Temperature dependences of the electrical conductivity and thermopower in TTT₂I₃ crystals

Ionel Sanduleac, Ion Balmus, Anatolie Casian

Technical University of Moldova

Chisinau, Moldova

ionel.sanduleac@mt.utm.md

Abstract—**The temperature dependences of the electrical conductivity and thermopower of the *p*-type tetrathiotetracene–iodide, TTT₂I₃ quasi-one-dimensional organic crystals are modeled in order to determine the optimal parameters of mentioned crystals for thermoelectric applications. The numerical calculations are performed in the frame of two-dimensional (2D) physical model for crystals with different carrier concentrations and different degrees of perfection. The possibilities to improve the thermoelectric efficiency of mentioned crystals are discussed.**

Index Terms— p-**type thermoelectric material, organic crystal, TTT₂I₃, electrical conductivity, thermopower.**

I. INTRODUCTION

In the last years, the possibilities of new materials and structures to be used for thermoelectric applications are intensively studied [1]. It is expected that organic materials will be more efficient and at lower cost than ordinary ones. The efficiency of the given material to be used in thermoelectric converters of thermal energy into electricity is determined by the dimensionless figure of merit *ZT*, where *T* is the temperature. Values of *ZT* > 3 are needed in order that the thermoelectric converters could be economically competitive with the ordinary ones. Values of *ZT* ≥ 3 have been reported [2, 3], but in very complicated and expensive structures.

The area of research of inorganic thermoelectric materials has meet new opportunities with the implementation of such ideas as the heavy atom masses scattering, complex unit cells, alloys scattering on phonons, bulk nanostructuring or band engineering [1, 4]. All these techniques are focused mainly on the diminution of the thermal conductivity of the structure. Recently, it was reported a value of 0.5 Wm⁻¹K⁻¹ for thermal conductivity in experimentally obtained Bi-Te samples [5]. In *n*-type PbTe - 4%InSb composites at 773 K, high values of *ZT* ~ 1.8 were reported [6]. In the last time, the scientific community is becoming more and more interested in the valorization of thermoelectric properties of organic materials. Organic compounds have lot o evident advantages, such as abundant raw materials, eco-friendly and inexpensive production techniques, solution process ability and low thermal conductivity. But, in almost cases, the carrier mobility is relatively low and some optimization procedures are needed in order to improve the electrical conductivity. Values of *ZT* ~ 0.4 and even *ZT* ~ 1 were reported in PEDOT: PSS thin films and

in PEDOT nanowire/PEDOT hybrid composites [7-9]. One of the main peculiarities of quasi-one dimensional organic structures consists in a disproportional grow of the electrical conductivity in relation to the thermal conductivity when the carrier concentration is varied. This phenomenon, known as the Wiedemann-Franz law violation [10], ensures the possibility to obtain high values of *ZT* by optimizing the carrier concentration.

II. CRYSTALS OF TETRATHIOTETRACENE-IODIDE (TTT₂I₃)

It was demonstrated theoretically, that quasi-one-dimensional (Q1D) organic crystals of TTT₂I₃ are prospective thermoelectric materials [11]. The internal structure of the crystal consists of segregate chains of planar molecules of tetrathiotetracene (TTT) and iodine ions. Along the chains of TTT, the overlap of π wavefunctions ensures the formation of a narrow conduction band of ~ 0.64 eV [12]. This direction is further denoted as *x* – direction. The nearest molecular chains are spaced at ~ 1.9 nm one from other (*y* – direction). The physical model of the crystal considers the charge transport along the TTT chains, with small corrections due to the weak interchain interactions. The scattering on impurity centers is also taken into account. The Hamiltonian of the crystal has the form:

$$H = \sum_{k} E(k)a_k^+ a_k + \sum_{q} \hbar\omega_q b_q^+ b_q + \sum_{k,q} A(k,q)a_k^+ a_{k+q}(b_q + b_{-q}^+) +$$

$$\left(I_i V_{0i} \sum_{l=1}^{N_i} e^{-iqr_l} + I_d V_{0d} e^{-E_0/k_0 T} \sum_{j=1}^{N_d} e^{-iqr_j} \right) V^{-1} \sum_{k,q} a_k^+ a_{k+q} \tag{1}$$

where the first term describes the energy of carriers, in the nearest-neighbor and tight-binding electrons approximations:

$$E(k) = -2w_1[1 - \cos(k_x b)] + 2w_2[1 - \cos(k_y a)] \tag{2}$$

here w_1 and w_2 are transfer energies of the hole from given molecule to the nearest one (the indices 1 and 2 indicate on the *x* and *y* directions, with corresponding lattice constants *b* and *a*, respectively); k_x, k_y are the projections of the quasi-wave vector **k**. Due to the pronounced quasi-one dimensionality of the crystal, w_2 ~ 0.01 w_1. The energy of holes is measured from the top of the conduction band. At relatively low temperatures (< 400 K), the carrier energy is relatively low and the scattering

