PEIERLS STRUCTURAL TRANSITION IN ORGANIC CRYSTALS OF TTT$_2$I$_3$: 2D MODELING

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Abstract. The Peierls structural transition in quasi-one-dimensional organic crystals of tetrathiotetracene iodide (TTT$_2$I$_3$) with a quarter filled zone is studied in a 2D physical model. A more complete crystal model is used which takes into account two main hole-phonon interactions. One of them is of deformation potential type and the other is similar to that of polaron. The ratios of amplitudes of the second interaction to the first one along the chains and in transversal directions are characterized by the parameters γ$_1$ and γ$_2$, respectively. The polarization operator as a function of temperature is calculated for different values of the parameter d, where d is the ratio of the transfer energy in the direction transversal to conductive chains to the transfer energy along the conductive chains. The Peierls critical temperature T$_p$ was determined for Fermi dimensionless quasi momentum k$_F$ = π/4 and for different values of γ$_1$.

Keywords: Peierls Transition, Peierls critical temperature, Tetrathiotetracene Iodide, 2D physical model, Polarization Operator.

1. Introduction:

In the last years the organic materials attract more and more attention. These materials can have much better properties compared with inorganic ones. A special interest is noticed in the applications of quasi-one-dimensional organic materials for thermoelectric devices, designed to convert the heat directly into electricity, or the electricity in cooling.

Among the best theoretically and experimentally studied quasi-one-dimensional organic crystals are those of TTT$_2$I$_3$ (tetrathiotetracene iodide) and of TTF-TCNQ (tetrathiofulvalinium-tetracyanoquinodimethane). But it is yet necessary to determine some parameters of these crystals. In this paper we propose to use Peierls structural transition phenomenon for this purpose. The Peierls transition was studied by many authors (see [1], [2] and references therein).

In [3] the effect of impurity scattering on Peierls structural transition in quasi-one-dimensional organic crystals of TTT$_2$I$_3$ type is discussed. It was shown that small rate of carrier scattering on impurity has negligible effect on Peierls structural transition. But a big value of impurity concentration changes considerably the Peierls critical temperature.

In [4] it is studied Peierls structural transition in Q1D crystals of TTF-TCNQ in 2D approximation. The polarization operator as a function of temperature is calculated for different values of *d*, where *d* is the ratio of the transfer energy in the direction transversal to conductive chains to the transfer energy along the conductive chains. The Peierls critical temperature T$_p$ was determined for different values of the parameter *d* in two cases: 1) when the conduction band is half filled and the dimensionless Fermi momentum $k_F = \pi/2$, and 2) when the conduction band is filled up to slightly more than a half of the Brillouin zone and $k_F = \pi/2 + \delta$, where δ represents the increase of the Fermi momentum, determined by the increase of carrier concentration. The results obtained in the 2D physical model were compared with those of 1D model.

In this paper the 2D physical model is applied to TTT$_2$I$_3$ crystals. It is simultaneously considered two the most important electron-phonon interactions. One of them is of deformation potential type and the other is similar to that of the polaron. The ratios of amplitudes of the second interaction to the first one along chains and in transversal directions are characterized by the parameters γ$_1$ and γ$_2$. The analytic expression for the phonon polarization operator is obtained in the random phase approximation. The polarization operator as a function of temperature is calculated for different values of *d*, when the values of parameter γ1 vary from 1.85 to 1.88.

2. Two-dimensional crystal model

The quasi-one-dimensional organic crystals TTT$_2$I$_3$ are formed of segregate chains or stacks of planar molecules of tetrathiotetracene TTT, and iodine. The compound is of mixed-valence: two molecules of TTT give one electron to iodine so that the iodine chains in crystal are constituted from I$_3^-$ ions. The overlapping

of electronic wave functions of iodine ions is very small. Therefore the electrical conductivity of iodine chains is very small too, and can be neglected. For TTT chains the overlapping of wave functions along chains is significant and the charge carriers are holes. These crystals admit a non-stoichiometric composition, $TTT_2I_{3\pm\delta}$, with a surplus or a deficit of iodine.

