Research Article

Charge Transport and Thermo-emf in TlFe$_{1-x}$Ga$_x$S$_2$ Solid Solutions

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1. Introduction

Ternary thallium sulfides TlFeS$_2$ and TlGaS$_2$ are representatives of anisotropic semiconductors with high magnetic, photosensitivity, and roentgensensitivity properties [1, 2]. Obtaining solid solutions with the base of these compounds is of interest because the study of their properties makes it possible to gain insight into general aspects of property-composition relationships. These ternary compounds crystallize in the monoclinic structure and have the following lattice parameters: $a$ = 11.36; $b$ = 5.304; $c$ = 6.799 Å; $\beta$ = 116.7°; and $Z$ = 4 (space group C2/m) for TlFeS$_2$ [1, 2] and $a$ = 10.29; $b$ = 10.284; $c$ = 15.175 Å; and $\beta$ = 99.603° (space group C2/c) for TlGaS$_2$ [3].

In [4], the $T-x$ phase diagram of the TlFeS$_2$–TlGaS$_2$ system has been constructed (simple eutectic system, eutectic at 80 mol.% TlGaS$_2$ with a melting point of 953 K). It was established that this system contains limited series of monoclinic solid solutions based on the ternary end-members. At an annealing temperature of 933 K, the solid solutions based on the end-members extend to 5 mol.% TlFeS$_2$ and 10 mol.% TlGaS$_2$. The band gap of TlGa$_{1-x}$Fe$_x$S$_2$ ($x = 0$; 0.005; 0.01) single crystals has been shown to decrease with increasing Fe concentration and increase with increasing temperature.

From the nature of the temperature dependence of the magnetic susceptibility and its magnitude, it follows that the TlFeS$_2$ is in the paramagnetic state at room temperature, while TlGaS$_2$ shows a typical diamagnetic state [5]. The temperature dependence of the magnetic susceptibility curve of TlFeS$_2$ revealed anomalies, indicating phase transitions in this compound. An increase in the content of gallium cations in TlFe$_{1-x}$Ga$_x$S$_2$ solid solutions reduces the specific magnetization and increases the differences in the temperatures of Curie–Weiss.

There are several review volumes devoted to the early works on physics of diluted magnetic semiconductors [6, 7] that are most popular these days [8, 9]. Various semiconductor chalcogenide materials based on solid solutions with varying properties are suitable for use in electronic devices [10–12].

The application of band theory to “magnetic” materials with partially filled 3d or 4f shells (for example, TlFeS$_2$) does not allow making any valuable predictions. Therefore, if we want to use magnetic semiconductors, it is necessary to establish regularities of changes in the properties of the
factors that change the concentration of charge carriers. In the TlFeS\(_2\) compound, the chemical bond is intermediate between pure ionic and covalent bond types. This is determined by the degree of electron affinity of anions and cations. The physical properties of TlFeS\(_2\) are strongly influenced by the contribution of the electrons of the doping components. Therefore, the study of the effect of doping components on the physical parameters, the mechanism of charge transfer, and temperature-concentration dependences of thermoelectric power, as well as the determination of correlations between them in materials of the TlFeS\(_2\) type is an urgent task. To date, of the temperature dependence of conductivity and thermoelectric power of materials based on TlFeS\(_2\), the composition of which is partially chemically modified, has not been systematically studied. This modification of the composition gives the material new properties and can be used to control physical parameters.

The results of our studies of the effect of gallium concentration on transport phenomena in the TlFeS\(_2\) magnetic material are given below. We compared the properties of TlFe\(_{1−x}\)Ga\(_x\)S\(_2\) solid solutions with the properties of pure TlFeS\(_2\). The study of the temperature dependence of electrical and thermoelectric properties of isostructural TlFe\(_{1−x}\)Ga\(_x\)S\(_2\) allows to establish the effect of the composition on the conductivity and thermoelectric power of the samples under study.

2. Materials and Methods

The starting chemicals used in our preparations were high-purity constituent elements: TI-00, gallium (5NGa), sulfur (OSCh 16-5), and iron (3N Fe). The ternary compounds TlFeS\(_2\) and TlGaS\(_2\) were synthesized by reaction of stoichiometric elemental mixtures, which were melted in silica tubes sealed off under a vacuum of 10\(^{-3}\) Pa. The completion of the synthesis of the ternary compounds TlFeS\(_2\) and TlGaS\(_2\) was checked by differential thermal analysis (DTA) and X-ray diffraction (XRD). The results were compared to earlier data [1–3]. The alloys were prepared by reacting the appropriate mixtures of the ternary compounds TlFeS\(_2\) and TlGaS\(_2\), respectively, at 1000 K for 5–7 h in silica tubes sealed off under a vacuum of 10\(^{-3}\) Pa. Next, the alloys were vacuum-annealed in two steps: first at 953 K for 200 h and then at 933 K for 500 h. The annealed alloys were furnace-cooled to room temperature. The phase composition of the obtained alloys was determined by XRD at room temperature on a DRON-2 diffractometer with CuK\(_\alpha\) radiation.