on optical phonons can be neglected. Only the acoustic phonons are considered (see the second term in (1)). Two main hole-phonon interaction mechanisms are considered: of the polaron type and of the deformation potential type. The first mechanism is determined by the fluctuation of polarization energies of the molecules from the neighborhood of the conducting hole. The coupling constant is proportional to the mean polarizability α_0 of TTT molecule. The second interaction is caused by the fluctuations of the transfer energy between the nearest molecules due to the variation of the intermolecular distance. The coupling constants of the second mechanism are proportional to the derivatives w'_1, w'_2 with respect to the intermolecular distance. The square of matrix element of the both hole-phonon interactions $A(\mathbf{k},\mathbf{q})$ from the Hamiltonian (1) has the form:

$$|A(\mathbf{k},\mathbf{q})|^2 = 2\hbar/(NM\omega_q)\{w'^2_1[\sin(k_x b) - \sin((k_x - q_x)b) + \gamma_1 \sin(q_x b)]^2 + w'^2_2[\sin(k_y a) - \sin((k_y - q_y)a) + \gamma_2 \sin(q_y a)]^2 \quad (3)$$

Here M is the mass of TTT molecule, N is the number of molecules in the basic region of the crystal, γ_1 and γ_2 indicate the ratios of amplitudes of the first interaction to the second one in the direction of chains and in transversal direction

$$\gamma_1 = 2e^2\alpha_0/(b^5 w'_1), \ \gamma_2 = 2e^2\alpha_0/(a^5 w'_2) \quad (4)$$

where e is the carrier charge. The last term in (1) describes the scattering of holes on impurities and crystal defects. The impurities that remain from the synthesis and the lattice defects are considered point-like, randomly distributed and electric neutral. In addition, the scattering on thermally activated defects, created as result of different thermal dilatation coefficients of TTT and iodine chains, is considered (E_0 - the activation energy of a defect).

III. ELECTRICAL CONDUCTIVITY AND THERMOPOWER

The kinetic equation of the Boltzmann type is deduced by the method of two-particle temperature dependent Green functions. In the given temperature interval the holes scattering can be considered elastic. Then the kinetic equation is solved analytically. The electrical conductivity σ_{xx} and the Seebeck coefficient S_{xx} along TTT chains can be expressed through the transport integrals R_n as follows:

$$\sigma_{xx} = \sigma_0 R_0, S_{xx} = (k_0/e)(2w_1/k_0 T)R_1/R_0$$
$$\sigma_0 = 2e^2 M v^2_{s1} w^3_1 r/\pi^2 \hbar ab(k_0 T_0)^2 w'^2_1(T_0/T), \quad (5)$$

where M is the mass of TTT molecule, r is the number of chains through the transversal section of the unit cell, v_{s1} is the sound velocity along chains and k_0 is the Boltzmann constant. Unfortunately, the R_n can be calculated only numerically.

$$R_n = \int_0^2 d\varepsilon \int_0^\pi d\eta [\varepsilon + d(1-\cos\eta) - (1+d)\varepsilon_F]^n \varepsilon(2-\varepsilon) \times$$
$$\times n_{\varepsilon,\eta}(1-n_{\varepsilon,\eta})[s_0\sqrt{\varepsilon(2-\varepsilon)}cth(s_0 T_0\sqrt{\varepsilon(2-\varepsilon)}/T) \times \quad (7)$$
$$\times \gamma^2_1(\varepsilon - \varepsilon_0)^2 + \frac{d^2}{8\varepsilon(2-\varepsilon)}(1+\gamma^2_2+2\sin^2\eta -$$
$$- 2\gamma_2\cos\eta) + D_0 + D_1\exp(-E_a/k_0 T)]^{-1}$$

Here ε_F is the dimensionless Fermi energy in units of $2w_1$, $\varepsilon_0 = (\gamma_1 - 1)/\gamma_1$ is the dimensionless resonance energy, $d = w_2/w_1 = w'_2/w'_1$ and $s_0 = \hbar v_{s1}/(ak_0 T_0)$. A new variable $\varepsilon = (1-\cos(k_x b))$ was introduced, which has the meaning of dimensionless kinetic energy of a hole along chains in units of $2w_1$, $\eta = k_y a$ is the dimensionless quasi momentum, $n_{\varepsilon,\eta}$ is the Fermi distribution function in these new variables. From (6) it is observed that, if the weak interchain interaction is neglected (i.e. $d = 0$), the expression under integral (and the relaxation time) has a maximum around $\varepsilon = \varepsilon_0$. This lead to a significant increase of the relaxation time due to the compensation of the mentioned above hole-phonon interaction mechanisms.

