

# 3D MODELING OF THE PEIERLS TRANSITION IN TTF-TCNQ ORGANIC CRYSTALS

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## Abstract

The Peierls structural transition in quasi-one-dimensional (Q1D) TTF-TCNQ organic crystals is studied in the 3D approximation. Two of the most important electron–phonon interactions are considered. The analytic expression for the phonon polarization operator is obtained in the random phase approximation. The polarization operator as a function of temperature is determined for different values of dimensionless Fermi momentum  $k_F$ . Different cases are analyzed:  $k_F = 0.59\pi/2$  and where the carrier concentration varies and  $k_F = 0.59\pi/2 \pm \delta$ , where  $\delta$  represents the variation of Fermi momentum  $k_F$ . In all cases, Peierls critical temperature  $T_p$  is determined.

## Introduction

Organic materials represent an important research direction, because it is assumed that they may have much better properties than inorganic materials known so far. The most extensively studied Q1D organic crystals include those of the tetrathiofulvalinium tetracyanoquinodimethane (TTF-TCNQ) type. For a complete description of the crystal model, it is necessary to determine the parameters of these crystals. In this paper, we propose to use the Peierls structural transition for this aim. According to this phenomenon, which has been theoretically predicted by Rudolf Peierls, at some lowered temperatures, the one-dimensional metallic crystal has to pass in a dielectric state. This temperature is referred to as Peierls critical temperature  $T_p$ . The Peierls transition has been studied by many authors (see [1–3] and references therein).

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

The 2D physical model for the same crystals has been investigated in [6–8]. The polarization operator as a function of temperature was numerically calculated for different values of parameters  $d$  and  $\delta$ , where  $d$  is the ratio of the electron transfer energy in the transversal direction to conductive chains to the transfer energy along the conductive chains and  $\delta$  represents the increase in Fermi momentum  $k_F$  determined by an increase in the carrier concentration. In all cases, the transition temperature has been determined.

In [9], a 3D physical model of the crystal has been studied. The structural transition has

been investigated in the case where the conduction band is filled up to a quarter of the Brillouin zone and the dimensionless Fermi momentum  $k_F = \pi/4$  and in the case where the carrier concentration varies and  $k_F = \pi/4 \pm \delta$ , where  $\delta$  represents the variation in Fermi momentum  $k_F$ . The critical temperature transition has been determined.

In this paper, we also investigate the 3D physical model of the crystal, but in a more realistic aspect. Computer modeling is performed and the Peierls transition is investigated for the case where the dimensionless Fermi momentum is  $k_F = 0.59\pi/2$  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 the  $x$  direction of conductive chains. Note that this value of  $k_F$  is estimated for real crystals of TTF-TCNQ. The polarization operator as a function of temperature is also calculated for different values of increase or decrease  $\delta$  in Fermi momentum  $k_F$  determined by an increase or decrease in the carrier concentration. For a complete description, two electron-phonon interactions are considered. The first is of deformation potential type and the second one is similar to that of the polaron. The analytic expression for the phonon polarization operator is obtained in the random phase approximation. Peierls critical temperature  $T_p$  is determined for different values of dimensionless Fermi momentum  $k_F \pm \delta$ . The results obtained in the 3D physical model are analyzed and commented in detail.

### 1. Three-dimensional crystal model

The compound of TTF-TCNQ forms quasi-one-dimensional organic crystals composed of TCNQ and TTF linear segregated chains. The TCNQ molecules are strong acceptors, and the TTF molecules are donors. The conductivity of TTF chains is much lower than that of TCNQ chains, and can be neglected 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  $a = 12.30 \text{ \AA}$ ,  $b = 3.82 \text{ \AA}$ ,  $c = 18.47 \text{ \AA}$ ,  $b$  is in the chains directions.

The Hamiltonian of the crystal was described in [6, 8] for the 2D physical model. Now it has the form:

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

In expression (1),  $\varepsilon(\mathbf{k})$  represents the energy of a conduction electron with 3D quasi-wave vector  $\mathbf{k}$  and projections  $(k_x, k_y, k_z)$ .

$$\varepsilon(\mathbf{k}) = 2w_1 \cos(k_x b) + 2w_2 \cos(k_y a) + 2w_3 \cos(k_z c), \quad (2)$$

where  $w_1$ ,  $w_2$  and  $w_3$  are the transfer energies of a carrier from one molecule to another along the chain (with lattice constant  $b$ ,  $x$  direction) and in a perpendicular direction (with lattice constant  $a$  in  $y$  direction and  $c$  in  $z$  direction). In (1)  $a_{\mathbf{k}}^+$ ,  $a_{\mathbf{k}}$  are the creation and annihilation operators of a conduction electron.

