EFFECT OF THE PEIERLS TRANSITION ON THE PHONON SPECTRUM IN TTF-TCNQ CRYSTALS

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Abstract: *It was demontrated theoretically that organic crystals of TTF-TCNQ are good candidates for thermoelectric materials. Because not all parameters of these materials are known, it is necessary to determine some of them. We'll use the Peierls transition phenomenon for this aim. In this work we study how the photon spectrum varies in quasi-one-dimensional organic crystal TTF-TCNQ close to Peierls transition. In the frame of the model, there are considered two the most important electron-phonon interactions. The equation for phonon Green function is deduced in the random phase approximation as a sum of diagrammatic ladder series of close loops of electronic Green functions. The renormalized phonon spectrum is presented for the Peierls model (with one molecule in an unit cell), and for the real model of the crystal (with two molecules in an unit cell).*

Key words: *phonon spectrum, Peierls transition, polarization operator, quasi-one-dimensional crystals, organic materials, phonon Green function.*

1. Introduction

The quasi-one-dimensional (Q1D) organic crystals of TTF-TCNQ (tetrathiofulvalinium tetracyanoquinodimethane) represent an important research object. These materials have promissing applications in thermoelectricity. Because not all parameters of these crystals are known, it is very important to apply different methods to determine them. We'll use the phenomenon of Peierls transition for this aim.

The structural Peierls transition was theoretically predicted by Rudolf Peierls who has established that the strictly one-dimensional lattice formed by ions with one conduction electron for each ion is unstable at zero temperature. Due to interaction of conduction electrons with the periodic field and with acoustic phonons, in terms of energy it is more convenient to deform uniform lattice and the constant of lattice to be doubled. It is said that lattice dimerization occurs. At dimerization the mechanical elastic energy of the lattice increases. But electron-lattice interaction leads to the renormalization of electronic spectrum and the energy of electron system decreases. Under certain conditions, the latter can overcome the increase of lattice energy, and then for whole system it is favorable to pass in dimerized state with lower total energy. But this leads to appearance of a forbidden energy band just above the Fermi energy. As a result, the crystal which before dimerization was metal after dimerization becomes dielectric. Usually, the factor which leads to dimerization state is the temperature decreasing. Thus, at a given temperature the one-dimensional metallic crystal has to pass in a dielectric state. The transition temperature is called the critical Peierls temperature.

The Peierls transition has been studied by many authors (see [1-2] and references therein). The aim of this paper is to describe in more detail Peierls transition phenomenon and to present the results obtained for the real model of the crystal, when the Fermi dimensionless quasi momentum is $k_F = 0.59\pi/2$.

In the previous papers [3-4] the Peierls structural transition in Q1D crystals of TTF-TCNQ type was investigated in a 1D physical model of the crystal. The renormalized phonon spectrum has been calculated for different temperatures in the case when the conduction band is half filled and the Fermi dimensionless quasi momentum is $k_F = \pi/2$ and in the case when the concentration of conduction electrons is reduced and the band is filled up to a quarter of the Brillouin zone, $k_F = \pi/4$, [4].

In this paper we also apply the 1D physical model, for a value of $k_F = 0.59\pi/2$, that corresponds to a real model of the crystal. For a more precise result, it was considered two important electron-phonon interactions. One of them is of deformation potential type and the other is similar to that of the polaron. The ratio of amplitudes of the second interaction to the first one along chains and in transversal directions is characterized by the parameter γ. The renormalized phonon spectrum was modeled for different values of γ.

2. The model of the crystal

The model of the crystal was described in detail in [4]. The TTF-TCNQ compound forms quasi-one-dimensional organic crystals composed of TCNQ and TTF linear segregated chains. The tranfer rate of

electrons from an one molecule of TCNQ to an one molecule of TTF is 0.59 and the crystal has a mixt valence. The TCNQ molecules are strong acceptors, and the TTF molecules are donors. Because the conductivity of TTF chains is much lower than that of TCNQ chains, the first one can be neglected in the first approximation. Also, we'll 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 an one-dimensional energy band.

