

# Effect of deviation from stoichiometry on transport and mechanical properties of $\text{Bi}_2\text{Se}_3$ polycrystals

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The dependences of electrical conductivity, the Hall coefficient, the Seebeck coefficient, thermoelectric power factor and microhardness of  $\text{Bi}_2\text{Se}_3$  polycrystals on the degree of deviation from stoichiometry 59.9–60.0 at. % Se and temperature (77–300 K) were obtained. The samples exhibited  $n$ -type conductivity in the studied ranges of compositions and temperatures. The boundaries of the  $\text{Bi}_2\text{Se}_3$  homogeneity region were estimated. A non-monotonic behavior of the concentration dependences of the properties in the studied composition range, associated with a change in the phase composition and defect structure under the deviation from stoichiometry, was observed. The calculation of the power coefficient in the temperature dependence of electron mobility showed that in a stoichiometric  $\text{Bi}_2\text{Se}_3$ , electrons are predominantly scattered by acoustic phonons, and under the deviation from stoichiometry the contribution of impurity scattering increases. Based on the experimental data, the Fermi energy  $E_F$  was calculated in the approximation of the relaxation time and within the framework of the single-band model with a quadratic dispersion law. The obtained values of  $E_F$  showed that both in stoichiometric and non-stoichiometric  $\text{Bi}_2\text{Se}_3$ , the conduction is mainly due to electrons in the lower conduction subband.

Keywords: bismuth selenide, stoichiometry, transport properties, defect structure.

## 1. Introduction

At present,  $\text{Bi}_2\text{Se}_3$  semiconductor compound attracts much attention, which is associated with its use in thermoelectricity as a material operating efficiently in the range close to room temperature [1]. In addition, recently it has been found out that  $\text{Bi}_2\text{Se}_3$  belongs to a new class of materials — topological insulators (dielectric with a conducting layer on the surface) [2], whose unique properties are of interest not only from a scientific but also from a practical point of view [3].

It is known that there are three phases  $\text{Bi}_2\text{Se}_3$ ,  $\text{BiSe}$ ,  $\text{Bi}_3\text{Se}_2$  in the Bi–Se system [4]. The  $\text{Bi}_2\text{Se}_3$  compound melts congruently at 979 K with an open maximum [4–6], which is deviated from stoichiometry to the Bi-rich side and located at  $(59.98 \pm 0.01)$  at. % Se [4, 7–10].  $\text{Bi}_2\text{Se}_3$  crystallizes in a rhombohedral structure with five atoms per unit cell [9]. The structural unit of  $\text{Bi}_2\text{Se}_3$  is a quintuple layer consisting of alternating monoatomic bismuth and selenium planes  $\text{Se}^1\text{–Bi–Se}^2\text{–Bi–Se}^1$  (superscripts 1 and 2 indicate the difference in positions of Se atoms in the crystal lattice). Atoms within a quintuple layer are connected by ionic-covalent bonds, while quintuple layers are bonded by Van der Waals forces.

In a number of works, the homogeneity region (HR) of  $\text{Bi}_2\text{Se}_3$  was studied. It is known, that the deviation from stoichiometry causes the appearance of intrinsic defects whose concentration varies within the HR, making it possible to control the properties of this compound. In [10], the boundaries of the  $\text{Bi}_2\text{Se}_3$  HR were determined for temperatures above 650 K by measuring the Hall coefficient  $R_H$  of  $\text{Bi}_2\text{Se}_3$  samples with different deviations from stoichiometry quenched from different temperatures. According to [10], the size of HR is maximal (59.984–59.997 at. % Se) at 900 K and corresponds to the interval of charge carrier concentrations (electrons)  $1.6 \cdot 10^{18}$ – $1.9 \cdot 10^{19}$   $\text{cm}^{-3}$ , and at 675 K the HR extends 59.984–59.997 at. % Se. The data on the HR boundaries at lower temperatures are not available in the literature, although  $\text{Bi}_2\text{Se}_3$  is used for thermoelectric applications at temperatures close to room temperature.

$\text{Bi}_2\text{Se}_3$  is a narrow-gap semiconductor with an energy gap 0.35 eV at room temperature [3]. It was found in [11–13] that there are two subbands (a six-valley subband of light electrons and a single-valley subband of heavy electrons) in the  $\text{Bi}_2\text{Se}_3$  conduction band. The distance between the subbands was theoretically estimated at 87 meV [11] and 40 meV [12]. The valence band also contains two sub-

bands that differ in the hole effective masses and are spaced apart by a distance of 24 meV [11].

