EFFECT OF IMPURITY SCATTERING ON PEIERLS STRUCTURAL TRANSITION IN TTT_2I_3 CRYSTALS

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Abstract. *Many quasi-one-dimensional organic crystals, known as synthetic metals at room temperature, become insulators when the temperature decreases, due to a Peierls transition. In the crystals with half-filled Brillouin zone the dimerization of lattice takes place at some critical temperature that determines the phase transition. The Peierls structural transition in tetrathiotetracene iodide (TTT_2I_3) crystals with a quarter filled zone is studied. A more complete crystal model is used which takes into account two main electron-phonon interactions. The polarization operator is calculated in two cases: when impurities are absent and when the scattering on impurities takes place.*

Keywords: *Peierls Transition, Quasi-One-Dimensional Organic Crystal, Tetrathiotetracene Iodide, Phonon Green Function, Polarization Operator.*

1. Introduction:

In the last years it is observed an increase of investigations of organic materials for electronic devices. A special interest is noticed in the applications of quasi-one-dimensional organic materials for thermoelectric devices, designed to convert the heat directly into electricity, or the 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 been increased significantly.

Among the best theoretically and experimentally studied quasi-one-dimensional organic crystals are those of TTT_2I_3 (tetrathiotetracene iodide) and of TTF-TCNQ (tetrathiofulvalinium-tetracyanoquinodimethane) [4]. Nevertheless, presently, not all parameters of these crystals are well determined and for this reason it is necessary to expand the number of experiments, including the comparison of theoretical results with those experimentally obtained to specify the values of certain parameters of these crystals. In this paper we propose to use Peierls structural transition phenomenon for this purpose (see [2] and references therein), namely effect of impurity scattering on Peierls structural transition in TTT_2I_3 crystals. The Peierls transition is currently studied in many papers (see [3], [4], [6] 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 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 temperature Peierls.

In the previous paper [4] the Peierls transition was studied in quasi-one-dimensional organic crystals of TTF-TCNQ. Unlike the other papers, the physical model of the crystal was completed by taken into account simultaneously two the most important interactions of conduction electrons with the longitudinal acoustic phonons. The first interaction mechanism is similar to that of the deformation potential and the second - to that of polaron, the latter being conditioned by the fluctuations of the polarization energy of the molecules surrounding the conduction electron. The ratio of amplitudes of the second interaction to that of the first one is characterized by the parameter γ. When $\gamma = 0$, it remains only the first mechanism of interaction.

In [4] the renormalized acoustic phonon frequencies $\Omega(q)$ were calculated, in two cases: when the Brillouin zone is half filled and the dimensionless Fermi momentum $k_F = \pi/2$, and when the concentration of

conduction electrons is reduced and the band is filled up to a quarter of the Brillouin zone, $k_F = \pi/4$. The results are compared with those obtained by other authors [2]. It was shown that a more detailed calculation made in this paper modifies considerably the dependencies $\Omega(q)$ even within the same crystal model ($\gamma = 0$). For larger values of γ the electron-phonon interaction becomes stronger and the modifications of $\Omega(q)$ become more pronounced. In the case, when $k_F = \pi/2$, the Peierls critical temperature remains ~ 59 K for all γ and corresponds to the experimental data. In the case, when $k_F = \pi/4$, the Peierls critical temperature T_p is different for different values of the parameter γ: T_p = 8.8 K, 54.2 K, 123.6 K and 176 K for γ = 0, 0.3, 0.5 and 0.6, respectively. With the increase of γ the sound velocity decreases considerably, especially in the case of a quarter filled band.

In [6] some proprieties of quasi-one-dimensional organic crystals of TTT_2I_3 were studied in the case when the concentration of conduction electrons varies and the band is filled up to slightly more than a quarter of the Brillouin zone, and Fermi momentum is $k_F = \pi/4 + \delta$. The dispersion equation for renormalized phonons was deduced in the random phase approximation and the renormalized phonon spectrum $\Omega(q)$ for $\gamma = 0$ was calculated, when k_F varies with 0.01, 0.04, 0.1 and 0.15. It was shown that with increasing Fermi momentum the Peierls transition temperature decreases.

2. Crystal model:

The physical model of the crystal was described in [1]. The quasi-one-dimensional organic crystals TTT_2I_3 are formed of segregate chains or stacks of planar molecules of tetrathiotetracene TTT, and iodine. The compound is of mixed-valence: two molecules of TTT give one electron to iodine so that the iodine chains in crystal are constituted from I_3^- ions. The overlapping of electronic wave functions of iodine ions is very small. Therefore the electrical conductivity of iodine chains is very small too, and can be neglected. For TTT chains the overlapping of wave functions along chains is significant and the charge carriers are holes. These crystals admit a non-stoichiometric composition, $TTT_2I_{3\pm\delta}$, with a surplus or a deficit of iodine (see [5] and references therein).

