# PEIERLS STRUCTURAL TRANSITION IN QUASI-ONE-DIMENSIONAL ORGANIC CRYSTALS

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## Abstract

Peierls transition in quasi-one-dimensional organic crystals of tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) type is studied in the case where the conduction band is half filled and 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, $k_F = \pi/4$. In the physical model of the crystal, it was simultaneously taken into account two the most important interactions of conduction electrons with the longitudinal acoustic phonons. The dispersion equation for renormalized phonons was deduced and solved numerically. The phonon frequency dependences on quasi momentum projection along molecular wires were calculated for different temperatures. The critical temperature of transition was determined.

## 1. Introduction

In the last years, an increase of investigations of organic materials for electronic devices has been observed. These materials have more diverse properties in comparison with the known inorganic ones and are expected to be cheaper and more efficient. A special interest is noticed in the applications of quasi-one-dimensional organic materials for thermoelectric devices designed to convert heat directly into electricity, or electricity in cooling. It was demonstrated theoretically (see [1] and references therein) that after the optimization of parameters, these crystals can have much better thermoelectric properties than those known so far. For this reason, the interest in the investigation of these crystals has increased significantly.

The best theoretically and experimentally studied quasi-one-dimensional organic crystals include those of tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ). At present, not all parameters of these crystals are well determined; for this reason, it is necessary to expand the number of experiments, including the comparison of theoretical results with the experimentally obtained data to specify the values of certain parameters of these crystals. In this paper, we propose to use Peierls structural transition phenomenon for this purpose [2]. The Peierls transition is currently studied in many papers (see [3] and references therein).

In previous papers [4-5], the Peierls transition in conductive chains of TCNQ was studied for the case in which the conduction band is half filled and Fermi quasi momentum $k_F = \pi/2b$, where $b$ is the lattice constant in the wire direction. The critical temperature transition value was also calculated, which corresponds to the experimental value. In this paper, we generalize the previous calculations and study the Peierls transition for the case where the conduction band is filled up to a quarter of the Brillouin zone, which means that the projection of Fermi quasi momentum along TCNQ conducting wire direction $k_F = \pi/4b$. The Peierls transition temperature in these cases is also determined. For comparison, the two cases are described in detail.

## 2. Crystal model

The 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. Moreover, we will neglect the interaction between TCNQ chains because electrical conductivity in the transversal to chains direction is almost three orders of magnitude smaller than along the chains. Thus, the conduction electrons move in a one-dimensional energy band.

We will apply the quasi-one-dimensional organic crystals model described in [6]. The Hamiltonian of a linear chain of molecules in the tight binding and nearest neighborhoods approximations is as follows:

$$H = \sum_k \varepsilon(k) a_k^+ a_k + \sum_q \hbar\omega_q b_q^+ b_q + \sum_{k,q} [A_1(k,q) + A_2(q)] a_k^+ a_{k-q} (b_q^+ + b_{-q}) \quad (1)$$

The first term is the energy operator of free electrons with wave vector projection $k$ along the chain and energy $\varepsilon(k) = 2w(1-\cos kb)$, where $w$ ($w > 0$) and $b$ are the transfer energy of an electron between the nearest molecules and lattice constant along the molecular chain, $a_k^+(a_k)$ are creation and annihilation operators. The second term in relation (1) is the energy of longitudinal acoustic phonons with the wave vector projection $q$ along the chain and the frequency $\omega_q = 2v_s b^{-1}|\sin qb/2|$, where $v_s$ is the speed of sound along the chains. It is supposed that $v_s$ is determined for the free phonons in the absence of conduction electrons. In this case $v_s$ can be easily calculated and we have $v_s = b\sqrt{c_0/(2M)}$, where $c_0$ is the generalized coefficient of elasticity which determines the force of interaction between nearest two molecules along the chain, and $M$ is the mass of TCNQ molecule.

The third term of equation (1) represents the electron-phonon interactions. Two interaction mechanisms are considered. The matrix element of the first interaction is determined by the energy transfer $w$ fluctuations, due to the intermolecular vibrations (acoustic phonons)

$$A_1(k,q) = 2i\hbar^{1/2} w'(2NM\omega_q)^{-1/2} [\sin kb - \sin(k-q)b], \quad (2)$$

where $M$ is the mass of a molecule, $N$ is the number of molecules in the basic region of the chain. This interaction is similar to that of deformation potential, and the coupling constant is proportional to the derivative $w'$ of $w$ with respect to the intermolecular distance, $w' > 0$.

