

STATE OF THE ART AND PROSPECTS  
OF THERMOELECTRICITY  
ON ORGANIC MATERIALS

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- *The aim of the paper is to analyze the expected thermoelectric opportunities of organic materials, including some highly conducting quasi-one-dimensional crystals. It is shown that interest of investigators in these materials has been growing recently. Quasi-one-dimensional organic crystals have high prospects for thermoelectric applications. These materials combine the properties of multi-component systems with more diverse internal interactions and of quasi-one-dimensional quantum wires with increased density of electronic states. It is shown that the values of the thermoelectric figure of merit  $ZT \sim 1.3 - 1.6$  at room temperature are expected in really existing organic crystals of tetrathiotetracene-iodide,  $TTT_2I_3$ , if the crystal parameters are approaching the optimal ones.*

## Introduction

It is known that conducting organic materials usually have much lower thermal conductivity than the inorganic materials. Moreover, the organic materials can be fabricated by simpler chemical methods, and it is expected that such materials will be less expensive in comparison with the inorganic ones. Exactly these properties attracted attention to such materials for the use in thermoelectric (TE) applications long time ago [1, 2]. In spite of relatively high value of the thermoelectric figure of merit  $ZT = 0.15$  at room temperature observed in polycopper phthalocyanine [2] as early as 1980, the thermoelectric properties of organic materials are still weakly investigated. This situation has the only explanation that thermoelectricians are still weakly interested in organic materials, and organic chemists are also weakly interested in thermoelectric materials. Moreover, in order to seek good organic thermoelectrics, it is necessary to organize multidisciplinary consortiums of physicists, organic chemists and engineers in the field of thermoelectricity.

The recent years have seen increasing efforts in the investigation of thermoelectric properties of organic materials [3 – 10] mainly in the scope to find low cost materials in order to convert even if a part of low-grade waste heat to electricity. It is known that almost 90% of world annual energy consumption (which now is around 15 terawatt-years and is expected to achieve nearly 30 terawatt-years by 2050 [11]) is generated by heat engines that use fossil fuel combustion, oil, natural gas and coal as a heat sources. These engines usually operate at 30 – 40 per cent efficiency. Thus, an enormous quantity of heat is lost to the environment. Automotive exhaust, industrial processes and home heating, all generate an enormous amount of unused waste heat. It is natural that there is a significant interest in finding cost-effective technologies for generating electricity from waste heat. It is expected that exactly low cost and more efficient thermoelectric generators based on organic materials will serve for these goals.

In [3] the thermoelectric properties of some organic charge-transfer compounds were measured with the aim to obtain predicted in [12, 13] improvement of thermoelectric efficiency. However, the measurements were made on compressed pellets and the samples do not correspond to

the theoretical model presented in [13].

In [4] a bilayer structure composed of an intrinsic pentacene layer and an acceptor tetrafluoro-tetracyanoquinodimethane layer is utilized with the electrical conductivity  $\sigma = 0.43$  S/cm, the Seebeck coefficient  $S \sim 200$   $\mu\text{V/K}$  and the power factor  $P = \sigma S^2 \sim 2.0$   $\mu\text{W/m}\cdot\text{K}^2$  when layer thickness is optimized. It was shown [5] that the iodine-doped pentacene thin films can be potential candidates for good organic thermoelectric materials. Conducting polymers have recently been suggested as thermoelectric materials for use in large-area thermogenerators. In [6] it is shown that the optimization of the power factor  $P = \sigma S^2$  ( $\sigma$  is the electrical conductivity,  $S$  is the thermopower or Seebeck coefficient) by accurate control of the oxidation level in poly (3, 4-ethylenedioxythiophene) (PEDOT) gave  $324$   $\mu\text{W}\cdot\text{m}^{-1}\text{K}^{-2}$  and combined with its low intrinsic thermal conductivity ( $\kappa = 0.37$   $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$ ) yielded a  $ZT = 0.25$  at room temperature and this material is air-stable.

In doped acetylene [7]  $ZT \sim 0.38$  at room temperature has been measured with parameters: the electrical conductivity  $\sigma = 11110$  S/cm, the Seebeck coefficient  $S = 28.4$   $\mu\text{V/K}$  and thermal conductivity  $\kappa = 0.7$   $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$ . One can observe that in spite of extremely high electrical conductivity, the thermal conductivity remains very low. It is a good result, but the problem is that this material is not stable even in air.