The Hamiltonian of the system was described in [5] and has the form:

$$H = \sum_k \varepsilon(k)a_k^+ a_k + \sum_q \hbar\omega_q b_q^+ b_q + \sum_{k,q}[A(k,q)a_k^+ a_{k-q}(b_q + b_{-q}^+)]. \tag{1}$$

In (1) the first term is the energy operator of free holes in the periodic field of the lattice, where k is two-dimensional wave vector with projections (k_x, k_y). a_k^+, a_k are the creation and annihilation operators. The energy of carriers measured form the top of conducting band has the form:

$$\varepsilon(k) = -2w_1(1-\cos(k_x b)) - 2w_2(1-\cos(k_y a)), \tag{2}$$

where w_1 and w_2 are transfer energies of a carrier from one molecule to another along the chain (with the lattice constant b, x direction) and in perpendicular direction (with the lattice constant a, y direction $a \sim 2b$). Due to the crystal quasi-one-dimensionality w_2 is much less than w_1.

The second term in the relation (1) is the energy of longitudinal acoustic phonons with two-dimensional wave vector q and frequency ω_q.

$$\omega_q^2 = \omega_1^2 \sin^2(q_x b/2) + \omega_2^2 \sin^2(q_y a/2), \tag{3}$$

where ω_1 and ω_2 are limiting frequencies for oscillations in x and y directions, ω_2 is much less than ω_1. In (1) b_q^+, b_q are the creation and annihilation operators of an acoustic phonon.

The third term in equation (1) represents the hole-phonon interactions. As it was mentioned above, two such interaction mechanisms are considered. The first interaction is determined by the fluctuations of energy transfer w_1 and w_2, due to the intermolecular vibrations (acoustic phonons). This interaction is similar to that of deformation potential, and the coupling constants are proportional to the derivatives w_1' and w_2' of w_1 and w_2 with respect to the intermolecular distances, $w_1' < 0$, $w_2' < 0$. The second interaction is of polaron type. This interaction is conditioned by the fluctuations of the polarization energy of the molecules around the conduction hole. The coupling constant of interaction is proportional to the average polarizability of the molecule α_0.

The square module of matrix element is represented in the following form:

$$|A(k,q)|^2 = 2\hbar w_1'^2/(\rho V \omega_q)\{[\sin(k_x b) - \sin(k_x - q_x, b) + \gamma_1 \sin(q_x b)]^2 +$$
$$+ d^2[\sin(k_y a) - \sin(k_y - q_y, a) + \gamma_2 \sin(q_y a)]^2\}, \tag{4}$$

where ρ is the crystal density, V is the volume of basic region of crystal, the parameters γ_1 and γ_2 have been explained above

$$\gamma_1 = 2e^2\alpha_0/b^5 w_1'; \gamma_2 = 2e^2\alpha_0/a^5 w_2'. \tag{5}$$

From exact series of perturbation theory for the phonon Green function [1] we sum up the diagrams containing 0, 1, 2 ... ∞ closed loops of two hole Green functions which make the most important contribution. This is the random phase approximation. We denote the phonons Green function in this approximation by $D(r-r', t-t')$, and the free phonons one by $D_0(r-r', t-t')$, where r and r' are spatial coordinates, t and t' - time coordinates. For the function $D(r-r', t-t')$ an integral equation is obtained. Performing Fourier transformation after spatial and time coordinates, we obtain for the Fourier component of the Green function $D(q,\Omega)$

$$D(q,\Omega) = D_0(q,\Omega) - D_0(q,\Omega)\Pi(q,\Omega)D(q,\Omega), \tag{6}$$

where $\Pi(q,\Omega)$ is the phonon polarization operator, q is the wave vector of longitudinal acoustic phonons and Ω is renormalized phonon frequency, determined from the equation

$$\Omega(q) = \omega_q[1 - \overline{\Pi}(q,\Omega)]^{1/2},$$

where $\overline{\Pi}(\boldsymbol{q},\Omega)$ is the dimensionless phonon polarization operator.

