INFLUENCE OF STRUCTURAL DEFECTS ON ELECTRICAL CONDUCTIVITY OF TTT_2I_3 CRYSTALS

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Abstract: *Effect of carriers' scattering on lattice structural defects is investigated for organic quasi-one-dimensional crystals of tetrathiotetracene-iodide, TTT_2I_3. It is considered that the charge carriers are moving only along the tetrathiotetracene, TTT, chains which are independent each of other. The defects are modeled by rectangular potential barriers, displaced into TTT chains. The linear kinetic equation is deduced and solved, taking into account that the scattering processes are elastic. The expression for relaxation time is obtained and analyzed. The electrical conductivity is calculated numerically as a function of Fermi energy for different parameters of structural defects.*

Key words: *tetrathiotetracene-iodide, quasi-one-dimensional crystal, organic crystal, structural defect, rectangular potential barrier, relaxation time, electrical conductivity.*

1. Introduction

In the last years it is observed an increased effort in the investigation of organic materials for electronic devices, especially for application in photo-voltaic solar cells and in thermoelectric modules used for the conversion of heat into the electrical energy or of the electrical energy into a cold. It is known that the organic materials have much more diverse and often even unusual physical properties in comparison with the inorganic materials. More over, it is expected that the organic materials will be more efficient and less expensive than known inorganic materials.

We are interested in the investigations of organic materials for thermoelectric applications. In doped acetylene [1] a value of the dimensionless thermoelectric figure of merit ZT of the order of 0,38 has been measured at room temperature. It is good result, but the problem is that this material is not stable. In poly (3,4 - ethilenedioxythiophene) (PEDOT) the value ZT = 0,25 has been observed at room temperature [2]. It is not as high as in [1], but this material is stable. The composite structures formed from inorganic thermoelectric materials and organic ones are also investigated [3]. It is expected that such composites will have better thermoelectric properties than the component materials alone.

We have predicted in TTT_2I_3 (tetrathiotetracene-iodide) crystals unusual high carriers mobilities [4]. After optimization of carriers concentration it is expected to obtain also high values of the thermoelectric power factor $P = \sigma S^2$ (σ is the electrical conductivity, S is the Seebeck coefficient) [5], and high values of ZT ~1,4 – 2,0 at room temperature [6, 7] in dependence on crystal perfection. Experimentally it is known that the electrical conductivity strongly depends on the impurity and defects content in crystal. Thus, for crystals grown from solution [8] σ varies between 800 and 1800 $\Omega^{-1}cm^{-1}$ and for those obtained by gas phase method [9] that are more perfect σ varies between 10^3 and 10^4 $\Omega^{-1}cm^{-1}$.

The aim of this paper is to investigate the effect of carriers scattering on structural defects on electrical conductivity of TTT_2I_3 crystals. For simplicity, the structural defects are modeled by a rectangular potential barrier of the height U_0 and of the width d.

2. Basic considerations

Organic ion-radical crystals TTT_2I_3 represent quasi-one-dimensional crystals formed from segregate linear chains of TTT and iodine. Crystals are of mixed valence: two molecules of TTT transfer one electron to iodine chain and the latter is formed of I_3^- ions. However, the wave functions of I_3^- are rather localized and the electrical conductivity of iodine chains is negligible small. Thus, the iodine plays the role of acceptors and the carriers are holes. The overlap of TTT molecular orbitals is important along the TTT chains, but is very small between the chains. Therefore, the crystals have needle-like structure with the length of 3-8 mm and the thickness ~30-60 microns. As a result, the electrical conductivity in the direction of TTT chains is approximately by three orders of magnitude greater than the conductivity in the transversal to

chains directions. In the first approximation the transversal conductivity can be neglected. So as the distance between the conducting chains of TTT is approximately 1 nm, these crystals can be considered as bulk nanostructured materials.

For the investigation of charge transport we apply the crystal model, described in [4]. The crystal is formed from independent linear conducting chains and the carriers move into a one-dimensional conduction band. The latter is calculated in the tight binding and the nearest neighbors' approximations. The direction along the TTT chain is taken as axis x. The variation of electron k and phonon q projections on axis x of quasi-moments into the whole Brillouin zone is considered.

