

ELECTRICAL CONDUCTIVITY AND THERMOELECTRIC POWER IN CRYSTALS OF TETRATHIOTETRACENE IODIDE

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Abstract. *Temperature dependences of electrical conductivity and of thermoelectric power in quasi-one-dimensional organic crystals of tetrathiotetracene iodide were calculated in a large temperature interval. Two electron-phonon interaction mechanisms: one of deformation potential type and other similar to that of polaron were considered. The scattering of carriers on impurities and on crystal defects was also taken into account. It is found that the presented crystal model describes rather well the temperature dependences in the interval from 300K up to ~ 150 K and can be applied for the modeling of thermoelectric properties. For lower temperature the calculated electrical conductivity grows faster, meaning that additional scattering mechanisms begin to be important.*

Keywords: *quasi-one-dimensional crystal, tetrathiotetracene iodide, electrical conductivity, thermoelectric power, temperature dependences.*

I. Introduction

Quasi-one-dimensional organic crystals of tetrathiotetracene iodide, TTT_2I_3 , were synthesized independently and nearly simultaneously by three scientific groups from former Soviet Union [1, 2], Switzerland [3] and USA [4]. The crystals were grown from solution [1, 2], from gas phase by cosublimation of tetrathiotetracene (TTT) and iodine in an inert gas flow [3] or in vacuum [4]. The aim was to create organic quasi-one-dimensional conductors in which the high temperature superconductivity could be realized. And even this aim was not achieved, it was found that these crystals have more diverse and often unusual physical properties from the point of view of ordinary materials. Later we have demonstrated theoretically [5, 6] that crystals of TTT_2I_3 after the optimization of carriers' concentration can have improved thermoelectric properties.

The crystals have chain-like structure. They are formed of separate stacks of almost planar molecules of TTT and of iodine. Two molecules of TTT give one electron to the iodine chain, so that the latter is formed from I_3^- ions. But the electronic wave functions of iodine ions are rather localized, therefore the iodine chains do not participate in the charge transport. The overlap of carriers' wave functions along the TTT stacks is large, whereas between the molecules of nearest chains the overlap is negligible. Thus, only TTT chains are conductible and the carriers are holes. But the electrical conductivity at room temperature along the chains is rather high. For crystals grown from solution it varies between 800 and $1800 \Omega^{-1}\text{cm}^{-1}$, but for those grown by gas phase is of the order of $10^3 - 10^4 \Omega^{-1}\text{cm}^{-1}$. These are the highest values of electrical conductivity measured in quasi-one-dimensional organic crystals until now. However, such large variation of experimental data obtained in different laboratories show that the conducting properties of TTT_2I_3 crystals strongly depend on the method of synthesis. The conditions of crystal grows determine the quality of crystals, their perfection and purity, the conducting properties being very sensitive to these factors.

In this paper we analyze the temperature dependences of electrical conductivity and thermoelectric power of TTT_2I_3 crystals in the frame of model described in [7]. It is found that this model describes rather well the temperature dependences in the interval from 300K up to ~ 150 K and can be applied for the modeling of thermoelectric properties around the room temperature.

II. Transport properties

The charge transport in quasi-one-dimensional organic crystals of TTT₂I₃ will be studied in the frame of physical model presented in [7]. Two mechanisms of carriers' interaction with longitudinal acoustic vibrations of crystalline lattice are considered. The first interaction is connected with the fluctuations of energy w of a hole transfer from one molecule to the nearest one along the chains. The coupling constant is proportional to the derivative w' of w with respect to the intermolecular distance. The second interaction is of polaron type, only the question is of the induced polarization. The coupling constant is proportional to the average polarizability of molecule a_0 . It is also taken into consideration the rates of carriers' scattering on impurities and on defects. The first is described by the parameter D_0 which is proportional to the concentration of impurity n_{im} . The second has the form $D_1 \exp(-E_d/k_0T)$, where the parameter D_1 is proportional to the concentration of defects, and E_d is the energy of defect formation. The charge transport is described in the approximation of tight binding electrons. So as the one-dimensional conducting band, related to carriers' motion along the TTT chains is not very large, the method of effective mass is not applied and the carrier energy is taken in the form $e(k) = 2w(1 - \cos ka)$, where k is the projection of carrier wave vector along chains and a is the lattice constant in the same direction. The variation of k is taken into the whole Brillouin's zone. On the same reason, for the longitudinal acoustic phonon frequency the exact expression is taken $w_q = 2v_s a^{-1} |\sin qa/2|$, where v_s is the sound velocity along the chains.

