Peierls Structural Transition in Organic Crystals of TTF-TCNQ in the 3D Model.

Andronic S., Balmus I., Casian A.
Technical University of Moldova
Chisinau, Moldova
andronic_silvia@yahoo.com

***Abstract* – Peierls transition in organic crystals of TTF-TCNQ type is studied in 3D approximation. For a more complete description of the crystal model, two the most important electron-phonon interactions are considered. The transition behavior is investigated in different cases, when the conduction band is filled up to a quarter of the Brillouin zone and the dimensionless Fermi momentum $k_F = \pi/4$ and when the carrier concentration varies and $k_F = \pi/4 \pm \delta$, where δ represents the variation of the Fermi momentum, k_F. In all cases the critical temperature of the transition is determined.**

***Key words* – Peierls transition, 3D physical model of TTF-TCNQ, polarization operator, Peierls critical temperature.**

I. INTRODUCTION

In the last years researchers attract more and more attention to the study of organic materials. It is observed a special interest in applications of quasi-one-dimensional (Q1D) organic materials for thermoelectric devices. If the parameters of these crystals will be optimized then they will have much better thermoelectric properties than those known so far (see [1] and references therein).

One of the best studied organic crystal is that of Tetrathiafulvene–Tetracyanoquinodimethane (TTF-TCNQ) type. There are different methods to determine the values of certain parameters of these materials. In this paper, we propose to use the Peierls structural transition phenomenon for this aim. The Peierls transition is currently studied in many papers (see [2-4] and references therein).

In the previous papers [5, 6] the Peierls structural transition in Q1D crystals of TTF-TCNQ was investigated in a 1D physical model of the crystal. It was studied Peierls transition in the case when the conduction band is half filled and the Fermi dimensionless quasi momentum is $k_F = \pi/2$ and also, it was analyzed the case when the concentration of conduction electrons is reduced and the band is filled up to a quarter of the Brillouin zone, $k_F = \pi/4$, [6]. The renormalized phonon spectrum has been calculated for different temperatures. The Peierls critical temperature was established in the both cases.

In [7-9] the Peierls transition was investigated in a 2D physical model for the same crystals. The polarization operator as function of temperature was calculated numerically for different parameters. It was determined the temperature of the transition.

In this paper we apply a 3D physical model of the crystal. For a complete description, two the most important electron-phonon interactions are considered. One of them is of deformation potential type and the other is similar to that of the polaron. The axis x is directed along conductive TCNQ molecular chains and y, z in transversal directions. The ratios of amplitudes of the second interaction to the first one in the x, y and z directions are characterized by the parameters γ_1, γ_2 and γ_3, respectively. The analytic expression for the phonon polarization operator is obtained in the random phase approximation. Peierls transition is investigated when the conduction band is filled up to a quarter of the Brillouin zone and the dimensionless Fermi momentum is $k_F = \pi/4$ for different values of parameters d_1 and d_2 which represents the ratio of the transfer energy in the transversal y and z directions to the transfer energy along x direction of conductive chains. The polarization operator as a function of temperature is calculated for different values of δ, where δ is the increase or the decrease of the Fermi momentum, k_F, determined by the increase or the decrease of carrier concentration. The Peierls critical temperature T_p is determined for different values of the dimensionless Fermi momentum $k_F \pm \delta$.

II. THREE-DIMENSIONAL CRYSTAL MODEL

The crystal of TTF-TCNQ was studied and described in many papers. Compound of TTF-TCNQ forms quasi-one-dimensional organic crystals composed of TCNQ and TTF linear segregated chains. The TTF molecules are donors, and TCNQ molecules are strong acceptors. Because the conductivity of TTF chains is much lower than that of TCNQ chains, we can neglect them in the first approximation. Thus, in this approximation, the crystal is composed of strictly one-dimensional chains of TCNQ that are packed in a three-dimensional crystal structure. The crystal lattice constants are a = 12.30 Å, b = 3.82 Å, c = 18.47 Å, b is in the chains directions.

The Hamiltonian of the crystal was described in [8, 9] for the 2D physical model. Now it 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, $\varepsilon(\boldsymbol{k})$ represents the energy of the electrons with 3D quasi-wave vector $\boldsymbol{k}$ and projections (k_x, k_y, k_z). In Eq. 1 $a_{\boldsymbol{k}}^{+} a_{\boldsymbol{k}}$ are the creation and annihilation operators of a conduction electron.

The second term in the Eq. 1 is the energy of longitudinal acoustic phonons with three-dimensional wave vector $\boldsymbol{q}$ and projections (q_x, q_y, q_z) and with frequency ω_q. In Eq. 1 $b_{\boldsymbol{q}}^{+} b_{\boldsymbol{q}}$ are the creation and annihilation operators of an acoustic phonon.

The third term in Eq. 1 describes the electron-phonon interaction. It contains two important mechanisms. The first one is of deformation potential type and is determined by the fluctuations of energy transfer w_1, w_2 and w_3, due to the intermolecular vibrations (acoustic phonons). The coupling constants 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, $w_1' > 0$, $w_2' > 0$, $w_3' > 0$. The second mechanism is similar to that of polaron.