Two interactions of holes with acoustic vibrations of crystalline lattice are taken into account. One interaction is similar to that of deformation potential. The other is similar to that of polaron, but determined by induced polarization of molecules surrounding the conduction electron. The scattering of carriers on impurities, considered as point-like is also considered. The latter is described by dimensionless parameter D_0 which is proportional to linear impurity concentration n_{im}. In this paper the scattering of holes on structural defects is added too. The defects of crystalline lattice are modeled by rectangular potential barriers of the height U_0 and the width d along the x-axis. This may be a linear dislocation. The probability of a carrier scattering on these defects from the state k' to the state k is

$$W(k,k') = (8\pi n_d U_0^2)/[\hbar L_1(k-k')^2]\sin^2[(k-k',d)/2]\delta[E(k)-E(k')], \quad (1)$$

where n_d is the defects' concentration, L_1 is the basic length of molecular chain, $E(k) = -2w(1-\cos kb)$ is the energy of carrier (hole) measured form the upper edge of conduction band down, w is the energy of charge transfer from one molecule to the nearest one along the chain, $w > 0$, $-4w \le E(k) \le 0$, b is the lattice constant along the chains.

The kinetic equation in a weak electrical field takes the form of Boltzmann equation. The scattering processes on structural defects are elastic. Then the kinetic equation is solved exactly and for electrical conductivity we obtain an analytical expression which, unfortunately, can be calculated only numerically

$$\sigma = \sigma_0 \Big\{ \int_0^1 \frac{n_\varepsilon(1-n_\varepsilon)\varepsilon(1-\varepsilon)d\varepsilon}{\frac{\hbar v_s[\varepsilon(2-\varepsilon)]^{1/2}}{bk_0T}\coth\frac{[\varepsilon(2-\varepsilon)]^{1/2}\hbar v_s}{bk_0T}(\gamma\varepsilon-\gamma+1)^2 + D_0 + D_d\frac{\sin^2[(d/b)\arccos(1-\varepsilon)]}{[\arccos(1-\varepsilon)]^2}} +$$

$$+ \int_1^2 \frac{n_\varepsilon(1-n_\varepsilon)\varepsilon(1-\varepsilon)d\varepsilon}{\frac{\hbar v_s[\varepsilon(2-\varepsilon)]^{1/2}}{bk_0T}\coth\frac{[\varepsilon(2-\varepsilon)]^{1/2}\hbar v_s}{bk_0T}(\gamma\varepsilon-\gamma+1)^2 + D_0 + D_d\frac{\sin^2[(d/b)[2\pi-\arccos(\varepsilon-1)]]}{[2\pi-\arccos(\varepsilon-1)]^2}} \Big\}, \quad (2)$$

where

$$\sigma_0 = [2ze^2Mv_s^2w^3/[\pi\hbar abc(k_0T)^2w'^2], \quad (3)$$

$$D_0 = n_{im}I^2l^2Mv_s^2/(4b^3w'^2k_0T), \quad D_d = n_dU_0^2d^2Mv_s^2/(4b^3w'^2k_0T). \quad (4)$$

Here e is the carrier charge; ε is the dimensionless carrier energy, expressed in unities of $2w$; $0 \le \varepsilon \le 2$, $4w$ is the width of the conduction band; v_s is the sound velocity along the chains; T is the temperature; z is the number of chains through the transversal section of the unit cell; $\gamma = 2e^2\alpha_0/a^5|w'|$ is the ratio of amplitudes of above mentioned hole-phonon interactions, α_0 is the mean polarizability of TTT molecule, w' is the derivative of w with respect to intermolecular distance; M is the mass of molecule TTT; k_0 is the Boltzmann constant; a, b, c are the lattice constants (axis x is along b); D_0 is a dimensionless parameter which describes the carriers scattering on impurity, considered point-like with the height I and width l; D_d is a dimensionless constant proportional to the potential barrier height U_0 and the width d, and to the defect concentration n_d. When $D_d = 0$, the both integrals in (2) joint together and we obtain the previous results from [6].

