

MODELLING OF THE THERMOELECTRIC POWER FACTOR IN QUASI-ONE-DIMENSIONAL ORGANIC CRYSTALS

A. Casian¹, Z. Dashevsky², H. Scherrer³, I. Balmus¹, and V. Duscic¹

¹*Technical University of Moldova, 168, Stefan cel Mare ave., MD-2004, Chisinau, Republic of Moldova*

²*Department of Materials Engineering, Ben-Gurion University, 84105, Beer-Sheva, Israel*

³*Laboratoire de Physique des Matériaux, Ecole des Mines, 54042, Nancy, France*

(Received 24 April 2008)

Abstract

Thermoelectric power factor is modelled in some quasi-one-dimensional organic crystals as a function of Fermi energy and different crystal parameters at room temperature. Two main electron-phonon interaction mechanisms and scattering of carriers on impurities are taken into account. Values of thermoelectric power factor $\sim 500 \mu\text{W}/\text{cmK}^2$ are predicted which are the highest calculated so far in such organic materials of *p*-type.

1. Introduction

The thermoelectric power factor is an important parameter, which determines the opportunity of the given material to be used as sensitive element for thermoelectric detectors of infrared radiation (IR). The power factor determines also the possibilities of materials for applications in thermoelectric devices [1], such as thermoelectric refrigerators and power generators. Materials with as high as possible values of power factor, $P = \sigma S^2$, are necessary, where σ is the electrical conductivity and S is the thermopower (Seebeck coefficient). However, in ordinary materials it is not possible to increase simultaneously σ and S . This requirement is contradictory, because an increase of σ leads to a decrease of S , and vice versa. Therefore, the search and investigation of new materials with more complicated electronic and phonon spectra that would overcome this contradiction is an important and urgent problem of solid state physics.

Presently the best bulk thermoelectric material Bi_2Te_3 has values of power factor on the order of $40 \mu\text{W}/\text{cmK}^2$. High values of power factor have been recently obtained in low – dimensional quantum well (QW) superlattice structures [2]. This increase of P is achieved due to the growth of the electronic density of states. As a result, the Fermi level is lowered in such a way, that the electron gas which in bulk material would be degenerate, in the QW structure it becomes nondegenerated or slightly degenerated. Thus, a possibility appears to somewhat increase the carriers concentration in order to obtain an increase of electrical conductivity and thermopower simultaneously. Values of power factor P of the order of $62 - 66 \mu\text{W}/\text{cmK}^2$ have been measured in *n*-type PbTe/PbEuTe QWs [3], which are much higher than in Bi_2Te_3 . Even higher values of P for these structures with optimized parameters have been predicted in [4-5]. Maximum calculated values of power factor P for (100) and (111) oriented QWs are $P_{100} = 175 \mu\text{W}/\text{cmK}^2$ and $P_{111} = 108 \mu\text{W}/\text{cmK}^2$, these are quite high values. Higher values of $P = 160 \mu\text{W}/\text{cmK}^2$ have been measured in *p*-type PbTe/PbEuTe QWs [6]. The highest calculated values of P for such QWs with optimal parameters are $\sim 250 \mu\text{W}/\text{cmK}^2$ [7]. But there is not full confidence that these optimal parameters can be achieved. Also, the technology for production

of such structures is complicated and expensive. Therefore, the search and investigate of new materials which will improve thermoelectric properties is very important and timely.

In the last years organic materials attract more and more attention as materials, which are less expensive and have more diverse and often unusual properties. These materials are already applied as active elements into new generations of organic-based devices such as light-emitting diodes and lasers for displays, photovoltaic cells, field-effect transistors, holographic optical recording and processing systems. It is also predicted to find among organic materials such, which will have improved thermoelectric properties [8-10].

In this paper we show that quasi-one-dimensional organic compounds are very promising materials which will have considerably increased thermoelectric power factor [11]. The highest value of the power factor calculated up to now in such materials is presented.