To examine the effect of the partial Ga\(^{3+}\) → Fe\(^{3+}\) cation substitution on the properties of the solid solutions of TlGaS\(_2\)–TlFeS\(_2\) system, TlFe\(_{1−x}\)Ga\(_x\)S\(_2\) (x = 0.025 and 0.1) was synthesized [4, 5]. For the experiments, we used freshly grown samples on the basis of TlFeS\(_2\) which practically do not deteriorate in the open air for a long time. TlFe\(_{1−x}\)Ga\(_x\)S\(_2\) samples for electrical measurements had the form of parallelepipeds with thickness d = 1.0–1.5 mm. Electrical contacts to their end faces were made by electrolytic copper deposition.

The electrical DC conductivity (\(\sigma\)) of the samples was measured by the four-probe method with an accuracy up to 3%. The thermopower of the prepared samples was measured to an accuracy of 5\%. Electrical and thermoelectric properties of TlFe\(_{1−x}\)Ga\(_x\)S\(_2\) were measured in the temperature range 80–355 K. The amplitude of the external DC electric field applied to the samples was from the Ohmic region of their current-voltage characteristics.

3. Results and Discussion

The results of X-ray phase analysis of TlFe\(_{1−x}\)Ga\(_x\)S\(_2\) (x = 0, 0.01, 0.025, 0.05, 0.075, and 0.1) heat-treated samples are shown in Figures 1 and 2. On the diffraction patterns of these samples, only X-ray lines of crystalline phase of TlFeS\(_2\) are present. The results of XRD samples indicate that they crystallize in monoclinic symmetry (C2/m) under normal conditions.

In TlFe\(_{1−x}\)Ga\(_x\)S\(_2\) (x = 0, 0.01, 0.025, 0.05, 0.075, and 0.1) crystals with increasing gallium concentration, parameter \(a\) decreases, parameter \(b\) increases, and the parameter \(c\) does not change substantially (Figure 2). For TlFeS\(_2\) crystals, \(a = 11.654(1)\), \(b = 5.292(2)\), \(c = 6.811(3)\) A, and \(\beta = 116.87^\circ\) which agrees well with data [1–4].

The results of the investigations into the electrical and thermoelectric properties of TlFe\(_{1−x}\)Ga\(_x\)S\(_2\) samples are presented below. Figure 3 depicts the temperature dependences of the thermopower for TlFe\(_{0.975}\)Ga\(_{0.025}\)S\(_2\) and TlFe\(_{0.0}\)Ga\(_{0.1}\)S\(_2\) (curves 2 and 3) in the temperature range 80–355 K. As the temperature increases from 80 to 150 K, the thermopower increases moderately and the sign of the thermo-emf is positive, which suggests that the studied crystal has \(p\)-type conductivity. With the further increase in the temperature up to 355 K, the thermopower sharply decreases and the inversion of the thermo-emf sign takes place. The negative sign of the thermopower indicates that electrons are the major charge carriers in TlFe\(_{0.975}\)Ga\(_{0.025}\)S\(_2\).

According to [16], the thermopower of \(p\)-type chalcogenide semiconductors can be represented in the form:

\[
\alpha(T) = -\frac{1}{e} \left[ \frac{\Delta E}{T} - y + k \right],
\]

where \(k\) is Boltzmann’s constant, \(e\) is the electron charge, \(\Delta E\) is the activation energy for conduction, and \(y\) is the temperature coefficient of the activation energy for conduction. The high-temperature \((T = 275 – 355\) K\) slope of the \(\alpha(1/T)\) curve was determined to be \(\Delta E^a = 0.047\) eV. Extrapolating the high-temperature portion of the \(\alpha(1/T)\) curve to the vertical axis \((1/T = 0)\), we obtained a vertical intercept of 212 \(\mu V/K\). The cutoff thermoelectric power according to equation (1) allowed us to find the temperature coefficient of the activation energy for conduction \((y)\), which was determined to be \(2.98 \times 10^{-4}\) eV/K. This made it possible to estimate the temperature coefficient of the optical band gap \((\beta)\) in TlFe\(_{0.975}\)Ga\(_{0.025}\)S\(_2\) as \(\beta = 2\gamma\) [16]. We obtained \(\beta = 5.96 \times 10^{-4}\) eV/K.