Several authors try to develop composite nanostructures from inorganic thermoelectric materials and organic ones. It is expected that composite materials consisting of inorganic TE nanostructures and polymer may have much better TE properties than pure polymer, as the composite materials could inherit the properties of both the polymer and the inorganic nanostructures and even have a synergistic effect [9]. And really, recently, several works on the inorganic-organic TE composites have been reported (see [9]). However, the obtained values of  $ZT$  are still very far from the required ones. A rather complete and good review of latest advances in semiconductor thermoelectric physics and materials is presented in [10].

It is known that increased values of  $ZT$  have been obtained in different low-dimensional quantum structures [14–16]. The improvement of TE properties in such structures is determined mainly by two factors: the increase of carriers' density of states, leading to the increase of power factor  $P$  and, to the maximum extent, by the decrease of thermal conductivity, caused by additional phonon scattering at the interfaces or by the reengineering of phonon spectrum.

Harman has reported the values of power factor of the order of  $6.2 - 6.6 \cdot 10^{-3}$   $\text{W/m}\cdot\text{K}^2$  in  $n$ -type  $\text{PbTe/PbEuTe}$  quantum wells (QW) [17] and  $\sim 1.6 \cdot 10^{-2}$   $\text{W/m}\cdot\text{K}^2$  in  $p$ -type one [18]. We have predicted theoretically for such (100) and (111) oriented  $n$ -QW<sub>s</sub>  $P_{100} = 1.75 \cdot 10^{-2}$   $\text{W/m}\cdot\text{K}^2$  and  $P_{111} = 1.08 \cdot 10^{-2}$   $\text{W/m}\cdot\text{K}^2$  [19, 20], and optimal value  $\sim 2.5 \cdot 10^{-2}$   $\text{W/m}\cdot\text{K}^2$  for  $p$ -type QW<sub>s</sub> [21]. These values are only for quantum well materials. A more rigorous theory of the thermoelectric power factor in nonowire-composit matrix structures [22] has demonstrated that care must be taken in the choice of matrix material as well as that of nanowires in order to optimize the thermoelectric power factor of composite structures. In a recent paper, Kim et al. [23] have revised the large thermoelectric power factor predicted in extremely small quantum wells or wires. They have shown that, if the thickness of confinement layers is taken into account, the actual improvement in the thermoelectric power factor per conduction channel is only 12 – 40%.

In [24]  $ZT = 2.4$  has been reported for  $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$  superlattices. High  $ZT \sim 3$  has been obtained by Harman in  $\text{PbTeSe}$  quantum dot superlattices [16] and even  $ZT \sim 3.5$  [25, 26].

Another direction in the improvement of thermoelectric properties of materials is a search for bulk multi-component systems which contain many atoms in the elementary cell and have more

complicate electronic and phonon spectra and more diverse internal interactions. One such example is the complex chalcogenide compound of the type  $AgPb_mSbTe_{2+m}$  with  $ZT \sim 2.2$  at 800 K as it was reported in [27]. Although to our knowledge the mechanism of  $ZT$  increase in this material is not yet completely understood, the result is impressive. The problem is that the technology to obtain such structures is complicated and expensive. Therefore, for practical applications there are still many difficulties. But the obtained high values of  $ZT$  show that a search for materials with improved TE properties give results and must be continued.

From this point of view the organic materials attract more and more attention in recent years. For example, in the highly conducting quasi-one-dimensional organic crystals the values of  $ZT$  of the order of 20 were predicted [28 – 31]. These materials can be considered to be bulk nanostructured, because they are formed of one-dimensional conducting chains of molecules displaced at approximately one nanometer one from other. They combine the TE properties of low-dimensional structures with increased density of states and of multi-component systems with more diverse internal interactions. Moreover, it was shown that in these crystals the Wiedemann-Franz law is violated [32, 33] and the Lorentz number can be diminished several times in comparison with the standard values.

The aim of this paper is to present briefly the state-of-the-art of investigations in the area of new organic thermoelectric materials and to describe the nearest expected results for really existing quasi-one-dimensional organic crystals of tetrathiotetracene-iodide,  $TTT_2I_3$ .

