

Peierls structural transition of TTF-TCNQ organic crystals in the 2D physical model.

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Abstract — Many quasi-one-dimensional (Q1D) organic crystals, known as synthetic metals at room temperature, become insulators when the temperature decreases, due to the Peierls transition. In the last years, it was demonstrated theoretically, that after the optimization of parameters, the organic crystals of TTF-TCNQ (tetrathiofulvalene-tetracyanoquinodimethane) are good candidates for thermoelectric materials. Peierls transition in Q1D crystals of TTF-TCNQ type is studied in a 2D physical model of the crystal. 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 polarization operator as a function of temperature is calculated for different values of the parameter δ , where δ is the increase of the Fermi momentum, k_F , that is determined by the increase of carrier concentration. The Peierls critical temperature T_p was determined for different values of δ .

Index Terms — Peierls transition, tetrathiofulvalene-tetracyanoquinodimethane, polarization operator, phonon Green function, Peierls critical temperature.

I. INTRODUCTION

In the last years an increasing interest in the use of organic materials in thermoelectric devices has been observed. Considerable research has been focused on the understanding and improving of the thermoelectric properties of such materials. A special interest is observed 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.

Among the best theoretically and experimentally studied quasi-one-dimensional organic crystals are those of tetrathiofulvalene-tetracyanoquinodimethane, TTF-TCNQ. But not all parameters of these crystals are well determined. Therefore, it is necessary to expand the number of experiments and form the comparison of theoretical results with the experimentally obtained data to improve the precision of some parameters.

In this paper, we propose to use the Peierls structural transition phenomenon to specify the values of certain parameters of these crystals [2]. The Peierls transition is currently studied in many papers (see [3] and references therein).

The structural Peierls transition was theoretical 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 the interaction of conduction electrons with the lattice 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. During this process, the mechanic 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. This leads to appearance of a forbidden energy band just above the Fermi energy. As a result, the crystal which before dimerization was a metal after dimerization becomes dielectric. Usually, this process is caused by the decreasing of temperature. Thus, at a given temperature the one-dimensional metallic crystal has to pass in a dielectric state. This temperature is called the Peierls critical temperature.

In the previous papers [4-7] the Peierls structural transition in Q1D crystals of TTF-TCNQ type was investigated in a 1D physical model of the crystal. Peierls transition was studied 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]. The renormalized phonon spectrum has been calculated for different temperatures.

In [8, 9] the Peierls transition in the same crystals was investigated in a 2D physical model. The polarization operator as function of temperature was calculated for different values of d , where d is the ratio of the transfer energy in the transversal direction to conductive chains to the transfer energy along the conductive chains.

In this paper we also apply a 2D physical model of the crystal. It is simultaneously considered two the most important electron-phonon interactions. One of them is of deformation potential type and the other is similar to that of the polaron. The ratios of amplitudes of the second

interaction to the first one along chains and in transversal directions are characterized by the 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 δ , where δ is the increase of the Fermi momentum, k_F , determined by the increase of carrier concentration. The Peierls critical temperature T_p is determined for different values of δ , so the Fermi momentum is $k_F + \delta$, and for different values of the parameter d (from 0 to 0.6). The results obtained in the 2D physical model are compared with those of 1D model.

II. 2D PHYSICAL MODEL OF THE CRYSTAL

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. However, the conductivity of TTF chains is much lower than that of TCNQ chains and can be neglected in the first approximation.

The Hamiltonian of the system was described in [10] and has the form:

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

Because the electron wave functions are strongly localized, the approximations of tight binding electrons and the nearest neighbors are applied.

In (1) the first term 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) . $a_k^+ a_k$ are the creation and annihilation operators. The energy of carriers has the form:

$$\varepsilon(\mathbf{k}) = 2w_1(1 - \cos(k_x b)) + 2w_2(1 - \cos(k_y a)), \quad (2)$$

where w_1 and w_2 are transfer energies of a carrier from one molecule to another along the chain (with the lattice constant b , x direction) and in perpendicular direction (with the lattice constant a , y direction). Due to the crystal quasi-one-dimensionality w_2 is much less than w_1 .

The second term in the relation (1) is the energy of longitudinal acoustic phonons with two-dimensional wave vector \mathbf{q} and frequency ω_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 limiting frequencies for oscillations in x and y directions, ω_2 is much less than ω_1 . In (1) $b_q^+ b_q$ are the creation and annihilation operators of an acoustic phonon.

