

Low Dimensional Organic Compounds as Promising Thermoelectric Materials

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Abstract

The thermoelectric properties of quasi-one-dimensional (Q1D) organic crystals with *p*-type conduction band are studied. Two main electron-phonon interaction mechanisms and carriers scattering on impurities are taken into account. The relaxation time as a function of carrier energy is analyzed for different values of crystal parameters. It is shown that under certain conditions, when the interference of both electron-phonon interactions is well manifested, the relaxation time takes the form of Lorentzian, the maximum of which is inversely proportional to the impurity concentration and can be very high and sharp, if the crystal is sufficiently pure. The thermoelectric figure of merit is modelled in such Q1D organic crystals as a function of Fermi energy for different parameters and different degree of purity. The highest calculated value of $ZT = 21$ at room temperature in these *p*-type crystals is presented.

Introduction

The early time of thermoelectric refrigeration has been rather fruitful. The famous scientist, Abram Ioffe has proposed to use heavily doped semiconductors as thermoelectric materials. He has predicted still 50 years ago that home and other thermoelectric refrigerators will rather soon replace the compressor based ones [1]. The best binary thermoelectric material at room temperature Bi_2Te_3 with the dimensionless thermoelectric figure of merit ZT near 1 was soon found. To date, however, Ioffe's predictions have not been realised yet. In spite of a big effort of a large number of scientists and of a multitude of investigated materials, the maximum value of ZT in bulk materials could not be increased essentially, and it remains rather low.

Presently, it is comprehended that the traditional methods applied to improve the thermoelectric properties of materials, formulated still many years ago, were practically exhausted. Other methods have been also proposed. Among them we can note artificial anisotropic materials [2], the use of barrier structures [3], the creation of materials with resonance scattering [4, 5], the application of structures with *p-n*-homo and heterojunctions [6]. Theoretical fundamentals of the thermoelectricity were also revised [7]. However, a significant increase of thermoelectric figure of merit has not been achieved, although there is no an upper limit for the thermoelectric figure of merit from the point of view of physical principles. Nevertheless, it became clear that in order to increase the electrical conductivity and the thermopower and to decrease the thermal conductivity, all in the same material, it is necessary to search for and investigate new, more complicated materials.

Different approaches in this direction are now developed. Two of them should be mentioned here. One consists in the search of bulk materials with many atoms in

the unit cell and more complicated electronic and phonon spectra able to possess simultaneously high electrical conductivity, high thermopower and low thermal conductivity. Promising materials are the semiconductor clathrates [8] and filled skutterudite systems [9]. Recently, high $ZT \sim 2.2$ at 800 K was reported in complex chalcogenide compounds of the type $\text{AgPb}_m\text{SbTe}_{2+m}$ [10]. The exact origin of such high ZT is not yet completely determined. The resonance states arising from the presence of different ordering arrangements of Ag-Sb atoms, considered as nanodots, were suggested to be related to such high figure of merit in these materials.

Another approach is the application of low dimensional systems such as two dimensional (2D) quantum-well structures, one dimensional (1D) quantum wires, and zero-dimensional (0D) quantum dot superlattices [11-14]. Really, all these structures are quasi-2D, quasi-1D and quasi-0D systems.

It has been demonstrated both theoretically and experimentally that when the dimensionality of a good thermoelectric material is reduced from 3D to lower dimensionality, an opportunity appears to improve the thermoelectric properties of the quantum well material and even of the whole superlattice structure. This opportunity is connected mainly with the increase of electronic density of states when the system dimensionality is reduced. The possibility appears to transform the carriers gas that in bulk 3D material would be degenerate, to a nondegenerate or slightly degenerate one in the low dimensional system. Thus, on the one side, one can increase the carriers concentration in order to compensate the reduction of electrical conductivity when the system dimensionality is diminished. On the other side, it is possible to maintain the carriers concentration at a rather low level in order to have nondegenerate electronic gas and high values of the thermopower. Moreover, the thermal conductivity can be reduced by interface scattering of phonons.

Harman [11] has experimentally demonstrated a value of $ZT \sim 3$ at elevated temperatures for PbTeSe quantum dot superlattice embedded in a conducting PbTe medium, and a $ZT = 2$ at room temperature in PbSnSeTe quantum-dot superlattice.