The critical temperature of Peierls transition is determined from the condition that at this temperature the renormalized phonon frequency is diminished up to zero, i.e. $\Omega(\boldsymbol{q}) = 0$. It means

$$1 - \operatorname{Re}\overline{\Pi}(\boldsymbol{q},\Omega) = 0, \tag{7}$$

where for $\operatorname{Re}\overline{\Pi}(\boldsymbol{q},\Omega)$ the following expression is obtained

$$\operatorname{Re}\overline{\Pi}(\boldsymbol{q},\Omega) = -\frac{1}{\pi^2\hbar\omega_q}\int_{-\pi}^{\pi}dk_x\int_{-\pi}^{\pi}dk_y|A(\boldsymbol{k},\boldsymbol{q})|^2\frac{n_k - n_{k+q}}{\varepsilon(\boldsymbol{k}) - \varepsilon(\boldsymbol{k}+\boldsymbol{q}) + \hbar\Omega}. \tag{8}$$

Here $A(\boldsymbol{k},\boldsymbol{q})$ is the matrix element of hole-phonon interaction presented in (4), $\varepsilon(\boldsymbol{k})$ is the energy operator presented in (2), n_k is the Fermi distribution function, and $\hbar$ is the Planck constant.

3. Results

The critical temperature of Peierls transition is determined from (7), when $\Omega = 0$, and dimensionless projections $q_x = \pi/2$, $q_y = \pi/2$. The polarization operator as a function of temperature is calculated for different values of d, when $k_F = \pi/4$ and γ_1 varies from 1.85 to 1.88. In Figs. 1, 2, 3, 4 (the polarization operator is named Polar) the results of calculation are presented.
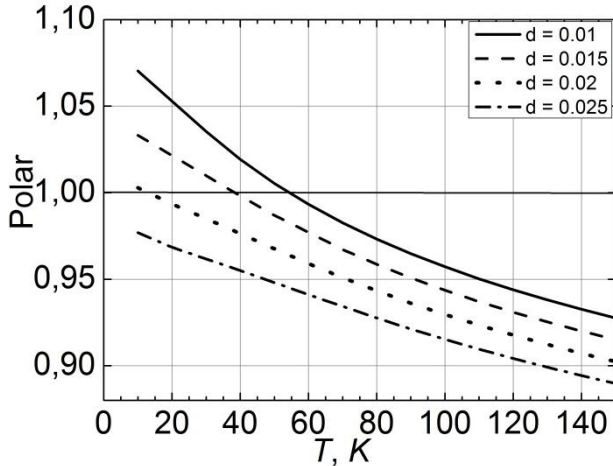

Fig.1. The polarization operator as a function of temperature, for different values of d and $\gamma_1 = 1.85$.
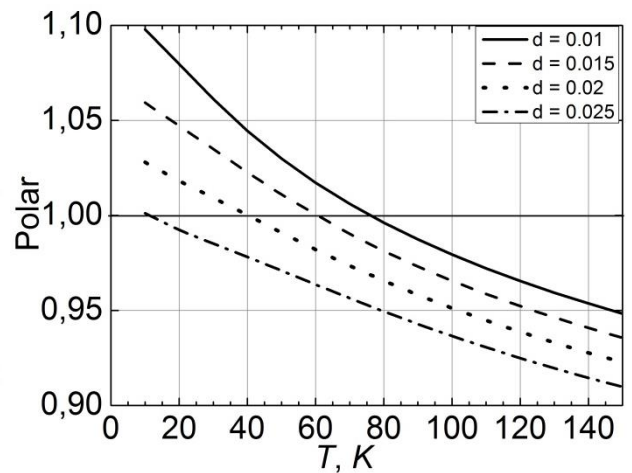
Fig.2. The polarization operator as a function of temperature, for different values of d and $\gamma_1 = 1.86$.

In all figures the continuous, the dash, dotted and dash-dotted lines correspond to $d = 0.01, 0.015, 0.02$ and 0.025, respectively. Note that the value $d = 0.015$ is estimated for real crystals of TTT_2I_3. The critical temperatures of Peierls transition are determined by the temperatures at which the curves in figures intersect the horizontal evidenced straight line for 1.00 value of polarization operator.

In Fig. 1 it is presented the case when $\gamma_1 = 1.85$. It is seen that for $d = 0.01$, $T_p \sim 54$ K; for $d = 0.015$, $T_p \sim 37$ K; for $d = 0.02$, $T_p \sim 13$ K; for $d = 0.025$ the transition disappear. It is observed that the T_p strongly decreases with the increase of the parameter d, i.e. when the deviation from the one-dimensionality is higher, the critical temperature T_p is lower.

In Fig. 2 it is presented the case when $\gamma_1 = 1.86$. It is observed that for $d = 0.01$, $T_p \sim 75$ K; for $d = 0.015$, $T_p \sim 62$ K; for $d = 0.02$, $T_p \sim 40$ K; for $d = 0.025$, $T_p \sim 10$ K. It is seen that with increasing of parameter γ_1 the critical temperature T_p also increase.