### Quasi-one-dimensional organic crystals of $TTT_2I_3$

The structure of quasi-one-dimensional organic crystals of tetrathiotetracene-iodide,  $TTT_2I_3$ , has been briefly described in [34]. These needle-like crystals are formed of segregate chains or stacks of planar molecules of tetrathiotetracene  $TTT$ , and iodine ions. The chemical compound  $TTT_2I_3$  is of mixed-valence: two molecules of  $TTT$  give one electron to the iodine chain which is formed from  $I_3^-$  ions. The conductivity of iodine chains is negligibly small, so that only  $TTT$  chains are electrically conductive and holes serve as carriers. The electrical conductivity  $\sigma$  along  $TTT$  chains at room temperature varies between  $10^3$  and  $10^4 \Omega^{-1}\text{cm}^{-1}$  for crystals grown by gas phase method [35], and between 800 and  $1800 \Omega^{-1}\text{cm}^{-1}$  for crystals grown from solution [36]. Thus, the conductivity is very sensitive to crystal impurity and perfection which depends on growth method. In the direction perpendicular to chains  $\sigma$  is by three orders of magnitude smaller than in the longitudinal direction and is neglected.

The  $TTT_2I_3$  crystals were intensively investigated more than 30 years ago in connection with a search for low-dimensional organic high critical temperature  $T_c$  superconductors. After the discovery of high  $T_c$  superconductivity in cuprates the investigations of  $TTT_2I_3$  crystals were stopped. In Fig. 1 the SEM image of a single  $TTT_2I_3$  crystal grown from solution [36] is presented.

As a result of needle-like structure, the charge and energy transport occurs into a one-dimensional conducting band. The crystal model presented in [12, 37] is applied. The holes motion is described in the tight binding and nearest neighbors' approximations. So as the conduction band is not

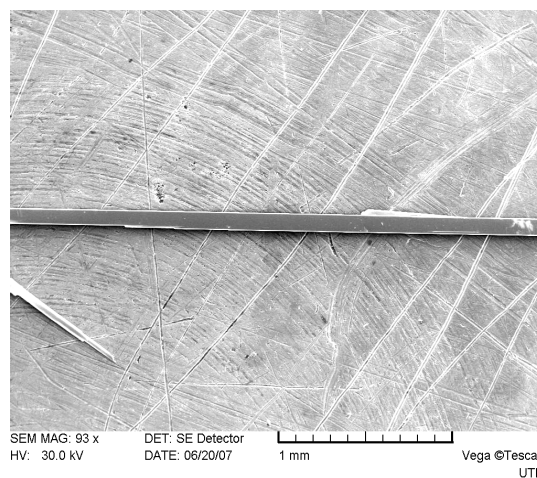


Fig. 1. SEM image of a  $TTT_2I_3$  single crystal.

very large, the variation of electron  $k$ , and phonon,  $q$  one-dimensional quasi-moments on the whole (1D) Brillouin zone is considered. The approximation of effective mass is not used.

Two most important hole-phonon interactions and scattering on impurities are taken into consideration. One interaction is similar to that of deformation potential. The coupling constant is proportional to the derivative  $w'$  with respect to the intermolecular distance of the transfer energy  $w$  of the hole from a given molecule to the nearest one. The second interaction is similar to that of polaron determined by induced polarization. The coupling constant of this interaction is proportional to the mean polarizability of molecule  $\alpha_0$ . In both interactions the same holes and acoustical phonons take part. Therefore, between these interactions the interference can take place. Due to the interference, both these interactions can compensate each other for a narrow strip of states in the conduction band. As a result, the relaxation time as a function of carrier energy obtains a high maximum for these states. The height of this maximum is limited by the rate of impurity scattering, determined by the dimensionless parameter  $D$

$$D = n_{im} I^2 d^2 M v_s^2 / (4b^3 w'^2 k_0 T), \quad (1)$$

where  $e$  is the charge of carrier,  $n_{im}$  is the linear concentration of impurity,  $I$  and  $d$  are the effective height and width of impurity potential,  $M$  is the mass of molecule,  $v_s$  and  $b$  are the sound velocity and the lattice constant along the chains,  $k_0$  is the Boltzmann constant and  $T$  is the temperature. The smaller is  $D$ , the higher is the maximum of relaxation time. From the expression (1) it is seen that the parameter  $D$  may be small, if the impurity concentration is small, i.e. if the crystal purity is high. Therefore in crystals grown by gas phase method which have a higher degree of purity, the electrical conductivity is much greater than in those grown from solution with a smaller purity. We are interested to realize as high as possible maxima of relaxation time, because high values of relaxation time will ensure high mobility of carriers in these states and high electrical conductivity, and sharp dependence on energy will ensure high values of thermopower. Thus, we expect to obtain high values of  $ZT$ . The parameter  $D$  will be varied for crystals of different purity, but in reasonable intervals.

