

PEIERLS TRANSITION IN QUASI-ONE-DIMENSIONAL CRYSTALS OF TTF–TCNQ TYPE IN A 2D APPROXIMATION

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Abstract

Peierls transition in quasi-one-dimensional organic crystals of TTF–TCNQ type is studied in a 2D physical model of the crystal. The two most important electron–phonon interactions are simultaneously 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 calculated for different values of 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. Peierls critical temperature T_p is determined for different values of d .

1. Introduction

Investigation of highly conducting quasi-one-dimensional (Q1D) organic crystals represents an important direction of solid state physics. It has been theoretically demonstrated that these crystals can have much more improved thermoelectric properties than those known so far (see [1] and references therein). The application of these materials for thermoelectric devices, which are designed to convert the heat directly into electricity, or the electricity in cooling, is one of important purposes of investigations. A great advantage in the use of these materials for thermoelectric devices is their low cost, relatively inexpensive technological process, and the ecological security in the application of these technologies. Furthermore, the use of these materials for thermoelectric devices allows us to solve many important issues, such as resource depletion, climate change, etc.

The best theoretically and experimentally studied Q1D organic crystals are those of TTT_2I_3 (tetrathiotetracene iodide) and TTF–TCNQ (tetrathiofulvalinium tetracyanoquinodimethane). A more complete physical model for these crystals is an essential element in the preparation of materials with a high thermoelectric efficiency. In this paper, we propose to study some properties of Q1D crystals of TTF–TCNQ type, namely, the Peierls structural transition. This phenomenon is connected with the Peierls statement that the one-dimensional crystalline lattice with one electron per ion is unstable. At a certain temperature, which is referred to as Peierls critical temperature T_p , it is energetically favorable that the lattice doubles the period: in this case, the diminution of the electron subsystem energy exceeds the increase in the lattice elastic energy. The Peierls transition was studied by many authors (see [2], [3] and references therein).

In the previous papers [4–7], the Peierls structural transition in quasi-one-dimensional crystals of TTF–TCNQ type was investigated in a 1D physical model of the crystal. Peierls transition was studied in the case where the conduction band is half filled and Fermi dimensionless quasi momentum $k_F = \pi/2$. The critical temperature of transition was determined

and it was found to correspond to the experimental value. The Peierls transition has been studied also in the case where the concentration of conduction electrons is reduced and the band is filled up to a quarter of the Brillouin zone, $k_F = \pi/4$ [4]. The renormalized phonon spectrum has been calculated for different temperatures.

In [8], the effect of impurity scattering on Peierls structural transition in quasi-one-dimensional organic crystals of TTF₂I₃ type is discussed. It is shown that a low rate of the impurity scattering of carriers has a negligible effect on the Peierls structural transition. However, a great value of impurity concentration considerably changes the Peierls critical temperature.

In this paper, we apply a more complete 2D physical model of the crystal. The two most important electron–phonon interactions are simultaneously considered. One of them is of deformation potential type and the other is similar to that of a polaron. The amplitude ratios between the second and first interactions along the chains and in transversal directions are characterized by parameters γ_1 and γ_2 , respectively. 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 , where d is the ratio of the transfer energy in the direction transversal to the conductive chains to the transfer energy along the conductive chains. Peierls critical temperature T_p is determined for different values of parameter d in two cases: (1) if the conduction band is half filled and the dimensionless Fermi momentum $k_F = \pi/2$ and (2) if 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 an increase in the carrier concentration. The results obtained in the 2D physical model are compared with those of the 1D model.

2. Two-dimensional crystal model

The structure of this crystal is described in [4]. A TTF–TCNQ compound 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. However, the conductivity of TTF chains is much lower than that of TCNQ chains and can be neglected in the first approximation.

As in 1D case, we will apply the quasi-one-dimensional organic crystal model described in [9]. The Hamiltonian of the 2D crystal in the tight binding and nearest neighborhoods approximations is as follows:

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

The first term in (1) is the energy operator of free electrons in the periodic field of the lattice, where \mathbf{k} is two-dimensional wave vector with projections (k_x, k_y) . The energy

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

where w_1 and w_2 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 , y direction). In Eq. (1), $a_{\mathbf{k}}^+$ ($a_{\mathbf{k}}$) are the creation and annihilation operators. The second term in relation (1) is the energy of longitudinal acoustic phonons with two-dimensional wave vector \mathbf{q} and frequency $\omega_{\mathbf{q}}$.