2. Quasi-one-dimensional organic compounds

The main particularity of quasi-one-dimensional organic crystals is that they are formed of chains or stacks of usually planar molecules [12]. The lattice constant along the chains is several times less than in transversal directions. As a result, the overlap of molecular orbitals along the chains is great and ensures a band-like conduction mechanism in the chain direction. Between the chains the overlap of electronic wave functions is very weak, determining a hopping-like conduction mechanism. In the first approximation the small transversal hopping conductivity can be neglected. We then obtain that the carriers are moving in a one-dimensional conduction band. The crystal model is described in more detail in [13, 14]. So as the molecular orbitals in molecular crystals are rather localized, the electronic states are described in the tight binding and nearest neighbor's approximations.

The Hamiltonian of 1D crystal chain can be presented in the form [14]

$$H = \sum_k \varepsilon(k) a_k^+ a_k + \sum_q \hbar \omega_q b_q^+ b_q + \sum_{k,q} [A_1(k, q) + A_2(q)] a_k^+ a_{k-q} (b_q + b_{-q}^+). \quad (1)$$

In order to obtain the Hamiltonian of whole crystal it is necessary to sum up (1) on all chains into the basic region of the crystal. Here a_k^+ and a_k are the creation and destruction operators of a carrier with the wave vector projection k along the chains, b_q^+ and b_q are the respective operators for longitudinal acoustic phonons. The first term in (1) is the energy operator of carriers with the energy $\varepsilon(k) = 2w(1 - \cos ka)$, where w is the energy of the electron transfer from one molecule to another along the chains, a is the lattice constant along the chains. The second term is the energy operator of free phonons with the frequency $\omega_q = 2v_s a^{-1} |\sin qa/2|$, where v_s is the sound velocity along the chains. And the third term describes two mechanisms of electron-phonon interaction. The first mechanism is similar to that of deformation potential and is proportional to the derivative w' of w with respect to the intermolecular distance. The matrix element $A_1(k, q)$ has the form

$$A_1(k, q) = [2i\hbar^{1/2} w' / (2NM\omega_q)^{1/2}] [\sin ka - \sin((k - q)a)] \quad (2)$$

and depends not only on the transfer momentum q , but also on the carrier state k . Here N is the number of molecules in the basic region of the chain, M is the mass of molecule. The second mechanism is similar to that of polaron, but the question is about the induced polarization. It is determined by the fluctuations of polarization energy of molecules surrounding the carrier and is proportional to the average polarizability of molecule α_0 . The matrix element $A_2(q)$ has the form

$$A_2(q) = [2i\hbar^{1/2} w' / (2NM\omega_q)^{1/2}] \gamma \sin qa. \quad (3)$$

One can demonstrate that the carriers interact only with the longitudinal acoustic phonons. The parameter γ is the ratio of amplitudes of above mentioned electron-phonon interaction mechanisms

$$\gamma = 2e^2\alpha_0 / a^5|w'|, \quad (4)$$

where e is the absolute value of carrier charge.

Since the conduction band, width is not very large, the effective mass approximation is not applicable and it is necessary to take into account the variation of electron and phonon quasi-momentums into the whole Brillouin zone. It is important to consider simultaneously two electron-phonon interactions because under certain conditions between them the interference can take place. Due to the interference, both electron-phonon interactions considerably compensate each other for a narrow strip of states in the conduction band. As a result, the relaxation time of carriers as a function of carrier energy takes the form of Lorentzian with a rather pronounced maximum. High values of relaxation time will ensure large electrical conductivity, and sharp dependence on energy will lead to enhanced values of the thermopower. Thus, it is favorable to expect a growth of the thermoelectric power factor P . The scattering of carriers on impurities is also taken into account, so as it determines the height of Lorentzian.