It is well known that  $\text{Bi}_2\text{Se}_3$  always exhibits *n*-type conductivity, which is associated with the presence of a large number of Se vacancies ( $V_{\text{Se1}}$ ) [3, 10, 14–25] acting as donors. The first assumptions about the existence of  $V_{\text{Se1}}$  in the  $\text{Bi}_2\text{Se}_3$  lattice were made in [19] based on comparing the experimentally measured values of density with the theoretically calculated ones using crystallographic data. The existence of Se vacancies was confirmed in later works [10, 20, 21, 24], where the authors obtained almost constant  $R_H$  value in the temperature range 80–330 K and, based on that, concluded that the ionization energy of vacancies was practically zero, and in [16], where voids on the (001) surface of  $\text{Bi}_2\text{Se}_3$  single crystals were observed by scanning tunneling microscopy. The coexistence of  $V_{\text{Se1}}$  and antisite defects (AD) — bismuth atoms in the positions of selenium ones ( $\text{Bi}_{\text{Se}}$ ), in the compound was suggested in [26, 27] based on the dependence of the electron concentration on the In impurity content in *n*- $\text{Bi}_2\text{Se}_3$ .

Theoretical works [14, 23] in which the formation energies of various types of defects in  $\text{Bi}_2\text{Se}_3$  were calculated also showed the dominance of donor-type defects ( $V_{\text{Se1}}$ ) under Bi excess, although it was demonstrated in [2, 25, 28] that under the deviation from stoichiometry, along with  $V_{\text{Se1}}$ , ADs ( $\text{Bi}_{\text{Se}}$ ), which act as acceptors, are formed. The authors of [28] also showed that if the spin-orbit interaction is taken into account when calculating the energy spectrum under excess Bi condition, the  $V_{\text{Se1}}$  remains the dominant defect type with a low formation energy, and the action of the  $\text{Bi}_{\text{Se}}$  defect changes from acceptor-like to donor-like.

Thus, by now the nature of defects in  $\text{Bi}_2\text{Se}_3$  under the deviation from stoichiometry to the Bi-rich side has not been identified unambiguously, although most authors believe that the predominate defects in  $\text{Bi}_2\text{Se}_3$  are  $V_{\text{Se1}}$  acting as donors.

The temperature (4.2–300 K) dependences of electrical conductivity  $\sigma$  and  $R_H$  of  $\text{Bi}_2\text{Se}_3$  crystals with the electron concentrations  $n \gtrsim 10^{18} \text{ cm}^{-3}$  exhibit a metallic behavior [29–32]. The temperature dependence of electron mobility  $\mu_H(T)$  becomes weaker than that typical of degenerate semiconductors, which is usually attributed to the increasing contribution of impurity scattering along with scattering by acoustic phonons [21, 29, 32]. It should be noted that the authors of [7] observed a minimum of  $\sigma$  for cast polycrystals with the composition 59.98 at. % Se, but did not comment on this result.

The following fact must also be pointed out. The properties of  $\text{Bi}_2\text{Se}_3$  were studied mainly for single crystals, while the data on the properties of polycrystals were reported in a limited number of works [33–36]. Meanwhile, pressed materials are widely used in thermoelectric (TE) converters. Pressing makes it possible to obtain samples with a high degree of uniformity and with a shape convenient for practical use. The presence of a large number of grain boundaries in pressed samples, on the one hand, increases mecha-

nical strength, and, on the other hand, leads to a decrease in the lattice component of thermal conductivity, which leads to an increase in the TE figure of merit of a material  $Z$  ( $Z = S^2 \cdot \sigma / \lambda$ , where  $\lambda$  is the total thermal conductivity of a TE material,  $S$  is the Seebeck coefficient). Thus, studying the properties of the pressed  $\text{Bi}_2\text{Se}_3$  is important from a practical point of view. However, a detailed investigation of galvanomagnetic (GM), thermoelectric and mechanical properties of cast and pressed  $\text{Bi}_2\text{Se}_3$  crystals under deviation from stoichiometry has not been carried out.

The goal of the present work is to study the effect of deviation from stoichiometry on the GM, TE and mechanical (microhardness) properties of pressed bismuth selenide polycrystals.

## 2. Experimental

Bi–Se polycrystals with Se concentrations varied in the range 59.9–60.0 at. % were synthesized by fusing high-purity (99.999 at. % of the main component) Bi and Se in evacuated quartz ampoules at a temperature about  $\sim 100$  K higher than the melting point of the compound ( $T = 979$  K). The melt was kept at this temperature for 3 h and to ensure its homogeneity vibrational stirring was applied. After that the alloys were subjected to homogenizing annealing for 200 h at  $T = 820$  K and then cooled down to room temperature in the turned-off furnace. All samples obtained in this way will be further called “cast samples”. The compositions of the prepared samples are given in Table 1.