Electrical conductivity σ_{xx}, the thermopower (Seebeck coefficient) S_{xx} (eq.5) were modeled numerically for the following parameters of TTT$_2$I$_3$ crystals: $M = 6.5\cdot10^5 m_e$ (m_e is the mass of the free electron), $a = 18.35$ Å, $b = 4.96$ Å, $w_1 = 0.16$ eV, $w'_1 = 0.26$ eVÅ^{-1}, $v_{s1} = 1.08\cdot10^3$ m/s, $E_F = 0.12$ eV, $d = 0.01$ [13]. Scattering rates on impurities and defects are described by the dimensionless parameters D_0 and $D_1\exp(-E_a/k_0 T)$. The parameters D_0 and D_1 are proportional to impurity and defect concentrations, respectively. Earlier [11, 13], the thermoelectric properties of the crystal were modeled at room temperature. By comparison with experimental data, it was deduced that for crystals growth from solution, the scattering parameter $D \approx 0.6$ and for crystal synthesized from gaseous phase, $D \approx 0.1$. In order to investigate the behavior of σ_{xx} and S_{xx} in a larger interval of T, the thermal activation of the defects and the influence of the thermal dilatation on the parameter γ_1 are considered.

In Fig.1. the electrical conductivity of TTT$_2$I$_3$ organic crystals as a function of temperature is presented.
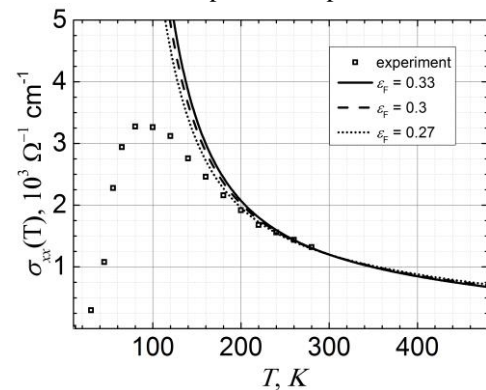

Fig.1. Electrical conductivity as a function of temperature T: rhombs – experiment; lines – numerical results.

The experimental data are taken from reported experimental results, measured only for $T \leq 300$ K in crystals with stoichiometric concentration of conducting holes [14]. It is observed that with decreasing temperature the electrical conductivity firstly increases, achieving a maximum at $T \sim 100$ K, then decrease rapidly. This decrease is explained by a smooth metal-dielectric transition of the Peierls type [15]. Numerical results are presented for $D_0 = 0.001$ and $D_1 = 0.8$. Different values of dimensionless Fermi energy ($\varepsilon_F = 0.33$, 0.3, 0.27 which corresponds to a concentration of conducting holes of: $n_h = 1.2$, 1.1 and $1 \cdot 10^{21}$ cm^{-3}) are considered. It is observed that theory describes very well the temperature dependence of σ_{xx} for a temperature interval from 180 K up to $\sim$ 300 K. For lower temperatures, probably it has to be considered the fluctuations of lattice constants before the metal-dielectric transition occurs. The diminution of σ_{xx} in this region may be conditioned by the opening of a small energy gap upon the Fermi energy, which increases when the temperature decreases.

In Fig.2 the temperature dependence of the Seebeck coefficient (thermopower) is presented. It is seen that numerical results for $\varepsilon_F = 0.33$ agree with experimental data [14] for a larger interval of T.
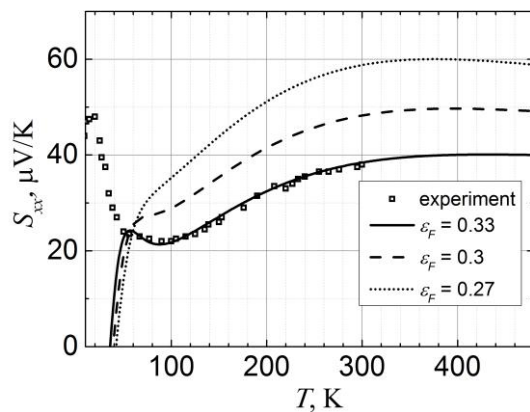

Fig.2. Thermopower as a function of temperature: rhombs – experiment; lines – numerical results.

The thermopower is proportional to the ratio R_1/R_0 (eq.5), which is less sensitive to the T variation. It is observed a very good fitting of numerical results with experimental data for 50 K $< T <$ 300 K. It is expected that the model will well describe also the behavior of S_{xx} for $T >$ 300 K and lower carrier concentrations. From Fig.2. it results that the S_{xx} increases for a wide interval of temperature with the diminution of carrier concentration, but achieves a smooth maximum at around 360 K. It is expected that the power factor $P_{xx} = \sigma_{xx} S_{xx}^2$ will have a maximum at this T. It would be interesting to verify experimentally this prediction.

CONCLUSIONS

The electric conductivity and thermopower of quasi-one-dimensional TTT$_2$I$_3$ organic crystal are modeled as a function of temperature in a two-dimensional physical model, considering the weak interchain interaction and the scattering on impurities and thermally activated defects. Experimental results for stoichiometric crystals are compared with the data of numerical modeling showing a good agreement in a rather large T interval. It is demonstrated that thermoelectric properties can be enhanced by diminution of carrier concentration and the optimal temperature for the heated part of the converter is $\sim$ 360 K.

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