Organic materials

Certainly, for thermoelectric cooling and energy conversion applications macroscopic bulk materials are required and not nanoscale systems. From this point of view, some new highly conducting organic compounds seem to be very promising thermoelectric materials. Unfortunately, the thermoelectric properties of organic materials are still weakly investigated, in spite of predictions, made even long ago [15-17] that among organic compounds it is expected to find materials with higher thermoelectric figure of merit than

that of the existing inorganic materials. Probably the thermoelectricians are not yet really interested in organic materials, and the organic chemists do not know enough about the thermoelectric possibilities of their compounds.

At our knowledge, the highest value of $ZT = 0.15$ at room temperature was reported in pCuPc (polycopper phthalocyanine) [16]. It is interesting to compare the parameters of this organic material: electrical conductivity $\sigma = 0.3 \Omega^{-1}\text{cm}^{-1}$, thermopower (Seebeck coefficient) $S = 3100 \mu\text{V/K}$, thermal conductivity $\kappa = 5.5 \text{ mW/cmK}$, with those of the best inorganic material Bi_2Te_3 . One can see that in this organic material the thermopower is 15 times higher, the thermal conductivity is 3 times lower, but the electrical conductivity is very low. Doping can increase the electrical conductivity, but the thermopower drops drastically. By the way, from the general principles of band theory it is difficult to explain such very high values of thermopower.

Presently, the organic compounds attract more and more the attention of investigators both as low cost replacements of ordinary conductors and semiconductors, and as materials with much more diverse physical properties as compared to those of inorganic materials. Such materials have already obtained large applications into new generations of organic based microelectronic devices.

Quasi-one-dimensional organic crystals

Among organic crystals the quasi-one-dimensional ones present a particular interest for us. Such compounds are not simply very anisotropic crystals, but present a separate, specific class. From the structural point of view, such crystals are formed from linear chains or stacks of molecules packed up into a three-dimensional crystalline structure. The distance between molecules along the chains is several times smaller than between molecules of different chains. Respectively, the interaction between the molecules along the chains is much stronger than between the molecules of nearest chains. As a result, the crystals have needle-like form with the length of usually $\sim 6\text{-}20 \text{ mm}$, and the thickness $\sim 20\text{-}60 \mu\text{m}$.

The overlap of molecular orbitals for conduction electrons is strong along the chains, but between the chains it is weak. Consequently, the conduction mechanism along the chains is band like, and between the chains is hopping like. In the first approximation the latter can be neglected and we obtain a 1D crystal model. The carriers move only along the chains where they have been created and do not hop from one chain to another.

The crystal model has been described in more detail in [18, 19]. So as the molecular orbitals are rather localized, the tight binding and nearest neighbours approximations are used. The effective mass and long wave length approximations are not applicable. The dispersion law for carriers is taken in the cosinusoidal form, usual for mentioned approximations, but for 1D longitudinal acoustic phonons the exact expression is considered. The model joins together the peculiarities of interactions in organic crystals and the increased density of states in Q1D quantum wires.

The model takes into account two more important electron-phonon interactions and scattering of carriers on impurities which always exist in the crystal. The first interaction is that of deformation potential. The energy of transfer w of the electron from one molecule to the nearest one along the chains strongly depends on the distance between the molecules. The acoustic thermal vibrations vary this distance leading to the coupling between electrons and acoustic phonons. The coupling constant is proportional to the derivative w' of transfer energy w with respect to the intermolecular distance. So as for p -type band w is positive, w' will have a negative sign.

The second interaction is similar to that of the polaron. The conduction electron polarizes the surrounding molecules and induces on them electrical dipoles. The polarisation energy of interaction of the conduction electron with the induced dipoles strongly depends on the distance between the electron and surrounding molecules. The same acoustic vibrations change this distance leading to another coupling between electrons and acoustic phonons. The coupling constant is proportional to the average polarizability α_0 of the molecule.

The ratio of amplitudes of the second interaction mechanism to the first one is characterized by the parameter γ . Thus, the parameter γ is proportional to the molecular polarizability α_0 , and is inversely proportional to the derivative w' . The molecular polarizability is roughly proportional to the volume of the molecule. If this volume is small, α_0 is small and $\gamma \ll 1$. Only the first interaction mechanism is important. This is the case of inorganic conductors and semiconductors formed of atoms and of materials formed of weakly polarizable molecules. The study of transport properties of Q1D organic crystals on the base of only the first interaction has been considered in literature [20].