Table 1. Compositions of the Bi–Se samples

№	at. % Se
1	59.90
2	59.95
3	59.98
4	59.985
5	59.99
6	59.995
7	59.998
8	59.999
9	60.0

The synthesized cast samples were used to make powders for pressing with particle size of 200  $\mu\text{m}$ . Pressed samples were prepared by cold pressing at a load of 400 MPa for 60 s with subsequent homogenizing annealing in evacuated quartz ampoules at 670 K for 250 h.

The Hall coefficient  $R_H$  and the electrical conductivity  $\sigma$  were measured by a *dc* method in the temperature range 77–300 K with an error not exceeding  $\pm 5$  %. The Hall carrier mobility  $\mu_H$  was calculated as  $\mu_H = R_H \sigma$ . The measurements of the Seebeck coefficient  $S$  were carried out by compensation method relative to Cu electrodes with an accuracy of  $\pm 3$  %. Based on the values of  $S$  and  $\sigma$ , the power factor  $P = S^2 \sigma$  was calculated. The microhardness  $H$  was measured on a PMT-3 device using a diamond

pyramid with a constant load of 30 g for 10 s with an accuracy of  $\pm 2\%$ . The phase composition of the samples was studied using X-Ray Diffractometer DRON-2.0 with the Bragg–Brentano focusing geometry in filtered radiation of a Cu anode.

### 3. Experimental results and discussion

The investigated samples were homogeneous in chemical composition and properties, which was confirmed by the results of measurements of  $H$ ,  $S$  and  $\sigma$  (the variation in the values of  $H$ ,  $S$  and  $\sigma$  within the sample did not exceed

the error of their measurement). The results of the x-ray diffraction study of the samples showed the presence of peaks corresponding to the Bi<sub>2</sub>Se<sub>3</sub> phase; the peaks of extraneous phases were not observed.

The measurements of  $S$  and  $R_H$  at room temperature showed that the cast and pressed samples exhibited  $n$ -type conductivity.

First, the room-temperature dependences of TE ( $S$ ), GM ( $\sigma$ ,  $R_H$ ), mechanical ( $H$ ) properties and  $P$  on the composition of the Bi–Se polycrystals were obtained for the pressed samples (Fig. 1). Then, the properties of the cast samples were measured (Fig. 2) to compare the behavior of