In TlFe\(_{0.4}\)Ga\(_{0.1}\)S\(_2\), the \(p\)-type conduction was observed in a more wide temperature range (85–327 K). With a further
increase in the temperature up to 355 K, the sign of the thermopower was negative. Figure 3 also shows the temperature dependence of thermoelectric power for TlFeS\textsubscript{2} (curve 1). The inversion of the thermo-emf\textsuperscript{5} sign in TlFeS\textsubscript{2} takes place at 130 K, i.e., the inversion point ($T_\alpha^i$) of thermopower sign in TlFe\textsubscript{1−x}Ga\textsubscript{x}S\textsubscript{2} crystals has been shown to increase from 130 to 327 K with increasing Ga concentration (Table 1).

Figure 4 shows typical temperature dependences of conductivity for TlFe\textsubscript{1−x}Ga\textsubscript{x}S\textsubscript{2} samples. High-temperature branches of the $\sigma(1/T)$ dependences had exponential character with slopes 0.33, 0.09, and 0.10 eV for $x = 0$, 0.025, and 0.1, correspondingly. As it was noted above, in TlFe\textsubscript{0.975}Ga\textsubscript{0.025}S\textsubscript{2}, the slope of $\alpha(1/T)$-dependence was found to be $\Delta E_\alpha = 0.047$ eV. This discrepancy in the values of $\Delta E_\alpha$ and $\Delta E_\sigma$, when $\Delta E_\sigma$ is two and more than twice as large as $\Delta E_\alpha$, was also observed in GaSb, Ge, and GaAs [16]. The discrepancy between $\Delta E_\alpha$ and $\Delta E_\sigma$ should be expected when the slope of the plot of $\ln \sigma$ against $1/T$ is contributed by the thermal activation of carrier mobility.

After the exponential decay, the conductivity of TlFe\textsubscript{1−x}Ga\textsubscript{x}S\textsubscript{2} crystals in the Arrhenius coordinates of the curve $\sigma(1/T)$ did not have a constant slope, i.e., was characterized by a monotonically decreasing activation energy with decreasing temperature. This behavior of the DC conductivity in TlFe\textsubscript{1−x}Ga\textsubscript{x}S\textsubscript{2} at low temperatures suggests that charge transfer occurs through the variable-range-hopping mechanism, provided the current is transferred by charge carriers at the states localized near the Fermi level [16]. This is also evidenced by the temperature dependence of conductivity in the form of a Mott plot: $\ln \sigma$ against $T^{-1/4}$ (Figure 5). From these plots ($T_\sigma$), the density of localized states near the Fermi level was evaluated as

$$ N_F = \frac{16}{T_\sigma k a^3}, $$

(2)
where \( l \) is the localization radius.

Obtained values for \( T_0 \) and \( N_F \) are listed in Table 2. The density of localized states near the Fermi level of TlFe\(_{1-x}\)Ga\(_x\)S\(_2\) crystals has been shown to increase by more than two orders with increasing Ga concentration. The localization radius was taken to be \( a_1 = 14 \text{ Å} \), by analogy with that in TlFeS\(_2\) [1]. Using the relation

\[
R(T) = \frac{3}{8} \cdot a_1 \left( \frac{T_0}{T} \right)^{1/4},
\]

we evaluate the hop distance in the TlFe\(_{1-x}\)Ga\(_x\)S\(_2\) crystals as a function of temperature. The average hop distances in studied crystals (Table 2) significantly (by 2–8 times) exceeded the average distance between the centers of localization of charge carriers.

From the expression given in [16],

\[
\Delta E = \frac{3}{2 \pi R^3 N_F},
\]

we estimated the scatter of the trapping states near the Fermi level: \( \Delta E = 70 \text{ meV} \) for TlFe\(_{0.975}\)Ga\(_{0.025}\)S\(_2\) and 50 meV for TlFe\(_{0.9}\)Ga\(_{0.1}\)S\(_2\). Knowing \( \Delta E \) and using the relation

\[
N_1 = N_F \Delta E,
\]

we calculated the trap concentration in TlFe\(_{1-x}\)Ga\(_x\)S\(_2\), whose values are shown in Table 2. The activation energy for hopping conduction in the studied crystals evaluated as [17]

\[
\Delta W = \frac{(kT)^{3/4}}{N_F \cdot a_1^r},
\]

is 65 meV for TlFe\(_{0.975}\)Ga\(_{0.025}\)S\(_2\) and 45 meV for TlFe\(_{0.9}\)Ga\(_{0.1}\)S\(_2\).