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

where ω_1 and ω_2 are limit frequencies for oscillations in x and y directions. In Eq. (1), b_q^+ (b_q) are the creation and annihilation operators of an acoustic phonon. The third term of equation (1) represents the electron–phonon interactions. Two 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 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 the polaron type. This interaction is conditioned by the fluctuations of the polarization energy of the molecules around the conduction electron. The coupling constant of interaction is proportional to the average polarizability of the molecule α_0 . This interaction is important for crystals composed of large molecules, such as TCNQ, so as α_0 is proportional to the volume of molecules. The Coulomb interaction between the carriers is not considered, because this interaction is significantly screened by polarization effects.

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

$$|A(\mathbf{k}, \mathbf{q})|^2 = 2\hbar/(NM\omega_q) \{w_1'^2 [\sin(k_x b) - \sin(k_x - q_x, b) + \gamma_1 \sin(q_x b)]^2 + w_2'^2 [\sin(k_y a) - \sin(k_y - q_y, a) + \gamma_2 \sin(q_y a)]^2\}, \quad (4)$$

where N is the number of molecules in the basic region of the crystal, M is the mass of the molecule, and parameters γ_1 and γ_2 have the sense of the amplitude ratio between the second and first electron–phonon interactions:

$$\gamma_1 = 2e^2 \alpha_0 / b^5 w_1'; \gamma_2 = 2e^2 \alpha_0 / a^5 w_2'. \quad (5)$$

From exact series of perturbation theory for the phonon Green function [10], we sum up the diagrams containing 0, 1, 2 ... ∞ closed loops of two electron Green functions that make the most important contribution. This is the random phase approximation. We denote the phonon Green function in this approximation by $D(\mathbf{r} - \mathbf{r}', t - t')$, and the free phonons one by $D_0(\mathbf{r} - \mathbf{r}', t - t')$, where \mathbf{r} and \mathbf{r}' are the spatial coordinates, t and t' are the time coordinates. For function $D(\mathbf{r} - \mathbf{r}', t - t')$, an integral equation is obtained. Performing Fourier transformation after spatial and time coordinates, we obtain the Fourier component of the Green function $D(\mathbf{q}, \Omega)$:

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

where $\Pi(\mathbf{q}, \Omega)$ is the phonon polarization operator, \mathbf{q} is the wave vector of longitudinal acoustic phonons, and Ω is the renormalized phonon frequency.

The critical temperature of Peierls transition is determined from the condition

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

where $\bar{\Pi}(\mathbf{q}, \Omega)$ is the dimensionless phonon polarization operator

$$\text{Re}\bar{\Pi}(\mathbf{q}, \Omega) = -\frac{1}{\pi^2 \hbar \omega_{\mathbf{q}}} \int_{-\pi}^{\pi} dk_x \int_{-\pi}^{\pi} dk_y |A(\mathbf{k}, \mathbf{q})|^2 \frac{n_{\mathbf{k}} - n_{\mathbf{k}+\mathbf{q}}}{\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k} + \mathbf{q}) + \hbar \Omega}. \quad (8)$$

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

3. Results

For a half filled conduction band, the critical temperature of Peierls transition is determined from (7) at $\Omega = 0$, $q_x = \pi$, and $q_y = \pi$. The polarization operator as a function of temperature is calculated for different values of d , where $d = w_2/w_1$. In Figs. 1, 3, 4, 5 (the polarization operator is named Polar) the results of calculation are presented.

In all figures the transition temperature does not depend on the values of γ_1 and γ_2 , because for $q_x = \pi$, $q_y = \pi$ the respective terms become equal to zero. The Peierls transition temperature depends only on the values of d and of k_F . In Figs. 1 and 3–5, the continuous lines correspond to the 1D physical model and $d = 0$. For 2D physical model of the crystal, the dash, dotted, and dash-dotted lines correspond to $d = 0.013$, 0.2 and 0.6, respectively. Note that the value $d = 0.013$ is estimated for real crystals of TTF–TCNQ.

Figure 1 shows the case where $k_F = \pi/2$. It is evident that, in the both physical models—1D and 2D—the Peierls transition takes place. For $d = 0$, $T_p \sim 60$ K; for $d = 0.013$, $T_p \sim 59$ K; for $d = 0.2$, $T_p \sim 32$ K; for $d = 0.6$, $T_p \sim 12$ K. It is observed that T_p strongly decreases with increasing parameter d ; that is, the larger the deviation from the one-dimensionality, the lower the critical temperature T_p .