The matrix element $A_2(q)$ describes the interaction which is conditioned by the fluctuations of the polarization energy of the molecules around the conduction electron

$$A_2(q) = 4i\hbar^{1/2} e^2 \alpha_0 b^{-5} (2NM\omega_q)^{-1/2} \sin qb. \quad (3)$$

Here $e$ is the electron charge. The coupling constant of this interaction is proportional to the average polarizability of the molecule $\alpha_0$. So as $\alpha_0$ is proportional to the volume of molecules, this interaction is important for crystals composed of large molecules such as TCNQ. Note that the same acoustic longitudinal phonons participate in (2) and (3). One can demonstrate that the carriers do not interact with the bend vibrations of the linear chains.

The matrix element *A(k,q)* is represented in the following form:

$$A(k,q) = [2i\hbar^{1/2} w'/(2NM\omega_q)^{1/2}][\sin kb - \sin((k-q)b) + \gamma \sin qb], \quad (4)$$

where the parameter $\gamma$ has the meaning of the amplitude ratio of second electron-phonon

interaction to the first one, $\gamma = 2e^2\alpha_0 / b^5 w'$. At $\gamma$ = 0, only the first mechanism of interaction remains.

In order to calculate the renormalized phonon spectrum, the method of retarded Green functions will be applied. We will use the Feynman diagrams technique for temperature-dependent Green functions [7], and then will analytically extend the previous functions from the discrete frequencies into the upper half plane of the complex frequency. The Green function pole will determine the phonon spectrum.

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

$$D(q,\omega) = D_0(q,\omega) - D_0(q,\omega)\Pi(q,\omega)D(q,\omega), \tag{5}$$

where $\Pi(\omega,q)$ is the polarization operator. Introducing instead of $\Pi(\omega,q)$ a new dimensionless polarization operator $\overline{\Pi}(q,\omega) = (1/\omega_q)\Pi(q,\omega)$, we will have

$$\mathrm{Re}\,\overline{\Pi}(q,\omega) = -\frac{2}{\pi\hbar\omega_q}\int_{-\pi}^{\pi} dk\left|A(k,-q)\right|^2 \frac{n_k - n_{k+q}}{\varepsilon_k - \varepsilon_{k+q} + \hbar\omega} \tag{6}$$

Here *A(k, q)* is the matrix element of electron-phonon interaction presented in (4), $n_k$ is the Fermi distribution function, and $\hbar$ is the Planck constant. The integral in (6) has singularities and must be calculated as Cauchy principal value. The renormalized acoustic phonons spectrum $\Omega(q)$ is determined by the pole of function $D(q,\omega)$ and is obtained from the transcendent dispersion equation

$$\Omega(q) = \omega_q[1 - \overline{\Pi}(q,\Omega)]^{1/2}. \tag{7}$$

Unfortunately, this equation can be calculated only numerically.

The results of calculation of $\Omega(q)$ for different temperatures in the case where the conduction band is half filled are presented in Figs. 1–6 for $k_F = \pi/2b$, where $\omega_q$ is denoted by $\omega(q)$. The crystal parameters are: $w$ = 0.125 eV, $w'$ = 0.2 eV Å$^{-1}$, $b$ = 3.82 Å, $v_s = 3.24\cdot10^5$ cm/s, $M = 3.7\cdot10^5 m_e$ ($m_e$ is the mass of the free electron). The parameter $\alpha_0$ is not known for the TCNQ molecule. We will take several values of $\alpha_0$ that will correspond to several values of $\gamma$.

Figure 1 shows the case where $\gamma$ = 0 and only the first mechanism of interaction remains, similar to that of the deformation potential, which was also considered in [2]. For comparison, Fig. 2 represents the result of [2]: (a) where the temperature $T$ is higher than the Peierls critical temperature $T_p$ and (b) where $T = T_p$. Comparing Figs. 1 and 2, we can state that the more detailed calculations even within the same model have modified the dependences $\Omega(q)$. The maximum frequency $\Omega(q)$ is now lower than the initial frequency $\omega(q)$, which corresponds to the same values of $q$. This means that, due to the electron-phonon interaction, the elasticity coefficient of the interaction force between molecules is reduced over a wide range of $q$. For values of $q$ close to $qb \sim \pi$ the elasticity coefficient considerably decreases with decreasing temperature.