3. Thermoelectric power factor

Near room temperature the scattering of carriers on acoustical phonons can be considered elastic and the kinetic equation can be solved as in [12]. The thermoelectric power factor can be expressed analytically through the transport integrals in the form

$$P = (R_1)^2 / (e^2 T^2 R_0), \quad (5)$$

where R_0 and R_1 are the transport integrals

$$R_n = -e^2 \int_0^\Delta (E - E_F)^n v^2(E) \tau(E) \rho(E) f'_0(E) dE. \quad (6)$$

Here T is the temperature, $v^2(E) = \hbar^{-2} a^2 E(\Delta - E)$ is the square of the carrier velocity as a function of energy E , $\Delta = 4w$ is the conduction band width, $0 \leq E \leq \Delta$, $\rho(E) = (2z / \pi abc) [E(\Delta - E)]^{-1/2}$ is the density of states per unit volume and energy, E_F is the Fermi energy, z is the number of chains through the transversal section of unit cell with the lattice constants b and c , $\tau(E)$ is the relaxation time, $f'_0(E)$ is the derivative of the Fermi distribution function with respect to the energy E .

The relaxation time has been calculated in [13] and has the form of Lorentzian as a function of carrier energy E

$$\tau(E) = \frac{\hbar M v_s^2 w^2 [E(\Delta - E)]^{1/2}}{2a^2 k_0 T w'^2 [\gamma^2 (E - E_0)^2 + 4w^2 D]}. \quad (7)$$

Here M is the mass of molecule, k_0 is the Boltzmann constant, E_0 has the meaning of the resonance energy in (7) which corresponds to the maximum of Lorentzian. For the crystals with hole conductivity considered here $E_0 = 2w(\gamma - 1) / \gamma$.

The parameter D describes the carrier scattering on impurities, and when the impurities are considered point-like, D has the form

$$D = n_{im} I^2 d^2 M v_s^2 / (4a^3 k_0 T w'^2) = D_0 T_0 / T, \quad (8)$$

where n_{im} is the concentration of impurities per a unity of chain length, I and d are the effective height and width of the impurity potential, D_0 is the value of D at $T = T_0 = 300\text{K}$.

4. Results and discussions

Expression (5) for the power factor P has been modeled for typical Q1D organic crystals, formed of p -type chains with parameters close to those of TTF chains in the TTF-TCNQ (tetrathiofulvalene-tetracyanoquinodimethane) crystal: $M = 3.7 \times 10^5 m_e$ (m_e is the mass of electron), $w = 0.16$ eV, $w' = 0.24$ eVÅ⁻¹, $v_s = 2 \times 10^5$ cm/s, $a = 12.3$ Å, $b = 3.82$ Å, $c = 18.47$ Å (the direction of chains is along b), $z = 2$. The parameter γ is unknown in quasi-one-dimensional organic crystals because the polarizability of molecule in crystal is unknown. Therefore we have modeled P as a function of dimensionless Fermi energy ε_F , expressed in unities of $2w$, for an interval of γ from 0.01 up to 2.5. For the parameter D values 0.2, 0.04, and 0.015 have been taken as more accessible. So as D is proportional to the impurity concentration, this means that the crystals must have high, but rather reasonable degree of purity. The interval of Fermi energy variation is from $\varepsilon_F = -0.5$ to the value when the thermopower changes the sign, what means that the hole conductivity is replaced by electronic one. The value $\varepsilon_F = -0.5$ corresponds to $E_F = -6k_0T_0$ ($T_0 = 300$ K) or to almost nondegenerated carrier gas.

In Fig. 1 the results for very small γ (0.01) are presented. In this case the polarizability of molecule is negligible and only the first interaction is displayed. It is seen that P has a maximum for ε_F close to the bottom of conduction band, but even in maximum the value of P is small. The dependence of crystal purity is weakly manifested. It is the case when the molecules are small, so as the molecule polarizability is roughly proportional to the volume of molecule. Such crystals have no prospects for thermoelectric applications.

In Fig. 2 the case when $\gamma = 0.05$ is shown. P is somewhat increased, but remains small. The resonance energy is yet in the forbidden band ($E_0 < 0$) and only slightly manifests itself. When $\gamma = 1$ (Fig. 3), the resonance energy is exactly at the bottom of conduction band, $E_0 = 0$, and the above mentioned interference begins to be important. P is increased considerably up to $150 \mu\text{W}/\text{cmK}^2$, but the maximum is a little displaced to lower values of Fermi energy. The dependence of crystal purity is now more pronounced.