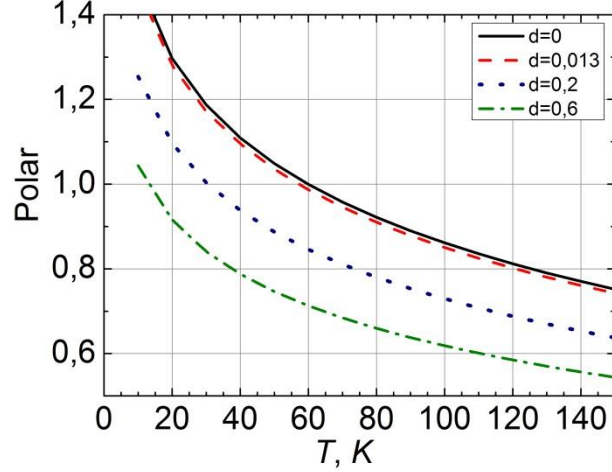


Fig. 1. Polarization operator as a function of temperature for different values of d and $k_F = \pi/2$.

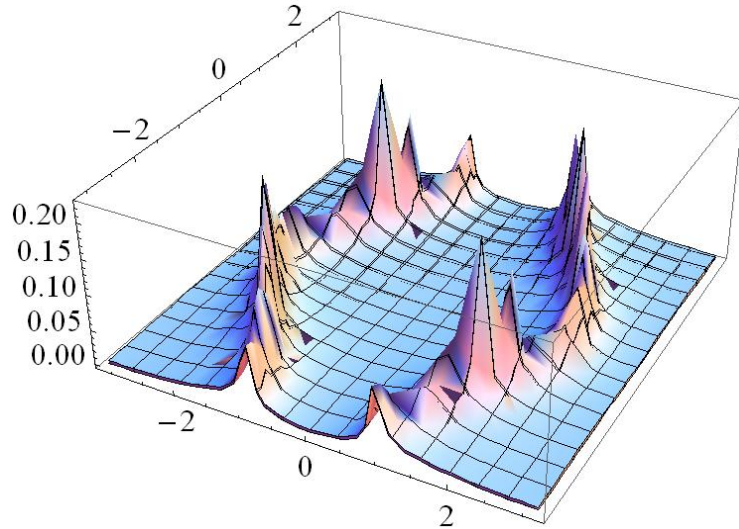


Fig. 2. Function under the integral in (8) for $d = 0.6$ and $k_F = \pi/2$ versus k_x and k_y .

Figure 2 shows the function under integral in (8) for $d = 0.6$ and $k_F = \pi/2$. It is observed that the integral has singular points, which makes the numerical calculation more difficult to carry out in order to attain the required precision.

Figure 3 shows the case of $k_F = \pi/2 + \delta$, where $\delta = 0.008$ or about 0.5% of the Fermi momentum increase. It is evident that, with an increase in the carrier concentration, the Peierls critical temperature is diminished. For $d = 0$, $T_p \sim 58$ K; for $d = 0.013$, $T_p \sim 55$ K; for $d = 0.2$, $T_p \sim 25$ K, and for $d = 0.6$ the Peierls transition disappears.

Figure 4 shows the case of $k_F = \pi/2 + \delta$, where $\delta = 0.016$. Now the additional increase in the carrier concentration leads to an increase by about 1% of the Fermi momentum. It is evident that, with a further increase in the carrier concentration, Peierls critical temperature T_p is more diminished; moreover, the transition disappears for $d = 0.2$ and $d = 0.6$. The Peierls transition take place only for $d = 0$, which corresponds to a simplified 1D physical model of the crystal and for $d = 0.013$, which corresponds to the real 2D physical model. For $d = 0$, $T_p \sim 50$ K and for $d = 0.013$, $T_p \sim 46$ K.

Figure 5 shows the case of $k_F = \pi/2 + \delta$, where $\delta = 0.02$, or about 1.3 % of the Fermi momentum increase. It is observed that, with an increase in the carrier concentration, the polarization operator decreases. The Peierls critical temperature also decreases. For $d = 0$, $T_p \sim 45$ K and for $d = 0.013$, $T_p \sim 35$ K, but for $d = 0.2$ and $d = 0.6$ there is no Peierls transition. It is also evident that, for $d = 0$ and $d = 0.013$, with a further decrease in temperature, the transition

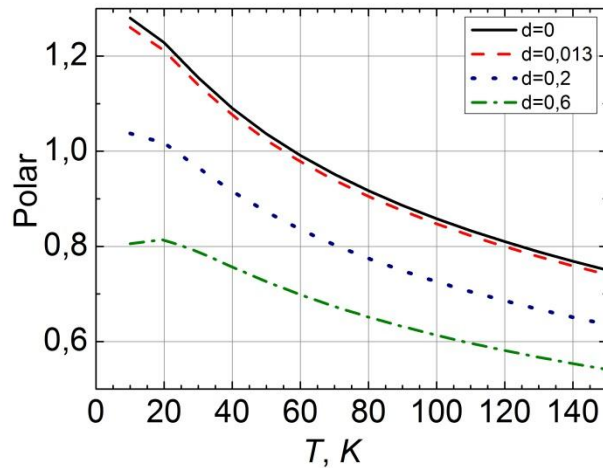


Fig. 3. The same as in Fig. 1 for $k_F = \pi/2 + 0.008$.