It is very important that both these interactions give simultaneously significant contributions, because under certain conditions the interference between them can take place. Due to the interference, these interactions compensate considerably each other for some states into the conduction band. For these states the carriers scattering rate is strongly reduced and the relaxation time is increased. As a function of carrier energy, the relaxation time has a pronounced maximum for energies, corresponding to these states into the conduction band.

The population of these states by carriers takes place as a consequence of thermal activation. And if these states are not far from the Fermi level, the activation energy is not big. In this case the contribution of respective carriers to the conductivity will be very important. The electrical conductivity of crystal will be considerably increased.

Due to sharp dependence of relaxation time on energy, and to increased density of states the thermopower will be also increased. At the same time, the thermal conductivity is expected not to be very high. This is favourable to expect an essential improvement of thermoelectric properties of some highly conducting Q1D organic materials.

Basic expressions

So as the conduction band in Q1D organic crystals is relatively narrow, the variation of electron and phonon quasimoments into the whole Brillouin zone must be considered. The scattering of carriers on impurities is elastic. The scattering on acoustic phonons can be considered elastic in a large temperature interval near the room temperature. In this approximation the kinetic equation is easily solved [18] and the expressions for electrical conductivity σ , thermopower S and electronic thermal conductivity κ^e can be written using the transport integrals

$$\sigma = R_0, \quad S = R_1 / eTR_0, \quad \kappa^e = (e^2 T)^{-1} (R_2 - R_1^2 / R_0), \quad (1)$$

where

$$R_n = - \int_0^\Delta (E - E_F)^n \sigma(E) f'_0(E) dE, \quad (2)$$

$$\sigma(E) = e^2 v^2(E) \tau(E) \rho(E) \quad (3)$$

Here e is the electron charge, T is the temperature, $v^2(E) = \hbar^{-2} a^2 E(\Delta - E)$ is the square of the carriers velocity as a function of energy E , $0 \leq E \leq \Delta$, Δ is the width of the conduction band, $\Delta = 4w$, E_F is the Fermi energy, f'_0 is the derivative of Fermi distribution function with respect to the energy E , $\rho(E)$ is the density of electronic states per unit volume and energy

$$\rho(E) = (2z / \pi abc) [E(\Delta - E)]^{-1/2}, \quad (4)$$

a , b and c are the lattice constants, z is the number of chains through the transversal section of the unit cell. The quantity $\tau(E)$ is the relaxation time

$$\tau(E) = \tau_0(E) L(E), \quad (5)$$

$$\tau_0(E) = \frac{\hbar M v_s^2 [E(\Delta - E)]^{1/2}}{8a^2 k_0 T w'^2}, \quad (6)$$

$$L(E) = \frac{4w^2}{\gamma^2 (E - E_0)^2 + 4w^2 D}. \quad (7)$$

Here $\tau_0(E)$ is the relaxation time for the case, when $\gamma = 0$ and $D = 0$, i.e. when only the first electron-phonon interaction exists, $L(E)$ describes the interference of both interactions and has the form of Lorentzian as a function of energy E , $E_0 = 2w(\gamma - 1) / \gamma$ is the resonance energy, which corresponds to the maximum of $\tau(E)$, M is the mass of molecule, v_s is the sound velocity along the chains. The

parameter γ which is the ratio of amplitudes of above mentioned electron-phonon interactions, has the form

$$\gamma = 2e^2 \alpha_0 / a^5 |w'|. \quad (8)$$

The carriers scattering on impurities, considered neutral and point-like is described by the dimensionless parameter D

$$D = n_{im} I^2 d^2 M V_s^3 / (4a^3 k_0 T w'^2), \quad (9)$$

where n_{im} is the linear concentration of impurity, I and d are the effective height and width of impurity potential.

The expressions for thermopower S and for thermoelectric power factor $P = \sigma S^2$ have been modelled in [21] and [22], respectively, for typical Q1D organic crystals, formed of chains with parameters close to those of TCNQ (*s*-type band) and TTF (*p*-type band) in the TTF-TCNQ (tetrathiofulvalene-tetracyanoquinodimethane) crystals. It has been demonstrated that under certain conditions unusually high values of S and P can be obtained in such crystals.