The square module of matrix element of electron-phonon interaction is represented in the following form:

$$\begin{aligned} |A(\boldsymbol{k},\boldsymbol{q})|^2 &= 2\hbar/(NM\omega_{\boldsymbol{q}}) \times \\ \{w_1'^2[\sin(k_x b) - \sin(k_x - q_x, b) + \gamma_1 \sin(q_x b)]^2 + \\ w_2'^2[\sin(k_y a) - \sin(k_y - q_y, a) + \gamma_2 \sin(q_y a)]^2 + \\ w_3'^2[\sin(k_z c) - \sin(k_z - q_z, c) + \gamma_3 \sin(q_z c)]^2\} . \end{aligned} \quad (2)$$

In Eq. 2, M is the mass of the molecule, N is the number of molecules in the basic region of the crystal; 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.

The analytic expression for the phonon polarization operator is obtained in the random phase approximation. The real part of the polarization operator is presented in the form:

$$\begin{aligned} \mathrm{Re}\,\overline{\Pi}(\boldsymbol{q},\Omega) = -\frac{1}{\pi^3 \hbar\omega_q} \int_{-\pi}^{\pi} dk_x \int_{-\pi}^{\pi} dk_y \int_{-\pi}^{\pi} dk_z |A(\boldsymbol{k},\boldsymbol{q})|^2 \times \\ \frac{n_{\boldsymbol{k}} - n_{\boldsymbol{k}+\boldsymbol{q}}}{\varepsilon(\boldsymbol{k}) - \varepsilon(\boldsymbol{k}+\boldsymbol{q}) + \hbar\Omega} , \end{aligned} \quad (3)$$

where $A(\boldsymbol{k},\boldsymbol{q})$ is the matrix element of electron-phonon interaction presented in Eq. 2, $\varepsilon(\boldsymbol{k})$ is the carrier energy, $n_{\boldsymbol{k}}$ is the Fermi distribution function, and $\hbar$ is the Planck constant.

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

$$1 - \mathrm{Re}\,\overline{\Pi}(\boldsymbol{q},\Omega) = 0 . \quad (4)$$

where $\mathrm{Re}\,\overline{\Pi}(\boldsymbol{q},\Omega)$ was represented in Eq. 3.

III. RESULTS

The critical temperature of Peierls transition is determined from Eq. 4, when $\Omega = 0$, and $q_x = 2k_F$, $q_y = 2k_F$, $q_z = 2k_F$. The polarization operator as a function of temperature was calculated for different values of parameter d_1 and a certain value of parameter d_2, where $d_1 = w_2/w_1 = w_2'/w_1'$, and $d_2 = w_3/w_1 = w_3'/w_1'$. Accordingly, it was determined the polarization operator as function of temperature for different values of k_F. It was analyzed different cases when $k_F = \pi/4$ and when $k_F \pm \delta$.

Computer modeling was performed for the following parameters: $w_1 = 0.125$ eV, $w_1' = 0.22$ eVÅ^{-1}, $a = 12.30$ Å, $b = 3.82$ Å, $c = 18.47$ Å. The sound velocity at low temperatures is $v_{s1} = 3.4 \cdot 10^5$ cm/s along chains, $v_{s2} = 5.25 \cdot 10^5$ cm/s in a direction and $v_{s3} = 5.25 \cdot 10^5$ cm/s in c direction [10], $M = 3.74 \cdot 10^5\, m_e$ (m_e is the electron rest mass), $d_1 = 0.015$ and $d_2 = 0.01$, $\gamma_1 = 1.28$, γ_2 and γ_3 are determined from the relations: $\gamma_2 = 32 \cdot \gamma_1 \cdot b^5/(a^5 \cdot d_1)$ and $\gamma_3 = 32 \cdot \gamma_1 \cdot b^5/(c^5 \cdot d_2)$.

In Figs. 1, 2, 3 (the polarization operator is named Polar) the results of calculation are presented. From all figures one can determine the transition temperatures from the intersections of calculated curves with the horizontal line at

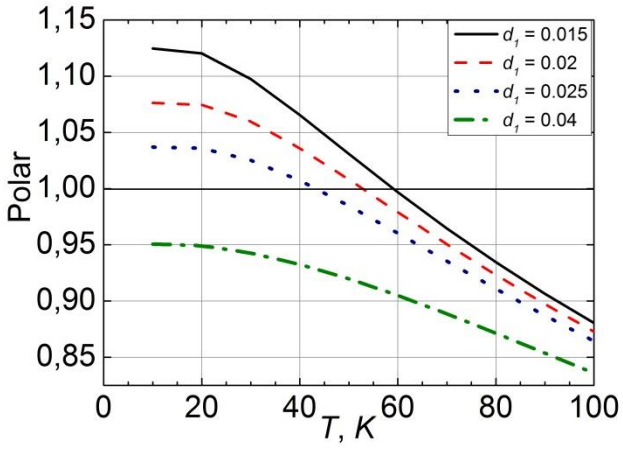

Fig. 1. The polarization operator as a function of temperature, for different values of d_1 and $d_2 = 0.01$ and $k_F = \pi/4$.