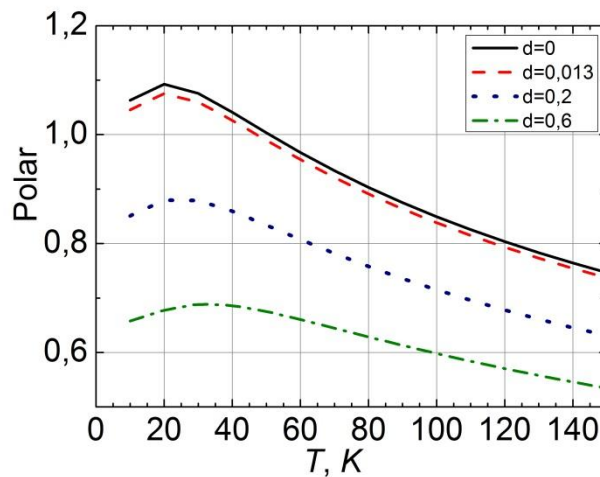


Fig. 4. The same as in Fig. 1 for $k_F = \pi/2 + 0.016$.

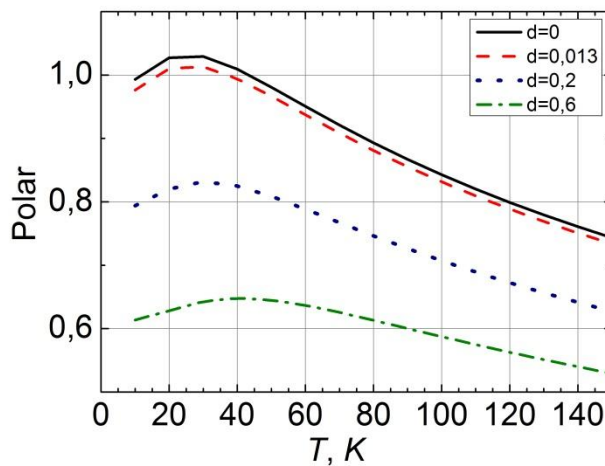


Fig. 5. The same as in Fig. 1 for $k_F = \pi/2 + 0.02$.

appears again. The physical nature of this additional transition has not yet been established.

4. Conclusions

We have studied the Peierls transition in quasi-one-dimensional organic crystals of TTF–TCNQ type in a 2D approximation. A more complete 2D physical model of the crystal has been applied. Two electron–phonon interactions have been considered. One of them is of the deformation potential type and the other is similar to that of a polaron. The amplitude ratios between the second and first interactions have been characterized by parameters γ_1 and γ_2 , respectively. The polarization operator as a function of temperature has been calculated in the random phase approximation for different values of parameter d , where d is the ratio of the transfer energy in the direction transversal to the conductive chains to the transfer energy along the conductive chains. Peierls transition temperature T_p has been determined. In this paper, we have investigated the cases where the conduction band is half filled and the dimensionless Fermi momentum $k_F = \pi/2$ and where 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 in the Fermi momentum determined by an increase in carrier concentration n . In both cases, the Peierls transition temperature does not depend on the values of γ_1 and γ_2 . It has been found that, in the case where $k_F = \pi/2$, T_p strongly decreases with an increase in parameter d and, for a certain value of this parameter, the Peierls transition does not take place. In the second case, where $k_F = \pi/2 + \delta$, T_p also decreases with an increase in carrier concentration n , and, for a certain value of n , the transition disappears too. The Peierls structural transition disappears for certain values of d , with an increase in the carrier concentration, only in the 2D physical model of the crystal. In 1D physical model, the transition does not disappear at these concentrations; however, T_p decreases with increasing carrier concentration. For $k_F = \pi/2$, $T_p \sim 60$ K, for $k_F = \pi/2+0.008$, $T_p \sim 58$ K, for $k_F = \pi/2+0.016$, $T_p \sim 50$ K and for $k_F = \pi/2+0.02$, $T_p \sim 45$ K.

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