The second term in Eq. (1) is the energy of longitudinal acoustic phonons with three-dimensional wave vector  $\mathbf{q}$  and projections  $(q_x, q_y, q_z)$  and with frequency  $\omega_{\mathbf{q}}$ :

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

where  $\omega_1$ ,  $\omega_2$  and  $\omega_3$  are the limit frequencies in the  $x$ ,  $y$  and  $z$  directions. In (1)  $b_{\mathbf{q}}^+$ ,  $b_{\mathbf{q}}$  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 the deformation potential type; it 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 derivatives  $w'_1$ ,  $w'_2$ , and  $w'_3$  of  $w_1$ ,  $w_2$ , and  $w_3$  with respect to 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:

$$\begin{aligned} |A(\mathbf{k}, \mathbf{q})|^2 = & 2\hbar / (NM \omega_{\mathbf{q}}) \times \{ w_1'^2 [\sin(k_x b) - \sin(k_x - q_x, b) + \gamma_1 \sin(q_x b)]^2 + \\ & + w_2'^2 [\sin(k_y a) - \sin(k_y - q_y, a) + \gamma_2 \sin(q_y a)]^2 + w_3'^2 [\sin(k_z c) - \sin(k_z - q_z, c) + \gamma_3 \sin(q_z c)]^2 \}, \end{aligned} \quad (4)$$

In Eq. (4),  $M$  is the mass of the molecule,  $N$  is the number of molecules in the basic region of the crystal; parameters  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$  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 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:

$$\text{Re } \overline{\Pi}(\mathbf{q}, \Omega) = - \frac{\overline{N}}{2\pi^3 \hbar \omega_{\mathbf{q}}} \int_{-\pi}^{\pi} dk_x \int_{-\pi}^{\pi} dk_y \int_{-\pi}^{\pi} dk_z |A(\mathbf{k}, -\mathbf{q})|^2 \times \frac{n_{\mathbf{k}} - n_{\mathbf{k}+\mathbf{q}}}{\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k}+\mathbf{q}) + \hbar\Omega}, \quad (6)$$

Here,  $\overline{N}$  is the number of elementary cells in the basic region of the crystal,  $N = r\overline{N}$ , where  $r$  is the number of molecules in the elementary cell,  $r = 2$ . In (6)  $A(\mathbf{k}, -\mathbf{q})$  is the matrix element of electron–phonon interaction presented in Eq. (2),  $\varepsilon(\mathbf{k})$  is the carrier energy,  $\hbar$  is the Planck constant,  $n_{\mathbf{k}}$  is the Fermi distribution function, and  $\Omega(\mathbf{q})$  is the renormalized phonon frequency.

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

$$1 - \text{Re } \overline{\Pi}(\mathbf{q}, \Omega) = 0. \quad (7)$$

where  $\text{Re } \overline{\Pi}(\mathbf{q}, \Omega)$  was represented in Eq. (6).

## 2. Results and discussion

Expression (7) shows that the critical temperature of Peierls transition is determined 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 parameters  $d_1$  and  $d_2$ , where  $d_1 = w_2/w_1 = w'_2/w'_1$ , and  $d_2 = w_3/w_1 = w'_3/w'_1$ . The polarization operator as a function of temperature was determined for different values of  $k_F$ . Different cases when

$k_F = 0.59\pi/2$  and when  $k_F = 0.59\pi/2 \pm \delta$  were analyzed.

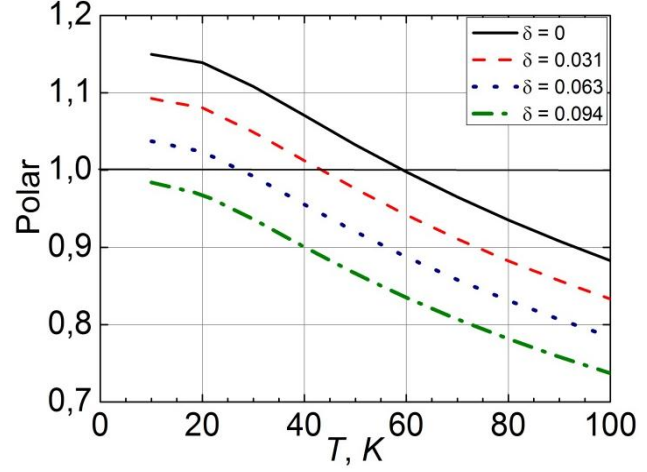
Numerical modeling was performed for the following parameters:  $M = 3.74 \cdot 10^5 m_e$  ( $m_e$  is the electron rest mass),  $w_1 = 0.125$  eV,  $w'_1 = 0.22$  eVÅ<sup>-1</sup>,  $a = 12.30$  Å,  $b = 3.82$  Å,  $c = 18.47$  Å. The sound velocity at low temperatures is  $v_{s1} = 3.4 \cdot 10^5$  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].  $\gamma_1 = 1.6$ ,  $\gamma_2$  and  $\gamma_3$  are determined from the relations:  $\gamma_2 = 32\gamma_1 b^5 / (a^5 d_1)$  and  $\gamma_3 = 32\gamma_1 b^5 / (c^5 d_2)$ .

