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Oksana Zamurujeva
 Halyna Myronchuk
 Oleh Parasyuk
 Hanna Shavarova
 Ludmyla Piskach

Hopping conductivity in $Tl_{1-x}In_{1-x}Si_xSe_2$ single crystals

The temperature dependence of the electrical conductivity in single crystals $Tl_{1-x}In_{1-x}Si_xSe_2$ ($x = 0,1; x = 0,2$) is investigated between the temperatures 77 and 300 K. It was found, that variable-range hopping conductivity over localized states near Fermi level takes place in titled solid solutions in the temperature range 125–215 K. The thermal activation energy of hopping is estimated to be $\sim 0,24$ eV and $0,22$ eV for $x = 0,1$ and $0,2$ respectively. At $T < 125$ K the non-activated hopping conductivity along crystal layers is observed.

Key words: chalcogenide solid solutions, Fermi level, activation energy, hopping conductivity, non-activated hopping conductivity.

Introduction. Thallium-containing ternary compounds $TlB^{III}C^{VI}_2$ (B=In, Ga, C=S, Se, Te) have pronounced layered-chain structure. They have anisotropy of physical properties due to high mobility of carriers intra the layers. Inter the layers mobility is limited. As a consequence carriers have different effective masses determined by correspond anisotropy of chemical bonds.

The structure and physical properties of ternary chalcogenide compound $TlInSe_2$ are described in [12–15; 17–20; 22]. Electric and photoelectric properties, that stipulate use of these compounds as materials for detectors of X-ray irradiation are reported in [16]. In [4; 23] the influence of Ag, Cu, Au Eu, Sm, Yb impurities on electric properties of $TlInSe_2$ has been investigated. The temperature dependences of permittivity and conductivity of $TlInSe_2$ and $TlGaTe_2$ single crystals in ac electrical fields are presented in [3].

Interest to the compounds $TlB^{III}C^{VI}_2$ (B=In, Ga, C=S, Se, Te) is caused by possibility of their applications in optoelectronic devices [2; 3; 8]. Based on $TlInTe_2$ and their structural analog $TlInSe_2$ low-inertial photoresistors, detectors of X-ray irradiation are created. To extend the operation opportunities of physical properties for the titled crystals promising is to study the possibility of the cationic substitution for the crystals $TlInSe_2$ and to investigate relevant solid solutions.

The goal of this work is to study electrical properties of $TlInSe_2$ – $SiSe_2$ solid solution and to define the conductivity mechanism in these crystals on dc.

Experimental. Crystals, grown by the method, described in [21], had layered structure, were homogenous and had very close parameters. For optical measurements samples were cleaved from the middle of the crystalline ingot along the cleavage plane. The studied samples had a form of parallelepipeds. The Ohmic contacts were applied by melt of indium on the opposite faces of the samples.

The studies of the temperature dependences of specific dark conductivity was performed using cryostat with Utrex thermoregulation. The temperature varied from 77 to 300 K with stabilization $\pm 0,1$ K.

Basic results and discussion. The single crystals $Tl_{1-x}In_{1-x}Si_xSe_2$ ($x = 0,1; 0,2$) are p-type semiconductors. Stoichiometric cation vacances which are situated in the down part of the forbidden gap are of acceptor type. They cause a hole type of conductivity which is typical for different kind of complex chalcogenides. Conductive type does not change with increasing x because the concentration of the Si decants is less than the concentration of the stoichiometric vacancies and other structural defects.

The temperature dependence of specific dark electroconductivity $\sigma(T)$ for the $Tl_{1-x}In_{1-x}Si_xSe_2$ at $x = 0,1; 0,2$ is represented on fig. 1 (a, c). The analysis of the experimental results shows that within the temperature range I (300–240 K and 315–270 K for the samples with $x = 0,1$ and $x = 0,2$, respectively), the temperature dependence can be well described by expression for disordered semiconductors [6]:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_A}{kT}\right) \quad (1)$$

where σ_0 is dependent on conductive mechanisms for disordered compounds.

Calculation of the activation energy from experimental data using an eq. (1) gives values $\sim 0,24$ eV and $0,22$ eV, for $x = 0,1$ and $0,2$; respectively.