As it is shown in Ref. 7 the scattering processes on acoustic phonons can be considered elastic up to temperature higher than 10 K. In this case the linear kinetic equation is solved exactly and for electrical conductivity σ and the thermoelectric power (Seebeck coefficient) S we obtain the expressions

$$s = \frac{e^2 z w^2 M v_s^2}{\hbar a b c w'^2 k_0 T_0} R_0, \quad S = \frac{k_0}{e} \frac{2w}{k_0 T_0} \frac{T_0}{T} \left(\frac{R_1}{R_0} - e_F \right), \quad (1)$$

where e is the electron charge, z is the number of chains through the transversal section of the unit cell, w is the energy of a hole transfer from one molecule to the nearest one along the chains M is the mass of molecule, a, b, c are the lattice constants, w' is the derivative of w with respect to the intermolecular distance, k_0 is the Boltzmann constant, $T_0 = 300$ K, $e_F = E_F/2w$ is the Fermi energy E_F in units of $2w$ and R_n are the transport integrals

$$R_n = - \int_0^2 \frac{e^{n+1} (2-e) f'_0(e) de}{\{s_0 \sqrt{e(2-e)} \text{cth}[s_0 (T_0/T) \sqrt{e(2-e)}] g^2 (e-e_0)^2 + D_0 + D_1 \exp(-E_d/k_0T)\}}. \quad (2)$$

Here e is the carrier energy E in unities of $2w$, $0 \leq e \leq 2$, $f'_0(e)$ is the derivative of Fermi distribution function with respect to e , $s_0 = \hbar v_s / (a k_0 T_0)$, γ is the ratio of amplitudes of above mentioned electron-phonon interactions $g = 2e^2 a_0 / (a^5 |w'|)$ and characterizes the relative role of these interactions, $e_0 = (\gamma - 1)/\gamma$ determines for $\gamma > 1$ the dimensionless energy for which the first term in denominator of (2) becomes zero, the dimensionless parameter D_0 describes the scattering of carriers on impurities

$$D_0 = n_{im} I^2 d^2 M v_s^2 / (4a^3 k_0 T_0 w'^2), \quad (3)$$

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

This model will be applied to the Q1D organic crystals of tetrathiotetracene–iodide, TTT_2I_3 , for which the parameters are: $w = 0.16 \text{ eV}$, $w' = 0.26 \text{ eV \AA}^{-1}$, the mass of molecule $M = 6.5 \cdot 10^5 m_e$ (m_e is the mass of free electron), the lattice constants $a = 18.35 \text{ \AA}$, $b = 4.96 \text{ \AA}$, $c = 18.46 \text{ \AA}$, the sound velocity along the chains $v_s = 1.5 \cdot 10^5 \text{ cm/s}$, the carriers concentration for stoichiometric crystals $n = 1.2 \cdot 10^{21} \text{ cm}^{-3}$. The one-dimensional chains are oriented along b direction. In TTT_2I_3 crystals the parameter γ is unknown. Earlier in [6] we have considered a value of $\gamma = 1.8$ ($\alpha_0 = 48 \text{ \AA}^3$), this value will be taken in this paper too. In rather pure and perfect crystals of TTT_2I_3 the second and third terms in the denominator of (2) can be made considerable less than unity. Consequently, the denominator becomes very small for energies $e \sim e_0$ and, if e_F is close to e_0 , these states will give big contribution to integral from (2), and the electrical conductivity will increase. Thus, e_0 determines a narrow strip of energy states in the conduction band the carriers from which will have increased mobility. Therefore, the difference between e_0 and e_F manifests itself as an energy gap in the energetic spectrum of crystal.

The measurements of electrical conductivity σ and of thermoelectric power S in TTT_2I_3 crystals are made on constant pressure. But the calculations are made on constant volume. In the same time it is known that the TTT_2I_3 crystals have rather large coefficient of thermal expansion. We will take into account this effect only in the parameter γ which determines the value of e_0 . The latter, as it was shown above, strongly influences the value of σ . Besides, the parameter γ most strongly depends on lattice constant a , being proportional to a^{-5} . Taking into account only the first approximation on the coefficient of thermal expansion β , we must replace in (2) γ at room temperature by γ_T at temperature T determined by relation $g_T = g[1 + 5b(T_0 - T)]$. We have taken $\beta = 8 \cdot 10^{-5} \text{ K}^{-1}$. Note that in ebonite $\beta = 7 \cdot 10^{-5} \text{ K}^{-1}$, but in TTT_2I_3 β must be a little greater.

The main purpose of this paper is to calculate accordingly to presented physical model the temperature dependences of electrical conductivity σ and of thermoelectric power S in TTT_2I_3 crystals and to compare calculated data with the experimental ones.

In Fig.1 the ratios of electrical conductivities at temperature T to conductivity at 300 K are presented for crystals grown from solution [8]. In Fig.2 the temperature dependences of thermoelectric power are presented [9]. Points are experimental data, lines – calculated ones, in Fig.1 for lower data and in Fig.2 for higher data. The same parameters are used in Figs 1 and 2: $e_F = 0.4$, $D_0 = 10^{-3}$, $D_1 = 3$, $E_d = 0.025 \text{ eV}$. It is seen that the continue lines describe well the experimental data for σ in the interval from 300 up to 150 K, and for S even up to 100K.

