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DENSITY OF STATES FOR AN ELECTRONIC SPECTRUM WITH A FORBIDDEN BAND

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Abstract. Quasi-one-dimensional organic crystals with high electrical conductivity at room temperature are prospect materials for thermoelectric applications. However, usually at some low temperature these materials manifest metal-dielectric transition of Peierls type. The aim of this paper is to calculate the density of electronic states and to show that the metal-dielectric transition is determined by the appearance of a forbidden band in the electronic spectrum exactly above the Fermi energy. While decreasing the temperature *T*, this forbidden band becomes larger and at some *T* prevails the value of k_0T, where k_0 is the Boltzmann constant and the carriers cannot be exited across the forbidden band. This temperature corresponds to metal-dielectric transition.

Keywords: *electrical conductivity, quasi-one-dimensional materials, organic compounds, thermoelectric figure of merit, thermoelectric converter.*

Introduction

Over the past few years, the quasi-one-dimensional (Q1D) organic crystals with high electrical conductivity at room temperature attract more attention of researchers being materials with prospect thermoelectric properties. These materials are used in thermoelectric convertors, which serve for direct transform of thermal energy into electricity without usual electrical generator, or to transform the electrical energy by cooling without a compressor. The possibility of the given material to be used in a thermoelectric convertor is characterized by its dimensionless figure of merit $ZT = \sigma S^2 T/\kappa$, where σ is the electrical conductivity, S is the thermopower or Seebeck coefficient, T *i*s the temperature, κ is the thermal conductivity. Values of ZT as high as possible are needed. However, the best commercially thermoelectric materials Bi_2Te_3 and its alloys for near room temperatures [1], and PbTe for intermediary temperature range have $ZT \sim 1$. It is a low value. Significant growth of the thermoelectric figure of merit value ZT at room temperature has been achieved in low-dimensional quantum-well structures [2]. The density of energetic states dramatically changes while the dimensionality is reduced. This phenomenon leads to significant changes in electronic and thermal transport properties [3, 5]. A value of $ZT \sim 15$

at room temperature has been predicted in molecular nanowires [6]. Even higher values of *ZT* ~ 20 we have predicted in quasi-one-dimensional organic crystals [7] under some conditions. However, these and above predictions were made on the base of a strictly dimensional physical model. Significant efforts were made over the past years in order to search and find new materials and structures with high thermoelectric figure of merit, see references [8]. Detailed modeling's of the thermoelectric properties taking into account the interchain interaction in 2D and 3D approximations in crystals of tetrathiotetracene-iodide, TTT_2I_3 of *p*-type, and of *n*-type tetrathiotetracene-tetracyanoquinodimethane, $TTT(TCNQ)_2$ are presented in [8 - 14]. Very promising results are predicted in TTT_2I_3 crystals. In crystals grown by gaseous phase with electrical conductivity σ_{xx} ~ 10^4 S/cm after diminishing the charge carrier concentration by 1.5 times with respect to stoichiometric one the value of *ZT* ~ 2.5 is predicted. Moreover, even *ZT* ~ 5 is predicted in more perfect crystals. In the case of $TTT(TCNQ)_2$ crystals, if by additional doping by donors, the concentration of conduction electrons is increased twice, *ZT* ~ 0.8 is expected. Even *ZT* ~ 1.5 is predicted in more perfect crystals.

Crystals of *p*-type TTT_2I_3

The Q1D crystals of tetrathiotetracene-iodide, TTT_2I_3, are formed from segregate stacks or chains of TTT molecules and iodine [15 - 17]. The TTT chains are strong donors. Two TTT molecules give one electron to iodine chain and the crystal is of mixed valence. Along the longitudinal direction, the overlap of π – electron wave functions of nearest TTT molecules is important, but being transversal to the chain direction, due to the significant interchain distance, the overlap of electron wave functions is insignificant. This fact determines that only TTT chains are conductive and the carriers are holes. Accordingly, the crystals have needle-like form with the dimensions 10-12 cm x 60 μm. The ratio of longitudinal electrical conductivity to the transversal one is of the order 10^2-10^3. Therefore, in the first approximation the transversal electrical conductivity can be neglected and we obtain the one-dimensional (1D) crystal model with the electrical conductivity along ***b*** direction. Due to relatively localized states, conduction electrons are described in the tight binding and nearest neighbors' approximations. The energy of a hole with the projection k_x of the wave vector along the chain direction *x*, measured from the top of conduction band has the form

$$E(k_x) = -2w_1(1-\cos k_x b), \tag{1}$$

where w_1 is the transfer energy of a hole from the given molecule to the nearest one along lattice vector ***b***, the axis *x* is directed along ***b*** of conductive chains. The corresponding density of states $\rho(E)$ for energetic spectrum (1) is

$$\rho(E) = \frac{2z}{\pi b[E(4w_1 - E)]^{1/2}} \tag{2}$$

where $E(k_x) = E$, and z = 4 is the number of molecular chains through the transversal section of the elementary cell.