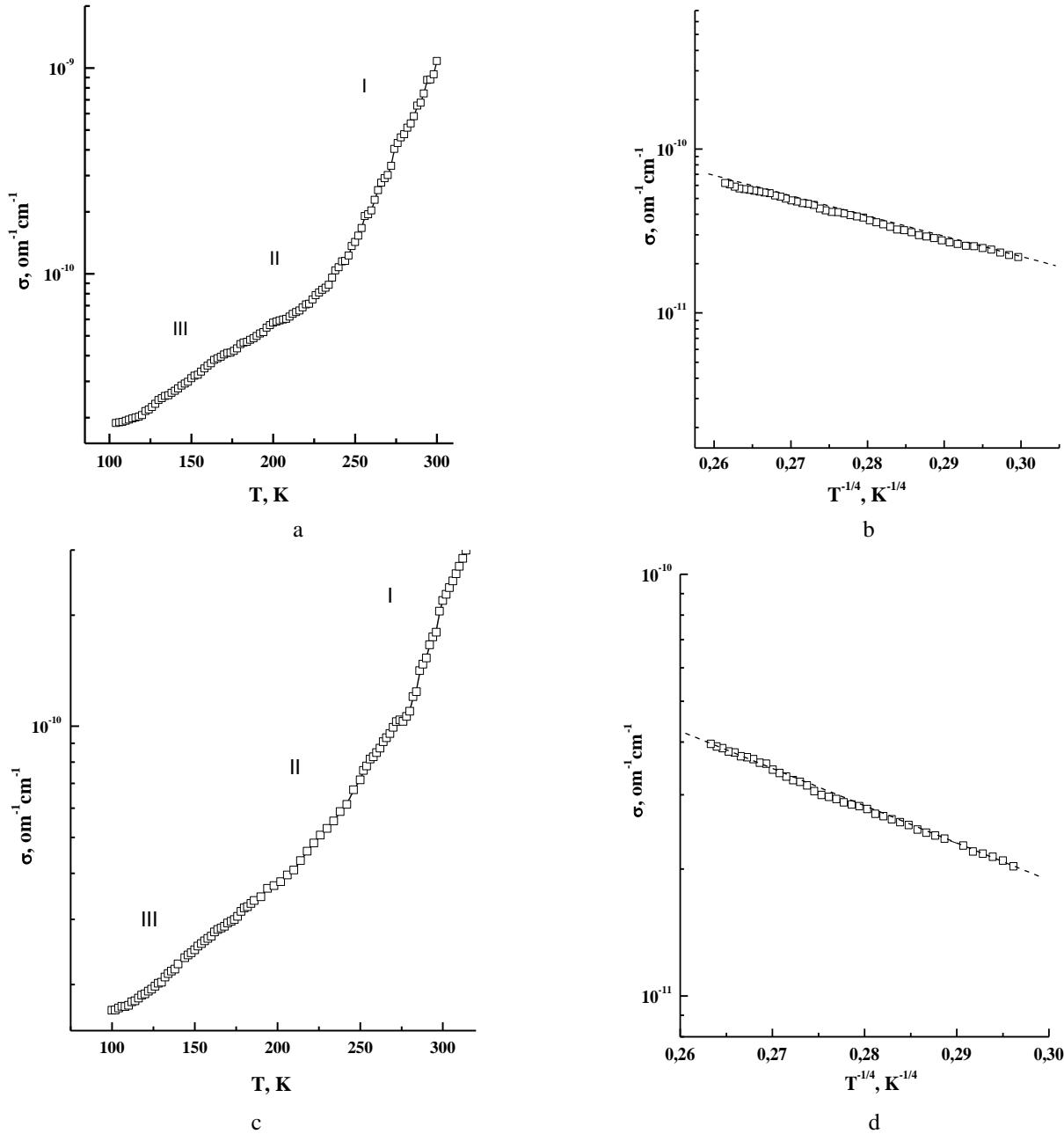


Fig. 1. Temperature dependences of specific dark electroconductivity for the single crystals $Tl_{1-x}In_{1-x}Si_xSe_2$:
a, b – $x = 0,1$; c, d – $x = 0,2$

Following the Mott criterion [6] the defined value of coefficient σ_0 for this range corresponds to electroconductivity mechanisms due to excitation of carriers from the levels near E_F to the localized states, which are situated in the tails of the valence band (for p-type semiconductors). In temperature region II (fig. 1 a, c) the activation energy continuously decreases with decreasing temperature to ~ 120 K.

Fig. 1 (b, d) represents conductivity values in this field, rebuilt in the coordinates $\ln(\sigma) - T^{-1/4}$. The temperature dependences are fitted by straights, so the conductivity can be described by the known Mott ratio [6]:

$$\sigma \sim \exp\left[-\left(T_0 / T\right)^{1/4}\right]. \quad (2)$$

This suggests that a charge transfer is carried out by means of hopping conduction carriers over localized states in a narrow band of energies near the Fermi level. At low temperatures the freezing out of doped carriers in the permitted area leads to the fact that the largest contribution to the conductivity is made by jumps of the carriers over localized impurity states without activation into permitted zone.

According to hopping conduction mechanism charge carriers make their jumps through a weak overlap tail part of the wave functions of neighbouring acceptors. Therefore this mechanism is characterized by extremely low mobility. But hopping conductivity exceeds band one for in hopping conduction every hole located on the acceptor takes part versus exponentially small part of the holes in valence zone [1].

