Peierls transition in organic crystals of TTT_2I_3 for different values of carrier concentration

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***Abstract* — Peierls transition in quasi-one-dimensional organic crystals of tetrathiotetracene-iodide, TTT_2I_3, is investigated in 3D approximation. For a more complete description of the crystal model, two the most important hole-phonon interactions are considered. 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 renormalized phonon spectrum is calculated in the random phase approximation for different temperatures applying the method of retarded Green functions. The transition behavior is investigated for different values of carrier concentration that is determined by the dimensionless Fermi momentum, k_F. In all cases the critical temperature of the transition is determined.**

***Key words* — Peierls transition, organic crystals, 3D physical model of TTT_2I_3, carrier concentration, Peierls critical temperature.**

I. INTRODUCTION

Quasi-one-dimensional (Q1D) organic crystals of TTT_2I_3 have been studied independently and nearly simultaneously [1-4] with the aim to find superconductivity in a low dimensional conductor. However, at low temperature these crystals showed a transition into a dielectric state. This transition was supposed to be of Peierls type. Also, these materials are of interest for thermoelectric applications [5, 6].

In [7] we have investigated the Peierls transition in a 2D physical model for a $TTT_2I_{3.1}$ crystal. In [8] the 3D approximation was analyzed for the same crystal. It has been established that Peierls transition begins at $T \sim 35$ K in TTT chains. Due to interchain interaction the transition is finished at $T \sim 9.8$ K. It is shown that the transition is of Peierls type, so as at $T \sim 10$ K the electrical conductivity achieves zero [4].

In this paper we also apply a 3D physical model of the crystal where the scattering on defects is also considered. It is analyzed the behavior of the Peierls structural transition for different values of carrier concentration, that is determined by the dimensionless Fermi momentum, k_F,. Two the most important hole-phonon interactions are taken into account. One is of deformation potential type and the other is similar to that of the polaron. The renormalized phonon spectrum is calculated in the random phase approximation for different temperatures applying the method of retarded Green functions. The Peierls critical temperature T_p is established.

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 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 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 $\boldsymbol{b}$.

The physical model of the crystal was described in more detail in [7]. The Hamiltonian of the 3D crystal in the tight binding and nearest neighbor approximations has the form:

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

In Eq. (1) 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). $b_{\boldsymbol{q}}^{+}$, $b_{\boldsymbol{q}}$ are creation and annihilation operators of an acoustic phonon with 3D wave vector $\boldsymbol{q}$ and frequency $\omega_{\boldsymbol{q}}$. The energy of the hole $\varepsilon(\boldsymbol{k})$, measured from the top of band, has the form:

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

where 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). The second term in the Equation (1) is the energy operator of longitudinal acoustic phonons [8]. The square module of matrix element $A(\boldsymbol{k},\boldsymbol{q})$ from Equation (1) can be written in the form:

$$|A(\mathbf{k},\mathbf{q})|^2 = 2\hbar w_1'^2 / (NM\omega_{\boldsymbol{q}}) \times$$
$$\{[\sin(k_x b) - \sin(k_x - q_x, b) - \gamma_1 \sin(q_x b)]^2 +$$
$$d_1^2[\sin(k_y a) - \sin(k_y - q_y, a) - \gamma_2 \sin(q_y a)]^2 +$$

$$d_2^2[\sin(k_z c) - \sin(k_z - q_z, c) - \gamma_3 \sin(q_z c)]^2\}. \quad (3)$$

In Equation (3), N is the number of molecules in the basic region of the crystal, M is the mass of the molecule. $d_1 = w_2/w_1$, $d_2 = w_3/w_1$, d_1 and d_2 represents the ratio of the transfer energy in the transversal y and z directions to that along the x direction. 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 [8]. It is necessary [7, 8] to take into account also the dynamical interaction of carriers with the defects. 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:

$$H_{def} = \sum_{\mathbf{k},\mathbf{q}} \sum_{n=1}^{N_d} B(q_x) \exp(-iq_x x_n) a_{\mathbf{k}}^{+} a_{\mathbf{k}-\mathbf{q}} (b_{\mathbf{q}} + b_{\mathbf{q}}^{+}), \quad (4)$$