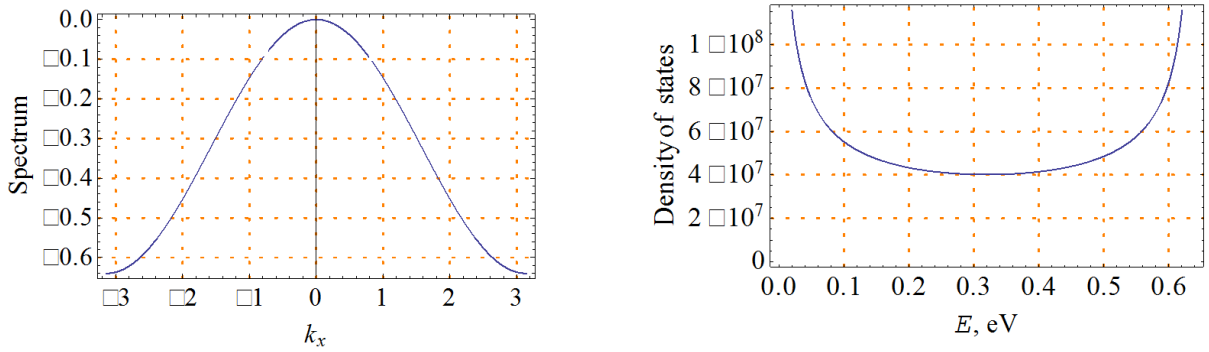
Let us now introduce the density of states for a hole spectrum with a forbidden band above the Fermi energy [17]

$$\tilde{\rho}(E)=\frac{4z}{2\pi^2 b}\{\int_0^{k_F}\frac{\delta dk}{(E-E_F+[(E(k)-E_F)^2+\Delta^2]^{1/2})^2+\delta^2}+\int_{k_F}^{\pi}\frac{\delta dk}{(E-E_F-[(E(k)-E_F)^2+\Delta^2]^{1/2})^2+\delta^2}\} \quad (3)$$

where $k = k_x b$ is dimensionless wave vector and k_F is dimensionless Fermi wave vector.

The numerical calculations of $\tilde{\rho}(E)$ were made with Mathematica. The parameters were chosen as follows: T_0 = 300K, δ = 0.00001, k_F = π/4. We have included in the energetic spectrum a forbidden band of the width Δ = 0.00005 (T_0 - T) depending on temperature. The value of Δ increases with the decrease of T and the coefficient 0.00005 was chosen in order to obtain a width of $k_0 T$ for the forbidden band at T = 100K At lower temperature the carriers will not be exited through the forbidden band.

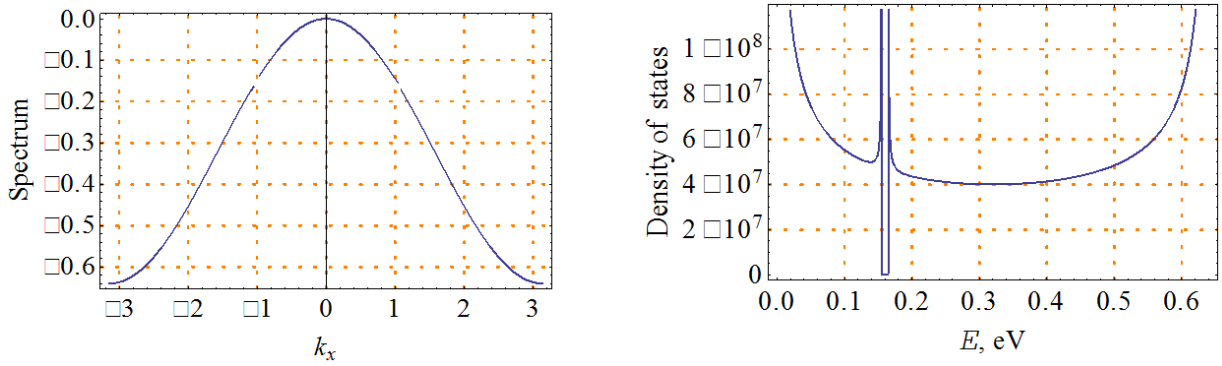
In Figure 1 the energetic spectrum and the density of electronic states at room temperature T_0 = 300 K are presented. It is seen that at this temperature, there is not a forbidden band in the energetic spectrum and in the density of states; the latter corresponds to expression Eq. (2). We have chosen that at 300 K there is not a forbidden band, considering the experimental reports on electrical conductivity behavior at room temperature.



a) b)

Figure 1. Energetic spectrum (a), and density of electronic states (b) for T = 300 K.

