Metal-Insulator Transition of Peierls Type in TTT_2I_3 Crystals in 3D Approximation

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***Abstract* — The metal-insulator transition in quasi-one-dimensional organic crystals of tetrathiotetracene-iodide, TTT_2I_3, is investigated in 3D approximation. A more complete physical model of the crystal is applied which takes into account two the most important hole-phonon interaction mechanisms. The first is similar to that of deformation potential and the second one is of polaron type. The scattering on defects is also considered. The phonon polarization operator and the renormalized phonon spectrum are calculated in the random phase approximation for different temperatures applying the method of retarded Green functions. The effect of lattice distortion on the dispersion of renormalized acoustic phonons is analyzed. The Peierls critical temperature is determined.**

***Index Terms* — Peierls transition, quasi-one-dimensional organic crystals, tetrathiotetracene-iodide crystals, polarization operator, renormalized phonon spectrum.**

I. INTRODUCTION

Quasi-one-dimensional (Q1D) organic crystals of TTT_2I_3 have been studied for the first time with 30 years ago with the aim to find superconductivity in a low dimensional conductor [1-4]. However, at low temperature these crystals showed not superconductivity, but a transition into a dielectric state. This transition is supposed to be of Peierls type. Also, these materials have been investigated as good candidates for thermoelectric applications [5, 6]. It was predicted [7, 8] that after optimization of the carrier concentration in such crystals values of dimensionless thermoelectric figure of merit ~ 4 could be realized. However, not all parameters of these crystals are determined experimentally. In this paper we have two main purposes: 1) to show that the transition is of Peierls type and 2) to use the investigation of the Peierls transition in order to determine more precisely some parameters of TTT_2I_3.

This phenomenon has been theoretically predicted by Rudolf Peierls [9]. According to Peierls, at some lowered temperatures, the one-dimensional metallic crystal with a half filled conduction band has to pass in a dielectric state with a dimerized crystal lattice. This temperature is called the Peierls critical temperature. The Peierls transition has been studied by many authors in other Q1D organic crystals (see [10-15] and references therein).

In TTF-TCNQ crystals, the transition takes place at 54 K into TCNQ stacks and at 38 K into TTF stacks with the opening of respective band gaps in the electronic spectrum above the Fermi energy and a strong diminution of electrical conductivity. We have also studied the behavior of the transition at 54 K in a more complete physical model [16-17]. With the lowering temperature, some modifications in the phonon spectrum take place [18-19], and at some temperature, the renormalized phonon frequency becomes equal to zero for a given value of the phonon wave vector. At this temperature the Peierls transition occurs.

Also, we have analyzed the Peierls transition in TTT_2I_3 crystals in 2D approximation [20]. It has been established that Peierls transition begins at $T \sim 35$ K in TTT chains and reduces considerably the electrical conductivity. Due to interchain interaction the transition is finished at $T \sim 19$ K. It is demonstrated that the hole-phonon interaction and the interactions with the structural defects diminish $\Omega(q_x)$ and reduce the sound velocity in a large temperature interval.

In this paper we will study the behavior of Peierls transition in the TTT_2I_3 crystals in 3D approximation, where the scattering on defects is also considered.

II. THE PHYSICAL MODEL OF THE CRYSTAL

TTT_2I_3 is a charge transfer compound. The orthorhombic crystal structure consists of segregated chains or stacks of plane TTT molecules and of iodine chains. The lattice constants are a = 18.40 Å, b = 4.96 Å and c =18.32 Å, which demonstrates a very pronounced crystal quasi-one-dimensionality. The highly conducting direction is along ***b***. The compound is of mixed valence. Two molecules of TTT give one electron to iodine chain formed of I_3^- ions that play the role of acceptors. Only TTT chains are conductive and the carriers are holes. The electrons on iodine ions are in a rather localized states and do not participate in the transport.