Consider now the temperature dependence of thermoelectric power in the region of hopping conduction in TlFe\(_{1-x}\)Ga\(_x\)S\(_2\). As it is seen from Figure 3, at low temperatures, when hopping conductivity takes place in studied crystals, the sign of thermopower is positive. The value of thermo-emf in samples has been shown to increase with increasing temperature. The temperature dependence of thermoelectric power in the region of hopping conduction is known to have the following form [16]:

\[
\alpha(T) = A + B T,
\]

where \( B \) is the temperature coefficient of thermoelectric power.

Obtained for solid solutions, TlFe\(_{1-x}\)Ga\(_x\)S\(_2\) low-temperature dependences \( \alpha(T) \) are linear functions of temperature, which is consistent with equation (7). The thermoelectric power at \( T = 0 \) (vertical intercept) is \( A_1 = -30 \mu V/K \) in TlFeS\(_2\). The temperature coefficient of thermoelectric power was determined to be \( B_1 = 0.4 \mu V/K^2 \); that is, low-temperature thermoelectric power of the TlFeS\(_2\) crystal can be represented by the formula:

\[
\alpha_1(T) = (0.4T - 30) \mu V/K.
\]

In TlFe\(_{0.9}\)Ga\(_{0.1}\)S\(_2\), the temperature coefficient of thermoelectric power at low temperatures was determined to be

\[
B_2 = \frac{\partial \alpha}{\partial T} = 0.06 \mu V/K^2,
\]

\[
A_2 = -1 \mu V/K.
\]

That is,

\[
\alpha_2(T) = (0.06T - 1) \mu V/K.
\]

The thermopower is determined primarily by the density of states and hence has positive sign in the region of hopping conduction. Thus, it was demonstrated that, at low temperatures when hopping conduction is dominant, the thermopower of TlFe\(_{1-x}\)Ga\(_x\)S\(_2\) is positive and proportional to the temperature.

In the study of temperature dependence of conductivity of TlFe\(_{1-x}\)Ga\(_x\)S\(_2\) solid solutions on curves ln \( \sigma \) vs \( 10^3/T \), the anomalies were observed (Figure 4). With the increase in temperature from 80 K, the conductivity of TlFe\(_{1-x}\)Ga\(_x\)S\(_2\) increases, then passing through a minimum value. The temperatures of conductivity minimum were equal to 171 K for TlFe\(_{0.975}\)Ga\(_{0.025}\)S\(_2\) and 164 K for TlFe\(_{0.9}\)Ga\(_{0.1}\)S\(_2\). These temperatures correspond to the temperature of the
antiferromagnetic phase transition ($T_N$) of type II in the studied solid solutions, when in the antiferromagnetic antiparallel orientation of the spins disappears and it becomes paramagnetic. In TlFe$_{1-x}$Ga$_x$S$_2$, Neel temperature determined from measurements of the magnetic susceptibility is equal to $T_N = 196$ K [3]. Thus, increasing the concentration of gallium ions in the TlFe$_{1-x}$Ga$_x$S$_2$ solid solutions led to the displacement of the Neel temperature to a lower temperature (Table 1).

### 4. Conclusions

At temperatures $T < 250$ K in a dc electric field, the TlFe$_{1-x}$Ga$_x$S$_2$ ($x = 0$, 0.025, and 0.1) crystals have been shown to exhibit the variable-range-hopping conduction through states localized near the Fermi level. In terms of hopping mechanism of charge transfer, the density of localized states near the Fermi level, their spread in energy, the activation energy, and the average hop distance have been evaluated. The density of localized states near the Fermi level of TlFe$_{1-x}$Ga$_x$S$_2$ crystals have been shown to increase by more than two orders, but average hop distance have been shown to decrease with increasing gallium concentration. The type of conductivity and the inversion point of thermopower sign have been determined for TlFe$_{1-x}$Ga$_x$S$_2$ from temperature dependences of thermo-emf. The inversion point ($T_\theta$) of thermopower sign in TlFe$_{1-x}$Ga$_x$S$_2$ crystals has been shown to increase from 130 to 327 K, and the temperature of phase transition ($T_N$) decreases from 196 to 164 K with increasing Ga concentration.

### Data Availability

The data used to support the findings of this study are included within the article.

### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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### References