Frequencies $\Omega(q)$ become lower, and at $T$ = 59 K $\Omega(q)$ is almost zero. In the middle range of $0 < qb < 2\pi$, when $qb = \pi$, a new edge of the Brillouin zone appears, which means that the lattice constant is doubled and the Peierls transition takes place. The Peierls critical temperature is ~59 K and corresponds to the experimental data. For long waves, the phonon spectrum hardly changes at all.

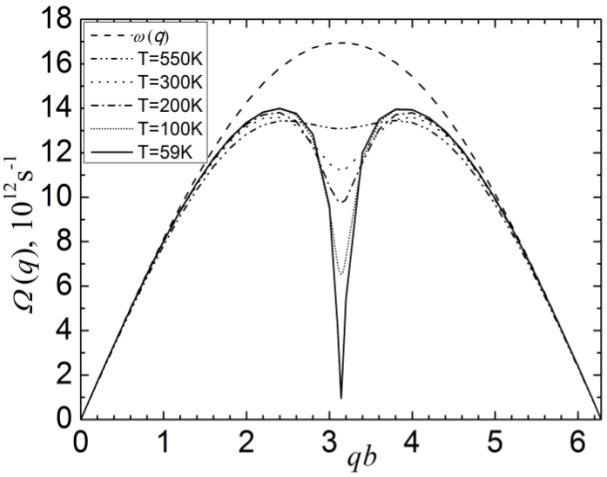


**Fig. 1.** Renormalized phonon spectrum $\Omega(q)$ for $\gamma = 0$ and different temperatures. The dashed line is for the spectrum of free phonons.

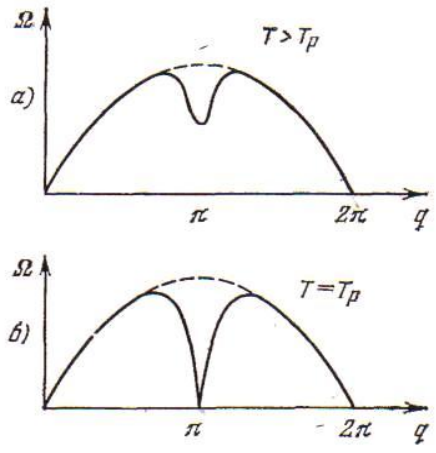


**Fig. 2.** Renormalized phonon spectrum $\Omega(q)$ from [2] for $\gamma = 0$ and different temperatures. The dashed line is for free phonons.

Figure 3 shows the calculations for the case where $\gamma = 0.5$. The maximum of $\Omega$ is now decreased. The speed of sound along the chains remains almost the same. The Peierls critical temperature has not changed.