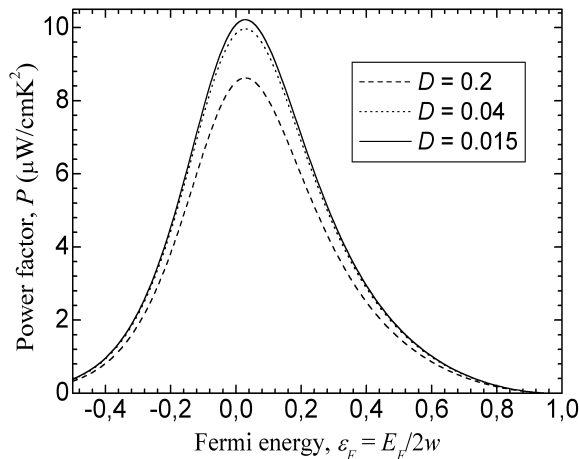


Fig. 1. Thermoelectric power factor P as a function of dimensionless Fermi energy for $\gamma = 0.01$.

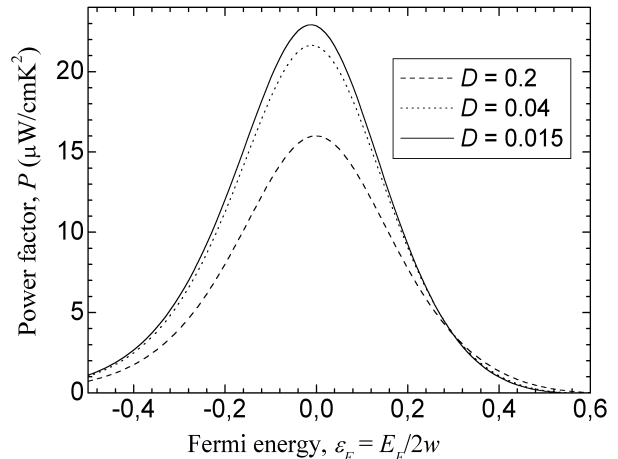


Fig. 2. Thermoelectric power factor P as a function of dimensionless Fermi energy for $\gamma = 0.05$.

At $\gamma = 1.5$ (Fig. 4) the maximum of P achieves $475 \mu\text{W}/\text{cmK}^2$, but now it is a little displaced into the conduction band. Even for crystals with lower purity ($D = 0.04$) the maximum of P is $\sim 200 \mu\text{W}/\text{cmK}^2$, a value which is five times higher than in Bi_2Te_3 .

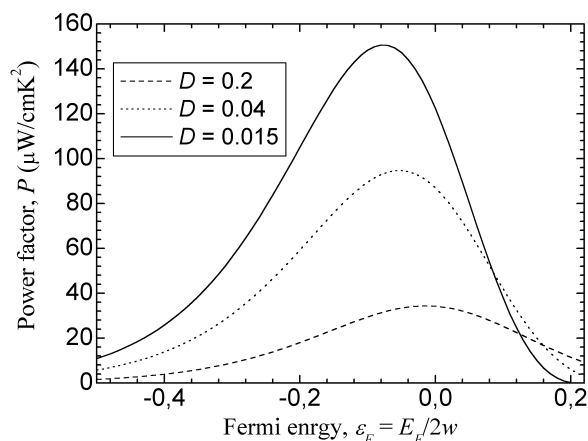


Fig. 3. Thermoelectric power factor P as a function of dimensionless Fermi energy for $\gamma = 1$.

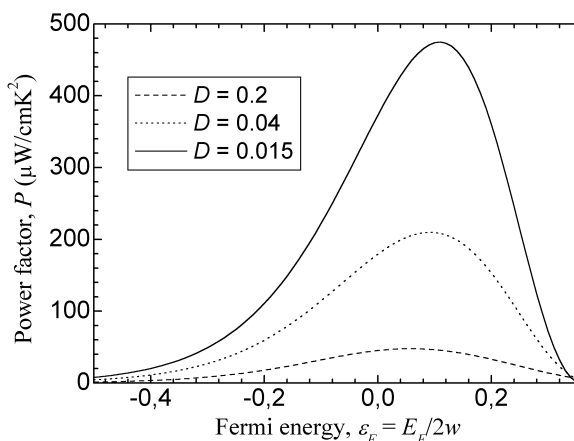


Fig. 4. Thermoelectric power factor P as a function of dimensionless Fermi energy for $\gamma = 1.5$.