The third term in equation (1) represents the electron-phonon interactions. There are considered two such interaction mechanisms. 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 the 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 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. Coulomb interaction between 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:

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

where N is the number of molecules in the basic region of the crystal, M is the mass of the molecule; parameters γ_1 and γ_2 have the sense of the amplitudes ratio of second electron-phonon interaction to the first one

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

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 electronic Green functions which make the most important contribution. This is the random phase approximation. We denote the phonons 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 spatial coordinates, t and t' – time coordinates. For the 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 renormalized phonon frequency, determined from the equation

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

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

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

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

where for $\text{Re} \bar{\Pi}(q, \Omega)$ the following expression is obtained

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

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_k is the Fermi distribution function, and \hbar is the Planck constant.

III. RESULTS

The critical temperature of Peierls transition is determined from (7), when $\Omega = 0$, and $q_x = \pi$, $q_y = \pi$. The polarization operator as a function of temperature is calculated for different values of δ , where δ is the increase of carrier concentration over the stoichiometric one. In Figs. 1, 2, 3, 4 (the polarization operator is named Polar) the results of calculation are presented.

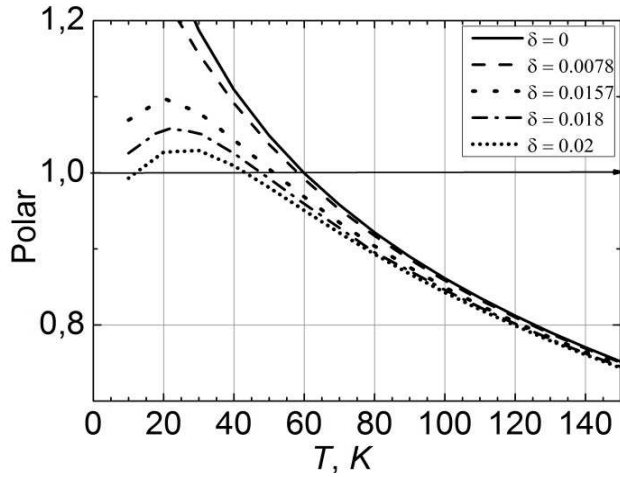


Fig.1. The polarization operator as a function of temperature, for different values of δ and $d = 0$.

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 , δ and of k_F . In Figs.1, 2, 3, 4 the continuous, dash, dotted, dash-dotted and short dotted lines correspond to $\delta = 0$ (or to a half filled band, Fermi momentum $k_F = \pi/2$), $\delta = 0.0078$ (or about 0.5 % of the Fermi momentum increase), $\delta = 0.0157$ (or to an additional increase in carrier concentration which leads to increase of about 1 % of the Fermi momentum), $\delta = 0.018$ (or about 1.2 % of the Fermi momentum increase) and $\delta = 0.02$ (or to about 1.3 % of the Fermi momentum increase), respectively. The transition temperatures are determined from the intersections of calculated curves with the horizontal line at 1.0.

In Fig. 1 it is presented the case when $d = 0$. This case corresponds to 1D physical model. It is seen that in the 1D physical model, the Peierls transition takes place for all values of parameter δ . For $\delta = 0$, $T_p \sim 60$ K; for $\delta = 0.0078$,

$T_p \sim 58$ K; for $\delta = 0.0157$, $T_p \sim 50$ K; for $\delta = 0.018$, $T_p \sim 47$ K; for $\delta = 0.02$, $T_p \sim 44$ K. It is observed that the T_p strongly decreases with the increase of the parameter δ , i.e. when the carrier concentration is higher the critical temperature T_p is lower. This means that with the increase of carrier concentration the diminution of electron subsystem energy, determined by the interaction with the lattice, is reduced.