1.0.

In Fig. 1 it is presented the case when $k_F = \pi/4$ and $d_2 = 0.01$. The continuous, dash, dotted and dash-dotted lines correspond to $d_1 = 0.015$, 0.02, 0.025 and 0.04, respectively. The value $d_1 = 0.015$ is estimated for real crystals of TTF-TCNQ.

From this graph it is observed that with the increase of the parameter d_1, the T_p strongly decreases. For $d_1 = 0.015$, $T_p \sim 59$ K as it was obtained experimentally. For $d_1 = 0.02$, $T_p \sim 53$ K; for $d_1 = 0.025$, $T_p \sim 43$ K and for $d_1 = 0.04$ the Peierls transition disappears. Thus, even with a small increase of the three-

dimensionality the transition temperature decreases considerably. This is explained by the fact that the Peierls structural transition is characteristic for crystals with very pronounced quasi-one-dimensional properties.

In Figs. 2, 3 it is shown the case when d_1 = 0.015 and d_2 = 0.01, but k_F is different. The continuous, dash, dotted and

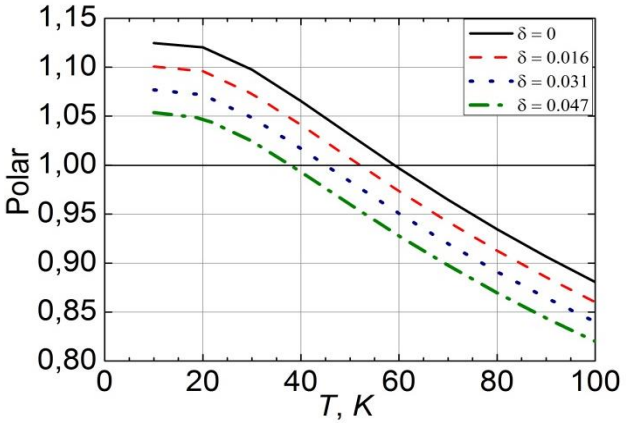

Fig. 2. The polarization operator as a function of temperature, for different values of δ and d_1 = 0.015; d_2 = 0.01; k_F = π/4 + δ.

dash-dotted lines correspond to δ = 0 (k_F = π/4), δ = 0.016 (~ 2 % variation of k_F), δ = 0.031 (~ 4 % variation of k_F) and δ = 0.047 (~ 6 % variation of k_F), respectively. In Fig. 2 it is presented the case when the conduction band is filled up to slightly more than a quarter of the Brillouin zone and the Fermi momentum increase with δ, so k_F = π/4 + δ. It is seen that with the increase of the parameter δ the T_p decreases. For

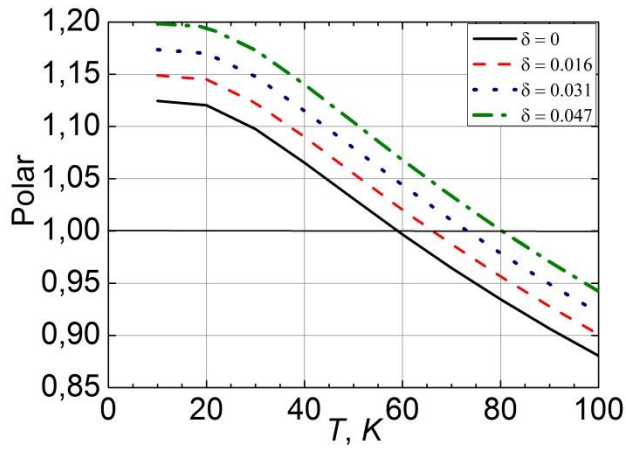

Fig. 3. The polarization operator as a function of temperature, for different values of δ and d_1 = 0.015; d_2 = 0.01; k_F = π/4 - δ.

δ = 0, T_p ~ 59 K; for δ = 0.016, T_p ~ 52 K; for δ = 0.031, T_p ~ 46 K and for δ = 0.047, T_p ~ 37 K. If we will increase more the carrier concentration the critical temperature T_p will be lower, and for a certain value of δ the Peierls transition will not take place.

In Fig. 3 it is presented the case when Fermi momentum decrease with δ and k_F = π/4 - δ. In this case for δ = 0, T_p ~ 59 K; for δ = 0.016, T_p ~ 66 K; for δ = 0.031, T_p ~ 73 K and for δ = 0.047, T_p ~ 80 K. It is observed that with decrease of carrier concentration the Peierls critical temperature increases.

IV. CONCLUSIONS

The Peierls transition is studied in quasi-one-dimensional organic crystals of TTF-TCNQ type in 3D approximation. The polarization operator as a function of temperature is calculated in the random phase approximation for different values of the parameters . It was observed that even with a small increase of the three-dimensionality the transition temperature decreases considerably. Thus, it means that the Peierls structural transition is characteristic for crystals with very pronounced quasi-one-dimensional properties.

Also, it was studied the behavior of Peierls transition when the carrier concentration varies. It was established that with the increase of carrier concentration, the T_p decreases and vice versa.

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