In order to determine the renormalized phonon spectrum, the method of Green functions will be applied. We will use the Feynman diagrams technique for temperature-dependent Green functions [5], 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 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 $D(q,\omega)$

$$D(q,\omega) = D_0(q,\omega) - D_0(q,\omega)\Pi(q,\omega)D(q,\omega), \tag{1}$$

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

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

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 (2) 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

$$\Omega(q) = \omega_q[1 - \overline{\Pi}(q,\Omega)]^{1/2} \tag{3}$$

This equation can be calculated only numerically.

3. Results and discutions

The numerical calculations for renormalized phonon spectrum, $\Omega(q)$, for different temperatures are presented in Figs. 1-6. In Figs. 1-3 are presented the calculations for Peierls model (with a single molecule in an unit cell), and in Figs. 4-6 are presented the calculations for the real model of the crystal (with two molecules in an unit cell). The calculations were performed for the following parameters: w = 0.125 eV, w' = 0.2 eV Å^{-1}, b = 3.82 Å, v_s = 3.24·10^5 cm/s (in the case when we have one molecule in an unit cell), v_s = 3.71·10^5 cm/s (in the case when we have two molecules in an unit cell). M = 3.7·10$^5 m_e$ (m_e is the mass of the free electron), z = 1 (in the case when we have one molecule in an unit cell) and z = 2 (in the case when we have two molecules in an unit cell).

In Fig. 1 it is considered the case when γ = 0.3 and z = 1. From the graph it is evident that the maximum of $\Omega(q)$ is diminished in comparison

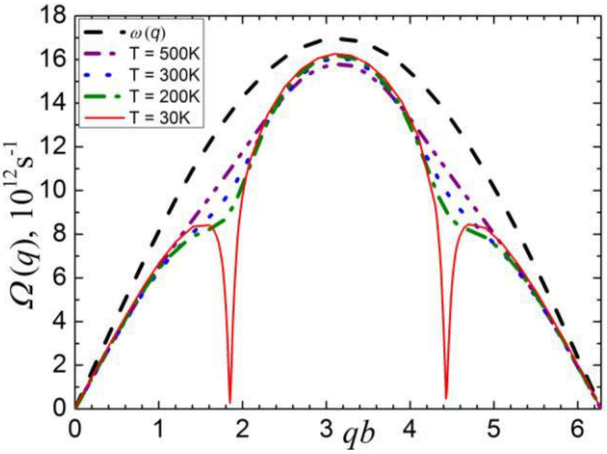

Fig. 1. Renormalized phonon spectrum $\Omega(q)$ for γ = 0.3, z = 1 and different temperatures. The dashed line is for the spectrum of free phonons.

with the frequency $\omega(q)$ in the absence of electron-phonon interaction. With a decrease in temperature the curves change their form, and in dependencies $\Omega(q)$ appear two minimums. These minimums become more pronounced at lower temperatures. At $T \sim 30$ K the frequency $\Omega(q)$ is about zero for $qb = 0.58\pi$ and $qb = 1.4\pi$. This means that, at this temperature, the structural Peierls transition takes place. The crystal lattice changes from the initial state with the lattice constant b to a new crystalline state with constant $4b$, that is four times larger.

In Fig. 2 it is shown the case where $\gamma = 0.44$ and $z = 1$. In this case the frequency $\Omega(q)$ becomes zero for $qb = 0.58\pi$ and $qb = 1.4\pi$ at $T \sim 54.1$ K. This means that Peierls transition occurs at a higher temperature. Note, that this value of temperature coresspond with the experimental data.

In Fig. 3 it is presented the case when $\gamma = 0.5$ and $z = 1$. From the graph it is seen that the slope of curves at small qb is diminished. This means that the elasticity force of interaction between two nearest molecules as a consequence of electron-phonon interaction decreases. As a result the sound velocity along the chains is diminished. The Peierls transition takes place at $T \sim 69$ K. It is observed that with increase of parameter γ, the Peierls critical temperature also increase.