$B(q_x) = \sqrt{\hbar/(2NM\omega_q)} \cdot I(q_x)$, 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.

$$I(q_x) = D(\sin(bq_x))^2, \quad (5)$$

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

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

$$\Omega(\mathbf{q}) = \omega_{\mathbf{q}}[1 - \overline{\Pi}(\mathbf{q}, \Omega)]^{1/2} \quad (6)$$

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

$$\mathrm{Re}\,\overline{\Pi}(\mathbf{q},\Omega) = -\frac{4}{\hbar\omega_q} \sum_{\mathbf{k}} \frac{\left[|A(\mathbf{k},-\mathbf{q})|^2 + |B(q_X)|^2\right](n_k - n_{k+q})}{\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k}+\mathbf{q}) + \hbar\Omega} \quad (7)$$

Here, n_k is the Fermi distribution function. The Equation (6) can be solved only numerically.

III. RESULTS

Computer modeling for the 3D physical model was performed for the following parameters [6]: $M = 6.5 \times 10^5\ m_e$ (m_e is the mass of the free electron), $w_1 = 0.16$ eV, $w_1' = 0.26$ eV·Å^{-1}, $d_1 = 0.015$, $d_2 = 0.015$, $\gamma_1 = 1.7$, 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 $v_{s1} = 1.5 \times 10^5$ 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.

It is simply to pass from 3D physical model of the crystal to 1D. It is sufficient to consider in expression (4) $d_1 = 0$, $d_2 = 0$.

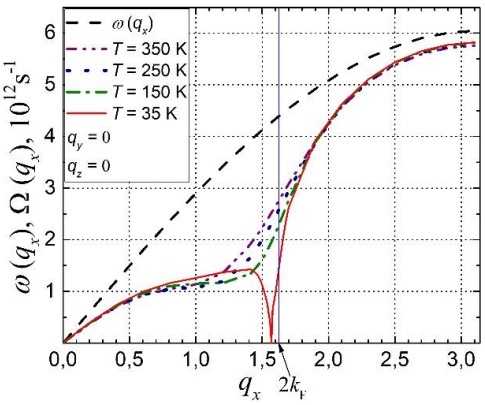

Fig. 1. Renormalized phonon spectrum $\Omega(q_x)$ for $\gamma_1 = 1.7$, $k_F = 0.517\pi/2$ and different temperatures. The dashed line is for the spectrum of free phonons. In this case $q_y = 0$, $q_z = 0$.

In figures 1-4 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 observed that in all graphs 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 see 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 shows the case, when $k_F = 0.517\pi/2$, $q_y = 0$ and $q_z = 0$. In this case the interaction between TTT chains is neglected. This value of k_F corresponds to crystal of composition $TTT_2I_{3.1}$. The Peierls transition begins at T = 35 K, as it is found experimentally.

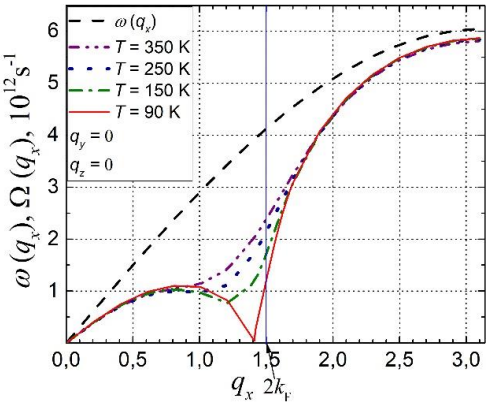

Fig. 2. Renormalized phonon spectrum $\Omega(q_x)$ for $\gamma_1 = 1.7$, $k_F = (0.517\pi/2)$-0.058 and different temperatures. The dashed line is for the spectrum of free phonons. In this case $q_y = 0$, $q_z = 0$.