The dimensionless thermoelectric figure of merit $ZT = \sigma S^2 T / (\kappa^L + \kappa^e)$, where κ^L is the lattice thermal conductivity, has been modelled in some Q1D organic crystals in [23, 24]. Values of ZT up to 20 have been predicted at room temperature. In [25] we have shown that even higher value of $ZT \sim 22$ can be expected in very perfect crystals with electronic conduction at optimal parameters. In this paper we will consider Q1D organic crystals with hole conduction and typical parameters: $M = 3.7 \cdot 10^5 m_e$ (m_e is the mass of free electron), $w = 0.125$ eV, $\kappa^L = 10$ mW/cmK, $w' = 0.2$ eV \Rightarrow^{-1} , $v_s = 2 \cdot 10^5$ cm/s, $a = 12.3 \Rightarrow$, $b = 3.82 \Rightarrow$, $c = 18.47 \Rightarrow$, $z = 2$. The direction of chains is along \mathbf{b} .

Relaxation time

Firstly, let's analyze the behaviour of the relaxation time after (5). The values of dimensionless parameter $D =$

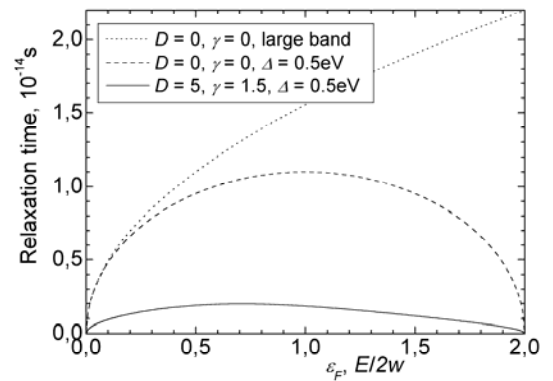


Fig.1. Relaxation time as a function of dimensionless carrier energy

$2 \cdot 10^{-2}$; $4 \cdot 10^{-3}$; 10^{-3} at room temperature are chosen for crystals with more accessible purity. As an example of very imperfect crystals the case when $D = 5$ is considered. In Fig.1 the dependences of relaxation time on dimensionless energy ε , expressed in unities of $2w$, $\varepsilon = E/2w$, is presented. So as $0\beta E\beta 4w$, it results that $0\beta \varepsilon \beta 2$. The dotted

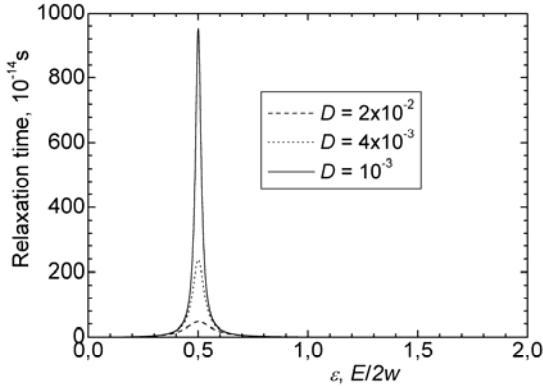


Fig.2. Relaxation time as a function of dimensionless carrier energy for $\gamma = 1.5$.

curve corresponds to the case of ordinary Q1D materials with large conduction band $\tilde{v} = 4w$ ($k_0 T_0$ ($T_0 = 300\text{K}$) and with only the first interaction mechanism (deformation potential). This dependence follows from (5) when $\gamma = 0$ and $D = 0$. It corresponds to $\tau(\varepsilon) \approx \sqrt{\varepsilon}$, as is expected in this case. The dashed curve corresponds to Q1D crystals also with only the first interaction mechanism ($D = 0$, $\gamma = 0$), but with not very large conduction band, when the variation of carrier quasi-momentum into the whole Brillouin zone must be taken into account. Maximum value of $\tau(\varepsilon)$ is $\sim 1.1 \cdot 10^{-14}$ s. The continuous curve corresponds to $\gamma = 1.5$ and $D = 5$. It is seen that $\tau(\varepsilon)$ is diminished for all energies. A weak and large maximum is observed near $\varepsilon = (\gamma - 1)/\gamma = 0.333$ that achieves only $\sim 0.16 \cdot 10^{-14}$ s. It is important to note that in all these cases the relaxation time is a smooth function on energy and is relatively small. This means that one can not expect high values of electrical conductivity and thermopower for such crystals, and such materials have weak prospects for thermoelectric applications.