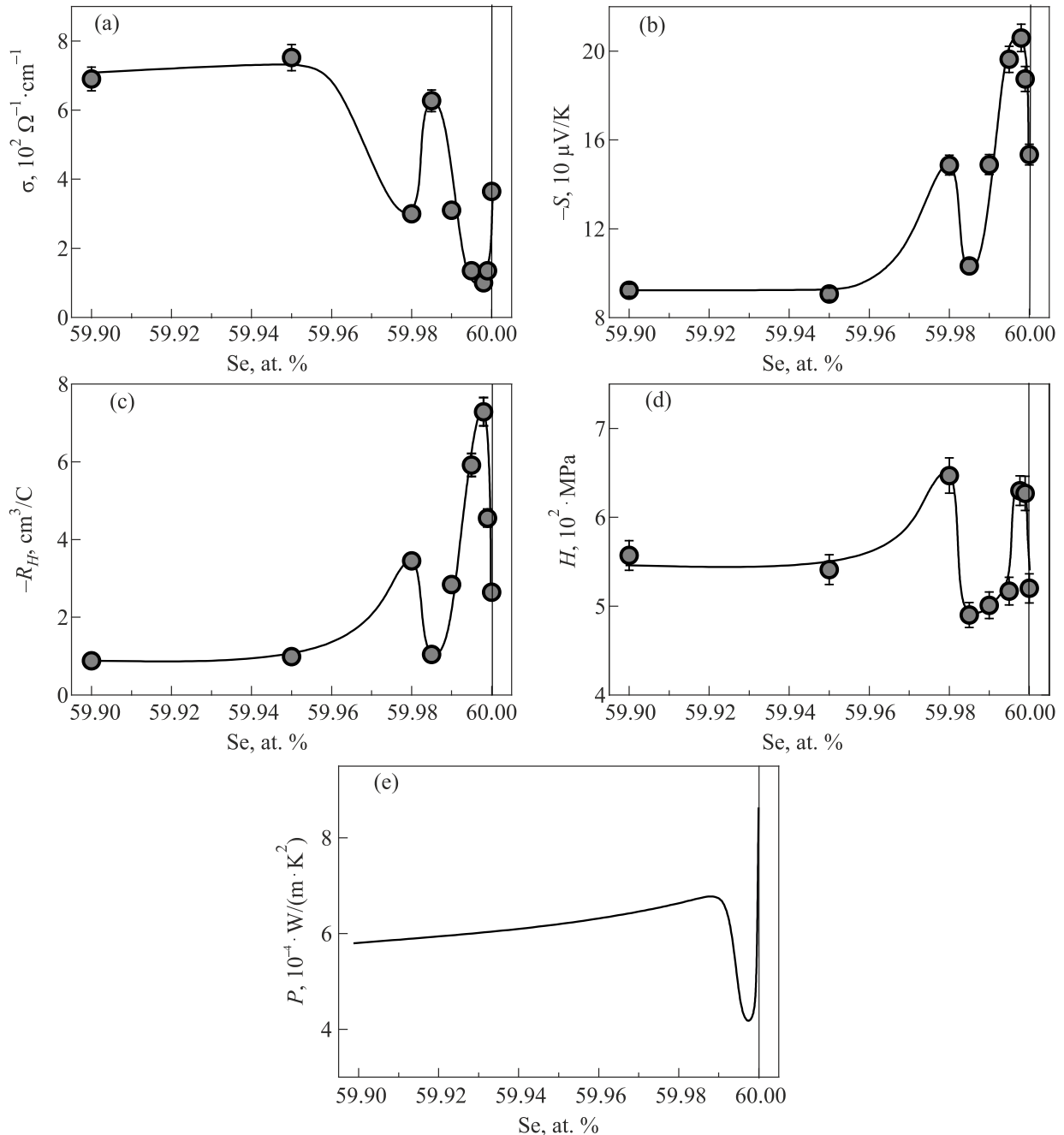


Fig. 1. Room-temperature dependences of electrical conductivity  $\sigma$  (a), Seebeck coefficient  $S$  (b), Hall coefficient  $R_H$  (c), microhardness  $H$  (d) and TE power factor  $P$  (e) on Se content in Bi–Se crystals.