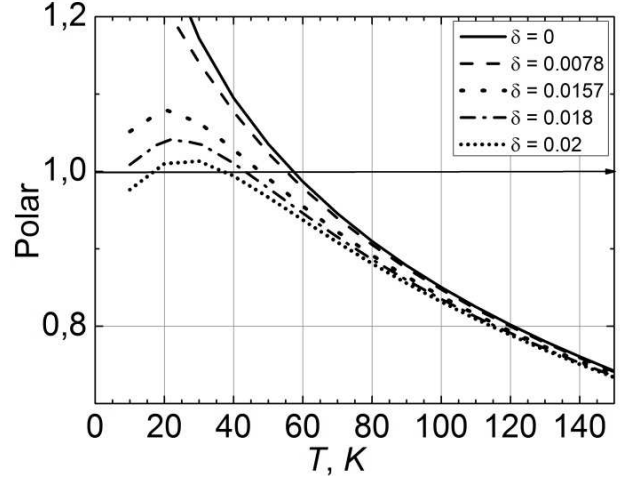


Fig. 2. The same as in Fig. 1 for $d = 0.013$.

In Fig. 2 it is presented the case when $d = 0.013$. Note that the value $d = 0.013$ is estimated for real crystals of TTF-TCNQ. It is seen that increasing the ratio of the transfer energy in the direction transversal to conductive chains to the transfer energy along the conductive chains, the Peierls critical temperature is diminished. For $\delta = 0$, $T_p \sim 57$ K; for $\delta = 0.0078$, $T_p \sim 55$ K; for $\delta = 0.0157$, $T_p \sim 47$ K; for $\delta = 0.018$, $T_p \sim 42$ K and for $\delta = 0.02$, $T_p \sim 35$ K. But the diminution of electron subsystem energy still prevails over the increase of lattice elastic energy and the structural transition takes place for all considered carrier concentrations, now at lower temperatures.

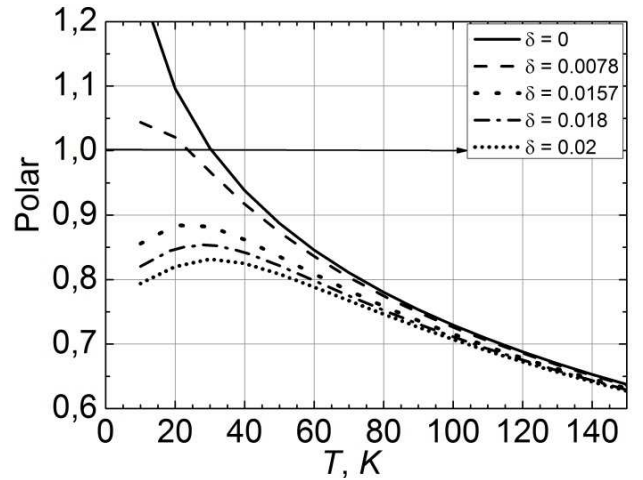


Fig. 3. The same as in Fig. 1 for $d = 0.2$.

In Fig. 3 it is presented the case when $d = 0.2$. It is seen that increasing more the parameter d , the Peierls critical temperature T_p is additionally diminished, and more over,

the transition disappears for $\delta = 0.0157$, $\delta = 0.018$ and $\delta = 0.02$. This means that in the last cases, due to the increase of deviation from the crystal quasi-one-dimensionality, the diminution of electron subsystem energy can not prevail over the increase of lattice deformation energy and the transitions do not take place. The Peierls transition appears only for $\delta = 0$, $T_p \sim 30$ K and for $\delta = 0.0078$, $T_p \sim 25$ K.

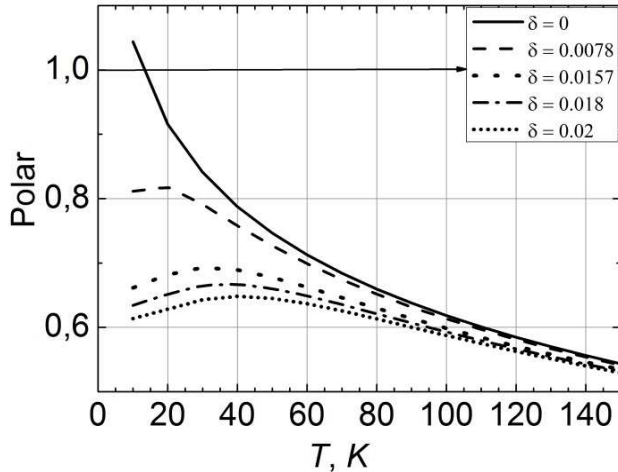


Fig. 4. The same as in Fig. 1 for $d = 0.6$.