From the steepness $\ln(\sigma) - T^{1/4}$ the magnitude of T_0 for electroconductivity along the chains of $Tl_{1-x}In_{1-x}Si_xSe_2$ is calculated to be $7,2 \times 10^5$ K and $4,6 \times 10^5$ K for $x = 0,1$ and $0,2$, respectively. According to [6]:

$$T_0 = \frac{16}{N_F k a^3}, \quad (3)$$

where k – is Boltzmann constant, a – radius of localization, N_F – is the density of states near the Fermi energy level. From ratio (3) we have estimated the density of localized states near Fermi levels: $N_F = 3,2 \times 10^{19}$ eV⁻¹cm⁻¹ and $5,02 \times 10^{19}$ eV⁻¹cm⁻¹ for $x = 0,1$ and $0,2$; respectively. Here we assumed the localization radius equal to radius of the first coulombic excitons [7]. For the crystals $A^{III}B^{III}C_2^{VI}a = 20$ Å.

The high value of N_F indicates that we deal with the single crystals with high degree of disorder. The highly deformed and broken chemical bonds lead to occurrence of acceptor properties. Such defects are typical for the crystals with layered and chain-like structures [7; 9].

From the ratio [10]:

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

one can evaluate the average jump length R for localized states near Fermi level. At $T = 125$ K, $R = 65$ Å, and at $T = 215$ K $R = 57$ Å. So the average lengths of the jumps within the temperature range 125–215 K for $x = 0,1$ is equal to $R_{av} = 61$ Å. For $x = 0,2$ $R = 58$ Å at $T = 130$ K and $R = 51$ Å at $T = 210$ K. The average jump distance for the titled crystals within the temperature range 130–210 K is equal to $R_{av} = 55$ Å. Assuming the average distances between the localized carrier centers a to be 20 Å, one can estimate the magnitude of R_{av}/a . It amounts 3 for $x = 0,1$ and 2,7 for $x = 0,2$. High value of the ratio R_{av}/a indicates the crank localization [6] in single crystals $Tl_{1-x}In_{1-x}Si_xSe_2$.

From [6] we have evaluated at different temperatures the distribution of the localized states for the titled crystals using following equation:

$$\frac{4\pi}{3} R^3 N_F \frac{\Delta E}{2} = 1. \quad (5)$$

For $x = 0,1$ $\Delta E = 53$ meV and 79 meV at $T = 125$ K and $T = 215$ K respectively, for $x = 0,2$ $\Delta E = 49$ meV and 70 meV at $T = 130$ K and $T = 210$ K.

In temperature region III at $T < 125$ K (fig. 1 a, c) the activation energy does not depend on the temperature. One can infer that along the crystal layers in this temperature range a hopping conduction is activation-free.

Conclusions. The studied $Tl_{1-x}In_{1-x}Si_xSe_2$ single crystals may be considered as crystals with high degree of disorder. High conductivity over localized states in the band gap is due to the existence of a high concentration of defect centers. In the temperature range 125–215 K ~ in the studied solid solutions one can observe a hopping conductivity with variable-length jumps over states localized near the Fermi level. In the temperature range $T < 125$ K the conductivity of single crystals is activation-free.

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Замуруєва Оксана, Мирончук Галина, Парасюк Олег, Шаварова Ганна, Піскач Людмила. Стрибкова провідність у монокристалах Tl_{1-x}In_{1-x}Si_xSe₂. Досліджена температурна залежність питомої електропровідності монокристалів Tl_{1-x}In_{1-x}Si_xSe₂ ($x = 0,1; x = 0,2$) в інтервалі температур 77–300К. Встановлено, що в досліджуваних твердих розчинах має місце стрибкова провідність зі змінною довжиною стрибка по станах, локалізованих поблизу рівня Фермі в температурному проміжку 125–215 К. Енергія термічної активації стрибків становить ~ 0,24 eV та 0,22 eV, для $x = 0,1$ та $0,2$ відповідно. При $T < 125$ К у досліджуваних твердих розчинах має місце безактиваційна стрибкова провідність уздовж шарів кристала.

Ключові слова: халькогенідні тверді розчини, рівень Фермі, енергія активації, стрибкова провідність, безактиваційна стрибкова провідність.

Замуруєва Оксана, Мирончук Галина, Парасюк Олег, Шаварова Анна, Піскач Людмила. Прыжковая проводимость в монокристаллах Tl_{1-x}In_{1-x}Si_xSe₂. Исследована температурная зависимость удельной электропроводности монокристаллов Tl_{1-x}In_{1-x}Si_xSe₂ ($x = 0,1; x = 0,2$) в интервале температур 77–300 К. Установлено, что в исследуемых твердых растворах имеет место прыжковая проводимость с переменной длиной прыжка по состояниям, локализованных близко к уровню Ферми в температурной области ~ 125–215 К. Термическая энергия активации прыжков составляет 0,24 eV и 0,22 eV для $x = 0,1$ и $0,2$ соответственно. При $T < 125$ К имеет место безактивационная прыжковая проводимость вдоль слоев кристалла.

Ключевые слова: халькогенидные твердые растворы, уровень Ферми, энергия активации, прыжковая проводимость, безактивационная прыжковая проводимость.

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