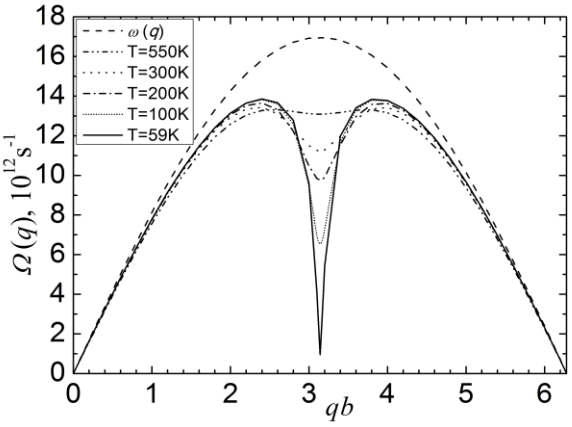


**Fig. 3.** The same as in Fig. 1 for $\gamma = 0.5$.

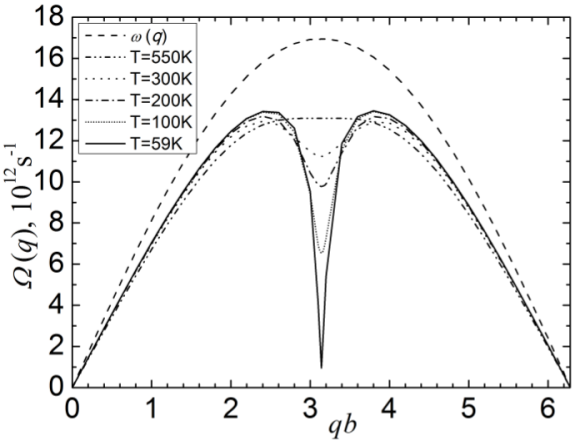


**Fig. 4.** The same as in Fig. 1 for $\gamma = 1$.

Figure 4 represents the calculations for the case where $\gamma = 1$. The two electron-phonon interaction amplitudes now have the same values. It is evident that the maximum of $\Omega$ is further decreased, but the speed of sound along the chains has also decreased; it is equal to the angular coefficient $d\Omega(q)/dq$ of curves for small $q$. The Peierls critical temperature is not changed.

Figure 5 represents calculations for the case where $\gamma = 1.5$. The electron-phonon interaction becomes stronger and the changes in spectrum $\Omega(q)$ become more pronounced, the maximum of $\Omega(q)$ is decreased to $12.7 \times 10^{12}$ $s^{-1}$, and the sound velocity has further decreased, the dependence of $\Omega$ on $q$ being almost linear up to $qb \sim 2$. The further diminution of sound velocity is due to a further decrease of elasticity force of interaction between molecules as a consequence of electron-phonon interaction. In the region of $qb \sim \pi$ the dependences $\Omega(q)$ remains the same as in Fig. 4 with the exception that the trace of $\Omega$ softening has disappeared at $T = 550$ K. The Peierls critical temperature is not changed.

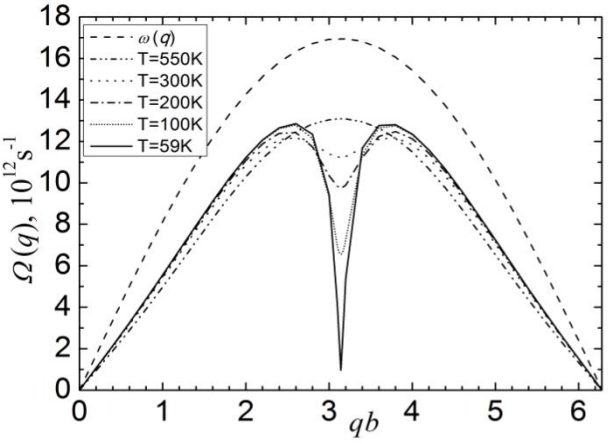


**Fig. 5.** The same as in Fig. 1 for $\gamma = 1.5$.

Figure 6 shows the calculations for the case where $\gamma = 1.8$. The changes in the spectrum $\Omega(q)$ become still more pronounced.

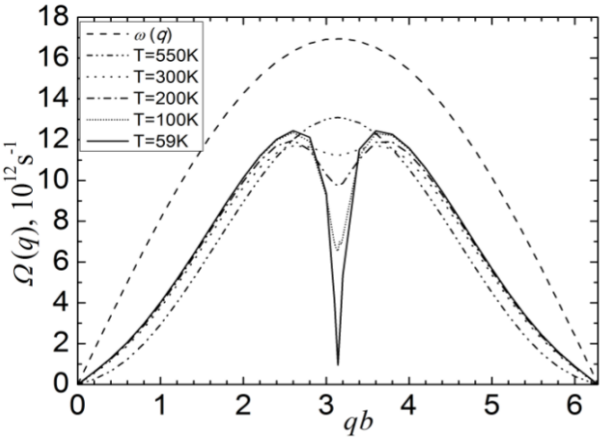


**Fig. 6.** The same as in Fig. 1 for $\gamma = 1.8$.

The results for the case where the conduction band is filled up to a quarter of the Brillouin zone ($k_F = \pi/4b$) are shown in Figs. 7 and 9–11.