Let us consider that a weak electrical field and temperature gradient are applied along the chains. The kinetic equation after linearization takes the form of Boltzmann equation. Around the room temperature the scattering processes can be considered elastic. In this case the kinetic equation is solved analytically and the electrical conductivity  $\sigma$ , the Seebeck coefficient  $S$ , the electron thermal conductivity  $\kappa^e$ , the dimensionless thermoelectric figure of merit  $ZT$  and the Lorenz number  $L = \kappa^e / \sigma T$  can be expressed through the transport integrals  $R_n$  as follows

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

$$ZT = \frac{R_1^2}{e^2 T^2 R_0^2 [\kappa_L / R_0 T + L]}, \quad L = \frac{k_0^2}{e^2} \frac{1}{(k_0 T)^2} \left[ \frac{R_2}{R_0} - \left( \frac{R_1}{R_0} \right)^2 \right], \quad (3)$$

where

$$R_n = \int_0^\Delta (E - E_F)^n \sigma(E) (-\partial f_0 / \partial E) dE, \quad (4)$$

$$\sigma(E) = e^2 v^2(E) \tau(E) \rho(E). \quad (5)$$

Here  $e$  is carrier charge,  $\kappa_L$  is the lattice thermal conductivity,  $E_F$  is the Fermi energy,  $E$  is the carrier energy,  $0 \leq E \leq \Delta$ ,  $\Delta$  is the width of the conduction band,  $\Delta = 4w$ ,  $\partial f_0 / \partial E$  is the derivative of

Fermi distribution function with respect to  $E$ ,  $v^2(E) = \hbar^{-2}b^{-2}E(\Delta - E)$  is the square of the carrier velocity as a function of energy  $E$ ,  $\rho(E) = (2z/\pi abc) [E(\Delta - E)]^{-1/2}$  is the density of electronic states per unit volume and energy,  $z$  is the number of chains through the transversal section of the unit cell,  $a$ ,  $b$  and  $c$  are the lattice constants, and  $\tau(E)$  is the relaxation time

$$\tau(E) \sim \frac{Mv_s^2 [E(\Delta - E)]^{1/2}}{[\gamma^2 (E - E_0)^2 + 4w^2D]}, \quad (6)$$

where  $E_0 = 2w(\gamma - 1)/\gamma$  is the resonance energy in (6),  $\gamma = 2e^2\alpha_0/b^5|w'|$  is the ratio of amplitudes of above mentioned electron-phonon interactions.

When only the first interaction is taken into account ( $\gamma = 0$ ), the dependence of  $\tau(E)$  on energy is a smooth function of usual form  $\tau(E) \sim [E(\Delta - E)]^{1/2}$ . Due to interference of both hole-phonon interactions and scattering on impurities, the denominator in (6) has appeared. It is seen that when  $E \sim E_0$ , the denominator in (6) becomes very small, when  $D$  is small. The relaxation time takes on the form of a Lorentzian, the height of which is limited by parameter  $D$  and may be very high in rather pure crystals (with  $D \approx 1$ ).

### Thermoelectric properties

Expressions (2) – (3) have been calculated in order to determine the thermoelectric properties of quasi-one-dimensional organic crystals of  $TTT_2I_3$  with different degrees of purity. The crystal parameters are:  $M = 6.5 \cdot 10^5 m_e$  ( $m_e$  is the mass of free electron),  $a = 18.35 \text{ \AA}$ ,  $b = 4.96 \text{ \AA}$ ,  $c = 18.46 \text{ \AA}$ ,  $v_s = 1.5 \cdot 10^3 \text{ m/s}$ ,  $w = 0.16 \text{ eV}$ ,  $w' = 0.26 \text{ eV \AA}^{-1}$ ,  $\kappa_L = 0.6 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$ ,  $z = 4$ . The value of polarizability  $\alpha_0$  in  $TTT_2I_3$  is not known, but it can be estimated approximately by comparison with the known polarizabilities of other molecules. In anthracene  $\alpha_0 = 25.3 \text{ \AA}^3$  [38], but  $TTT$  molecule is bigger and  $\alpha_0$  must be greater, too. We have taken  $\alpha_0 = 45 \text{ \AA}^3$ , that corresponds to  $\gamma = 1.7$ . For parameter  $D$  we have chosen the values: 0.6 that corresponds to crystals grown from solution [36] with  $\sigma \sim 1800 \text{ \Omega}^{-1} \text{cm}^{-1}$ ; 0.1 that corresponds to crystals grown by gas phase method [35] with  $\sigma \sim 10^4 \text{ \Omega}^{-1} \text{cm}^{-1}$  and 0.04 which corresponds to purer crystals with somewhat higher  $\sigma \sim 2 \cdot 10^4 \text{ \Omega}^{-1} \text{cm}^{-1}$ .