In Fig. 2 the dependences of relaxation time on energy is presented for three crystals with $\gamma = 1.5$ and different, but high degree of purity ($D \ll 1$). The other parameters are those mentioned above. It is seen that the variation becomes very sharp. The relaxation time has a pronounced maximum at $\varepsilon = 0.333$ which in the purest crystal with $D = 10^{-3}$ achieves $9.2 \cdot 10^{-12}$ s. Even in the less pure crystal with $D = 2 \cdot 10^{-2}$ the maximum of $\tau(\varepsilon)$ is still high and achieves $4 \cdot 10^{-13}$ s. It is expected that the Q1D organic compounds with such parameters will be promising thermoelectric materials. High values of relaxation time, if these states are populated by carriers, will lead to high electrical conductivity, and sharp dependence on energy will ensure simultaneously high values of the thermopower.

Thermoelectric figure of merit

The results of thermoelectric figure of merit modelling are presented in Figs. 3-7. Calculations are made for room temperature $T_0 = 300$ K as a function of dimensionless Fermi energy ε_F , expressed in unities of $2w$, $0 \leq \varepsilon_F \leq 2$. In Fig. 3 the parameter γ is small, $\gamma = 0.01$. This means that the polarizability of molecules is very weak and only the first electron-phonon interaction mechanism is manifested. It is seen that the maximum value ZT corresponds to $\varepsilon_F \sim 0$ and is small, of the order of 0.29.

The Q1D organic crystals are mixed-valence compounds. The carriers are created by transfer of electrons from donor molecules to acceptor ones. We consider the case when the donor molecules form their chains, and acceptor molecules their chains, and only the donor chains are highly conducting. Thus, the electron transfer takes place from one chain to another. In many cases the degree of transfer is such that the conduction band is filled to the order of 1/4. In these crystals the Fermi energy ε_F is close to 0.5, or carrier concentration $n \sim 1.2 \cdot 10^{21} \text{cm}^{-3}$. From Fig. 3 it is seen that for $\varepsilon_F = 0.5$ (typical for these compounds) the value of ZT is only ~ 0.02 . For optimal parameters we have $\varepsilon_F = 0$ ($n \sim 2.3 \cdot 10^{20} \text{cm}^{-3}$), $\sigma = 290 \Omega^{-1} \text{cm}^{-1}$, $S = 193 \mu\text{V/K}$, $\kappa^e = 1.2 \text{ mW/cmK}$, ($\kappa = 11.2 \text{ mW/cmK}$). Electrical conductivity is very small. This is the situation in crystals formed from very weakly polarizable molecules. Such Q1D organic crystals are not promising thermoelectric materials, even if the optimal ε_F (optimal concentration) is achieved.

The resonance energy E_0^p is placed deeply into the forbidden band and the interference of both electron-phonon interactions does not take place. The three curves which

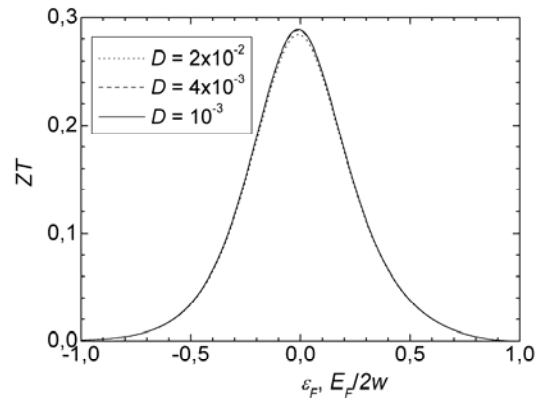


Fig.3. ZT as a function of dimensionless Fermi energy for $\gamma = 0.01$

correspond to different values of D coincide, so as the relaxation time, determined by carriers scattering on impurities is much greater than that determined by acoustical phonons.