Figure 7 shows the case where $\gamma = 0$, which was earlier also considered in [2]. It is evident that the maximum of $\Omega(q)$ is diminished in comparison with the frequency $\omega(q)$ in the

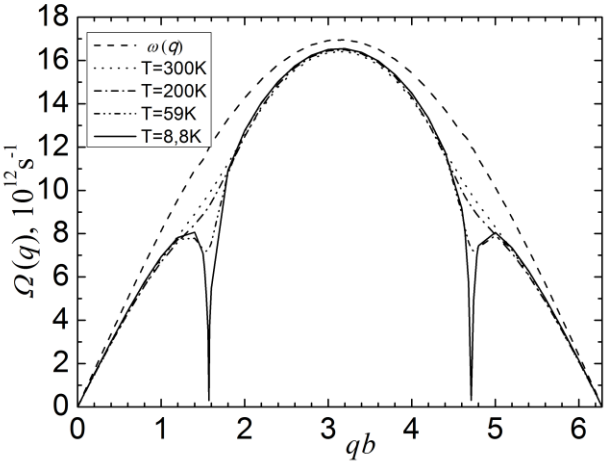


**Fig. 7.** Renormalized phonon spectrum $\Omega(q)$ for $\gamma = 0$ and different temperatures. The dashed line is for the spectrum of free phonons.

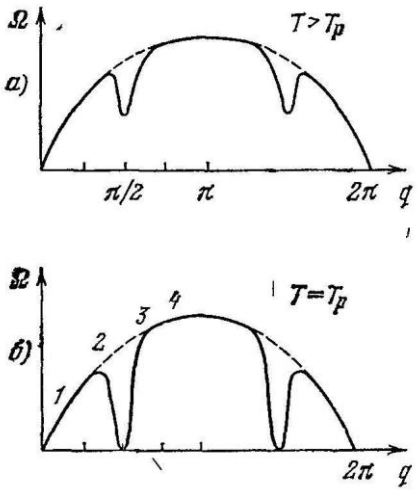


**Fig. 8.** Renormalized phonon spectrum $\Omega(q)$ from [2] for $\gamma = 0$ and different temperatures. The dashed line is for free phonons.

absence of electron-phonon interaction. With a decrease in temperature, two minimums appear in dependences $\Omega(q)$, which become more pronounced at lower temperatures. At $T \sim 8.8$ K the frequency $\Omega(q)$ becomes zero for $qb = \pi/2$ and $qb = 3\pi/2$. This means that, at this temperature, the structural Peierls transition occurs. The crystal lattice changes from the initial state with the lattice constant $b$ to a new crystalline state with constant $4b$, four times larger. Figure 8 represents dependences $\Omega(q)$ taken from [2] and measured for the same physical model and values of crystal parameters as in Fig. 7. By comparing Figs. 7 and 8, one can observe that more detailed calculations in Fig. 7 have determined considerable modifications of phonon spectrum. Firstly, the renormalized frequency $\Omega(q)$ is decreased almost in the entire interval of $0 \le qb \le 2\pi$. Secondly, the minimums at $qb = \pi/2$ and $qb = 3\pi/2$ are much more sharp.

Figures 9 and 10 show the cases where $\gamma = 0.3$ and $\gamma = 0.5$. It is evident that the slope of curves at small $qb$ is diminished. This means that the sound velocity along the chains is diminished. As in the case where $k_F = \pi/2b$, this diminution is due to a decrease in the elasticity force of interaction between two nearest molecules as a consequence of electron-phonon interaction. The transition temperature now becomes different for different values of $\gamma$. The transition temperature is 54.2 K for $\gamma = 0.3$ and 123.6 K for $\gamma = 0.5$. So as the Peierls transition appears as competition between the diminution of the electron subsystem energy and the increase in the elastic lattice energy caused by lattice deformation, one can conclude that in the considered cases where the parameter $\gamma$ increases, the overcome of electron subsystem energy is increased. Accordingly, with an increase in $\gamma$, the critical transition temperature increases too.

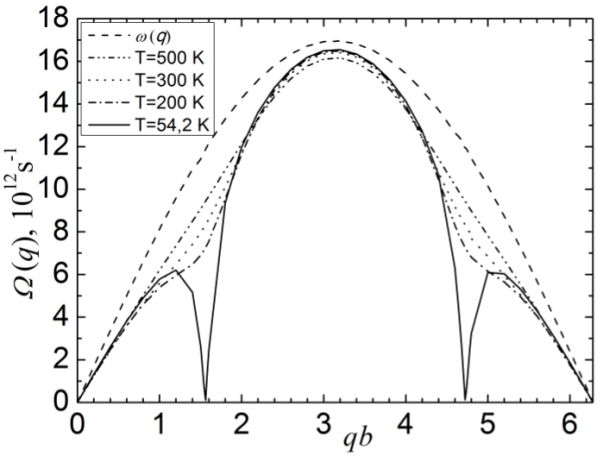


**Fig.9.** Renormalized phonon spectrum $\Omega(q)$ for $\gamma = 0.3$ and different temperatures. The dashed line is for the spectrum of free phonons.

