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Modeling of thermoelectric properties of *n* – type organic crystals of $TTT(TCNQ)_2$: 3D physical model.

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Thermoelectric properties of quasi-one-dimensional $TTT(TCNQ)_2$ organic crystals are investigated in order to appreciate the prospect of using this compound as *n* – type thermoelectric material. A more complete three-dimensional (3D) physical model is elaborated. It takes into account two the most important interactions of conduction electrons with longitudinal acoustic phonons, the electrons' scattering on neighbor molecular chains, as well as the scattering by impurities and defects. The electrical conductivity, thermopower, the power factor, electronic thermal conductivity and the thermoelectric figure of merit in the direction along conductive molecular chains are calculated numerically for different degrees of crystal purity. It is shown that in stoichiometric compounds the thermoelectric figure of merit *ZT* remains small even after the increase of crystal perfection degree. The thermoelectric properties may be significantly enhanced by simultaneous increase of crystal perfection and of electron concentration. The latter can be achieved by additional doping with donors. For less pure crystals, the interaction with impurities predominates over the weak interchain interaction and the simpler one-dimensional (1D) physical model is applicable. When the impurity scattering is reduced, the interchain interaction begins to limit the carrier mobility and the application of the 3D physical model is required. The optimal parameters permitting to predict $ZT \sim 1$ are determined.

Key words: $TTT(TCNQ)_2$, electrical conductivity, Seebeck coefficient, power factor, thermal conductivity, thermoelectric figure of merit.

INTRODUCTION

Environmental problems facing humanity require a widespread implementation of renewable energy sources. Due to the abundance of low-level heat, thermoelectric devices are very promising to recover even a part of wasted energy. The search and investigations of high-efficient thermoelectric materials represent a priority purpose toward an eco-friendly technology for global and local power generation systems, cooling systems and for infrared sensors. In the last decade, thermoelectric properties of materials with complex crystalline structure, of low-dimensional systems, of superlattices with quantum dots and of nanostructured organic materials were successfully investigated in order to achieve high conversion efficiency.

In *n* – type clathrate crystal, thermoelectric figure of merit $ZT \sim 1 – 1.3$ was reported at $T = 800 – 1000$ K [1, 2]. In multiple-filled skutterudites, $ZT = 1.7$ at 850 K was realized [3]. High values of $ZT \sim 2.5$ were obtained also in low-dimensional systems, such as Bi_2Te_3/Sb_2Te_3 superlattices, and in superlattices with quantum dots PbTe/PbSe, with $ZT \sim 3$ at 600 K [4, 5]. New promising results were reported recently in $Mg_2Sn_{0.75}Ge_{0.25}$ compound – $ZT \sim 1.4$ at $T = 800$ K [6]. However, the wide scale implementation of thermoelectric devices based on inorganic materials requires very sophisticated production technology and expensive raw materials.

Recent investigations revealed that nanostructured organic materials might be very promising candidates as thermoelectric material. Their internal structure joins together the properties of low-dimensional systems and of complex compounds with much more diverse internal interactions. Moreover, thermoelectric properties are well-tunable by molecular chemistry methods. In DMSO – treated PEDOT: PSS, $ZT \sim 0.42$ was achieved by minimizing the total dopant volume [7]. High values of *ZT* were reported in mixed organic and inorganic compounds, such as hybrid material composed of nanoparticles of a polymer complex, carbon nanotubes and poly(vinyl chloride), $ZT \sim 0.3$ [8]. Important value, $ZT = 0.57$ at room temperature was measured in phenyl acetylene-capped silicon nano particles [9].

Earlier it was predicted theoretically [10] that in molecular structures consisting of nanowires of conducting polymers values of $ZT \sim 15$ may be achieved, and even $ZT \sim 20$ in charge transfer compounds [11], if the crystal purity is sufficiently high. In [12-14] the organic nanostructured crystals of tetrathiotetracene-iodide, TTT_2I_3, were proposed as prospect thermoelectric materials of *p*-type.

The aim of this paper is to propose and analyze the opportunity of organic crystal of $TTT(TCNQ)_2$ type as candidate for *n* – type thermoelectric material. A more complete three-dimensional (3D) physical model is elaborated, taking into account two the most important interactions of conduction electrons with longitudinal acoustic phonons, the electrons' scattering on neighbor