In Fig. 4 it is shown the renormalized phonon spectrum $\Omega(q)$ for $\gamma = 1.5$, $z = 2$ and different temperatures. From the graph one can see that unlike the previous case, when $z = 1$, the maximum of $\Omega(q)$ is diminished less. It happens because the sound velocity increased slightly. It is evident that in the real model of the crystal, when $z = 2$, the parameter γ increased significantly. As in the first case it is observed that at lower temperatures the minimums become more pronounced. The frequency $\Omega(q)$ is about zero for $qb = 0.58\pi$ and $qb = 1.4\pi$ at $T \sim 40.2$ K. This means that Peierls transition occurs at this T.

From Fig. 5 one can observe that the Peierls transition takes place at $T \sim 54.1$ K, which corresponds to the experimental data. This temperature corresponds to $\gamma = 1.6$. From the figure it is seen that the slope of curves at small qb is diminished.

In Fig. 6 it is shown the case for $\Omega(q)$ when $\gamma = 1.7$ and $z = 2$. It is observed that the slope of curves at small qb is diminished more. This means that the sound velocity along the chains is diminished additionally. The Peierls critical temperature in this case has a value of $T \sim 71.9$ K. For the real model of the crystal also it is observed an increase in temperature with the increase of parameter γ.

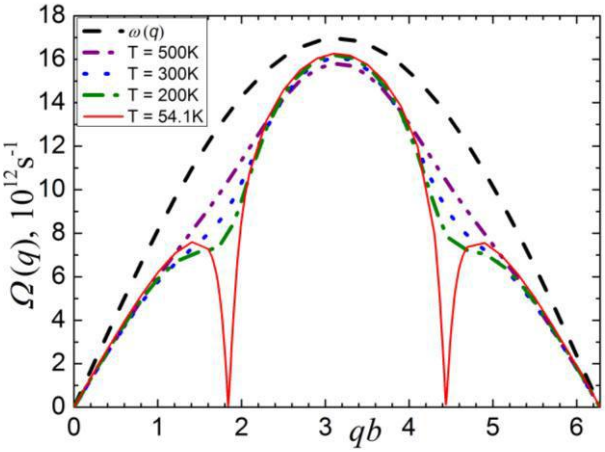

Fig. 2. Renormalized phonon spectrum $\Omega(q)$ for $\gamma = 0.44$, $z = 1$ and different temperatures. The dashed line is for the spectrum of free phonons.

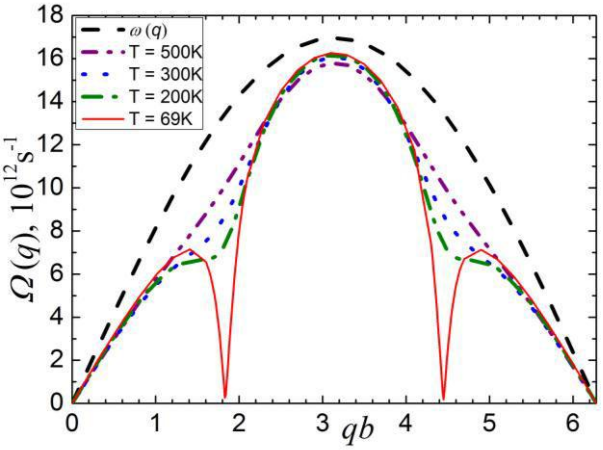

Fig. 3. Renormalized phonon spectrum $\Omega(q)$ for $\gamma = 0.5$, $z = 1$ and different temperatures. The dashed line is for the spectrum of free phonons.

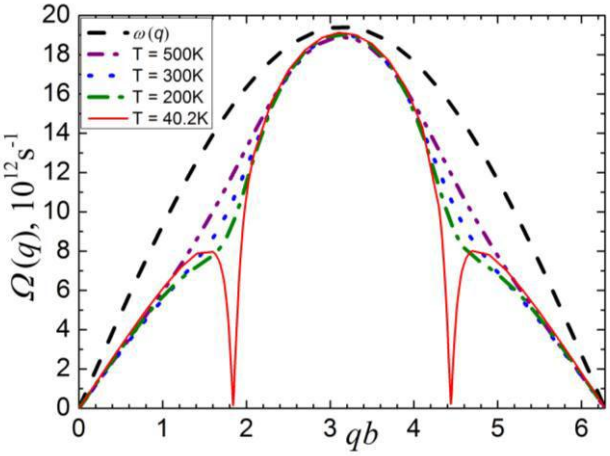

Fig. 4. Renormalized phonon spectrum $\Omega(q)$ for $\gamma = 1.5$, $z = 2$ and different temperatures. The dashed line is for the spectrum of free phonons.