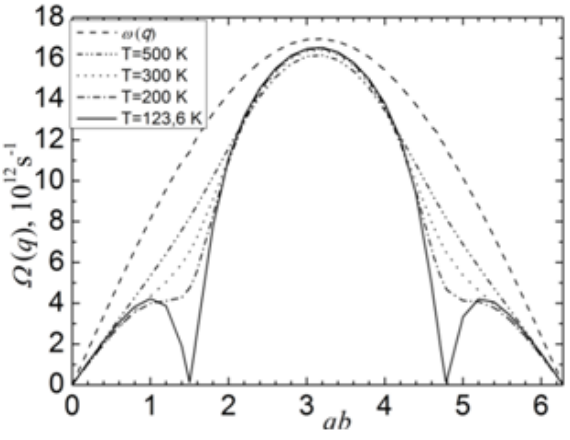


**Fig. 10.** Renormalized phonon spectrum $\Omega(q)$ for $\gamma = 0.5$ and different temperatures. The dashed line is for the spectrum of free phonons.

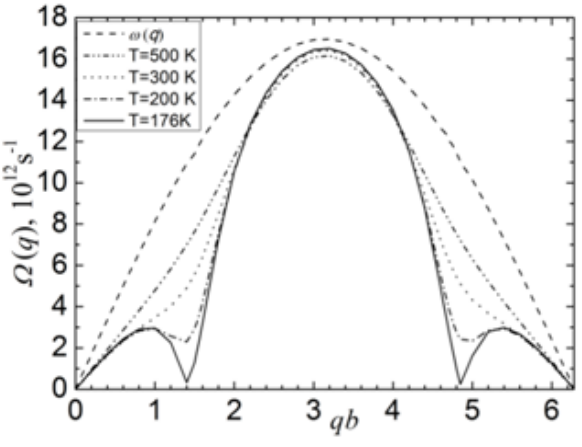


**Fig. 11.** Renormalized phonon spectrum $\Omega(q)$ for $\gamma = 0.6$ and different temperatures. The dashed line is for the spectrum of free phonons.

Figure 11 represents the results for $\gamma = 0.6$. In this case, the transition temperature is 176 K. It is also seen that the slope of curves is further increased at small $qb$. This means that the sound velocity along the chains is further decreased and this effect is much more pronounced that in the previous case where $k_F = \pi/2b$ and $\gamma = 0.6$. In the scheme of reduced bands, we will have four dispersion curves. At temperatures lower than $T_p$, the renormalized phonon spectrum will consist of one acoustic branch and three optical branches. However, this issue will be considered in a separate paper.

## 3. Conclusions

We have studied the Peierls transition in quasi-one-dimensional organic crystals of TTF-TCNQ type. A more complete crystal model is applied, which takes into account two the most important electron-phonon interactions. One interaction is of deformation potential type and the other is similar to that of polaron. The ratio of amplitudes of the second interaction to that of the first one is characterized by the parameter $\gamma$. At $\gamma = 0$, there remains only the first interaction, which was considered earlier by other authors. The renormalized acoustic phonon frequencies $\Omega(q)$ are calculated in two cases: where the conduction band is half filled and the dimensionless Fermi 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, $k_F = \pi/4$. The results are compared with those obtained by other authors. It is shown that a more detailed calculation made in the present paper considerably modifies the dependences $\Omega(q)$ even within the same crystal model ($\gamma = 0$). For larger values of $\gamma$, the electron-phonon interaction becomes stronger and the modifications of $\Omega(q)$ become more pronounced. In the case where $k_F = \pi/2$, the Peierls critical temperature remains to be ~59 K for all $\gamma$ and corresponds to the experimental data. In the case where $k_F = \pi/4$, the Peierls critical temperature $T_p$ is different for different values of the parameter $\gamma$: $T_p$ = 8.8, 54.2, 123.6, and 176 K for $\gamma$ = 0, 0.3, 0.5, and 0.6, respectively. With an increase in $\gamma$, the sound velocity considerably decreases, especially in the case of a quarter filled band.

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