HOPPING CONDUCTION AND POOLE-FRENKEL EFFECT IN $TlGaTe_2$

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Göstərilmişdir ki, $TlGaTe_2$ kristallında keçiricilik sıçrayışlıdır. Lokallaşdırmış şəviyyələrin hal sıxlığı N_F, aktivasiya enerjisi E_a, R sıçrayışların uzunluğu, Fermi səviyyəsinə yaxın enerji şəviyyələri arasında fərq ΔE , N_t dərin tələlərin konsentrasiyası hesablanmışdır. $\sigma \sim (E^{1/2})$ əsasında tədqiqatlar göstərir ki, $TlGaTe_2$ kristallında həm parallel həmdə perpendikulyar istiqamətdə cərəyan, qeyri-xətti oblastda zəif sahə effektlərilə əlaqədardır. İonlaşmış mərkəzlərin konsentrasiyası , sərbəst qaçış məsafəsi λ, Frenkel faktorunun qiyməti β hesablanmış və potensial çəpərin forması müəyyən edilmişdir.

Показано наличие прыжковой проводимости в монокристаллических образцах $TlGaTe_2$. Рассчитаны значения плотности локализованных состояний N_F, энергии активаций E_a, длины прыжков R, разность между энергиями состояний вблизи уровня Ферми ΔE и концентрации глубоких ловушек N_t. На основе исследований зависимости $\sigma \sim (E^{1/2})$ показано, что ток в нелинейной области обусловлен слабым полевым эффектом как при измерениях параллельном так и перпендикулярном кристаллографической оси тетрагонального кристалла $TlGaTe_2$. Определены рассчитанные значения концентрации ионизованных центров, длина свободного пробега λ, значения коэффициент Френкеля β, форма потенциальной ямы в кристаллах $TlGaTe_2$.

It is shows the existence of hopping conductivity in samples of $TlGaTe_2$ monocrystalline. The values of the density of localized states N_F, activation energy E_a, the length of jumps R, the difference between the energy states near the Fermi level ΔE and concentration of deep trap N_t were calculated. Based on the research of dependence $\sigma \sim (E^{1/2})$ it is shown that the current in nonlinear range due to a weak effect when measured both in parallel and perpendicular to the crystallographic axis of $TlGaTe_2$ tetragonal crystal. The values of ionized centers concentration, the length of free path λ, the value of Frenkel coefficient β, the form the potential well in crystals $TlGaTe_2$ were calculated.

1. INTRODUCTION

Semiconductor crystals $TlGaTe_2$ belong to a class of $A^{III}B^{III}C^{VI}_2$ compounds group, crystallized in tetragonal space group of D_{4h}^{18} (structural type TlSe). TlSe and TlS are the most studied compounds of the compounds of this group. Studies of coherent and incoherent inelastic neutron scattering, Raman scattering of first and second order [1-3], revealed a gap in the density of phonon states in TlSe and TlS crystals. This fact allows dividing the energy spectrum of these crystals on intrachain fluctuations, and interchain interactions consider as a weak perturbation, resulting in Davydov splitting. The gap presence in the density of states, maximum anisotropic-chain structure in crystals of this class allows the expected features in the mechanism of the electrical conductivity associated with a low-dimensional structure of crystals. On the other hand, this class of compounds, for their physical and technological properties are promising materials for use in Optoelectronic Technology.

A characteristic feature of crystals of the above type is that they are a chain of Ga - Te elongated along the tetragonal axis of the crystal. Tetragonal axis is the optical axis. Univalent atoms Tl^+ have octahedral surrounding of Te atoms.

The calculation of band structure of $TlGaTe_2$ performed pseudopotential method is given in [4]. These calculations showed that the limit of the valence band is in high-symmetry point T on the surface Brillouin zone, and the bottom of a zone of conductivity on the line D. The lowest energy direct transition occurs between states of T_3 and T_4, and is forbidden in dipole approximation. The width of the band gap, obtained on the basis of the calculations was equal to 0.86 eV.