3. Results and discussion

The expression (2) has been calculated numerically for TTT_2I_3 crystals with different values of D_0 (of impurity concentration). The parameters of TTT_2I_3 are: the mass of molecule $M = 6.5 \square 10^5 m_e$ (m_e is the mass of free electron), the lattice constants $a = 18.35$ Å, $b = 4.96$ Å, $c = 18.46$ Å, the sound velocity along the chains $v_s = 1.5 \square 10^5$ cm/s, the carriers concentration for stoichiometric crystals $n = 1.2 \square 10^{21}$ cm^{-3} which

corresponds to the value of $\varepsilon \sim 0.37$, z = 4. The transfer energy w of the hole is estimated as $w = 0.16$ eV [8, 10]. The value of the polarizability of TTT molecule α_0 in TTT$_2$I$_3$ crystals is not known, therefore the parameter γ is not known. But α_0 is roughly proportional to the volume of molecule and can be estimated approximately by comparison with the known polarizability of other molecules. We have chosen $\alpha_0 = 47$ Å^3 that corresponds to $\gamma = 1.8$, as in [6]. For the parameter D_0 we have taken values: 0.7 which corresponds to crystals grown from solution, 0.1 which corresponds to more perfect crystals grown by gas phase and 0.04 which corresponds to still more perfect crystals which could be obtained in the future.

From Eq. (2) it is seen that the term in the integrand expression, containing the factor $(\varepsilon\gamma - \gamma + 1)^2$ is transformed in zero, when $\varepsilon = (\gamma - 1)/\gamma$. For this value of ε the integrand expression will have a maximum, if the other terms, describing the scattering on impurities and on defects will be small. The height of this maximum strongly depends on the values of parameters D_0 and D_d. It is a consequence of dependence of relaxation time on ε which has a respective maximum. Certainly, the addition of carriers scattering on structural defects will diminish this maximum and will reduce the electrical conductivity too.

In the Fig. 1 the dependencies of electrical conductivity σ on dimensionless Fermi energy ε_F are presented for $D_0 = 0.7$ (crystals grown from solution) at room temperature. The solid line 1 is calculated in the absence of defects, $D_d = 0$. For stoichiometric crystals with $\varepsilon_F = 0.37$ the electrical conductivity $\sigma = 1.7 \times 10^3$ Ω^{-1}cm^{-1}. For curves $2 - 4$ the concentrations of defects is taken smaller by an order of magnitude than the concentration of impurities. It is seen, that the scattering on defects has diminished σ. Now σ takes values 1.5×10^3, 1.2×10^3 and 1.1×10^3 Ω^{-1}cm^{-1}, or smaller than in absence of defects by 11%, 29% and 35%, respectively for curves $2 - 4$.

In the Fig. 2 the dependences of σ on ε_F are presented for more perfect crystals grown by gas phase method with $D_0 = 0.1$. This means that the impurity concentration is diminished by 7 times with respect to the previous case. The defects concentration is diminished too. Now σ is increased and in stoichiometric crystals takes the values 9.6×10^3, 8.6×10^3, 7.3×10^3 and 6.4×10^3 Ω^{-1}cm^{-1}, respectively for curves $1 - 4$. Absolute differences of σ between the cases when the defects are not included and are included have increased considerably, but the relative ones have slightly decreased. It is also seen, that with the decrease of carriers concentration (decrease of ε_F) these difference are reduced.

In the Fig. 3 the dependences of σ on ε_F are presented for still more perfect crystals with $D_0 = 0.04$, i.e. with the impurity concentration diminished additionally by 2.5 times. It is expected that such
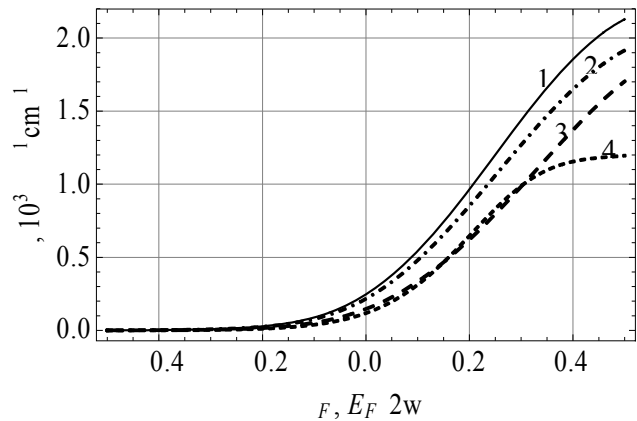

