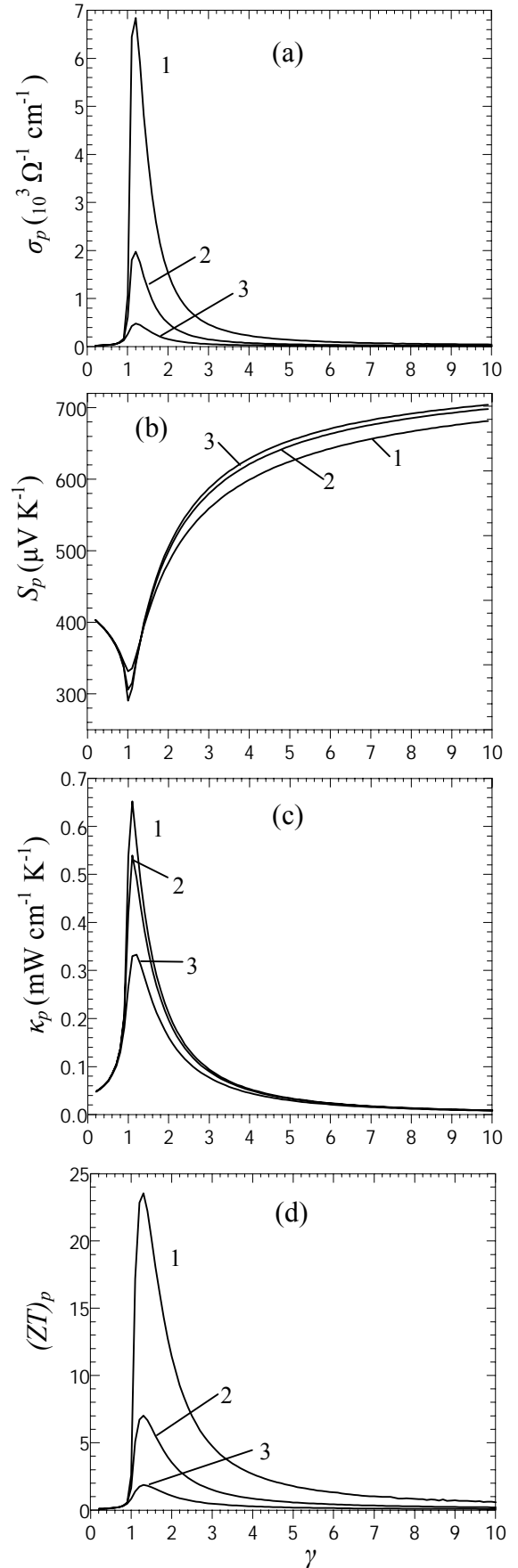


Figure 1. Calculated: (a) - σ_p ; (b) - S_p ; (c) - κ_p^e ; and (d) - $(ZT)_p$ as a function of γ . D_0^2 : 1- 10^{-4} ; 2- 10^{-3} ; 3- 10^{-2} .

mentioned ones for the other crystal parameters, we obtain at $T = 300 \text{ K}$ $(ZT)_p = 2.1 \times 10^{-1} D_0^{-1}$, i.e. $(ZT)_p = 21$ for $D_0 = 10^{-2}$. Numerical calculation after the exact expressions of σ , S , κ^e and ZT gives for these parameters $(ZT)_p = 20.2$, a value very close to the approximate one. This fact confirms the applicability of used approximations for the given range of crystal parameters. To this value of $(ZT)_p$ corresponds $\sigma_p = 3.90 \times 10^3 \Omega^{-1} \text{cm}^{-1}$, $S_p = 423 \mu\text{V/K}$, $\kappa^e = 0.369 \text{ mW/cmK}$. If the parameter D_0 is a little greater, $D_0 = 10^{-3/2}$, from (12) follows $(ZT)_p = 6.6$, still a very good value. For larger values of D_0 numerical calculation is needed. Obtained values of $(ZT)_p$ are not yet optimized with respect to crystal parameters. So, even higher values of $(ZT)_p$ can be expected.

The results of numerical calculation of σ_p , S_p , κ_p^e and $(ZT)_p$ as functions of the parameter γ for a p -type crystal with the above mentioned physical parameters and different values of D_0 are shown in Fig.1. It is seen that at small γ ($\gamma \ll 1$) the values of all kinetic coefficients do not depend on D_0 and ZT is rather small. The mutual compensation of electron-phonon interactions does not take place. When $\gamma > 1$, σ_p grows considerably, especially at small D_0 (curve 1 in Fig.1a) due to important increase of carrier mobility, and has a pronounced maximum, which depends essentially on D_0 . The interference of interaction mechanisms considerably affects σ_p . When σ_p increases, S_p decreases, but remains at rather high values. The dependence of S_p on D_0 is weak. Even for such high carrier concentration as $4 \times 10^{19} \text{ cm}^{-3}$, κ_p^e is rather small, due to large carrier effective masses. The maximum value $(ZT)_p = 23.5$ is achieved for $\gamma = 1.3$ and $D_0 = 10^{-2}$. With the increase of D_0 this maximum decreases considerably.

Conclusions

A mechanism for large enhancement of ZT in Q1D organic semiconductors is proposed. It is related to the mutual compensation of two main electron-phonon interaction mechanisms for a narrow range of carrier states in the conduction band. As a result, the relaxation time as a function of carrier energy takes the form of a sharp Lorentzian. The carriers in these states have significantly increased mobility. The Seebeck coefficient attains large values as well due to strong dependence of relaxation time on energy. As a result, it is predicted that the room temperature ZT can be as high as 20 in such materials.

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