In Fig. 2 the dependences of electrical conductivity  $\sigma$  on holes concentration are presented for different values of parameter  $D$  and  $\gamma = 1.7$  at room temperature. For stoichiometric crystals it corresponds to  $n = 1.2 \cdot 10^{21} \text{ cm}^{-3}$ . It is seen from Fig. 2 that for this concentration  $\sigma$  really takes on the above mentioned values. With further increase in holes concentration,  $\sigma$  increases slightly and achieves maxima at  $n = 1.51, 1.37$  and  $1.34 \cdot 10^{21} \text{ cm}^{-3}$ . The maximum is higher in purer crystals (with smaller  $D$ ). After the maximum the carriers become electrons, their concentration decreases, because the conduction band has a finite width, and  $\sigma$  decreases, too.

In the case when only one hole-phonon interaction is taken into account ( $\gamma = 0$ ) the maximum of  $\sigma$  is achieved at holes concentration for which the Fermi energy is exactly in the middle of conduction band, when  $n = 2.2 \cdot 10^{21} \text{ cm}^{-3}$ . Here, due to the interference of both hole-phonon interactions, the maxima of  $\sigma$  are displaced to lower concentrations. For smaller  $D$  the interference is more pronounced and the displacement of  $\sigma$  maximum is larger.

In Fig. 3 the dependences of thermopower (Seebeck coefficient)  $S$  on carriers' concentration at room temperature are presented. It is seen that in the  $p$ -type region  $S$  can reach unusually high values, especially in the purest crystal (continuous line,  $D = 0.04$ ). It is also seen that  $S$  changes the

sign at  $n = 1.51 \cdot 10^{21} \text{ cm}^{-3}$  for less pure crystals with  $D = 0.6$ , at  $n = 1.37 \cdot 10^{21} \text{ cm}^{-3}$  in crystals with  $D = 0.1$ , and at  $n = 1.34 \cdot 10^{21} \text{ cm}^{-3}$  in the purest crystals with  $D = 0.04$ . These values of  $n$  correspond to carriers' concentrations for which  $\sigma$  achieves maximums in Fig. 2. At stoichiometric concentration  $n = 1.2 \cdot 10^{21} \text{ cm}^{-3}$   $S$  depends very weakly on crystal purity and takes the values 45, 42 and 41  $\mu\text{V/K}$  for  $D = 0.6$ , 0.1 and 0.04, respectively. These values of  $S$  for this concentration are in the interval of measured ones [39, 40].

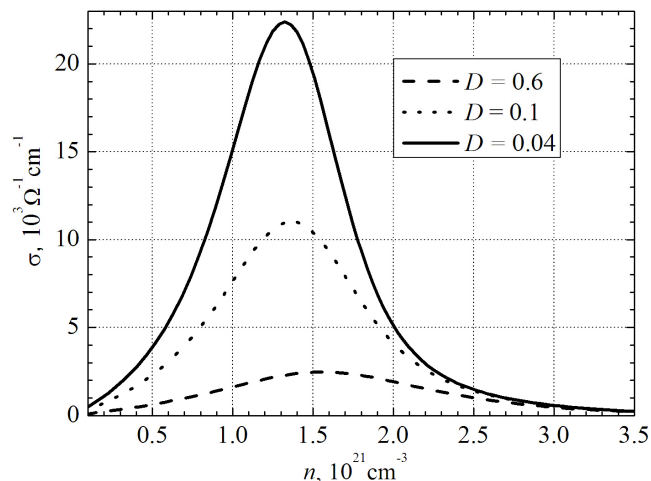


Fig. 2. Electrical conductivity  $\sigma$  as a function of carriers' concentration  $n$ .