Fig. 1. Dependencies of electrical conductivity σ on Fermi energy ε_F for $D_0 = 0.7$. $1 - D_d = 0$; $2 - 4 - D_d = 0.1\, D_0$. d: $2 - 6b$; $3 - 10b$; $4 - 20b$.
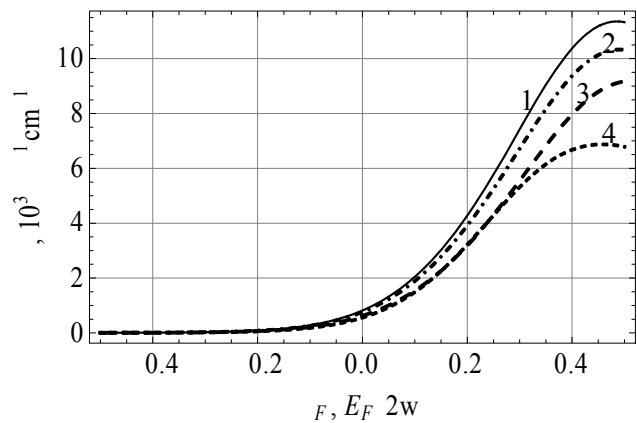

Fig. 2.The same as in Fig. 1 for more perfect crystals with $D_0 = 0.1$.
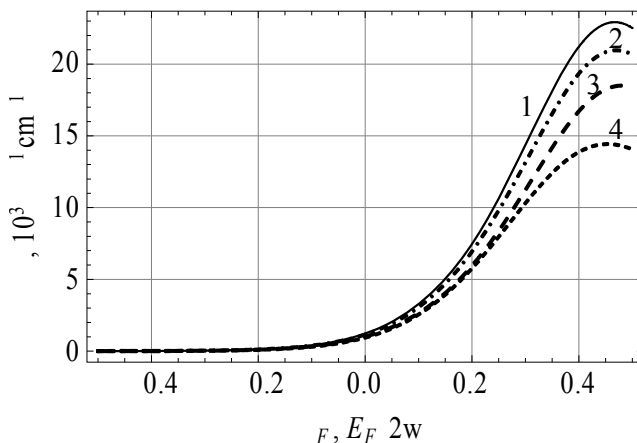

Fig. 3.The same as in Fig. 1 for still more perfect crystals with $D_0 = 0.04$.

crystals can be synthesized in the future. It is seen that σ is increased additionally and in stoichiometric crystals takes the values 19×10^3, 17×10^3, 15×10^3 and 13×10^3 $\Omega^{-1} cm^{-1}$, respectively for curves $1 - 4$. The differences of σ between the case, when the defects are absent and the cases, when they are included, grow considerably with the improvement of crystal perfection, especially for increased values of Fermi energy (or carriers' concentration). This fact must be taken into consideration, when the thermoelectric properties will be investigated.

Conclusions

The effect of carriers scattering on structural defects on electrical conductivity of TTT_2I_3 (tetrathiotetracene-iodide) crystals is investigated theoretically. For simplicity, the structural defects are modeled by a rectangular potential barrier of the height U_0 and of the width d. It is considered that the crystal is formed from independent linear conducting chains of TTT and the carriers move into a one-dimensional conduction band. The latter is calculated in the tight binding and the nearest neighbors' approximations.

For the investigation of the charge transport two hole-phonon interaction mechanisms are considered. One is similar to that of deformation potential and is determined by the variation of transfer energy w of the hole from a molecule to the nearest one along the molecular chain, caused by acoustical vibrations. The second mechanism is similar to that of polaron and is determined by variation of polarization energy of molecules, surrounding the conduction hole, caused by the same acoustical phonons. The carriers scattering on point-like impurities is described by the parameter D_0 which is proportional to impurity concentration. The carriers scattering on defects is described by the parameter D_d which is proportional to the concentration of defects.

The dependences of electrical conductivity σ are calculated as a function of dimensionless Fermi energy ε_F, expressed in unities of $2w$, for different values of D_0 and D_d. Different widths of potential barrier describing the defect are considered. The concentration of defects is taken by one order of magnitude smaller than that of impurity. It is found that the defects reduce σ in stoichiometric crystals up to more than 30%.

Acknowledgements

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