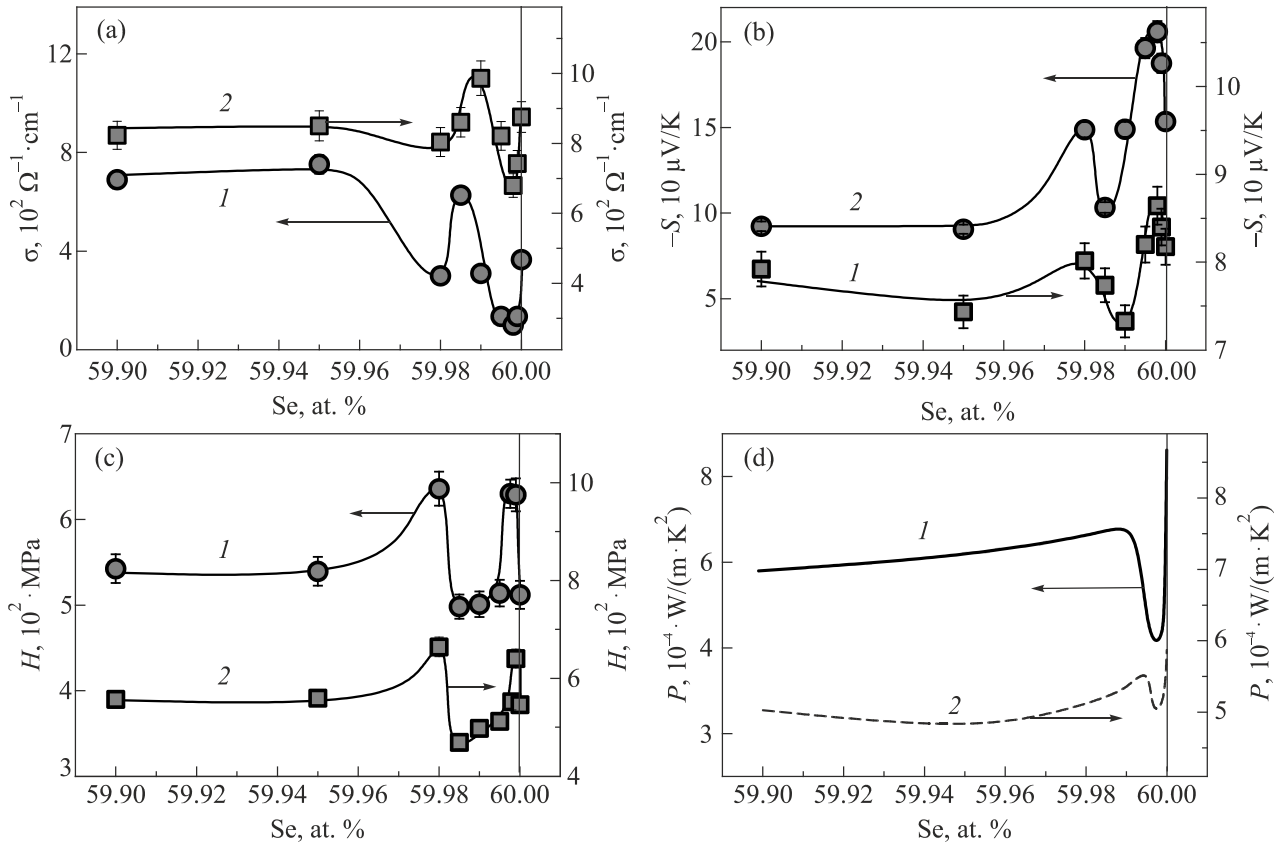


Fig. 2. Room-temperature dependences of electrical conductivity  $\sigma$  (a), Seebeck coefficient  $S$  (b), microhardness  $H$  (c) and TE power factor  $P$  (d) on Se content in pressed (1) and cast (2) Bi–Se crystals.

the composition-property dependences for cast and pressed Bi–Se polycrystals.

As can be seen from Fig. 1, under the deviation from the stoichiometric composition of  $\text{Bi}_2\text{Se}_3$  to the Bi-rich side, general tendencies toward an increase in  $\sigma$  and a decrease in  $R_H$  and  $S$  are observed, and starting from  $\sim 59.95$  at. % Se, the values of  $\sigma$ ,  $R_H$ ,  $S$  and  $H$  practically do not change. It can also be seen that in the studied composition range (59.95–60 at. % Se) the concentration dependences of these parameters are non-monotonic and exhibit an oscillating behavior. Within the studied range of compositions, five regions with different behaviors of properties can be identified:

- (1) 60.0–59.998 at. % Se:  $\sigma$  decreases, and  $R_H$ ,  $S$  and  $H$  increase.
- (2) 59.998–59.985 at. % Se:  $\sigma$  increases, and  $R_H$ ,  $S$  and  $H$  decrease.
- (3) 59.985–59.980 at. % Se:  $\sigma$  decreases again, and  $R_H$ ,  $S$  and  $H$  increase.
- (4) 59.98–59.95 at. % Se:  $\sigma$  increases and  $R_H$ ,  $S$  and  $H$  decrease.
- (5) 59.95–59.90 at. % Se: transport coefficients and  $H$  practically do not change.

From Fig. 2 it can be seen that the character of the concentration dependences of the properties for the cast samples is very similar to that for the pressed samples (see Fig. 1): the positions of the observed maxima and minima of  $\sigma$ ,

$S$ ,  $H$ , and  $P$  for the cast and pressed polycrystals coincide. In the pressed samples, the values of  $S$  are higher and the values of  $\sigma$  are lower than in the cast ones, which can be explained by the increased contribution of scattering by the grain boundaries, which appear as a result of pressing. The values of  $H$  for the cast and pressed crystals with the same composition practically do not differ.

A non-monotonic behavior of the composition dependences of properties of alloys generally indicates the crossing of the phase boundary, but within a single-phase region (in this case, the HR of  $\text{Bi}_2\text{Se}_3$ ) indicates the self-organization processes occurring in the crystal and associated with the redistribution of atoms and non-stoichiometric defects. Taking into account the long-term isothermal annealing at 670 K after pressing Bi–Se crystals, it can be assumed that a state close to the equilibrium state at 670 K is reached, and that the subsequent rapid cooling down to room temperature (in a turned-off furnace) does not significantly change this state.

It is known [4, 7, 9] that  $\text{Bi}_2\text{Se}_3$  is a bertollide with the HR shifted towards the Bi excess (at least at  $T > 675$  K [10]) and the maximum of the melting curves is also shifted towards the Bi excess (59.98 at. % Se) [4, 7–10]. Thus, it follows that under the deviation from stoichiometry to the Bi-rich side, a narrow two-phase region ( $\text{Bi}_2\text{Se}_3 + \text{Se}$ ) should exist. As the temperature decreases below 675 K (in our

case, the samples are cooled in a turned-off furnace), the phase boundary may shift, and this shift is most likely to occur towards a lower concentration of Se, taking into account how the boundary shifts with temperature decreasing from 900 to 675 K [4, 10]. Therefore, it can be assumed that the concentration interval 60.0–59.998 at. % Se corresponds to the two-phase region ( $\text{Bi}_2\text{Se}_3 + \text{Se}$ ), which is in the state of homogeneous decomposition of the solid solution. The behavior of the composition dependences of properties in this region depends on many factors, in particular, on the size and number of precipitated particles, annealing time, cooling rate, *etc.*

The next region — 59.998–59.985 at. % Se, from our point of view, determines the boundaries of HR. As noted above [4, 7–10],  $V_{\text{Se}1}$ , is the predominant type of non-stoichiometric defects in  $\text{Bi}_2\text{Se}_3$ , which are responsible for the  $n$ -type conductivity of this compound. Therefore, we can assume that the deviation from stoichiometry to the Bi-rich side leads to an increase in the concentration of Se vacancies, which are electrically active defects whose appearance causes an increase in electron concentration (reduces  $R_H$  and  $S$ ).