Valence bands, according to [4], are divided conditionally into three groups. Lowest near-11eV is formed 5s states of Te. Another group in range (4-6) eV is mainly due to states 6s of Tl and 4s states of Ga. The top group in the 0-4 eV is formed from the 5p states of Te, and 6p states of Tl and 4p states of Ga. These data are consistent with the results of [5], which studied photoemissive spectra, as well as a zone structure of $TlGaTe_2$ was calculated by the method of associated plane waves. The authors of [6], in studies of heat capacity and X-ray diffraction revealed the existence of the second kind of phase transition in $TlGaTe_2$ crystal at a temperature of 98.5K. The temperature behavior of the intensity of Bragg reflections enabled the authors to suggest the existence of incommensurate superstructure. Electrical conductivity and current-voltage characteristics (I-V) of $TlGaTe_2$ crystals were studied in [7,8]. In [7] from the electrical measurements for the width of the band gap the value of 1.2 eV was obtained. The authors [8] in the study of nonlinear range of I-V characteristics watched Volt oscillations which lasted indefinitely long. The frequency of oscillations was within a few hertz, is chaotic and changing with time.

The purpose of this work is to establish the mechanism of conductivity in the ohm range of I-V characteristics and the features of Poole-Frenkel effect in a nonlinear range of I-V characteristics of $TlGaTe_2$ crystal. I-V characteristics measurements conducted with the direct direction, with increasing applied constant voltage along and perpendicular to the axis. The measurements were carried out at fixed temperatures in the range 80 - 300K.

2. EXPERIMENTAL RESULTS

Figure 1 and 2 are presented I-V characteristics of $TlGaTe_2$ crystals at various temperatures and two geometries of experiment with parallel and perpendicular to tetragonal axis. On I-V characteristics two ranges are identified: ohm ($J \propto U$) and range of sharper voltage rise ($J \propto U^n$, $n > 1$). With an increase of temperature a linear site is broaden, and a voltage of transition increases. With increasing of voltage the quadratic range of the dependence ($J \propto U$) moves in a great value, but with increasing temperature the threshold voltage, which begins with the quadratic region, moves towards lower values of voltage, and n decreases. This shows that the sharp increase of current due to ionization of the local level in the field.

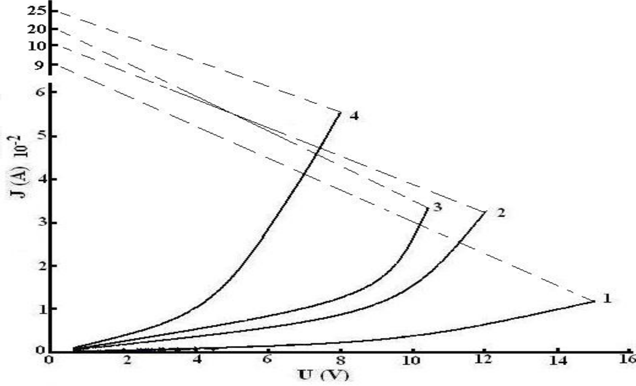

Fig.1. I-V characteristics of $TlGaTe_2$ crystal parallel to tetragonal axis **c** at temperatures: 1-90 K, 2-120K, 3-200K and 4-300 K.

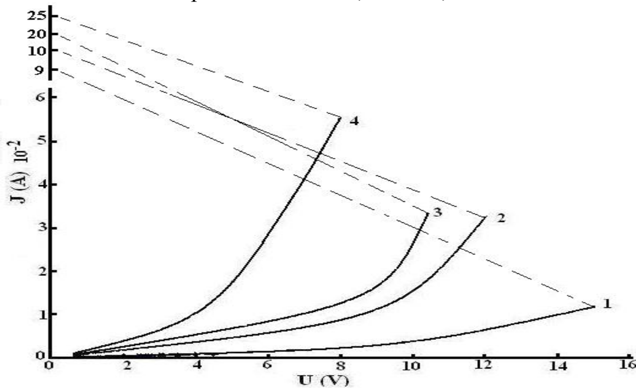

Fig.2. I-V characteristics of $TlGaTe_2$ crystal perpendicular to tetragonal axis **c** at temperatures: 1-90 K, 2-150K, 3-300K.