From exact series of 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 $\Pi(q,\Omega)$ is the phonon polarization operator, q is the projection along TTT chain of longitudinal acoustic phonons wave vector and Ω is renormalized phonon frequency.

3. Polarization operator:

The critical temperature of Peierls transition is determined from the condition

$$1 - \mathrm{Re}\,\overline{\Pi}(q,\Omega) = 0 \tag{2}$$

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

$$\mathrm{Re}\,\overline{\Pi}(q,\Omega) = -\frac{w'^2 a^2}{\pi M v_s^2 w \sin(q/2)} \int_{-\pi}^{\pi} \frac{\{[\cos(x+(q/2)) + \gamma\cos(q/2)]^2 + imp\}(n_x^0 - n_{x+q}^0)}{\sin(x+(q/2)) + \hbar\Omega}\, dx, \tag{3}$$

here we have introduced for the scattering rate of carriers on impurities the following notation

$$imp = \varepsilon_0^2 L v_s M /(w'^2 a^2 \hbar \sin(q/2)). \quad (4)$$

where ε_0 is a parameter which describes the energy of carrier interaction with impurities, n_x is the Fermi distribution function, w is the transfer energy of an electron between the nearest molecules along the TTT chain, M is the mass of a molecule, w' is derivative of w with respect to the intermolecular distance, $w' > 0$, v_s is the speed of sound along the chains, a is lattice constant along the molecular chain, L is length of linear chain of molecules.

The critical temperature of Peierls transition is determined from the condition (2) when $\Omega = 0$ and $q = \pi/2$.

The polarization operator as function of temperature, for different values of γ is calculated, considering the effect of impurity scattering on Peierls structural transition. In Figs. 1, 2, 3, 4, 5 (the polarization operator is named Polaris) the results of calculation are presented in two cases: a) when the effect of impurity scattering on Peierls structural transition is neglected (*imp* = 0) and b) when the effect of impurity scattering on Peierls structural transition is taken into account (*imp* ≠ 0).

In all Figs. the transition temperature is different for different values of γ. For γ = 0.5 and γ = 2 there is no Peierls transition.

In Fig. 1 it is presented the case when the *imp* = 0 and the *imp* = 0.001. From graphs it is seen that for a small value of impurity concentration, the Peierls critical temperature is the same as in the case when the *imp* = 0. For γ = 0, T_p ~ 90 K, for γ = 2.35, T_p ~ 75 K. Thus, the small impurity concentration does not change the Peierls critical temperature.

In Fig. 2 it is presented the case when the *imp* = 0 and the *imp* = 0.01. From graphs it is seen that increasing the impurity concentration, the Peierls critical temperature has changed. For γ = 0, T_p ~ 92 K, for γ = 2.35, T_p ~ 80 K.

In Fig. 3 it is presented the case when the *imp* = 0 and the *imp* = 0.03. In this case impurity concentration has more influence on the Peierls critical temperature. Thus, for γ = 0, T_p ~ 100 K, for γ = 2.35, T_p ~105 K.

In Fig.4 it is presented the case when the *imp* = 0 and the *imp* = 0.05. The Peierls critical temperature has changed more. For γ = 0, T_p ~ 106 K, for γ = 2.35, T_p ~120 K. It is observed from graphs that the Peierls critical temperature has increased.

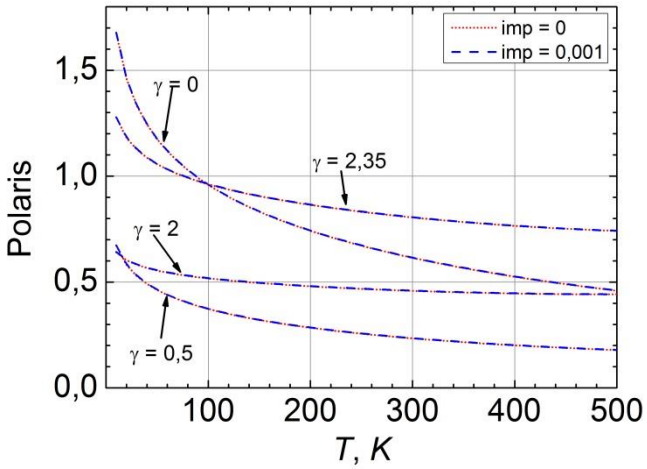

Fig.1. The polarization operator as function of temperature, for different values of γ and *Imp* = 0.001.