The physical model of the crystal was described in more detail in [20]. The Hamiltonian of the 3D crystal in the tight binding and nearest neighbor approximations has the form:

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$$H = \sum_{\boldsymbol{k}} \varepsilon(\boldsymbol{k}) a_{\boldsymbol{k}}^{+} a_{\boldsymbol{k}} + \sum_{\boldsymbol{q}} \hbar\omega_{\boldsymbol{q}} b_{\boldsymbol{q}}^{+} b_{\boldsymbol{q}} + \sum_{\boldsymbol{k},\boldsymbol{q}} A(\boldsymbol{k},\boldsymbol{q}) a_{\boldsymbol{k}}^{+} a_{\boldsymbol{k}+\boldsymbol{q}} (b_{\boldsymbol{q}} + b_{-\boldsymbol{q}}^{+}) \quad (1)$$

where the first term is the energy operator of free holes in the periodic field of the lattice, $a_{\boldsymbol{k}}^{+}$, $a_{\boldsymbol{k}}$ are the creation and annihilation operators of such hole with a 3D quasi-wave vector $\boldsymbol{k}$ and projections (k_x, k_y, k_z). The energy of the hole $\varepsilon(\boldsymbol{k})$, measured from the top of band has the form:

$$\varepsilon(\boldsymbol{k}) = -2w_1(1-\cos k_x b) - 2w_2(1-\cos k_y a) - 2w_3(1-\cos k_z c) \quad (2)$$

Here w_1, w_2 and w_3 are the transfer energies of a hole from one molecule to another along the chain (x direction) and in perpendicular (y and z directions). In Equation (1) $b_{\boldsymbol{q}}^{+}$, $b_{\boldsymbol{q}}$ are creation and annihilation operators of an acoustic phonon with 3D wave vector $\boldsymbol{q}$ and frequency $\omega_{\boldsymbol{q}}$. The second term in the Equation (1) is the energy operator of longitudinal acoustic phonons

$$\omega_{\boldsymbol{q}}^2 = \omega_1^2 \sin^2(q_x b/2) + \omega_2^2 \sin^2(q_y a/2) + \omega_3^2 \sin^2(q_z c/2) \quad (3)$$

where ω_1, ω_2 and ω_3 are the limit frequencies in the x, y and z directions. The third term in equation (1) represents the hole-phonon interactions. As it was mentioned above, two interaction mechanisms are considered: the first is similar to that of deformation potential and the second is of polaron type. The coupling constants of the first interaction are proportional to the derivatives w_1', w_2' and w_3' of w_1, w_2, and w_3 with respect to the intermolecular distances. The coupling constant of second interaction is proportional to the average polarizability of the molecule α_0. This interaction is important for crystals composed of large molecules as TTT, so as α_0 is roughly proportional to the volume of molecule.

The square module of matrix element $A(\boldsymbol{k},\boldsymbol{q})$ from Equation (1) can be written in the form:

$$\begin{aligned} |A(\boldsymbol{k},\boldsymbol{q})|^2 &= 2\hbar w_1'^2/(NM\omega_{\boldsymbol{q}}) \times \\ &\{[\sin(k_x b) - \sin(k_x - q_x, b) - \gamma_1 \sin(q_x b)]^2 + \\ &d_1^2[\sin(k_y a) - \sin(k_y - q_y, a) - \gamma_2 \sin(q_y a)]^2 + \\ &d_2^2[\sin(k_z c) - \sin(k_z - q_z, c) - \gamma_3 \sin(q_z c)]^2\}. \end{aligned} \quad (4)$$

In Equation (4), M is the mass of the molecule, N is the number of molecules in the basic region of the crystal, $d_1 = w_2/w_1 = w_2'/w_1'$, $d_2 = w_3/w_1 = w_3'/w_1'$, parameters γ_1, γ_2, and γ_3 describe the ratio of amplitudes of polaron-type interaction to the deformation potential one in the x, y and z directions:

$$\gamma_1 = 2e^2\alpha_0/b^5 w_1', \gamma_2 = 2e^2\alpha_0/a^5 w_2', \gamma_3 = 2e^2\alpha_0/c^5 w_3' \quad (5)$$