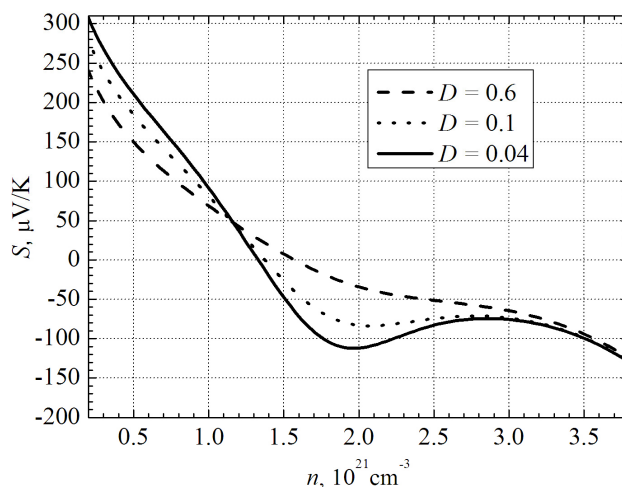


Fig. 3. Dependences of Seebeck coefficient  $S$  on carriers' concentration  $n$ .

The dependencies of the electron thermal conductivity  $\kappa^e$  on carriers' concentration  $n$  are presented in Fig. 4. For  $n$  which corresponds to stoichiometric crystals,  $\kappa^e$  receives the values 1.0, 3.6 and 5.6  $\text{W/m}\cdot\text{K}$  for crystals with  $D = 0.6$ , 0.1 and 0.04, respectively. Thus,  $\kappa^e$  is increased, especially in the purest crystals, but relatively not so much as  $\sigma$ . It is seen that  $\kappa^e$  has also maxima, as  $\sigma$  in Fig. 2, but there are two important differences in comparison with Fig. 2: the maxima of  $\kappa^e$  are displaced to a little higher carriers' concentrations than the maxima of  $\sigma$ , and they are somewhat larger than those of  $\sigma$ . So, the maxima of  $\kappa^e$  are reached at  $n = 1.71$ , 1.54 and  $1.51 \cdot 10^{21} \text{ cm}^{-3}$ , respectively. This means that the value of relaxation time maxima and their position on the energy scale have different effects on electrical conductivity and on electron thermal conductivity which is determined by addition factor  $(E - E_F)^2$  in (4).

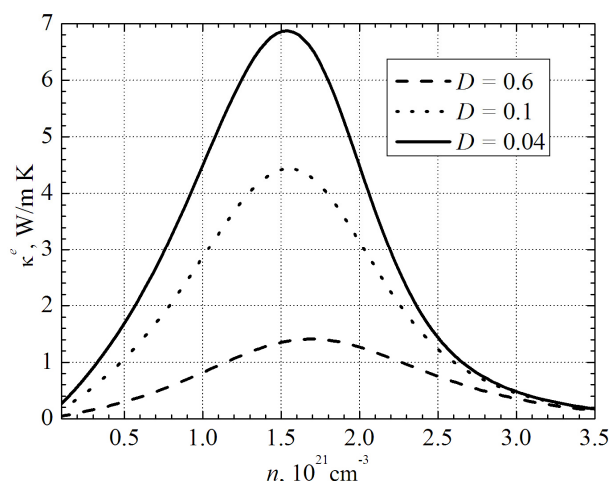


Fig. 4. Dependences of electron thermal conductivity  $\kappa^e$  on  $n$ .

In Fig. 5 the dependences of the Lorentz number  $L$  on  $n$  are presented. In the case of a large conduction band ( $w = 1.6$  eV) and of only the first hole-phonon interaction ( $\gamma = 0$ ) the Wiedemann-Franz law takes place. For non degenerate hole gas the Lorentz number  $L = 2 (k_0/e)^2$  and for degenerate gas  $L = (\pi^2/3)(k_0^2/e^2)$ , as it is expected for high temperatures and scattering on acoustical phonons (dash-dot-dot-line, the horizontal parts). In  $TTT_2I_3$  crystals the room temperature can be considered high, so as the Debye temperature is  $\sim 90$  K. If the conduction band is narrower, as in  $TTT_2I_3$  crystals ( $w = 0.16$  eV), the Wiedemann-Franz law is violated. The Lorentz number is diminished in the whole interval of considered concentrations (dash-dotted line) due to the reduction of the electron thermal conductivity in a narrower conduction band. But the Wiedemann-Franz law is violated most strongly, when both hole-phonon interactions are taken into consideration ( $\gamma \neq 0$ ) and their interference is more pronounced. In less pure crystals ( $D = 0.6$ ) the maximum of relaxation time is low and  $L$  is only slightly diminished for  $0.4 \cdot 10^{21} \text{ cm}^{-3} < n < 2.1 \cdot 10^{21} \text{ cm}^{-3}$  in comparison with the previous case.

