RENORMALIZED PHONON SPECTRUM IN QUASI-ONE-DIMENSIONAL ORGANIC CRYSTALS OF TETRATHIOTETRACENE-IODIDE

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Abstract: *The metal-insulator transition in quasi-one-dimensional organic crystals of tetrathiotetracene-iodide, TTT_2I_3, is studied in the 2D approximation. In the frame of the crystal model two the most important hole-phonon interaction mechanisms are considered. One is similar to that of deformation potential and the other is of polaron type. The scattering on defects is also considered and it is crucial for the explanation of the transition. The renormalized phonon spectrum is calculated in the random phase approximation for different temperatures applying the method of Green functions. We show that the transition is of Peierls type. The effect of lattice distortion on the dispersion of renormalized acoustic phonons is analyzed.*

Keywords: *Metal-insulator transition, Peierls transition, renormalized phonon spectrum, TTT_2I_3, interchain interaction.*

1. Introduction

Organic crystals attract more and more attention as prospective materials for thermoelectricity. Tetrathiotetracene-iodide, TTT_2I_3 is a charge transfer compound. The orthorhombic crystal structure consists of segregated chains or stacks of flat TTT molecules and of iodine chains. The lattice constants are a = 18.35 Å, b = 4.96 Å and c =18.46 Å, which demonstrates a very pronounced quasi-one-dimensionality. The highly conducting direction is along ***b*.** The compound is of mixed valence. Two molecules of TTT give one electron to iodine chain formed of ions that play the role of acceptors. Only TTT chains are conductive and the carriers are holes. The electrons on iodine ions are in a rather localized states and do not participate in the transport. In the crystals grown by sublimation of TTT and iodine in an inert gas flow [1] the room electrical conductivity σ along ***b*** direction achieves (10^3 - 10^4) $\Omega^{-1}\cdot cm^{-1}$, but in those grown from solution [2–3] σ ~ (800 - 10^3) $\Omega^{-1}\cdot cm^{-1}$. Such variation in σ of crystals, grown in different laboratories, shows that the conductivity properties of TTT stacks are highly sensitive to defects and impurities. It is caused by the purity of initial materials and the conditions of crystal growth. In all crystals, with the lowering of temperature the conductivity firstly grows, reaches a maximum after that falls. The temperature of the maximum, T_{max}, and the value of the ratio $\sigma_{max}/\sigma_{300}$ depends on the iodine content. Crystals with a surplus of iodine, $TTT_2I_{3.1}$, have T_{max} ~ (34 - 35) K and very sharp fall of σ(T) after the maximum.

The aim of present paper is to demonstrate that this sharp decrease of σ(T) is determined by the Peierls structural transition in the TTT chains. This phenomenon has been theoretically predicted by Rudolf Peierls. According to Peierls, at some lowered temperature, the one-dimensional metallic crystal with a half-filled conduction band has to pass in a dielectric state with a dimerized crystal lattice. This temperature is called the Peierls critical temperature.

The Peierls transition in TTT_2I_3 was studied theoretically in [4]. Unlike of [4], in this paper we study the Peierls structural transition and the renormalized phonon spectrum in $TTT_2I_{3.1}$ and 2D model, but for a larger temperature interval.

The physical model of the crystal is described in detail in [4]. Here we will present only the simulations for the renormalized acoustic phonon spectrum $\Omega(\boldsymbol{q})$, that is determined by the pole of the phonon Green function $D(\boldsymbol{q},\Omega)$ and is obtained from the transcendent dispersion equation ($\boldsymbol{q}$ is the phonon quasi-wave vector with the projections q_x, q_y, $\overline{\Pi}(\boldsymbol{q},\Omega)]$ is the polarization operator)

$$\Omega(\boldsymbol{q}) = \omega_{\boldsymbol{q}}[1-\overline{\Pi}(\boldsymbol{q},\Omega)]^{1/2} \qquad (1)$$

This equation can be calculated only numerically.

2. Results and discussions

Numerical modeling was performed for the parameters from [4, 5]. Lower the parameter γ_1 has the mean of the ratio of amplitudes of above-mentioned hole-phonon interactions along ***b*** direction, γ_1 = 1.7.

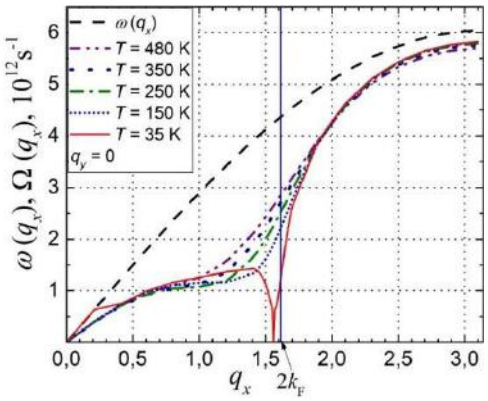

Fig. 1. Renormalized phonon spectrum $\Omega(q_x)$ for γ_1 = 1.7 and different temperatures. The dashed line is for the spectrum of free phonons. In this case $q_y = 0$.

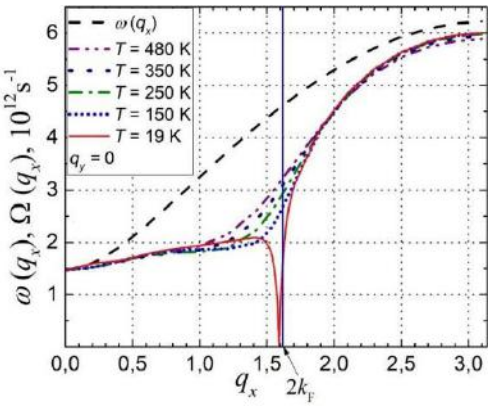

Fig. 2. Renormalized phonon spectrum $\Omega(q_x)$ for γ_1 = 1.7 and different temperatures. The dashed line is for the spectrum of free phonons. In this case $q_y = \pi$.

In Fig. 1-2 the dependences of renormalized phonon frequencies $\Omega(q_x)$ as functions of q_x for different temperatures and different values of q_y are presented. One can observe that with a decrease of temperature T the curves change their form, and in dependencies $\Omega(q_x)$ a minimum appears. This minimum becomes more pronounced at lower temperatures. In the same graphs, the dependences for initial phonon frequency $\omega(q_x)$ are presented too. It is seen that the values of $\Omega(q_x)$ are diminished in comparison with those of frequency $\omega(q_x)$ in the absence of hole-phonon interaction. This means that the hole-phonon interaction and structural defects diminish the values of lattice elastic constants.

In Fig. 1 it is presented the case when the interaction between TTT chains is neglected ($q_y = 0$). The Peierls transition begins at T = 35 K. When the interaction between TTT chains is taken into account ($q_y = \pi$), the Peierls transition is finished at T ~ 19 K (Fig. 2).

3. Conclusions

The behavior of phonons near Peierls structural transition in quasi-one-dimensional organic crystals of TTT_2I_3 (tetrathiotetracene iodide) has been investigated in 2D approximation. It was established that Peierls transition begins at T = 35 K when the interaction between TTT chains is neglected and reduces considerably the electrical conductivity. Due to interchain interaction the transition is finished at T ~ 19 K. It is demonstrated that the hole-phonon interaction and the interactions with the structural defects diminish $\Omega(q_x)$ and reduce the sound velocity in a large temperature interval.

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