Deviations from Wiedemann-Franz law in quasi-one-dimensional organic crystals

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Abstract — **The physical reasons that lead to deviations from the Wiedemann-Franz law in low-dimensional organic crystals with electronic type conduction are investigated. The kinetic coefficients were modeled as functions of Fermi energy. It is shown that the Lorentz number becomes dependent on crystal purity and unlike the case of ordinary materials has a maximum in the domain of intermediary electronic concentrations. At higher concentrations the Lorentz number may be diminished in the purest crystals by an order of magnitude and even more. This diminution gives important contribution to the increase of the thermoelectric figure of merit. It is favorable for thermoelectric applications of such materials.**

Index Terms — **organic crystals, Lorentz number, nanostructured organic crystals, thermoelectric efficiency, Wiedemann-Franz law.**

I. INTRODUCTION

The search and investigation of materials with a higher thermoelectric figure of merit was and remains to be an important and urgent problem of solid state physics. Such materials are needed for the utilization in thermoelectric direct converters of electrical energy into cold and of heat into electrical energy. In the last years, the demand for thermoelectric converters, as solid state coolers, especially for microelectronics and computers, or as power generation systems, in particular for recuperation of waste heat, has increased considerably. The thermoelectric materials are used also as sensitive elements in the detectors of infra red radiation.

It is well known that the thermoelectric converters have evident advantages with respect to traditional ones: no moving parts, high reliability, compactness, noiseless operation, no environment pollution. Also, they can be made very small and, relatively, no expensive. However, large application of thermoelectric converters is limited by their low efficiency. The latter is determined by low thermoelectric figure of merit ZT of used materials. In order to increase ZT, it needs to increase in the same material the electrical conductivity σ, the thermopower (Seebeck coefficient) S, and to diminish the thermal conductivity k at operating temperature T. However, this strategy applied to known bulk materials has not yet produced materials with $ZT > 1$ at room temperature, because σ, S and k are not independent each of other.

Now the best bulk thermoelectric materials have values of dimensionless figure of merit, ZT near 1. It is rather low value. But it is expected that new more efficient materials will be found and the market of thermoelectric devices will grow quickly in the nearest future. For example, a ZT value of 3 or higher would make solid-state home refrigerators economically competitive with the compressor-based one [1].

An increase of the thermoelectric figure of merit has been obtained in different low dimensional structures such, as the IV-VI based multiple quantum-well [2, 3] and quantum-dot [4] superlattices. A value of $ZT \sim 2.4$ has been measured [5] at room temperature in *p*-type Bi_2Te_3/Sb_2Te_3 superlattice structures. Even higher values of ZT were measured in B_4C/B_9C and Si/SiGe multilayer quantum-well films [6]. At Hi-Z Technology, Inc. it has been recently demonstrated a conversion efficiency of 14% of a quantum-well couple fabricated on the base of above mentioned films [6].

We have investigated theoretically the opportunities to increase the figure of merit of material in PbTe/PbEuTe quantum-well structures [7, 8] and have elaborated some recommendations for these purposes. The integrated superlattice micro coolers, grown directly on the microelectronic chip surface have been also fabricated [9]. Impressive high $ZT \sim 3$ has been obtained by Harman in PbTeSe quantum dot superlattices [10], and even $ZT \sim 3.5$ [11, 12].

However, the technology to obtain such structures is complicated and very expensive. In the last years the organic materials attract more and more attention as materials which are less expensive and have more diverse and often unusual properties in comparison with the inorganic materials. It exists already a new generation of organic based electronic devices. It was also predicted that some quasi-one-dimensional organic materials may have improved thermoelectric properties too, and values of $ZT \sim 20$ at room temperature [13-16]. New possibilities to increase ZT open recent prediction of the violation of Wiedemann-Franz law [17] and the diminution of the Lorentz number in the crystals of tetrathiotetracene–iodide, TTT_2I_3, which are of hole type conduction.

The aim of this paper is to study in more detail the physical reasons of Lorentz number reduction in low-dimensional nanostructured organic crystals with electronic type conduction and to evaluate the effect of this reduction on the increase of ZT.

II. CRYSTAL MODEL

Quasi-one-dimensional are named such organic crystals which are formed from linear chains or stacks of molecules that are packed into a three-dimensional crystal. Many organic crystals have Q1D structure [18]. We will consider the Q1D crystals with electronic conduction and with the

parameters of TCNQ chains in TTF-TCNQ (tetrathiofulvalene-tetracyanoquinodimethane) crystals.