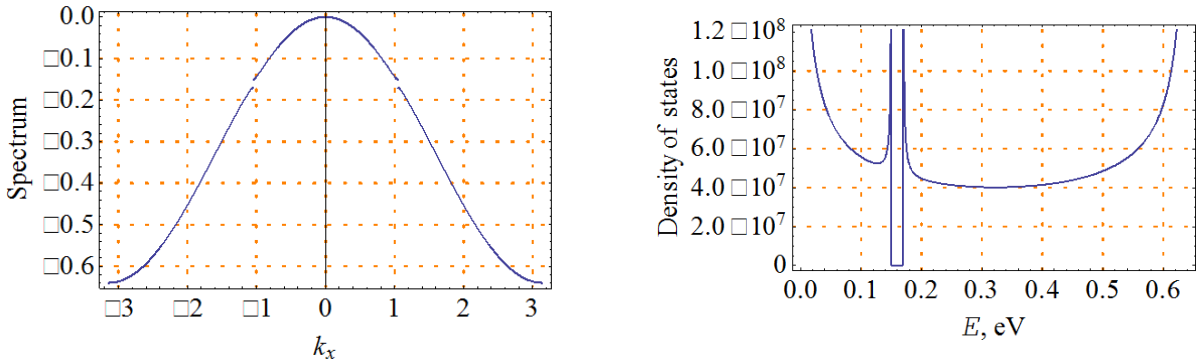
In "Figure 2" the energetic spectrum and the density of electronic states are presented at temperature T = 200 K. It is seen that a small forbidden band has appeared in the energetic spectrum and in the density of states.



a) b)

Figure 2. Energetic spectrum (a), and density of electronic states (b) for T = 200 K.

This will lead to some diminution of the electrical conductivity, because a small part of holes cannot be exited across the forbidden band.



a) b)

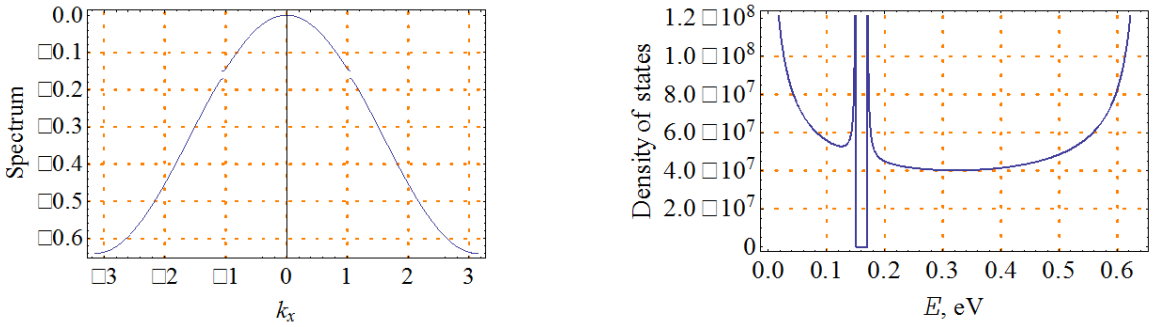
Figure 3. Energetic spectrum (a), and density of electronic states (b) for T = 100 K.

At T = 100 K Figure 3 the width of forbidden band is considerably increased and equals to k_0T at this temperature.

The additional holes cannot be exited across the forbidden band. As a result, the electrical conductivity will cease to grow.

At least, at T = 90 K the width of forbidden band becomes much larger than k_0T at this temperature and the holes in general cannot be exited across the forbidden band.

At this temperature, the metal-dielectric transition must take place.



a) b)

Figure 4. Energetic spectrum (a), and density of electronic states (b) for T = 90 K.

Conclusions

We have calculated the density of electronic (holes) states for an energetic spectrum with a forbidden band depending on a temperature in the crystal of TTT2I3 of p-type.

When temperature decreases, the width of the forbidden band increases, leading to the decrease of electrical conductivity, because a part of holes cannot be exited across the forbidden band.

From T ~ 100 K and below, the electrical conductivity ceases to grow because the width of the forbidden band match k_0T at this temperature.

At T = 90 K the width of forbidden band becomes larger than k_0T at this temperature and the holes in general cannot be exited across the forbidden band.

At this temperature, the metal-dielectric transition must take place, as the experiment shows [15, 16].

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