The further decrease in the Se concentration (59.985–59.980 at. % Se) should result in a further increase in the concentration of non-stoichiometric defects. It is possible that the appearance of a new type of non-stoichiometric defects, for example, acceptor type  $\text{AD-Bi}_{\text{Se}}$  [2, 28] becomes thermodynamically favorable. And this can lead to an increase in the elastic stresses of the lattice and, correspondingly, to an increase in  $H$ .  $\text{Bi}_{\text{Se}}$  defects can partially compensate for the donor action of  $V_{\text{Se}1}$ , leading to an increase in  $R_H$  and  $S$  in this region.

In the concentration range 59.98–59.95 at. % Se, a further deviation from stoichiometry, which leads to the slight decrease in  $R_H$ ,  $S$ ,  $H$  and increase in  $\sigma$ , presumably corresponds to the reaching of the boundary of the  $\text{Bi}_2\text{Se}_3$  HR from the Bi-rich side. Further (in the range 59.95–59.90 at. % Se),

the properties of the crystals practically do not change, which, probably, indicates the precipitation of a second phase (possibly  $\text{BiSe}$  [4]) upon crossing the solidus line. Based on the analysis of the experimental data (Fig. 1), it can be assumed that the boundary of the  $\text{Bi}_2\text{Se}_3$  HR on the Se-rich side corresponds to 59.998 at. % Se, and on the Bi-rich side it lies in the interval of 59.98–59.95 at. % Se.

Let us note that the position of the minimum of  $\sigma$  observed at the composition of 59.98 at. % Se [Fig. 1(a)] is in good agreement with the results reported in [7].

As can be seen in Fig. 1(d), the TE power factor also exhibits a non-monotonic behavior under the deviation of  $\text{Bi}_2\text{Se}_3$  from the stoichiometry to the Bi-rich side. A deep minimum of  $P$  is observed at 59.998 at. % Se. It should be noted that the highest value of TE power factor  $P = 8.3 \cdot 10^{-4} \text{ W}/(\text{K} \cdot \text{m}^2)$  corresponds to the stoichiometric composition, which is important from a practical point of view.

The GM properties of the pressed Bi–Se samples were investigated in the temperature range (77–300) K. The results of the  $R_H$  measurements showed that all samples were  $n$ -type in the entire temperature range. The investigated crystals were degenerate semiconductors: with increasing temperature  $\sigma$  and  $\mu_H$  decreased, and  $R_H$  practically did not change (Fig. 3), which is consistent with the available literature data [29–32].

In alloys deviated from stoichiometry due to changes in the phase composition and defect structure, one can expect a change in the mechanism of charge carrier scattering. On the basis of the temperature dependences of charge carrier mobility  $\mu_H(T)$  plotted on logarithmic scale, the exponents  $\nu$  in the  $\mu_H \sim T^{-\nu}$  dependences were determined (Fig. 4). The analysis of the obtained  $\nu$  values allowed us to identify the prevailing mechanisms of electron scattering in the samples.

For the stoichiometric  $\text{Bi}_2\text{Se}_3$  we obtained  $\nu = 0.8 \pm 0.1$ , which is consistent with the reported in the literature weakening of the  $\mu_H(T)$  dependence for degenerate statis-