The analysis shows that the Hamiltonian from the Equation (1), as in 2D physical model, can not explain the sharp decrease of electrical conductivity for temperatures lower than T_{max} = 35 K. It is necessary to take into account also the dynamical interaction of carriers with the defects. The static interaction will give contribution to the renormalization of hole spectrum. The defects in TTT_2I_3 crystals are created due to different coefficients of dilatation of TTT and iodine chains. The Hamiltonian of this interaction H_{def} is presented in the form:

$$H_{def} = \sum_{\boldsymbol{k},\boldsymbol{q}} \sum_{n=1}^{N_d} B(q_x) \exp(-iq_x x_n) a_{\boldsymbol{k}}^{+} a_{\boldsymbol{k}-\boldsymbol{q}} (b_{\boldsymbol{q}} + b_{\boldsymbol{q}}^{-}) \quad (6)$$

Here $B(q_x)$ is the matrix element of a hole interaction with a defect and it is presented in the form: $B(q_x) = \sqrt{\hbar/(2NM\omega_q)} \cdot I(q_x)$, where $I(q_x)$ is the Fourier transformation of the derivative with respect to intermolecular distance from the energy of interaction of a carrier with a defect, x_n numbers the defects, which are considered linear along x-direction of TTT chains and distributed randomly.

$$I(q_x) = D(\sin(bq_x))^2 \quad (7)$$

where the constant D = 1.03 and determines the intensity of hole interaction with a defect.

The renormalized phonon spectrum, $\Omega(\boldsymbol{q})$ is determined by the pole of the Green function and is obtained from the transcendent dispersion equation

$$\Omega(\boldsymbol{q}) = \omega_{\boldsymbol{q}}[1 - \overline{\Pi}(\boldsymbol{q},\Omega)]^{1/2} \quad (8)$$

where the principal value of the dimensionless polarization operator takes the form:

$$\mathrm{Re}\,\overline{\Pi}(\boldsymbol{q},\Omega) = -\frac{4}{\hbar\omega_q} \sum_{\boldsymbol{k}} \frac{\left[|A(\boldsymbol{k},-\boldsymbol{q})|^2 + |B(q_x)|^2\right](n_k - n_{k+q})}{\varepsilon(\boldsymbol{k}) - \varepsilon(\boldsymbol{k}+\boldsymbol{q}) + \hbar\Omega} \quad (9)$$

Here, $|A(\boldsymbol{k},-\boldsymbol{q})|^2$ and $|B(q_x)|^2$ are, respectively, the square module of matrix elements of the hole-phonon interaction from Equation (4), and of hole interaction with defects from Equation (6), n_k is the Fermi distribution function. The Equation (8) can be solved only numerically.

III. RESULTS AND DISCUSSIONS

Computer simulations for the 3D physical model of the crystal are performed for the following parameters [21]: M = 6.5 × 10^5 m_e (m_e is the mass of the free electron), w_1 = 0.16 eV, w_1' = 0.26 eV·Å^{-1}, d_1 = 0.015, d_2 = 0.015, γ_1 = 1.7, γ_2 and γ_3 are determined from the relations: $\gamma_2 = \gamma_1 b^5/a^5 d_1$, $\gamma_3 = \gamma_1 b^5/c^5 d_2$. The sound velocity along TTT chains v_{s1} = 1.35 × 10^5 cm/s. For v_{s2} and v_{s3} in transversal directions (in a direction and in c direction) we have taken 1.35 × 10^5 cm/s and 1.3 × 10^5 cm/s respectively.

In figures 1-2 the dependences of renormalized phonon frequencies $\Omega(q_x)$ as functions of q_x for different

temperatures and different values of q_y and q_z are presented. In the same graphs, the dependences for initial phonon frequency $\omega(q_x)$ are presented too. It is seen that the values of $\Omega(q_x)$ are diminished in comparison with those of $\omega(q_x)$ in the absence of hole-phonon interaction. This means that the hole-phonon interaction and structural defects diminish the values of lattice elastic constants. Also, one can observe that with a decrease of temperature T the curves change their form, and in dependencies $\Omega(q_x)$ a minimum appears. This minimum becomes more pronounced at lower temperatures.