Fig.3 shows the temperature dependence of specific electrical conductivity of single $TlGaTe_2$ crystals along the tetragonal axis ***c*** (curve 1) and perpendicular to it (curve 2), presented in Arrhenius coordinates. High-temperature branch of given dependence was exponential in temperature range 300 - 220K for $\sigma_{//}(T)$ and 300-180K for $\sigma_{\perp}(T)$. In this temperature range the conduction of thermally generated impurity charge carriers in the allowed zone is dominated. The decrease of temperature is accompanied by a rapid decrease of concentration of impurity charge carriers, that is, at temperatures below 220K for $\sigma_{//}(T)$, and 180K for $\sigma_{\perp}(T)$ they are the ranges of freezing of impurity charge carriers. The resulting activation energy of impurity charge carriers was $\sigma_{//}(T) \approx \sigma_{\perp}(T) = 0.26$ eV.

In insertion of Fig.3 the dependences of $\sigma_{//}(T)$ and $\sigma_{\perp}(T)$ are given in the temperature region 140<T<180K in the Mott coordinates. As can be seen from the figure the experimental points are aligned well in the specified coordinates. This fact testifies that in this the temperature range the charge transfer along the chains and perpendicular to them in $TlGaTe_2$ monocrystals done through hopping conductivity of charge carriers in localized states, lying in a narrow band of energies near the Fermi level.

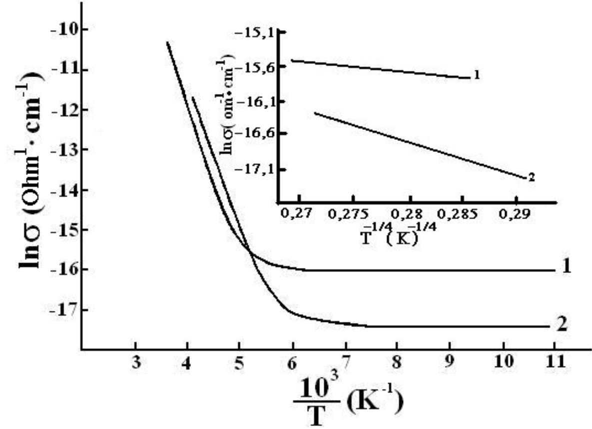

Fig.3. The temperature dependence of specific electrical conductivity of single $TlGaTe_2$ crystals along the tetragonal axis **c** (curve 1) and perpendicular to it (curve 2). In insertion the dependences of $\sigma_{//}(T)$ and $\sigma_{\perp}(T)$ are given in the temperature region 140<T<180K in the Mott coordinates.

In this case, conductivity is described by a well-known Mott relation [9]:

$$\sigma \sim \exp\left[-\left(T_0/T\right)^{1/4}\right], \quad T_0 = \frac{\beta}{kN_F a^3} \tag{1}$$

Here N_F is the density of localized states near the Fermi level, *a* is the radius of localization, k is Boltzmann constant, β is the number depending on the dimension of the task.

A feature of hopping mechanism of conductivity is low mobility, since the jumps of charge carriers are occurred on the weak overlap of the rear wave functions nearby acceptor levels. With lowering of temperature the rapid emptying of charge carriers is occurred in the conduction zone, and this has resulted in the greatest role in the electrical conductivity begins to play jumping charge on individual impurity states without activation in the permitted area.

The temperature dependence of the activation energy of hopping conductivity is described by relation [10]:

$$\varepsilon_0(T) = \frac{(kT)^{3/4}}{\left[N_F a^3\right]^{1/4}} \tag{2}$$

It is also known as conductivity with monotonically decreasing activation energy.

Figure 4 presents temperature dependences of the activation energy $\varepsilon_0(T)$, experimentally defined as the derivative $d(\ln\rho)/d(kT)^{-1}$ in range of hopping conductivity at a given temperature T. As can be seen from the figure, in range of hopping conductivity with variable-length jump, the activation energy is monotonous decrease at decreasing temperature, and the dependence of $\varepsilon_0(T^{3/4})$ is well extrapolated by straight lines.

Slope of lgσ line on $T^{-1/4}$ is equal $T_0=1.1\cdot10^7$ K for conductivity parallel to the axis ***c*** of the $TlGaTe_2$ crystal. Taking β=21 [10], *a* = 20Å [11, 12] (*a* is the radius of localization of states equal to the typical radius of Coulomb

states in a group of $A^{III}V^{III}C^{VI}_2$ crystals), it is possible to estimate the density of localized states near the Fermi level in $TlGaTe_2$ monocrystals: $N_F=2.8\cdot10^{18}$ $eV^{-1}cm^{-3}$.