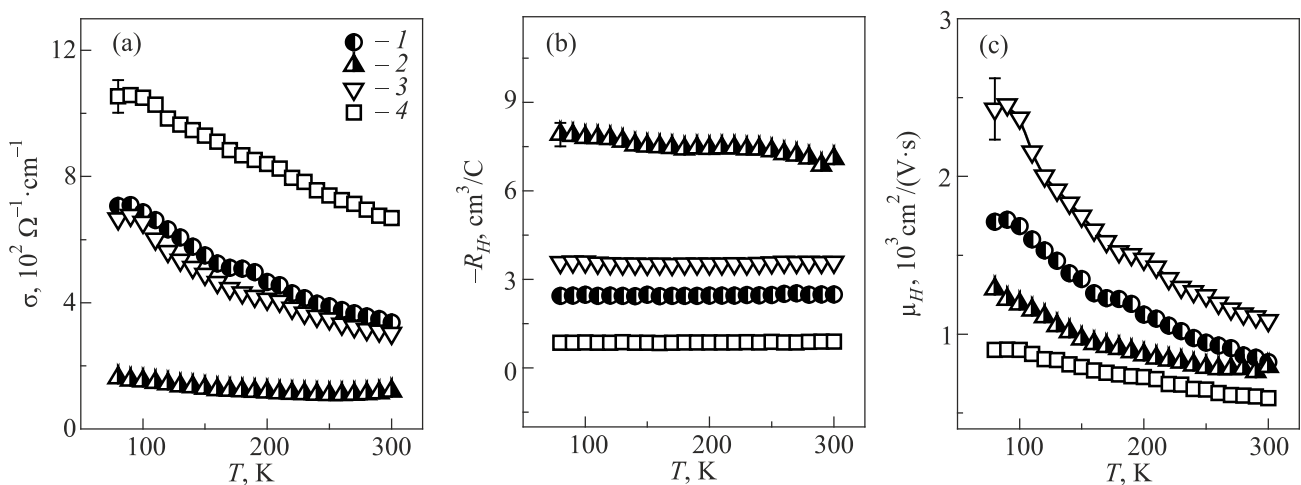


Fig. 3. Temperature dependences of electrical conductivity  $\sigma$  (a), Hall coefficient  $R_H$  (b) and charge carrier mobility  $\mu_H$  (c) of Bi–Se pressed crystals with Se content, at. %: 60.0 (1), 59.998 (2), 59.98 (3), 59.9 (4).

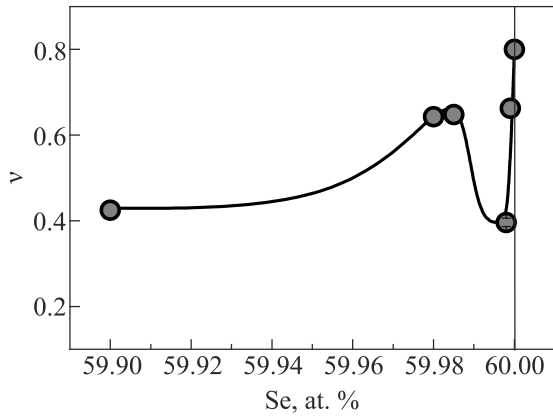


Fig. 4. The dependence of the exponent  $\nu$  in the temperature dependence of the electron mobility on Se content in the pressed Bi–Se crystals.

tics associated with the increasing role of impurity scattering [21]. For the crystal with Se concentration 59.998 at. % [this sample had the highest value of  $R_H$  and the lowest value of  $\sigma$ , Figs. 1(a) and 1(c)], the parameter  $\nu$  was the lowest  $\nu = 0.4 \pm 0.1$  among all the studied samples, which indicates a significant increase in the contribution of impurity scattering. It should also be noted that the positions of the extrema in the concentration dependence of  $\nu$  (Fig. 4) coincide with the positions of the extrema in the dependences of TE, GM, and mechanical properties of the samples (Fig. 1).

The isotherms of the properties of Bi–Se crystals in the vicinity of the  $\text{Bi}_2\text{Se}_3$ -compound were plotted. It should be noted that the non-monotonic, oscillatory behavior of the properties is preserved at 77 K. As an example in Fig. 5 the isotherms of  $\sigma$  of the Bi–Se pressed samples are shown.

Within the framework of a single-band model and in the relaxation time approximation, assuming a parabolic dispersion law, the Seebeck coefficient value can be expressed as [37]:

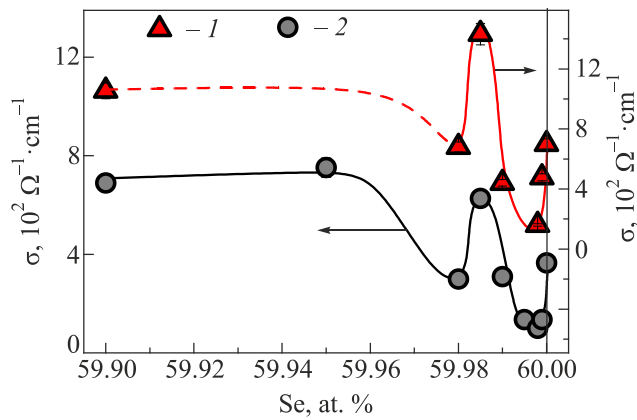


Fig. 5. The composition dependences of electrical conductivity  $\sigma$  in pressed Bi–Se crystals at 77 K (1) and 300 K (2).