But in purer crystals the Wiedemann-Franz law is strongly violated. The Lorentz number is diminished in some intervals of concentrations, and is increased in the others, but has pronounced minima. In the purest crystal ( $D = 0.04$ , continuous line) the minimum of  $L$  is attained at stoichiometric concentration  $n = 1.2 \cdot 10^{21} \text{ cm}^{-3}$  and  $L_{\min} = 1.2 (k_0/e)^2$ , i.e. it is by 2.75 times lower than in conventional materials. Even in less pure crystal (with  $D = 0.1$ , dotted line)  $L_{\min} = 1.6 (k_0/e)^2$ , still 2 times smaller than in the usual case. It is also observed that the minima of  $L$  are rather smooth and large. This situation is favorable for the increase of  $ZT$ , because it permits to vary the carriers' concentration in a large interval.

The dependences of the thermoelectric figure of merit  $ZT$  on holes concentration are presented in Fig. 6. Only the samples with  $p$ -type conductivity are considered. At stoichiometric concentration  $n = 1.2 \cdot 10^{21} \text{ cm}^{-3}$   $ZT$  is very small  $\sim 0.1$  even in the purest crystals. But  $ZT$  grows with the decrease of  $n$ , especially quickly in purer crystals. So, if  $n$  decreases 1.5 times up to  $0.8 \cdot 10^{21} \text{ cm}^{-3}$ ,  $ZT$  increases up to 0.29, 0.87 and 1.4, respectively for crystals with  $D = 0.6, 0.1$  and  $0.04$ . If  $n$  decreases 2 times up to  $0.6 \cdot 10^{21} \text{ cm}^{-3}$ ,  $ZT$  increases up to 0.60, 1.3 and 2.0, respectively. Although the  $TTT_2I_3$  are crystals of mixed valence, the diminution of  $n$  is possible, because  $TTT_2I_3$  admit nonstoichiometric compounds with surplus and deficiency of iodine.

It is interested to know the parameters for the two above mentioned concentrations. For the first concentration we have, respectively for  $D = 0.6, 0.1$  and  $0.04$ :  $\sigma = 1.16, 4.92$  and  $9.08 \cdot 10^3 \Omega^{-1} \text{ cm}^{-1}$ ,  $S = 98.9, 124$  and  $143 \mu\text{V/K}$ ,  $\kappa^e = 0.57, 2.02$  and  $3.19 \text{ W} \cdot \text{m}^{-1} \text{ K}^{-1}$ ,  $L = 2.2, 1.8$  and  $1.5 (k_0/e)^2$ . For the second

concentration:  $\sigma = 0.75, 2.84$  and  $4.88 \cdot 10^3 \Omega^{-1} \text{cm}^{-1}$ ,  $S = 135, 168$  and  $193 \mu\text{V/K}$ ,  $\kappa^e = 0.36, 1.27$  and  $2.03 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$ ,  $L = 2.1, 2.0$  and  $1.8 (k_0/e)^2$ . All parameters are reasonable. Nevertheless, if because of technological difficulties the highest crystal purity (with  $D = 0.04$ , continuous line) will be not possible to attain, there remains the possibility to obtain  $ZT \sim 1.3 - 1.4$ , may be somewhat more in crystals with the initial conductivity  $\sigma \sim 10^4 \Omega^{-1} \text{cm}^{-1}$  (dotted line) after the reduction of carriers concentration in the direction to optimal one. Crystals with such conductivity were obtained earlier in connection with a search for high  $T_c$  superconductivity. If in these crystals  $n$  is diminished 3 times, up to  $0.4 \cdot 10^{21} \text{ cm}^{-3}$ , it is expected to obtain  $ZT \sim 1.6$ . We hope that the achievements of modern chemistry will allow resolving this specific problem and even will permit the synthesis of better thermoelectric materials.