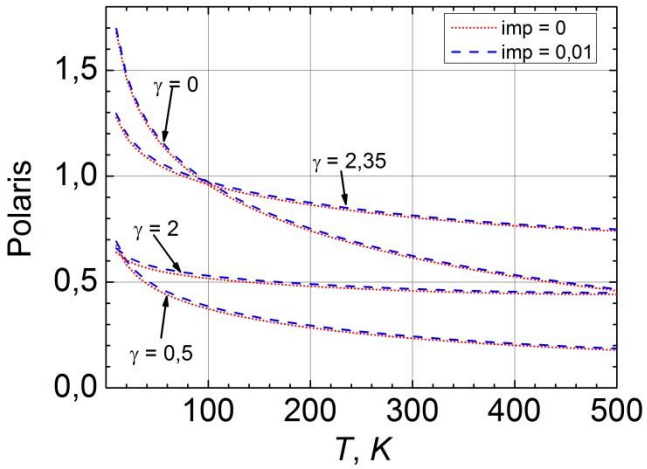

Fig.2. The same as in Fig.1 for *imp* = 0.01

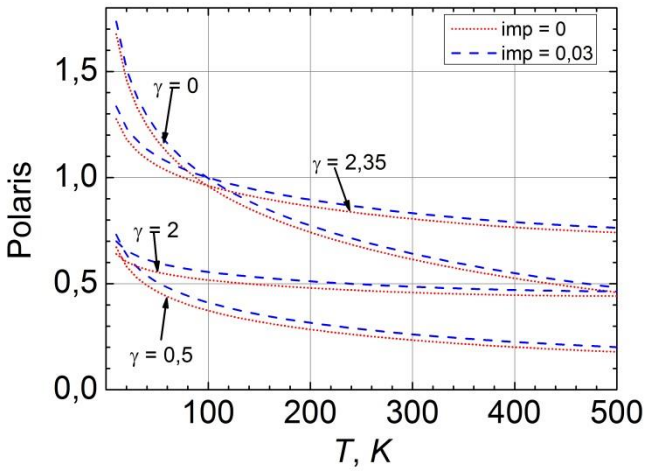

Fig.3. The same as in Fig.1 for *imp* = 0.03

In Fig.5 it is presented the case when the *imp* = 0 and the *imp* = 0.1. In this case it is better observed the effect of impurity scattering on Peierls structural transition. For γ = 0, T_p ~ 135 K, for γ = 2.35, T_p ~170 K. So, a great value of impurity concentration changes considerably the Peierls critical temperature.

3. Conclusions:

We have investigated the effect of impurity scattering on Peierls structural transition in quasi-one-dimensional organic crystals of TTT_2I_3 (tetrathiotetracene iodide) 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 γ. When γ = 0, it remains only the first interaction, considered earlier by other authors. 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 function of temperature, for different γ values is calculated, in two cases: when the effect of impurity scattering on Peierls structural transition is neglected (*imp* = 0), and when the effect of impurity scattering on Peierls structural transition is taken into account (*imp* ≠ 0). It is shown that small rate of carrier scattering on impurity (*imp* = 0.001) has negligible effect on Peierls structural transition. But when the scattering rate is increased up to 0.1, the Peierls critical temperature is considerably increased from T_p ~ 90 K in the absence of impurity up to 135 K for γ = 0, and from T_p ~ 75 K in the absence of impurity up to 170 K for γ = 2.35.

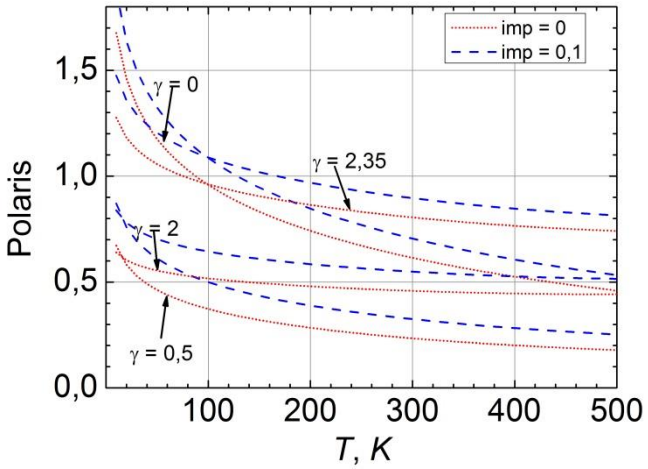

Fig.5. The same as in Fig.1 for *imp* = 0.1

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