In Fig. 2 it is presented the case when the interaction between TTT chains is also neglected, but the carrier concentration is smaller and k_F = (0.517π/2)-0.058. One can observe that with a decrease in carrier concentration the Peierls transition begins at higher T = 90 K. Experimentally [2], it is observed that in some crystals the electrical conductivity achieves a smooth maximum at this temperature, after that decreases slowly up to zero at T ~ 20 K.

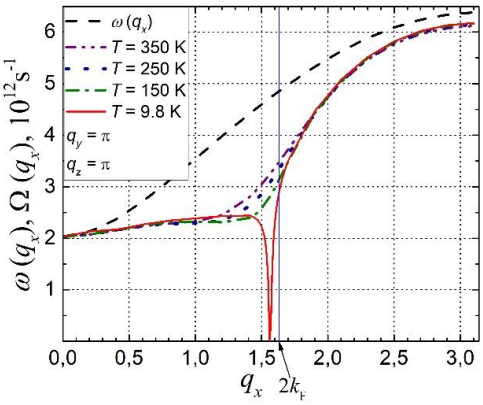

Fig. 3. Renormalized phonon spectrum Ω(q_x) for γ_1 = 1.7, k_F = 0.517π/2 and different temperatures. The dashed line is for the spectrum of free phonons. In this case q_y = π, q_z = π.

In Fig. 3 the dependences of Ω(q_x) on q_x for q_y = π, q_z = π and different temperatures are presented. It is observed that the temperature, when Ω(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 ~ 10 K. Thus, our calculations show that the transition is of Peierls type and is finished at this temperature for $TTT_2I_{3.1}$ crystal. A new superstructure must appear. In 2D approximation, the Peierls critical temperature, T = 19 K, for values of q_y = π and q_z = π is obtained [7]. According to the graph of the electrical conductivity [4], one can observe that 3D physical model explains more exactly the behavior of Peierls transition.

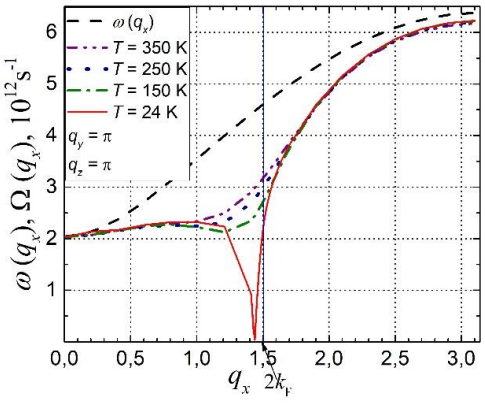

Fig. 4. Renormalized phonon spectrum Ω(q_x) for γ_1 = 1.7, k_F = (0.517π/2)-0.058 and different temperatures. The dashed line is for the spectrum of free phonons. In this case q_y = π, q_z = π.

In Fig. 4 the same dependences of Ω(q_x) on q_x for q_y = π, q_z = π and different temperatures are presented but for k_F = (0.517π/2)-0.058. In this case the metal-dielectric transition is finished at T = 24 K. It is observed that with a decrease in carrier concentration, the Peierls structural transition is finished at this T and the critical temperature increases. Our modeling explains rather well the experimental data.

IV. CONCLUSIONS

The Peierls transition is studied in quasi-one-dimensional organic crystals of TTT_2I_3 type in 3D approximation. The renormalized phonon spectrum Ω(q_x) as function of q_x for different values of q_y and q_z and different temperatures is calculated in the random phase approximation.

Also, it is studied the behavior of metal-dielectric transition in TTT_2I_3 crystals, when the carrier concentration varies. It is found that when the carrier concentration decreases, the metal-dielectric transition begins at higher temperature and is finished at higher temperature too. The Peierls critical temperature is calculated for different carrier concentrations.

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