In Fig. 4 the case, when the molecule polarizability is a little greater, so that $\gamma = 0.5$, is presented. It is seen that the maximum value of ZT is increased almost two times and is a

little displaced into the forbidden band, but still remains low, $ZT = 0.57$. For $\varepsilon_F = 0.5$ (typical for these compounds), the value of ZT is decreased down to 0.01. The dependence of ZT on D is also not manifested. The resonance energy E_0^p is still far from the band edge and the interference of both

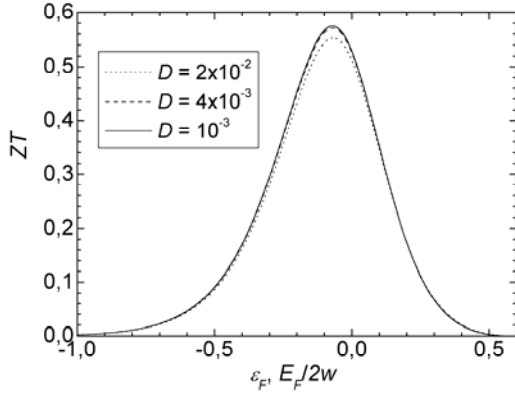


Fig.4. ZT as a function of dimensionless Fermi energy for $\gamma = 0.5$

electron-phonon interactions is not manifested.

When $\gamma = 1$, Fig. 5, the resonance energy E_0^p achieves the edge of the conduction band. One half of Lorentzian from relaxation time is into the conduction band. The interference of both electron-phonon interactions begins to manifest itself. Maximum of ZT rises to 5.5, but is achieved for lower value of $\varepsilon_F = -0.25$. The dependence of ZT on D is well pronounced, the difference between the highest and

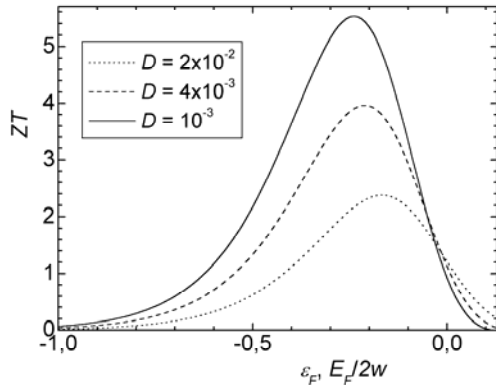


Fig.5. ZT as a function of dimensionless Fermi energy for $\gamma = 1$

the lowest maximums is 3.2.

In Fig. 6 the dependence of ZT on ε_F for $\gamma = 1.5$ is presented. It is seen that ZT achieves the value of 21 in the purest crystal, the highest calculated value in such materials of p -type. The maximum of ZT corresponds to $\varepsilon_F = -0.1$, or to carriers concentration $n = 1.1 \cdot 10^{20} \text{ cm}^{-3}$. Note that this optimal concentration is 11 times lower than the typical one for considered mixed valence crystals. But even for higher Fermi energy $\varepsilon_F = 0.2$ a value of $ZT \sim 7$ is expected, also

an excellent result. It is seen that in a large interval of Fermi energy from -0.5 up to 0.3 values of ZT greater than unity are predicted. Should technological difficulties limit the crystal purity to its lowest level, values of $ZT \sim 4$ can still be expected (dotted curve in Fig. 6), a very good result. It is interesting to know the thermoelectric parameters for the crystal with the highest value of ZT . The calculation gives: $\sigma = 1.2 \cdot 10^4 \Omega^{-1} \text{ cm}^{-1}$, $S = 342 \mu\text{V/K}$, $\kappa^e = 10 \text{ mW/cmK}$, $\kappa = 20 \text{ mW/cmK}$. Seebeck coefficient S is especially high, but all

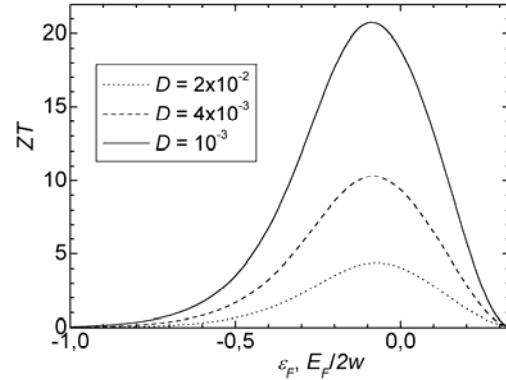


Fig.6. ZT as a function of dimensionless Fermi energy for $\gamma = 1.5$

parameters are, in general, rather reasonable.