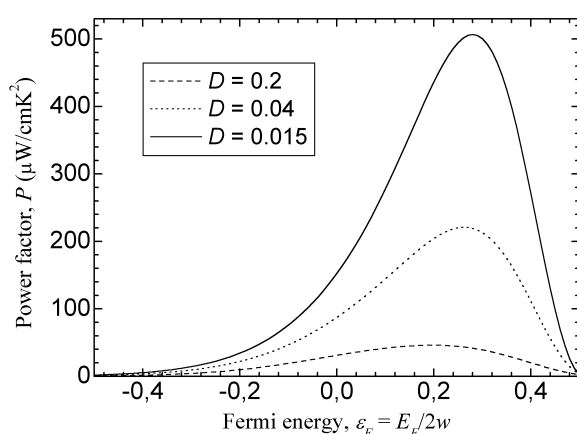


Fig. 5. Thermoelectric power factor P as a function of dimensionless Fermi energy for $\gamma = 2$.

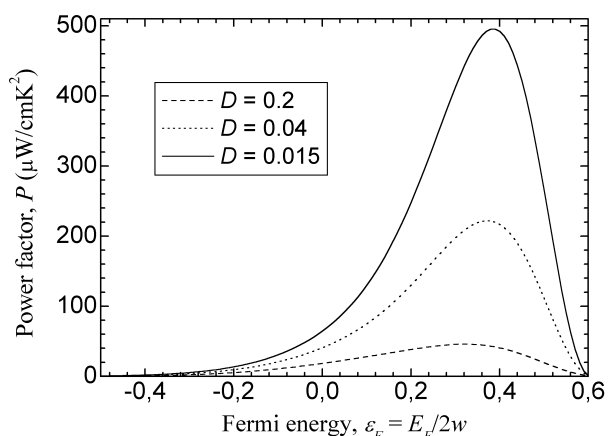


Fig. 6. Thermoelectric power factor P as a function of dimensionless Fermi energy for $\gamma = 2.5$.

For $\gamma = 2$ and $D = 0.015$ (Fig. 5) $P = 507 \mu\text{W}/\text{cmK}^2$. It is the highest value calculated so far in such materials of p -type, but it is achieved at lower values of Fermi energy, $\varepsilon_F = 0.28$, than the typical one for this crystal for which $\varepsilon_F \sim 0.45$. At this value of ε_F the power factor P is only $\sim 100 \mu\text{W}/\text{cmK}^2$, but it is also a good result.

When γ is increased up to 2.5 (Fig. 6), the maximum values of power factor are very little diminished and slightly displaced to higher values of Fermi energy. For $\varepsilon_F \sim 0.45$ and $D = 0.015$ the power factor P is $422 \mu\text{W}/\text{cmK}^2$, a value which is more than ten times higher than in Bi_2Te_3 . In this case the electrical conductivity $\sigma = 2.9 \times 10^4 \Omega^{-1}\text{cm}^{-1}$ and the thermopower $S = 121 \mu\text{V}/\text{K}$. Even for lower purity ($D = 0.04$) P achieves $180 \mu\text{W}/\text{cmK}^2$ at $\varepsilon_F \sim 0.45$. An average molecule polarizability $\alpha_0 = 17 \text{ \AA}^3$ corresponds to $\gamma = 2.5$ for given crystal parameters. It is not high value, taking into account that in anthracene [15] $\alpha_0 = 25 \text{ \AA}^3$. With the further increase of γ the maxima of power factor decrease, due to the decrease of electrical conductivity. Thus, in order to increase considerably the power factor P it is necessary to choose crystals with well pronounced quasi-one-dimensional properties formed from as bigger as possible molecules so as to have $\gamma \sim 2$ -2.5, to raise the crystal purity, after that, in dependence on concrete value of γ , it is necessary to optimize the carrier concentration. Rather high values of the thermoelectric power factor are expected. Such crystals have big prospects for different thermoelectric applications.