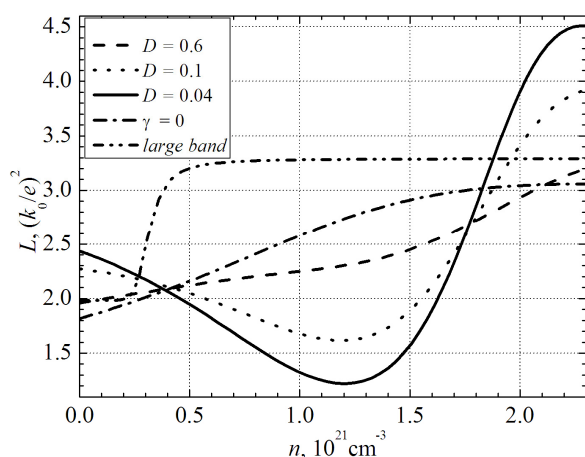


Fig. 5. Dependences of Lorentz number  $L$  on  $n$ .

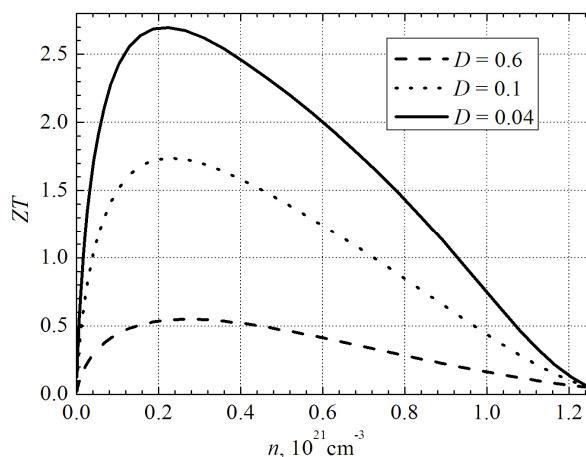


Fig. 6. Dependences of the thermoelectric figure of merit  $ZT$  on  $n$ .

A more detailed analysis shows that the main contribution to the increase of  $ZT$  comes from the growth of the power factor. But the contribution from the decrease of the Lorentz number is also very important because it reduces significantly the electronic thermal conductivity and, as result, reduces the parasitic thermal flux.

## Conclusions

The state-of-the-art of research on new organic materials for thermoelectric applications is analyzed. It is shown that the interest of investigators in these materials has been growing in recent years. The highest value of  $ZT \sim 0.38$  at room temperature has been measured in doped acetylene, with the only problem that this material is not stable. Accurate control of the oxidation level in poly (3, 4-ethylenedioxythiophene) (PEDOT) gave the power factor  $324 \mu\text{W} \cdot \text{m}^{-1} \text{K}^{-2}$  and in combination with its low intrinsic thermal conductivity ( $\kappa = 0.37 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$ ) yielded  $ZT = 0.25$  at room temperature, and this material is air-stable.

Quasi-one-dimensional organic crystals have good prospects for thermoelectric applications. These materials combine the properties of multi-component systems with more diverse internal interactions and of quasi-one-dimensional quantum wires with increased density of electronic states. The prospects of existing quasi-one-dimensional organic crystals of tetrathiotetracene-iodide,  $TTT_2I_3$ , are analyzed in more detail. The dependences of the electrical conductivity  $\sigma$ , the Seebeck coefficient  $S$ , the electron thermal conductivity  $\kappa^e$ , the Lorenz number  $L$  and the dimensionless thermoelectric figure of merit  $ZT$  on carriers' concentrations  $n$  are calculated and presented graphically.

It is shown that, if  $n$  decreases 1.5 times from  $1.2 \cdot 10^{21} \text{ cm}^{-3}$  up to  $0.8 \cdot 10^{21} \text{ cm}^{-3}$ ,  $ZT$  increases up to 0.29, 0.87 and 1.4, respectively for crystals with the scattering rate on impurity  $D = 0.6, 0.1$  and



0.04. The values of the Lorenz number in this case are  $L = 2.2, 1.8$  and  $1.5 (k_0/e)^2$ , i.e. they are reduced considerably in comparison with the usual value  $(\pi^2/3)(k_0^2/e^2) \sim 3.3 (k_0/e)^2$ . Due to the reduction of the Lorenz number and of  $\kappa^e$  the parasitic thermal flux is reduced approximately 1.5 times in comparison with conventional materials. If  $n$  decreases 2 times up to  $0.6 \cdot 10^{21} \text{ cm}^{-3}$ ,  $ZT$  increases up to 0.60, 1.3 and 2.0, respectively. Thus, it is expected that in the existing crystals of  $TTT_2I_3$  it will be possible to realize the values of  $ZT \sim 1.3 - 1.6$  at room temperature after optimization of crystal parameters.

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