If we increase more the molecule polarizability, so that $\gamma = 2$ (Fig. 7), the maximum value of ZT in the purest crystal remains high, but is diminished down to 15 and is displaced to Fermi energy $\varepsilon_F = 0.1$ into the conduction band ($n \sim 4.2 \cdot 10^{20} \text{ cm}^{-3}$). In the crystal with the lowest purity the maximum is diminished down to 3.5. These values of ZT are also very good. The interval of Fermi energy for which ZT is greater than unity is enlarged up to $\varepsilon_F = 0.4$. Now the thermoelectric parameters which correspond to the highest value of ZT are: $\sigma = 2.1 \cdot 10^4 \Omega^{-1} \text{ cm}^{-1}$, $S = 292 \mu\text{V/K}$, $\kappa^e = 25 \text{ mW/cmK}$, $\kappa = 35 \text{ mW/cmK}$. We observe that σ and κ^e have grown, but the thermopower S is diminished.

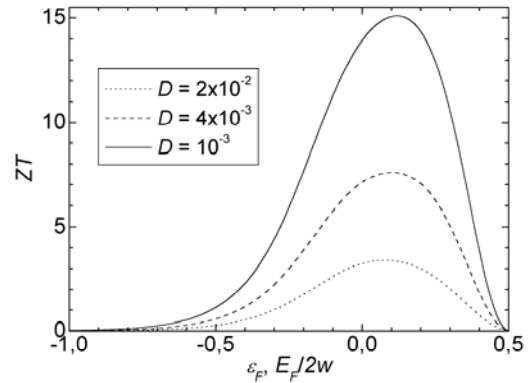


Fig.7. ZT as a function of dimensionless Fermi energy for $\gamma = 2$

With the further increase of parameter γ up to $\gamma = 5$, the thermopower continues to decrease, but the electronic part of

thermal conductivity is also diminished, so that the maximum of ZT remains at the level of 15. This means that such Q1D organic compounds are very promising thermoelectric materials.

Let's estimate the parameter γ . We do not know the value of molecule polarizability α_0 . Therefore we will appreciate α_0 from Eq. (8). We obtain that for above mentioned crystal parameters, when γ varies from 1 to 5, the polarizability α_0 changes from $6 \Rightarrow^3$ to $30 \Rightarrow^3$. These values of α_0 are rather reasonable.

Conclusions

The dimensionless thermoelectric figure of merit ZT has been calculated at room temperature as a function of Fermi energy in some quasi-one-dimensional organic crystals with hole conduction band and typical parameters for such compounds. The crystals have chain structure with band transport along chains and hopping one between chains. The hopping transport usually is small and in the first approximation is neglected.

Two more important electron-phonon interaction mechanisms and carriers 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. Under certain conditions the interference between these two interactions becomes possible.

Due to the interference, the relaxation time as a function of carrier energy obtains a maximum for a strip of states into the conduction band. The behaviour of relaxation time for different values of crystal parameters γ (which is the ratio of amplitudes of both electron-phonon interactions) and D (which describes the scattering on impurities) is presented. For γ close to zero and D greater than unity, when the interference does not manifest itself, the relaxation time is a smooth function on energy and is small ($\sim 10^{-14}$ s). For $\gamma = 1.5$ and $D = 10^{-3}$ (very pure crystal) the relaxation time has a sharp maximum which is 820 times higher than in the previous case.

Due to such behaviour of the relaxation time, the electrical conductivity obtains in this case $1.2 \cdot 10^4 \Omega^{-1} \text{cm}^{-1}$, the thermopower obtains 342 $\mu\text{V/K}$, the electronic thermal conductivity – 10 mW/cmK and the thermoelectric figure of merit achieves a value of 21. This is the highest value, calculated to date in such materials of p -type. However, optimal concentration is 11 times lower than the typical one for considered mixed-valence compounds. Even in crystals with lowest purity ($D = 0.02$) and $\gamma = 1.5$ values of $ZT \sim 4$ are predicted, a very good result. When the parameter γ varies up to 5, maximum of ZT diminishes to ~ 15 , but remains rather high. Values of ZT greater than unity are predicted in a large interval of concentrations. Thus, such well purified Q1D organic crystals are promising thermoelectric materials.

Acknowledgments

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