THERMOELECTRIC PROPERTIES OF THE TTT(TCNQ)$_2$ CRYSTALS: 3D MODELING

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Thermoelectric properties of quasi-one-dimensional (Q1D) organic crystals of *n*-type TTT(TCNQ)$_2$ are investigated theoretically in order to estimate the possibility to apply this compound for thermoelectric applications. A more complete three-dimensional (3D) physical model is applied. Two the most important electron-phonon interactions are taken into account simultaneously. One interaction is similar to that of deformation potential. Three coupling constants of this mechanism are proportional to the derivatives w_1', w_2' and w_3' with respect to the intermolecular distance of transfer energies w_1, w_2 and w_3 of an electron from the given TCNQ molecule to the nearest one along lattice vectors ***c, b, a***. The other is of polaron type. The coupling constant of this interaction is proportional to the mean polarizability of TCNQ molecule α_0. The ratios of amplitudes of second interaction to the first one in the *x* direction on chains and in transversal directions *y*, *z*, respectively are described by the parameters γ_1, γ_2 and γ_3. The electrons' scattering by impurities and defects is also considered. The electrical conductivity, thermopower, the electronic thermal conductivity and the thermoelectric figure of merit in the direction of conductive molecular chains are calculated numerically for different degrees of crystal purity.

Crystals of TTT(TCNQ)$_2$ have the aspect of dark-violet needles of length of 3 – 6 mm. Conductive molecular chains of TCNQ are arranged along ***c*** direction, further considered as *x* – axis. The carriers are electrons. The transfer energy of an electron from a given TCNQ molecule to the nearest one in this direction has been taken as in TTF-TCNQ crystals, $w_1 = 0.125$ eV. In transversal to chain directions the transfer energies $w_2 = d_1 \cdot w_1$ and $w_3 = d_2 \cdot w_1$ are small and the transport mechanism is of hopping-type. The parameters d_1 and d_2 were estimated earlier for TTT_2I_3 crystals. By analogy we can put $d_1 = 0.015$ and $d_2 = 0.01$ for TTT(TCNQ)$_2$. In the previous paper [1] we have taken for the sound velocity along TCNQ chains the value $v_{s1} = 2.8 \cdot 10^3$ m/s as in TTF-TCNQ crystals. However, the modeling of Peierls structural transition have shown that in TTT(TCNQ)$_2$ the sound velocity must be larger, $v_{s1} = 3.9 \cdot 10^3$ m/s. The average value $\alpha_0 = 10$ Å^{-3} was estimated which leads to $\gamma_1 = 1.8$. Note that the results are not very sensitive to small variation of γ_1. The stoichiometric concentration of electrons in TTT(TCNQ)$_2$ crystals was estimated to $n = 1.1 \cdot 10^{21}$ cm^{-3} or $\varepsilon_F = 2w_1/E_F = 0.35$, where E_F is the Fermi energy and ε_F is the dimensionless Fermi energy.

The thermoelectric figure of merit $(ZT)_{xx}$ along TCNQ chains as function of ε_F is presented in Fig.1. Three different values of the dimensionless parameter describing the impurity scattering processes are considered: $D_0 = 0.1$ as in TTT_2I_3 crystals growth from gaseous phase method, and $D_0 = 0.05$, $D_0 = 0.02$ for ultra-pure crystals, not obtained yet. From Fig.1. it is observed that in stoichiometric crystals $(ZT)_{xx} \sim 0.05$ even for crystals of high purity. This phenomenon is explained by the simultaneous increase of both the electrical and electronic thermal conductivity. The optimisation of thermoelectric properties may be performed by aditional dopping with donor impurities. Thus, if the concentration of electrons is increased by two times compared to the stoichiometric one, $n = 2.2 \cdot 10^{21}$ cm^{-3} or $\varepsilon_F = 1.05$, $(ZT)_{xx} = 0.4$, 0.56 and even 0.8 may be obtained, depending on crystal purity.

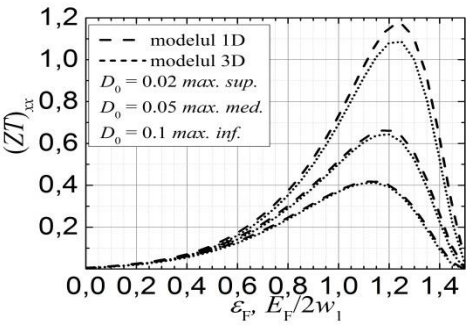

Fig.1. Thermoelectric figure of merit, $(ZT)_{xx}$ along TCNQ chains

[1] I. Sanduleac, A. Casian. *J. of Electron. Materials*, DOI: 10.1007/s11664-015-4018, 2015, 7 pages.