It should be noted that such a relatively high concentration of localized states in the forbidden zone is characteristic for crystals of $A^{III}B^{VI}$ group [11,12] and $A^{III}B^{III}C^{VI}_2$ [11-13], crystallized in layered and chain structures. An issue relating to the cause of such a high concentration of defects in anisotropic crystals is raised each time as the measurements of electrical conductivity, and in the study of dielectric properties.

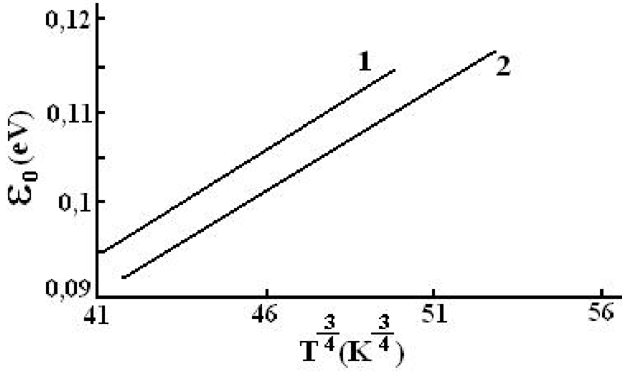

Fig.4. Temperature dependences of the activation energy ε_0 in range of hopping conductivity with variable-length jump at movement of charge along the tetragonal axis **c** (curve 1) and perpendicular to it (curve 2).

According to [13], hopping conductivity in layered GaSe and GaS associated with anionic vacancies, and also that the such conductivity due to defects in forming the chain interlaminate space. According to [14-15], the cause of a defect structure may be a wide range of homogeneity of crystals of $A^{III}B^{III}C^{VI}_2$ group, up to 6-8 mol.%. The coefficient of segregation in the field homogeneity is less than one, so when growing single crystals, there is a high probability of deviations from stoichiometry. This in turn will contribute to the emergence of a large number of defects join layers, vacancies, dislocations, upset translational invariance of the crystal lattice, and as a consequence of any localized states with energies in the range of values that are prohibited in the ideal crystal.

Average hop length of charge carriers on the localized states near the Fermi level at a given temperature can be estimated as [9]:

$$\frac{R}{a}=\frac{3}{8}\left(\frac{T_0}{T}\right)^{1/4} \quad (3)$$

As can be seen from this formula, with decreasing temperature the average hop length of charge carriers increases. This is due to the fact that with decreasing temperature the probability of jumps of charge carriers increases in a spatially more distant but energetically closer localization centers. The activation energy of which determines the width of the band energy near the Fermi level, which occur jumps of charge carriers, is almost all electric. According to [9], at a given temperature, the activation energy can be estimated as:

$$\varepsilon=\frac{3}{4\pi R^3 N_F} \quad (4)$$

From relations (3) and (4) at temperature T = 180K the average hop length of carriers R=117Å and dispersion of energy of localized states ε=50 meV were calculated. The same parameters at temperature T = 150K, respectively, equal to R=123Å and ε=46 meV. Thus, with decreasing temperature the charge carriers hop more spatially distant, but more of near energy centers of localization. Calculated according to (4) the activation energy is in good agreement with the values of $d(\ln\rho)/d(kT)^{-1}$, presented in Fig.4. In the same time, the charge carriers commit hop to distance R, is almost 6 times greater than the radius of localization of α.

Similarly, for electrical conductivity perpendicular to the direction of chains of $TlGaTe_2$ single crystals from fig.4. (curve 2) on a slope of a curve $\lg\sigma_\perp(T^{-1/4})$ the value of $T_0=0.92\cdot10^7$ K is calculated. Taking into account that the previously calculated density of localized states was $N_F=2.8\cdot10^{18}$ $eV^{-1}cm^{-3}$, from (1) we can be determine the radius of localization of charge carriers when moving in the direction perpendicular to the chains α_2=1.1Å, α_1=21Å. Thus, the wave function of localized states, as well as in the case of a structural analogue of the investigated $TlInTe_2$ crystal [11] is anisotropic and possesses ellipsoidal symmetry with semiaxises α_1=20, and α_2=21Å. Besides, a large semiaxis is oriented along the direction of strong bond. Average hop length of charge calculated on the basis of (3), at a temperature of 175K is 120Å, but at 140K – is 126Å. Accordingly, the variance of energy of localized states, according to (4), is equal to ε=42 meV at 175K and ε=36 meV at 140K, which agrees well with the values presented in fig.4 (curve 2).