In Q1D crystals the interaction between the molecules along the chains is much greater than between those of different chains. Accordingly, the crystals have needle-like form. In the chains direction the conduction mechanism is band-like, and in transversal to chains direction it is hopping-like. The ratio of longitudinal conductivity to the transversal one is of the order of 10^3. Therefore, in the first approximation the transversal conductivity can be neglected and we obtain the one-dimensional (1D) crystal model. The model has been described in [19].

Two more important electron-phonon interactions are taken into account simultaneously. The first interaction is deformation potential similar and is determined by the variation of the energy w of electron transfer between nearest molecules long chains, caused by the thermal vibrations of crystalline lattice (longitudinal acoustic phonons). The coupling constant is proportional to the derivative w' of w with respect to the intermolecular distance. The second interaction is similar to that of polaron. The coupling constant of this interaction is proportional to the mean polarizability of molecule α_0.

We consider the charge and energy transport along the chains under a weak electric field and a temperature gradient applied in the direction of chains. The linearized kinetic equation is solved as in [19] and for the electrical conductivity σ, the Seebeck coefficient S, the electronic thermal conductivity κ^e, the power factor P, the thermoelectric figure of merit ZT and the Lorenz number L we obtain

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

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

(1)

where R_n are the transport integrals

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

Here E is the carrier energy, $0 \le E \le \Delta$, $\Delta = 4w$, $f_0'(E)$ is the derivative of Fermi distribution function with respect to E, k_L is the lattice thermal conductivity, z is the number of chains through the transversal section of the unit cell, e is the electron charge, k_0 in the Boltzmann constant, E_F is the Fermi energy, a, b and c are lattice constants, $\tau(E)$ is the relaxation time

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

where v_s is the sound velocity, γ is the ratio of amplitudes of above mentioned electron-phonon interactions $\gamma = 2e^2 \alpha_0 /(a^5 w')$, $E_0 = 2w(\gamma + 1)/\gamma$ is the resonance energy which corresponds to the maximum of

$\tau(E)$, when $0 \le E_0 \le \Delta$. The dimensionless parameter D in Eq. (3) describes the scattering of carriers on impurities

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

Thus, the crystal model is characterized by two main parameters that can be varied: the parameters γ and D. The latter determines the crystal purity.

III. MODELING OF KINETIC COEFFICIENTS

The kinetic coefficients were modeled as functions of dimensionless energy $\varepsilon = E/2w$, or Fermi energy $\varepsilon_F = E_F/2w$, measured in unities of $2w$, for different values of crystal parameters. The parameters of TCNQ chains (electronic conduction) in the TTF-TCNQ crystal are: the mass of molecule $M = 3.7 \square 10\ m_e$ (m_e is the mass of electron), $w = 0.125$ eV, $w' = 0.2$ eV Å^{-1}, $v_s = 2 \square 10^5$ cm/s, $a = 12.3$Å, $b = 3.82$Å, $c = 18.47$Å, $z = 2$. We will choose $\gamma = 2$ and $D = 0.05, 0.01, 0.005$.
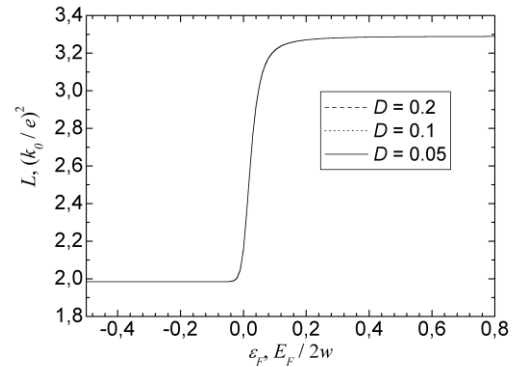

Fig.1. Lorenz number L as a function of Fermi energy ε_F for $\gamma = 0$ and a large conduction band.

In the Fig. 1 the dependence of Lorenz number L on Fermi energy ε_F is presented for a material with $\gamma = 0$ and w, w' increased by ten times (large conduction band). It is seen that for nondegenerate carriers L is very close to $2(k_0^2/e^2)$, and for degenerate one L is close to $(\pi^2/3)(k_0^2/e^2)$ as for scattering on acoustic phonons. It is seen that the Wiedemann-Franz law occurs in this case (horizontal parts of solid line) and L does not depend on D.