Figures 1–4 show the calculation results (the polarization operator is denoted by Polar). From all figures, one can determine the transition temperatures from the intersections of the calculated curves with the horizontal line at 1.0.

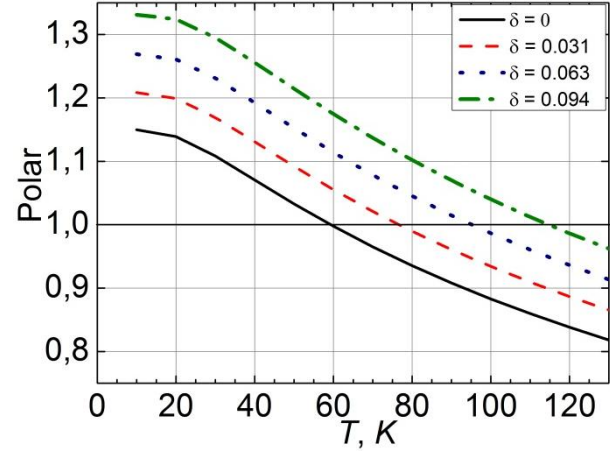
Figures 1 and 2 shows the calculations for  $d_1 = 0.015$  and  $d_2 = 0.01$  and different values of the dimensionless Fermi momentum  $k_F$ . The solid, dashed, dotted, and dash-dotted lines correspond to  $\delta = 0$  ( $k_F = 0.59\pi/2$ ),  $\delta = 0.031$  ( $\sim 3.35\%$  variation of  $k_F$ ),  $\delta = 0.063$  ( $\sim 6.8\%$  variation of  $k_F$ ), and  $\delta = 0.094$  ( $\sim 10.15\%$  variation of  $k_F$ ), respectively. Figure 1 shows the case where the Fermi momentum increase with  $\delta$ , so  $k_F = 0.59\pi/2 + \delta$ . It is evident that  $T_p$  decreases with an increase in parameter  $\delta$ . For  $\delta = 0$ ,  $T_p \sim 59$  K; for  $\delta = 0.031$ ,  $T_p \sim 43$  K; for  $\delta = 0.063$ ,  $T_p \sim 26$  K and for  $\delta = 0.094$  Peierls transition does not take place.

Figure 2 shows the case where the Fermi momentum decrease with  $\delta$  and  $k_F = 0.59\pi/2 - \delta$ . In this case, for  $\delta = 0$ ,  $T_p \sim 59$  K; for  $\delta = 0.031$ ,  $T_p \sim 75$  K; for  $\delta = 0.063$ ,  $T_p \sim 93$  K and for  $\delta = 0.094$ ,  $T_p \sim 114$  K. It is observed that the Peierls critical temperature considerably increases with decreasing carrier concentration.

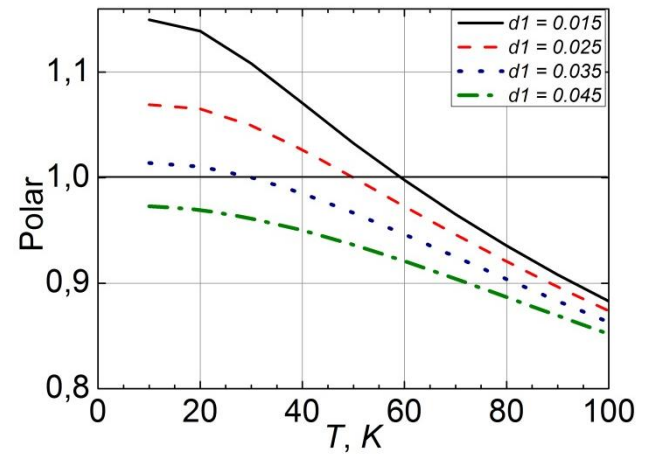
Figure 3 shows the case where  $k_F = 0.59\pi/2$ ,  $d_2 = 0.01$  and  $d_1$  takes different values. The solid, dashed, dotted, and dash-dotted lines correspond to  $d_1 = 0.015$ , 0.025, 0.035, and 0.045,



**Fig. 1.** Polarization operator as a function of temperature for different values of  $\delta$  and  $d_1 = 0.015$ ;  $d_2 = 0.01$ ;  $k_F = 0.59\pi/2 + \delta$ .