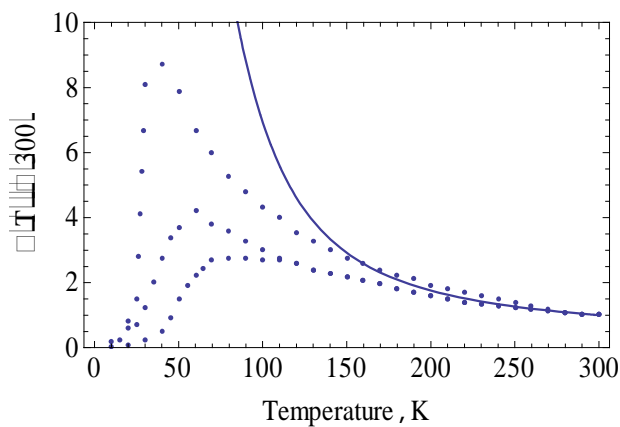


Fig.1. Ratio of electrical conductivity at temperature T to that for 300 K: points – experiment, line – calculation for lower data.

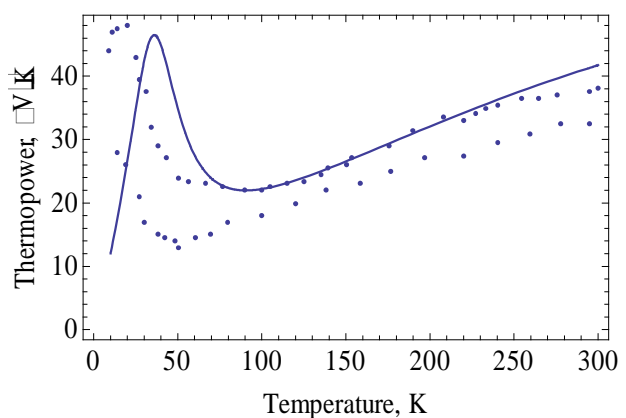


Fig.2. Temperature dependences of thermoelectric power: points – experiment, line – calculation for higher data.

In Figs. 3 and 4 the same dependences are presented, only in this case calculations for σ were made for higher data and for thermopower – for lower data. Unlike of previous case, the value of e_F was increased up to 0.43.

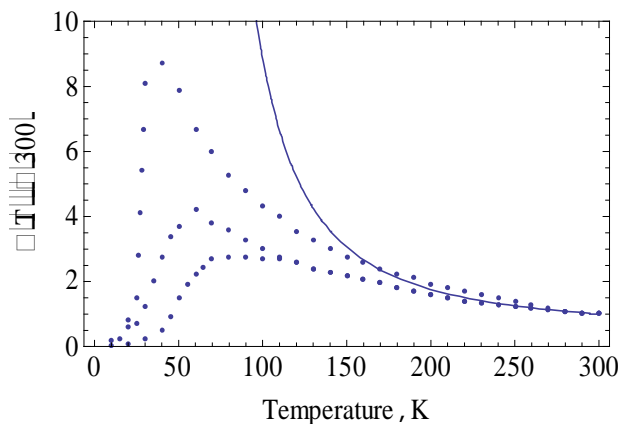


Fig.3. The same as in Fig.1 : points – experiment, line – calculation for higher data.

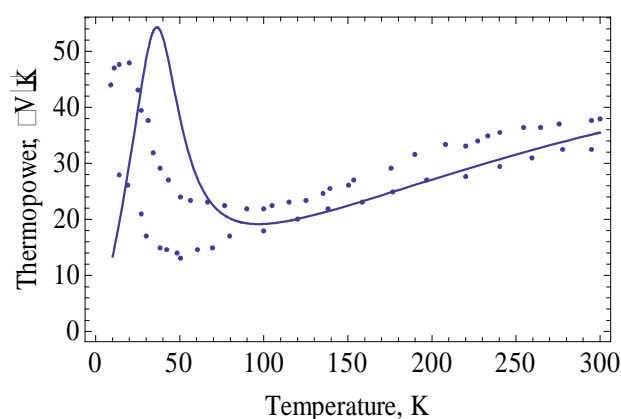


Fig.4. The same as in Fig.2 : points – experiment, line – calculation for lower data.

Thus, the presented physical model of charge transport in TTT_2I_3 can be applied for the modeling of thermoelectric properties of these crystals for temperatures higher than ~ 150 K. For lower temperature the calculated electrical conductivity grows faster, meaning that additional scattering mechanisms begin to be important.

III. Conclusions

Temperature dependences of electrical conductivity and thermoelectric power were calculated for quasi-one-dimensional crystals of TTT_2I_3 in the frame of a more complete physical model which takes into account two electron-phonon interactions and carriers' scattering on impurities and defects. It is shown that theoretical calculations agree well with the experimental data in the temperature interval from 300 to 150 K and can be used for the modeling of thermoelectric properties. For lower temperatures the model must be completed by additional interactions.

V. References

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