Thus, in $TlGaTe_2$ monocrystals with temperatures down the conductivity on the allowed zone in the direction of chains and perpendicular to them is carried out by thermally generated impurity charge carriers with activation energy of 0.26 eV. With temperatures down the movement of charge is carried out by means of hops of charge carriers on localized states near the Fermi level, is energetically more favorable, while more spatially distant, which is typical for hopping conduction with a variable length of hop. Upon further the temperature down the normal hopping conductivity is observed, where the average length of charge carriers hop is the value of the order of the average distance between impurities and does not change at the temperature change.

In a strong electric field, when the drop of the potential energy of the electron eER(T) in the typical hop length R(T) is compared with the width of the band of energy around the Fermi level Δε(T), in which hops occur, the electron can move in the direction of the field, emitting phonons with each hop. According to Mott [9] in this case the current does not depend on temperature and increases with increasing field in law

$$I(E)\sim \exp\{-(E_0/E\}^{1/2} \quad (5)$$

In fig. 5 for the range a sharp current increase the dependence of electrical conductivity on the electric field at temperatures of 90K and 300K in $\ln\sigma\sim\sqrt{E}$ coordinates are represented. As is known, the theory of exponential growth of the conductivity was first supposed by Frenkel [16-17].

$$\sigma=\sigma_0\exp(\beta\sqrt{E}) \quad (6)$$

Here: β is coefficient of Frenkel:

$$\beta = \frac{\sqrt{e^3}}{kT\sqrt{\pi\varepsilon\varepsilon_0}} \qquad (7)$$

e is electron charge,, ε is permittivity of free space, κ is Boltzmann constant, *T* is absolute temperature. From fig.6 on slope of a curve at various temperatures the values of β were determined. They are in range of $2.4\text{x}10^{-2}$–$7.2\text{x}10^{-3}$ $(\text{cm/V})^{1/2}$. Determined at various temperatures the temperature dependence of β is shown in fig.5.

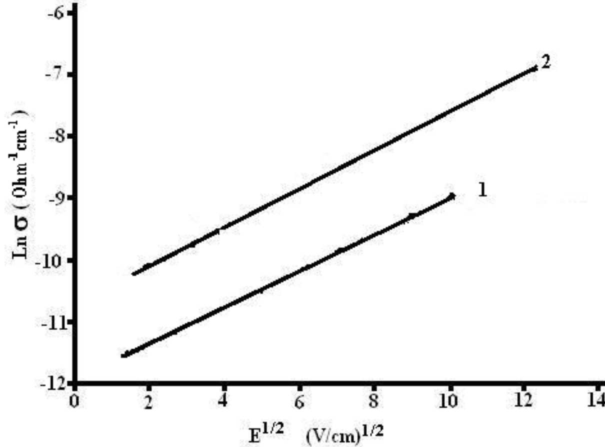

Fig.5. Dependence of conductivity of $TlGaTe_2$ crystals on field intensity E at temperatures T of: 1 – 90K; 2 – 300K; parallel (curve 1) and perpendicular (curve 2) to tetragonal axis **c**.

From figure 6, with temperature down we can see an increase of β, and in the same time the dependence of $\beta \sim 10^3/T$ is well held. Also the temperature change of β is agree with the theory of Frenkel; and according to the formula (6) the extrapolation by $\beta \sim 10^3/T$ resulting to origin of coordinates. In [18] it is shown that the minimum value of electric field corresponding to nonlinear dependence of σ~f(E), contains information on the concentration of defects responsible for thermo field ionization and conductivity of the $TlGaTe_2$ crystal.