**Fig. 2.** Polarization operator as a function of temperature for different values of  $\delta$  and  $d_1 = 0.015$ ;  $d_2 = 0.01$ ;  $k_F = 0.59\pi/2 - \delta$ .



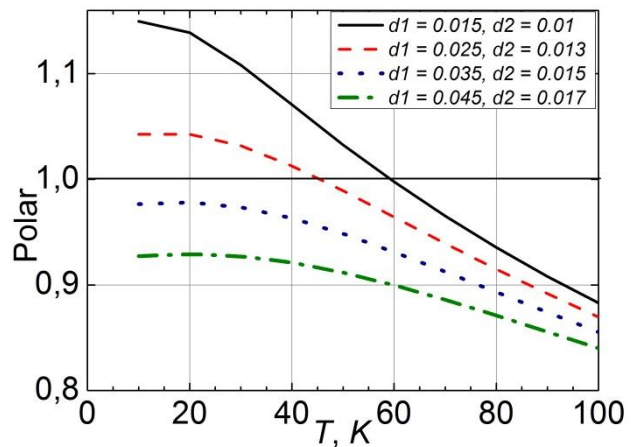
**Fig. 3.** Polarization operator as a function of temperature for different values of  $d_1$  and  $d_2 = 0.01$  and  $k_F = 0.59\pi/2$ .

0.035, and 0.045, respectively. The value  $d_1 = 0.015$  is estimated for real crystals of TTF-TCNQ.

This graph shows that  $T_p$  strongly decreases with increasing parameter  $d_1$ . For  $d_1 = 0.015$ ,  $T_p \sim 59$  K, as it was obtained experimentally. For  $d_1 = 0.025$ ,  $T_p \sim 50$  K; for  $d_1 = 0.035$ ,  $T_p \sim 30$  K; and for  $d_1 = 0.045$ , the Peierls transition disappears.

Figure 4 corresponds to the case where  $k_F = 0.59\pi/2$  and parameters  $d_1$  and  $d_2$  vary. In this graph the solid, dashed, dotted, and dash-dotted lines correspond to  $d_1 = 0.015, 0.025, 0.035,$  and  $0.045$  and  $d_2 = 0.01, 0.013, 0.015,$  and  $0.017$ , respectively. In this case,  $T_p$  decreases faster. For  $d_1 = 0.015$  and  $d_2 = 0.01$ ,  $T_p \sim 59$  K; for  $d_1 = 0.025$  and  $d_2 = 0.013$ ,  $T_p \sim 46$  K. In the other two cases, i.e., for  $d_1 = 0.035$ ,  $d_2 = 0.015$  and  $d_1 = 0.045$ ,  $d_2 = 0.017$ , the Peierls transition will not take place.

From Figs. 3 and 4, one can observe that even a small increase in three-dimensionality leads to a considerable decrease in the transition temperature. This feature is attributed to the fact that the Peierls structural transition is characteristic of crystals with pronounced quasi-one-dimensional properties.



**Fig. 4.** Polarization operator as a function of temperature for different values of  $d_1$  and  $d_2$  and  $k_F = 0.59\pi/2$ .

#### 4. Conclusions

The Peierls transition has been studied in quasi-one-dimensional organic crystals of the TTF-TCNQ type in the 3D approximation. The polarization operator as a function of temperature has been calculated in the random phase approximation for different values of parameters  $d_1$  and  $d_2$ , where  $d_1$  and  $d_2$  are the ratio of the transfer energy in the transversal  $y$  and  $z$  directions to the transfer energy along the  $x$  direction of conductive chains. For a more complete description of the crystal model, two the most important electron–phonon interactions were considered. The first is of the deformation potential type and the second one is similar to that of a polaron. The amplitude ratios between the second and first interactions are characterized by parameters  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$ , respectively. Peierls transition temperature  $T_p$  has been determined. In this paper, the behavior of Peierls structural transition where the carrier concentration varies has been studied. We have investigated the cases where the dimensionless Fermi momentum  $k_F = 0.59\pi/2$  and  $k_F = 0.59\pi/2 \pm \delta$ , where  $\delta$  represents the variation in the Fermi momentum determined by a variation in carrier concentration  $n$ . It has been established that, with an increase in carrier concentration, the  $T_p$  value decreases and vice versa.

In addition, it has been shown that, with an increase in three-dimensionality, the transition temperature considerably decreases, and for some values of parameters  $d_1$  and  $d_2$  the Peierls structural transition will not occur. This feature is attributed to the fact that the Peierls structural transition is characteristic only of crystals with pronounced quasi-one-dimensional properties.

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