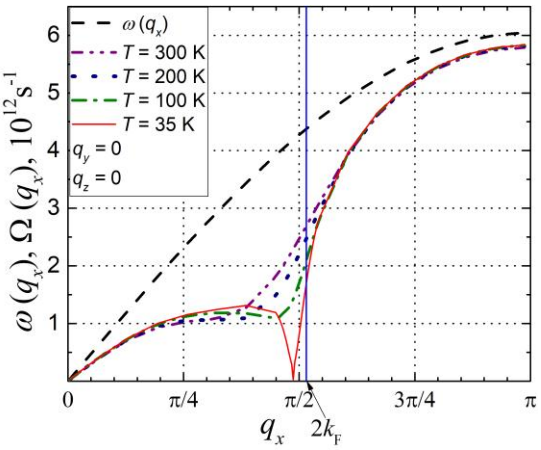

Fig. 1. Renormalized phonon spectrum $\Omega(q_x)$ for $\gamma_1 = 1.7$ and different temperatures. The dashed line is for the spectrum of free phonons. In this case $q_y = 0$, $q_z = 0$.

Fig.1 shows the case, when $q_y = 0$ and $q_z = 0$. In this case the interaction between TTT chains is neglected. The Peierls transition begins at $T = 35$ K. At this temperature, the electrical conductivity is strongly diminished, so as a gap in the carrier spectrum is fully opened just above the Fermi energy. In addition, it is seen that the slope of $\Omega(q_x)$ at small q_x is diminished in comparison with that of $\omega(q_x)$. This means that the hole-phonon interaction and structural

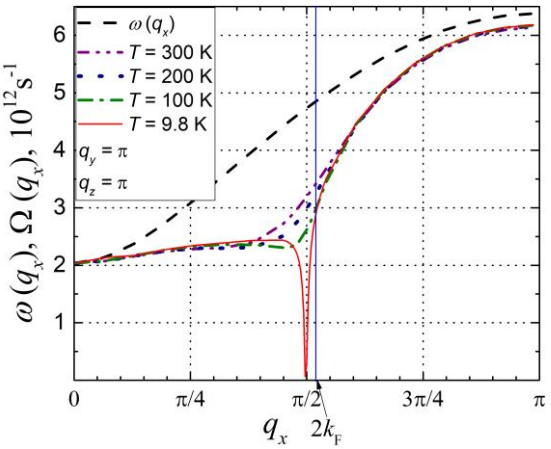

Fig. 2. Renormalized phonon spectrum $\Omega(q_x)$ for $\gamma_1 = 1.7$ and different temperatures. The dashed line is for the spectrum of free phonons. In this case $q_y = \pi$, $q_z = \pi$.

defects have reduced also the sound velocity in a large temperature interval.

In Fig. 2 the dependences of $\Omega(q_x)$ on q_x for $q_y = \pi$, $q_z = \pi$ and different temperatures are presented. It is observed that the temperature, when $\Omega(q_x) = 0$, decreases and equals $T = 9.8$ K. As it is seen from [4], the electrical conductivity is strongly reduced, and achieves zero at $T \sim 10$ K. Thus, our calculations show that the transition is of Peierls type and is finished at this temperature. A new superstructure must appear. In 2D approximation, the Peierls critical temperature, $T = 19$ K, for the values of $q_y = \pi$ and $q_z = \pi$ is obtained [20]. According to the graph of the electrical conductivity [4], one can observe that 3D physical model explain more exactly the behavior of Peierls transition. Unfortunately, at our knowledge, such experiments were not realized. It would be interesting to verify experimentally our conclusions.