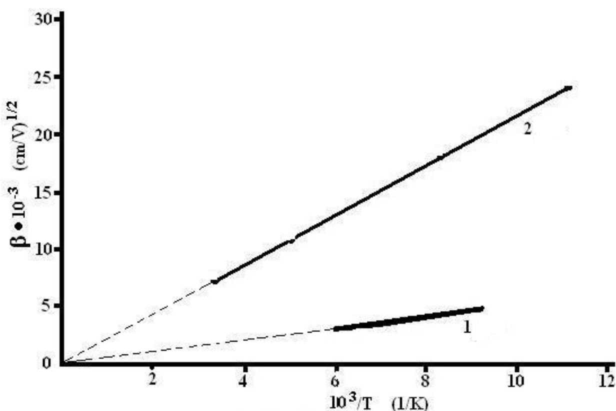

Fig.6. Temperature dependence of Frenkel coefficient β; parallel (curve 1) and perpendicular (curve 2) to tetragonal axis **c**.

According to the expression

$$N_f = \left(\frac{2e}{kT\beta}\sqrt{E_e}\right)^3 \qquad (8)$$

If they are known values of minimum electric field E_c at which the nonlinear dependence of σ on E starts, we can estimate the concentration of ionized centers N_f for crystal $TlGaTe_2$: $N_t = 1{,}8 \text{ x } 10^{13}\ \text{cm}^{-3}$.

It is important to define the form the potential well. Function $\varphi(x)$ is potential energy that depends on the distance to the impurity center or trap (x is distance along the direction of applied electric field), under the impact of an electric field, it changes [18]. From [18,19] follows that

$$\varphi(x) = -\frac{kT\beta}{2}\sqrt{E} = eEx \qquad (9)$$

$$x = \frac{kT\beta}{2e\sqrt{E}} \qquad (10)$$

From experimental data using (9) and (10) a form of potential well in TlGaTe2 was defined, which is shown in Fig.7. If the form of a curve of potential energy for interaction with a concrete center is known, it is possible to obtain information about the structure of the trapping center. As shown in [18-19], that an electron lefts the center, should the condition $\varepsilon_e > E_0 - \Delta U_0$. It is necessary that the electron preserved energy until such time as it bypasses the cross point and lost it in the thermal collisions. This takes place only when the length of free path of electrons is more than effective sizes of the potential well. In this time, the length of free path of carriers is determined by the formula [18,19]:

$$\lambda = \frac{1}{e} f(E_e) = \frac{kT\beta}{2e\sqrt{E}} \qquad (11)$$

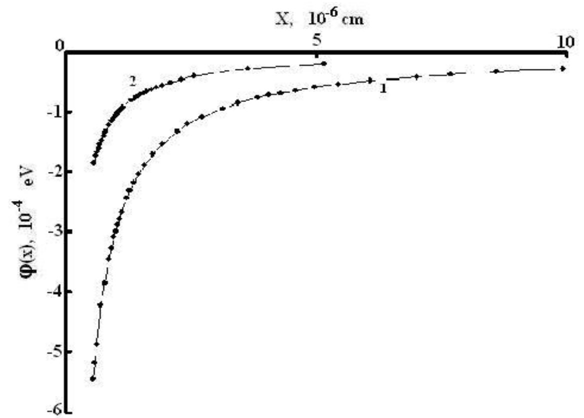

Fig.7. The form of potential well connected with electron trap in $TlGaTe_2$: parallel (curve 1) and perpendicular (curve 2) to tetragonal axis **c**.

The length of free path of electrons in monocrystals $TlGaTe_2$, calculated on the basis of experimental data, according to this formula, approximately is equal along the axis ***c*** $\sim 12 \cdot 10^{-7}$cm, perpendicular to axis ***c*** $\sim 9{,}8 \text{ x } 10^{-6}$ cm.

3. CONCLUSIONS

Thus, the values of the density of localized states N_F, activation energy E_a, the length of jumps R, the difference between the energy states near the Fermi level ΔE and concentration of deep trap N_t (in ohm region) were calculated. Based on the research of dependence $\sigma \sim (E^{1/2})$ it is shown that the current in nonlinear range (taking into

account Poole-Frenkel effect) due to a weak effect when measured both in parallel and perpendicular to the crystallographic axis of $TlGaTe_2$ tetragonal crystal. The values of ionized centers concentration N_t, the length of free path λ, the value of Frenkel coefficient β, the form the potential well in crystals $TlGaTe_2$ were calculated.

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