In the Fig.2 the dependence of relaxation time on carrier energy is presented. The lowest dash-dotted line
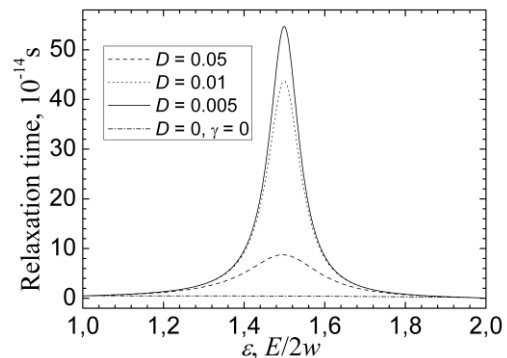

Fig.2. Relaxation time as a function of energy in the conduction band.

corresponds to the case, when only the first electron-phonon interaction mechanism is included ($\gamma = 0$). It is seen that in this case the relaxation time is a very smooth function of energy with a very small maximum which is even not observed in this scale. The anomalies of kinetic coefficients are connected with the behavior of relaxation time, when both electron-phonon interactions are included (dash, dotted and continue lines in Fig.2). In this case the interference of above mentioned electron-phonon interactions leads to their mutual compensation for a narrow strip of states in the conduction band. The maximums of relaxation time are limited by impurity scattering.

In the Fig. 3 the dependencies of thermopower (Seebeck coefficient) S on ε_F are presented. It is seen that the domain of electronic conduction ($S < 0$) which in the case when $\gamma = 0$ is up to $\varepsilon_F = 1$, is enlarged up to $\varepsilon_F = 1.5$. It is due to the contribution of carriers thermally excited from the states near the Fermi level to states near the maximum of relaxation time. For $\varepsilon_F > 1.5$ the carriers become holes and $S > 0$. The values of S can be rather high.
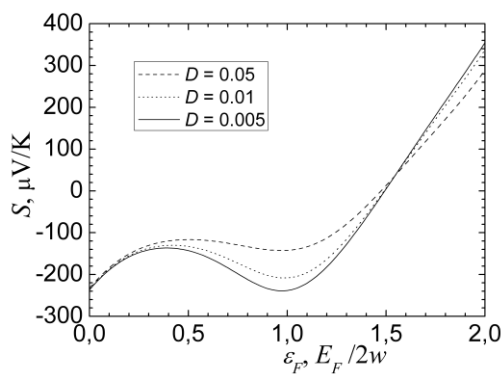

Fig.3. Thermopower S as a function of dimensionless Fermi energy ε_F for $\gamma = 2$.

Let now analyze the behavior of the Lorentz number. From Fig.4 it is seen that the dependences of L on ε_F are total different in comparison with those from Fig.1. At
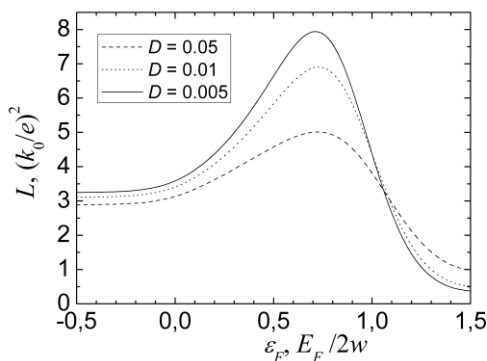

Fig.4. Lorentz number L as a function of dimensionless Fermi energy ε_F for $\gamma = 2$.

ε_F less than approximately 1.5 and up to $\varepsilon_F \sim -0.1$, L is increased and achieves very high maximum at $\varepsilon_F \sim 0.7$. The maximum is higher in purest crystals. From other hand, for $\varepsilon_F > 1.1$ the Lorentz number is diminished and achieves at $\varepsilon_F = 1.5$ values of 0.37, 0.51 and $0.98(k_0/e)^2$ for $D = 0.005$, 0.01 and 0.05, respectively. In the purest crystal L is diminished by 9 times as compared with the respective values in ordinary materials (see Fig.1). It is important for thermoelectric applications. Such behavior of L is caused by the behavior of relaxation time.

In general form, the Lorentz number is defined as $L = \kappa_e / \sigma T$. The minimums of L are determined by the carriers with energies around the maximums of relaxation time. These carriers give significant contribution to σ which obtains high maximums at $\varepsilon_F \sim 1.5$. The electronic thermal conductivity k_e is increased too, but not so strongly as σ, due to narrower interval of energy of carriers that give main contribution to the energy transport. The maximums of κ_e are relatively lower and larger than those of σ and besides, are displaced to lower values of Fermi energy $\varepsilon_F \sim 1.28 - 1.33$ in dependence of crystal purity. In the purest crystal the maximum of L is almost 2.5 higher than in ordinary materials.