5. Conclusions

The thermoelectric power factor P has been modeled for typical quasi-one-dimensional organic crystals formed of p -type chains with parameters close to those of TTF chains in the TTF-TCNQ (tetrathiofulvalene-tetracyanoquinodimethane) crystal. Two interactions of carriers with longitudinal acoustic phonons are considered. The first is similar to that of deformation potential, and the second is similar to that of polaron, caused by induced polarization. Under certain conditions between these interactions the interference takes place. Due to the interference, both electron-phonon interactions considerably compensate each other for a narrow strip of states in the conduction band. As a result, the relaxation time is considerably increased for these states. The scattering of carriers on impurities is also taken into account. The crystal model is characterized by two main parameters: γ , which is the ratio of amplitudes of both electron-phonon interactions, and D , which describes the scattering on impurities.

The power factor P has been modeled as a function of Fermi energy for an interval of γ from 0.01 up to 2.5, and values of $D = 0.2, 0.04,$ and 0.015 as more accessible. In all cases P has a maximum at optimal Fermi energy. For $\gamma \ll 1$, when only the first interaction is displayed, the power factor P is small even in maximum. For $\gamma > 1$ the interference of both interactions begins to manifest itself and P grows considerably. For $\gamma = 2$ and $D = 0.015$ $P = 507 \mu\text{W}/\text{cmK}^2$. It is the highest value calculated up to now in such materials of p -type, but it is achieved at lower values of Fermi energy, $\varepsilon_F = 0.28$, than the typical one for this crystal for which $\varepsilon_F \sim 0.45$. In order to obtain high values of P it is necessary to increase the crystal purity and to optimize the carrier concentration. It would be interesting to verify experimentally these theoretical predictions.

References

- [1] H.J. Goldsmid, *J. of Thermoelectricity*, 4, 14, (2005).
- [2] M.S. Dresselhouse and J.P. Heremance, In: *Thermoelectric Handbook, Macro to Nano*, Ed. by Rowe, CRC press, Boca Raton, FL, Chap. 39, 1229, 2006.
- [3] T.C. Harman, P.J. Taylor, M.P. Walsh, and B.E. LaForge, *Science*, 297, 2229, (2002).
- [4] A. Casian, I. Sur, H. Scherrer, and Z. Dashevsky, *Phys. Rev. B*, 61, 15965, (2000).
- [5] A. Casian, Z. Dashevsky, V. Kantser, H. Scherrer, I. Sur, and A. Sandu, *Phys. Low-Dim. Struct.*, 5/6, 49, (2000).
- [6] T.C. Harman, D.L. Spears, D.R. Callaway, S.H. Groves, and M.P. Walsh, In: *Proc. of 16th Int. Conf. on Thermoel.*, Dresden, Germany, 416, (1997).
- [7] I. Sur, A. Casian, and A. Balandin, *Phys. Rev. B*, 69, 035306, (2004).
- [8] A. Casian (Kasiyan), *J. of Thermoelectricity*, 3, 5, (1996).
- [9] R. Dusciac, V. Dusciac, and A. Casian, *J. of Thermoelectricity*, 1, 30, (2006).
- [10] A. Casian, In: *Thermoelectric Handbook, Macro to Nano*, Ed. by Rowe, CRC press, Boca Raton, FL, Chap. 36, 1229, 2006.
- [11] A. Casian and V. Dusciac, *J. of Thermoelectricity*, 1, 29, (2007).
- [12] M. Pope and C.E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd Ed., Oxford University Press, Oxford, 1999.
- [13] A. Casian, V. Dusciac, and Iu. Coropceanu, *Phys. Rev. B*, 66, 165404, (2002).
- [14] A. Casian, A. Balandin, V. Dusciac, and Iu. Coropceanu, *Phys. Low-Dim. Struct.*, 9/10, 43, (2002).
- [15] R.J.W. LeFevre and K.M.S. Sundaram, *J. Chem. Soc.*, 1963, 4442, (1963).