In Fig. 4 it is presented the case when $d = 0.6$. It is observed that additional increase of the deviation from the crystal quasi-one-dimensionality (parameter d) leads to additional decrease of the polarization operator and the Peierls transition disappears for all values of δ with the exception of $\delta = 0$. For this value the critical temperature is strongly reduced, $T_p \sim 12$ K. Thus, for the realization of Peierls structural transition it is necessary that the crystal have pronounced quasi-one-dimensional properties and the carrier concentration does not prevails strongly over the stoichiometric one.

IV. CONCLUSION

We have studied the Peierls transition in quasi-one-dimensional organic crystals of TTF-TCNQ type in 2D approximation. It is applied a more complete 2D physical model of the crystal. It was simultaneously considered two the most important electron-phonon interactions. One of them is of deformation potential type and the other is similar to that of polaron. The ratios of amplitudes of the second interaction to the first one are characterized by the parameters γ_1 and γ_2 , respectively.

The phonon Green function is obtained in the random phase approximation. The polarization operator as a function of temperature is calculated for different values of the parameter δ , where δ is the variation of the Fermi momentum over the value $k_F = \pi/2$ for stoichiometric crystals. The Peierls transition temperature T_p is determined for different values of 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. It is found that for 1D model of the crystal the T_p strongly decreases from 60 K down to 12 K with the increase of the parameter

δ from 0 up to 0.02, or up to about 1.3 % of the Fermi momentum considered in this paper. In the 2D physical model, the T_p also decreases with the increase of carrier concentration n , and for a certain value of n the transition even disappears.

The Peierls critical temperature decreases, when the deviation from the crystal quasi-one-dimensionality increases and it decreases additionally when the parameter δ increases. One can conclude that for the realization of Peierls structural transition it is necessary that the crystal have pronounced quasi-one-dimensional properties and the carrier concentration does not prevails strongly over the stoichiometric one.

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REFERENCES

- [1] A. I. Casian, B. M. Gorelov, and I. V. Dubrovin, "State of art and prospects of thermoelectricity on organic materials" J. of Thermoelectricity, Nr 3, 7-16, 2012.
- [2] Л. Н. Булаевский "Структурный (Пайерлсовский) переход в квазиодномерных кристаллах", УФН, т. 115, 2636, 1975.
- [3] M. Hohenadler, H. Fehske, and F.F. Assaad, "Dynamic charge correlations near the Peierls transition", Phys. Rev. B, 83, 115105, 2011.
- [4] S. Andronic, A. Casian, "Peierls structural transition in quasi-one-dimensional organic crystals". In: MJPS, V. 12, N. 3-4, p. 192-198, 2013.
- [5] A. Casian, S. Andronic, "Fononii în apropierea tranziției de fază Peierls în cristale organice cvasiunidimensionale" Proc. 4th Int. Conf. on Telecom., Electron. and Inform., ICTEI 2012, V. 1, p. 258-261, Chisinau, 2012.
- [6] A. Casian, V. Duscic, S. Andronic, "Effect of Peierls phase transition on the phonons spectrum in quasi-one-dimensional organic crystals" Abstr. 9th Int. Conf. on Phys. and Adv. Mater., ICPAM-9, 20-23, Iasi, Romania, p. 95-96, September, 2012
- [7] A. Casian, S. Andronic, V. Duscic, "Influența tranziției de fază Peierls asupra spectrului fononilor în cristallul organic cvasiunidimensional TTF-TCNQ" Studia Universitatis Moldaviae, N.7 (67), 2013.
- [8] S. Andronic "Peierls transition in quasi-one-dimensional crystals of TTF-TCNQ type in 2D approximation ". In: MJPS 2014, accepted for publication.
- [9] S. Andronic, A. Casian, V. Duscic, "Peierls structural transition in Q1D crystals of TTF-TCNQ type for different values of carrier concentration" Abstr. 10th Int. Conf. on Phys. and Adv. Mater., ICPAM-10, 22-28 September, 2014, Iasi, Romania, p. 95.
- [10] I. Sanduleac, A. Casian, J. Pflaum, "Thermoelectric Properties of Nanostructured Tetrathiotetracene Iodide Crystals in a Two-Dimensional Model", J. Nanoelectronics and Optoelectronics 9, p. 247-252 2014.