In the Fig.7 the dependences of thermoelectric figure of merit ZT on ε_F are presented. It is seen that ZT has also maximums. In the purest crystals ZT achieves value as high
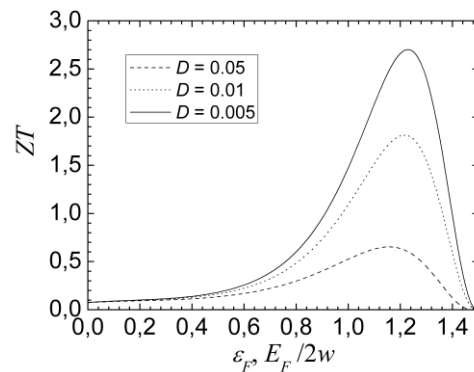

Fig.5. ZT as a function of dimensionless Fermi energy ε_F for $\gamma = 2$.

as 2.7. Even in less pure crystals (dotted line in Fig.5) the maximum of ZT is still 1.8, very good result. Unlike the case of crystals with hole conduction, considered earlier [17, 20], the maximums are displaced at higher carrier's concentrations. This means that in order to increase ZT it is necessary to increase the electron's concentration n. If in ordinary stoichiometric crystals $n = 1.4 \times 10^{21}$ cm^{-3}, to the maximum of ZT in the purest crystals it corresponds $n = 2.7 \times 10^{21}$ cm^{-3}, i.e. the carrier's concentration must be increased by 1.9 times.

For crystals with such carriers concentration the values of electrical conductivity σ are expected to be 2.6×10^4, 2.0×10^4 and 9.6×10^3 Ω^{-1}cm^{-1}, respectively for three degrees of purity, when $D = 0.005$, 0.01 and 0.05. The

thermopower S must be (-167, 151, and -104) μV/K, respectively. The electronic thermal conductivity must be (7.4, 6.5 and 4.1) W/m·K. The values of Lorentz number are expected to be (1,21, 1.45, and 1.92) $(k_0/e)^2$, i.e. approximately 2.7, 2.3 and 1.7, times smaller than for ordinary materials. These results are very promising for thermoelectric applications.

In the same times, a value of $ZT = 2$ can be achieved in the purest crystal at lower concentration $n = 2.5 \times 10^{21}$ cm^{-3}, or $\varepsilon_F = 1.08$. At this concentration in less pure crystals ZT achieves still 1.4 (dotted line) and 0.6 (dashed line).

For crystals with such carriers concentration the values of electrical conductivity σ are expected to be (9800, 7900 and 9600) Ω^{-1}cm^{-1}, respectively for same three degrees of purity. The thermopower S must be (-226, -200, and -136) μV/K, respectively. The electronic thermal conductivity must be (6.5, 5.6 and 3.4) W/m·K. The values of Lorentz number are expected to be (2.94, 2.65, and 2.82) $(k_0/e)^2$, i.e. approximately 1.1 - 1.2, times smaller than for ordinary materials.

In order to evaluate the importance of the Lorentz number reduction let's introduce dimensionless power factor $S_0 = S/(k_0/e)$, dimensionless Lorentz number $L_0 = L/(k_0/e)^2$, and rewrite the expression for ZT in the following form

$$ZT = \frac{S_0^2}{k_L/[\sigma T(k_0/e)^2] + L_0} = \frac{S_0^2}{D_0}, \qquad (5)$$

where k_L is the lattice thermal conductivity. In the best bulk thermoelectric material Bi$_2$Te$_3$ the contribution to ZT from two terms in the denominator is $D_0 = 3.4 + 3.3 = 6.7$. It is seen that the contribution from L_0 is important,

approximately 50%. In considered here crystals $k_L = 1.0$W/m.K and for σ = 1000 Ω^{-1}cm^{-1} in the absence of interference (γ = 0) $D_0 = 2.7 + 3.3 = 6$. The contribution from L_0 even dominates, but D_0 is a little decreased. In the presence of interference, when both electron-phonon interactions are considered, for σ = 2.6×10^4 Ω^{-1}cm^{-1} we have $D_0 = 0.17 + 1.21 = 1.38$. The contribution to D_0 from the Lorentz number dominates too, but it is diminished by 2.7 times, and the denominator in (5) it self is diminished by 2.4 times. From this comparison it is seen the importance of Lorentz number diminution for the increase of the thermoelectric power factor.

IV. CONCLUSIONS

We consider the charge and energy transport in quasi-one-dimensional nanostructured organic crystals under a weak electric field and a temperature gradient applied in the direction of chains. Two more important electron-phonon interactions are taken into account simultaneously. The first interaction is deformation potential similar and the second is of the polaron type. The carrier's scattering on impurity is also considered. It is shown that unlike the case of ordinary materials, the Lorentz number has a maximum in the domain of intermediary electronic concentrations. The maximum is higher in the purest crystals. At higher concentrations the Lorentz number has a minimum which is deeper also in the purest crystals with a value diminished by an order of magnitude and even more in comparison with the case of ordinary materials. It leads to increase of the thermoelectric efficiency and is favorable for thermoelectric applications of such materials.

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