Fig. 3 corresponds to the case when $\gamma_1 = 1.87$. In this case it is seen that increasing more the parameter γ_1 the Peierls critical temperature T_p is additionally increased. One can observe that for $d = 0.01$, $T_p \sim 102$ K; for $d = 0.015$, $T_p \sim 85$ K; for $d = 0.02$, $T_p \sim 66$ K and for $d = 0.025$, $T_p \sim 42$ K.
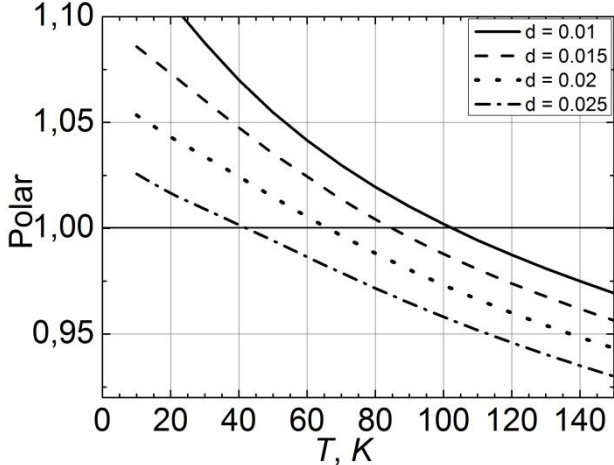
In Fig. 4 it is presented the case when $\gamma_1 = 1.88$. Also, the dependences indicate that the growth of the

Fig.3. The polarization operator as a function of temperature, for different values of d and $\gamma_1 = 1.87$.

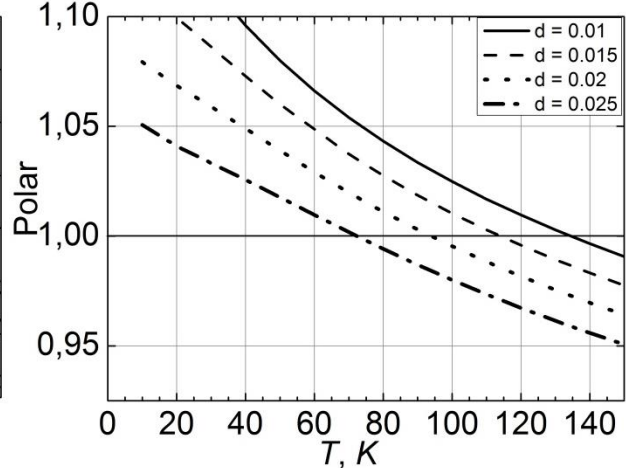Fig.4. The polarization operator as a function of temperature, for different values of d and $\gamma_1 = 1.88$.

parameter γ_1 leads to a significant increment of the Peierls critical temperature. In such a way, for $d = 0.01$, $T_p \sim 135$ K; for $d = 0.015$, $T_p \sim 113$ K; for $d = 0.02$, $T_p \sim 92$ K and for $d = 0.025$, $T_p \sim 70$ K.

4. Conclusion

In this paper we have studied the Peierls transition in the quasi-one-dimensional organic crystals of TTT_2I_3 type in 2D approximation. It is applied a more complete 2D physical model of the crystal. It was simultaneously considered two the most important hole-phonon interactions. One is of deformation potential type and the other is similar to that of polaron. The ratios of amplitudes of the second interaction to the first one are characterized by the parameters γ_1 and γ_2, respectively.

The expression for the phonon Green function is obtained in the random phase approximation. The polarization operator as a function of temperature is calculated for different values of the parameter d, where d is the ratio of the transfer energy in the direction transversal to conductive chains to the transfer energy along the conductive chains. The Peierls transition temperature T_p is determined for different values of d when Fermi dimensionless momentum is $k_F = \pi/4$ and the parameter γ_1 has different values. It is found that the T_p strongly decreases with increase of the parameter d. Also, it is observed from the figures that a small variation of the parameter γ_1 significantly change the Peierls transition temperature. For the value of the real crystal of TTT_2I_3, and namely $d = 0.015$, the T_p increase from 37 K for $\gamma_1 = 1.85$ to 113 K for $\gamma_1 = 1.88$.

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