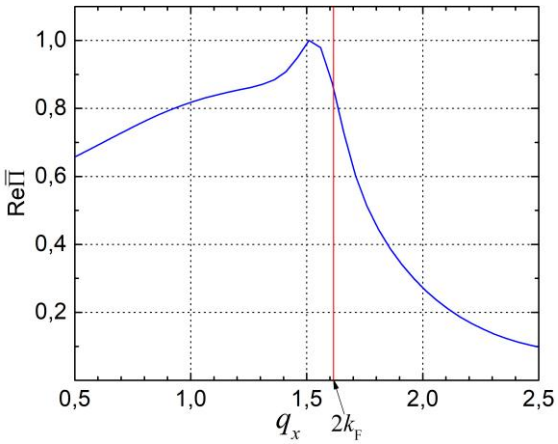

Fig. 3. Polarization operator as function of q_x for $q_y = 0$, $q_z = 0$ and T = 35 K.

Fig. 3 and Fig. 4 show the dependencies of the real part of dimensionless polarization operator $\mathrm{Re}\,\overline{\Pi}(q_x, \Omega)$ as function of q_x for different values of q_y, q_z and different temperatures at $\Omega = 0$. In Fig. 3, it is presented the case, when $q_y = 0$, $q_z = 0$ and the interaction between TTT

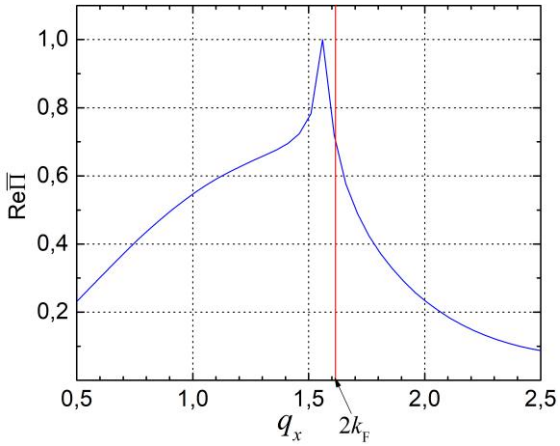

Fig. 4. Polarization operator as function of q_x for $q_y = \pi$, $q_z = \pi$ and T = 9.8 K.

chains is not taken into account. It is observed a not very pronounced peak near the value of unity. This means that the Peierls transition begins at $T = 35$ K.

In Fig. 4 it is presented the same dependence of polarization operator as function of q_x, but for $q_y = \pi$ and $q_z = \pi$. From this graph it is observed that, when the

interaction between TTT chains is taken into account, the Peierls critical temperature decrease and a pronounced transition is finished at $T = 9.8$ K.

IV. CONCLUSION

We have investigated the behavior of phonons near Peierls structural transition in quasi-one-dimensional organic crystals of TTT_2I_3 (tetrathiotetracene iodide) type in 3D approximation. A more complete crystal model is applied which takes into account two the most important hole-phonon interactions. The first is of deformation potential type and the second one is similar to that of polaron. The ratios of amplitudes of second hole-phonon interaction to the first one along chains and in transversal direction are noted by γ_1, γ_2 and γ_3, respectively. The interaction of holes with the structural defects in direction of TTT chains is taken into account too. Analytical expression for the polarization operator was obtained in random phase approximation. The method of retarded temperature dependent Green function is applied. The numerical calculations for renormalized phonon spectrum, $\Omega(q_x)$, for different temperatures are presented in two cases: 1) when $q_y = 0$, $q_z = 0$ and the interaction between transversal chains is neglected and 2) when $q_y \neq 0$, $q_z \neq 0$ and interactions between the adjacent chains are considered. It has been established that Peierls transition begins at $T \sim 35$ K in TTT chains and reduces considerably the electrical conductivity. Due to interchain interaction the transition is finished at $T \sim 9.8$ K. It is demonstrated that the transition is of Peierls type, so as at $T \sim 10$ K the electrical conductivity achieves zero. The hole-phonon interaction and the interactions with the structural defects also diminish $\Omega(q_x)$ and reduce the sound velocity in a large temperature interval.

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