$$S = \pm \frac{k_B}{e} \left[ \frac{\left( r + \frac{5}{2} \right) F_{r+\frac{3}{2}}(\eta)}{\left( r + \frac{3}{2} \right) F_{r+\frac{1}{2}}(\eta)} - \eta \right], \quad (1)$$

where  $k_B$  is the Boltzmann constant,  $e$  is the electron charge,

$F_i(\eta) = \int_0^\infty \frac{x^i dx}{1 + e^{x-\eta}}$  is the Fermi integral,  $\eta = E_F / (k_B T)$  is the

reduced Fermi energy,  $x = E / (k_B T)$  is the reduced energy,  $r$  is the scattering parameter. In this model the value of  $E_F$  is measured upward from the bottom of the conduction band (for  $n$ -type conduction) or downward from the top of the valence band (for  $p$ -type conduction). Using Eq. (1) and taking into account the experimentally measured values of  $S$ , as well as the fact following from the analysis of the  $\mu_H(T)$  dependence, that in the stoichiometric  $\text{Bi}_2\text{Se}_3$  crystal electrons are predominantly scattered by acoustic phonons (scattering parameter  $r = -1/2$  [37]), the value of  $E_F$  was calculated as 24 meV. A similar estimation of the Fermi energy yielded  $E_F = 62$  meV for the crystal containing 59.998 at. % Se, for which the contribution of impurity scattering is the largest (Fig. 4), and the value  $r = 3/2$  corresponding to scattering only by ionized impurities was taken into account [37]. Positive values of  $E_F$  for the stoichiometric  $\text{Bi}_2\text{Se}_3$  and for the crystal with a significant contribution of impurity scattering indicate that the Fermi level is located in the conduction band.

As was noted above [11–13], the conduction band of  $\text{Bi}_2\text{Se}_3$  consists of the two subbands. Taking into account that in the present work the value  $E_F$  for  $\text{Bi}_2\text{Se}_3$  (24 meV) was smaller than theoretical estimates of the distance between the conduction subbands [11, 12] one can conclude that the Fermi level is located between the bottom of the lower conduction subband and the bottom of the upper conduction subband. The result of the calculation of  $E_F$  indicates that both in the stoichiometric and non-stoichiometric  $\text{Bi}_2\text{Se}_3$ , the electrons in the upper subband practically do not take part in the conductivity process.

#### 4. Conclusions

The effect of the deviation from stoichiometry to the Bi-rich side 59.9–60.0 at. % Se on the galvanomagnetic, thermoelectric and mechanical properties of the cast and pressed  $\text{Bi}_2\text{Se}_3$  samples subjected to a long-term annealing at 670 K with subsequent cooling in the turned-off furnace in the temperature range 77–300 K was studied. The boundaries of the  $\text{Bi}_2\text{Se}_3$  homogeneity region were estimated.

The non-monotonic behavior of the composition-property dependences in the investigated temperature range was observed and attributed to a change in the defect structure and phase composition under the deviation from stoichiometry.

It was established that the samples of all compositions exhibited *n*-type conductivity in the entire temperature range (77–300 K). The values of  $\sigma$  and  $\mu_H$  decrease, and  $R_H$  practically does not change with temperature, which is typical of degenerate semiconductors. An analysis of the exponents in the temperature dependences of electron mobility showed that electron scattering by acoustic phonons prevails in the stoichiometric Bi<sub>2</sub>Se<sub>3</sub>, and under the deviation from stoichiometry the contribution of defect scattering increases.

The calculation of the Fermi energy within the framework of the single-band model with a parabolic dispersion law and in the approximation of the relaxation time showed that it is mainly electrons located in the lower conduction subband that take part in the conductivity of stoichiometric and non-stoichiometric Bi<sub>2</sub>Se<sub>3</sub>.

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## Вплив відхилення від стехіометрії на транспортні та механічні властивості полікристалів $\text{Bi}_2\text{Se}_3$

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Отримано залежності електропровідності, коефіцієнта Холла, коефіцієнта Зеєбека, термоелектричної потужності та мікротвердості полікристалів  $\text{Bi}_2\text{Se}_3$  від ступеня відхилення від стехіометрії 59.9–60.0 ат. % Se та температури (77–300 K). У досліджуваних діапазонах складів та температур зразки демонстрували провідність  $n$ -типу. Зроблено оцінку меж області гомогенності  $\text{Bi}_2\text{Se}_3$ . Встановлено, що концентраційні залежності властивостей у досліджуваному діапазоні складу мають немонотонний характер, який пов'язано зі зміною фазового складу та дефектної структури при відхиленні від стехіометрії.

Розрахунок величини степеневого параметра в температурній залежності рухливості електронів показав, що у стехіометричному  $\text{Bi}_2\text{Se}_3$  переважає розсіяння електронів на акустичних фонах, та за відхилення від стехіометрії зростає внесок домішкового розсіяння. На основі експериментальних даних у наближенні часу релаксації в межах однозонної моделі з квадратичним законом дисперсії розраховано енергію Фермі  $E_F$ . Отримані значення  $E_F$  показують, що як у стехіометричному, так і в нестехіометричному  $\text{Bi}_2\text{Se}_3$ , у провідності беруть участь переважно електрони, які знаходяться в нижній провідниковій зоні.

Ключові слова: селенід вісмуту, стехіометрія, транспортні властивості, дефектна структура.