4. Conclusions

We have studied the effect of Peielrs transition on the phonon spectrum in organic crystals of TTF-TCNQ. The renormalized acoustic phonon frequencies $\Omega(q)$ are calculated in two cases: when we have one molecule in an unit cell (z = 1), this is Peierls model, and when we have two molecules in an unit cell (z = 2), that corresponds to the real model of the crystal. Unlike other papers, we applied a more complet crystal model, that takes into account two the most important electron-phonon interactions. The first interaction is of deformation potential type and the second one 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 γ. It is evident that for the real crystal model the parameter γ it is much higher. In both cases, the Peierls critical temperature is different for different values of γ. In the case when z = 1, for $\gamma = 0.3$, $T \sim 30$ K ; for $\gamma = 0.44$, $T \sim 54.1$ K and for $\gamma = 0.5$, $T \sim 69$ K. When z = 2, for $\gamma = 1.5$, $T \sim 40.2$ K ; for $\gamma = 1.6$, $T \sim 54.1$ K and for $\gamma = 1.7$, $T \sim 71.9$ K. It is observed that in both cases with an increase in γ, the Peierls critical temperature increase and the sound velocity considerably decreases. It was shown that for larger values of γ, the electron-phonon interaction becomes stronger and the modifications of $\Omega(q)$ become more pronounced. In all cases the frequency $\Omega(q)$ is about zero for $qb = 0.58\pi$ and $qb = 1.4\pi$, having a different transition temperature. This means that, at this temperature, the structural Peierls transition takes place. The crystal lattice changes from the initial state with the lattice constant b to a new crystalline state with constant $4b$.

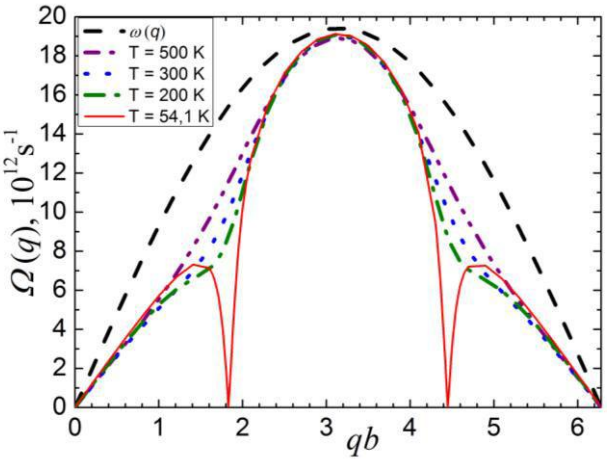

Fig. 5. Renormalized phonon spectrum $\Omega(q)$ for $\gamma = 1.6$, z = 2 and different temperatures. The dashed line is for the spectrum of free phonons.

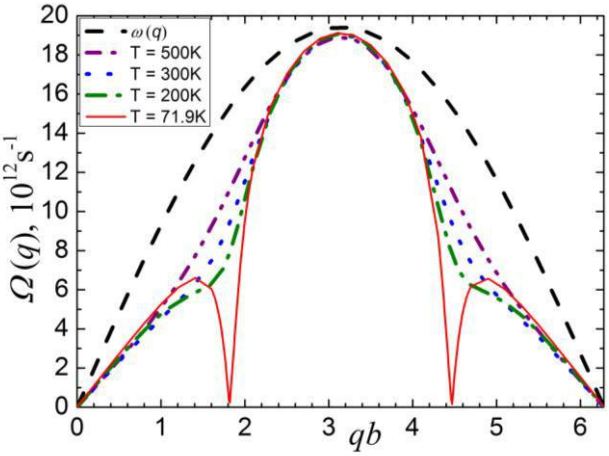

Fig. 6. Renormalized phonon spectrum $\Omega(q)$ for $\gamma = 1.7$, z = 2 and different temperatures. The dashed line is for the spectrum of free phonons.

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