The work was performed at the Institute of Physics of Azerbaijan National Academy of Sciences, laboratory "Resonance spectroscopy of ferromagnetic substances"

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GENERAL DESCRIPTION OF THE WORK

The actuality of work. Over the past 25-30 years, alloys (Bi-Sb) have found wide application in the creation of thermostatic elements of electronic devices and infrared radiation receivers.

In medicine and biology, semiconductor refrigerators have become widespread, allowing you to cool sections of organic tissues. On the basis of (Bi-Sb) alloys, thermoelectric devices for deep cooling are being developed, which are used in vacuum technology as traps for freezing oil vapors of steam-oil pumps, in installations for growing epitaxial layers of single crystals, in studies of high-temperature superconductivity, etc. In connection with the growing use of this material in science and technology, the relevance of research on alloys (Bi-Sb) is beyond doubt.

Alloying single-crystal alloys (Bi-Sb) with impurities in small doses (less than 0.5 at.%) from the fourth (Sn, Pb) or sixth (Se, Te) groups of the periodic table gives the alloys electrical conductivity, respectively, of the acceptor or donor types. Thus, on the basis of bismuth by varying the concentration of antimony and dopants, can be obtained a whole family of semiconductor single crystals for various fields of science and technology.

Crystals of semimetals of bismuth and antimony have a similar structure and under normal conditions crystallize in a rhombohedral lattice of the As type, which is a corrugated layer. In each layer, atoms are located in two parallel planes so that an atom of one plane has three nearest neighbors in the second plane and three neighbors at a great distance in an adjacent layer. Chemical bonds between double layers are weak - van der Waals, and in double layers - covalent. To describe the structure of crystals of the Bi type, in addition to the rhombohedral lattice, hexagonal and face-centered pseudocubic is used.

Since bismuth and antimony are electronic analogs, have the same type of chemical bond and crystal structure (the difference in atomic radii for Bi and Sb is ~ 7.5%), they form a continuous series of solid solutions. With an increase in the concentration of antimony, the type of crystal structure in the Bi-Sb system remains unchanged,

only the parameters of the unit cell change. When bismuth is doped with antimony, the band structure characteristic of bismuth changes. It is known that at antimony concentrations of 2–3 at. % there is a transition to a gapless state and an inversion of energy bands at the L-point of the Brillouin zone, and at antimony concentrations of 6–7 at.% - a semimetal-semiconductor phase transition. The authors observed anomalies on the concentration dependences of the galvanomagnetic and thermoelectric properties at the indicated compositions. For example, measurements of the unit cell parameters of Bi-Sb alloys in the concentration range 0 - 12.5 at.% Sb showed that at helium temperatures the concentration dependence of the parameter "c" is nonlinear.

It was noted that the observed deviations from Vegard's law are observed in the region of the transition of alloys from a semi-metallic to a semiconducting state, which, naturally, is reflected in the electronic spectra of Bi-Sb solid solutions. Note that the nature of the overlapping bands leading to the semi-metallic behavior for elementary Bi and Sb is different. The bands drastically change energy depending on the composition of the $Bi_{1-x}Sb_x$ alloy, and at values of "x" from 0.07 to 0.23, a real semiconductor is observed. In narrow-gap semiconductor compositions, the states of the valence band and the conduction band can be inverted in energy , surface states change, with the 111 or 001 basal plane having triple rotation symmetry and topological surface states crossing the Fermi energy an odd number of times. The Fermi surface for electrons in surface states is rather complicated, but the $Bi_{0.9}Sb_{0.1}$ composition turns out to be less than an ideal material for studying topological surface states. Accordingly, studies of the scattering mechanisms of charge carriers are becoming relevant. However, the analysis of galvanomagnetic phenomena in $Bi_{1-x}Sb_x$ alloys in order to obtain information on the mobility of charge carriers is hampered by the complex shape of isoenergetic surfaces.

Doping of semimetals, semiconductors and their solid solutions with donor and acceptor impurities is widely used to study the structure of the energy spectrum of carriers near the bottom of the conduction band and the top of the valence band, since by shifting

doping the Fermi level, it is possible to fill mainly either the electronic or hole states and thereby simplify calculations of zone parameters. However, such questions remain unclear to what extent the overlying energy valleys make themselves felt.

Note that, the doping of bismuth with an isovalent impurity with antimony in a wide concentration range is a convenient tool for studying phonon scattering by impurities, which can be compared with the effect of isotopic scattering, since bismuth occurs naturally in the form of a monoisotope and the atomic mass of bismuth is 1.7 times that of antimony. The low density of states in the valence band and in the conduction band of bismuth and its alloys with antimony makes it possible, when doped with other electrically active impurities, to significantly shift the Fermi level of charge carriers in energy, and thus to include in the transfer phenomena little studied, remote energy bands. In this case, studies of the mechanisms of scattering of charge and heat carriers in alloys with a complex multiextremum energy spectrum are of independent interest. Note that scientific publications on electronic processes of charge carriers in the region of intrinsic conductivity from different energy subbands are ambiguous.

Experimental research and practical application of bismuth, antimony and their alloys are facilitated by the manufacturability of materials: low melting points, developed methods of purification from impurities and the technique of growing perfect crystals.

Bismuth and its alloys with antimony have long found practical application as sensitive bolometers, strain gauges and magnetic field meters, in the creation of working elements for thermoelectric, thermomagnetic and anisotropic energy converters. It is interesting to note that scientific research on these alloys is still relevant. A group of scientists from the Moscow Institute of Physics and Technology (Russia), the University of Twente and the University of Amsterdam (the Netherlands) discovered the ability of one of the topological materials - non-conducting bismuth doped with antimony - to conduct a superconducting current inside its volume. Researchers at the Massachusetts Institute of Technology (USA) found that a thin film of $Bi_{1-x}Sb_x$ compound exhibits

characteristics that MIT professor Mildred Dresselhaus claims indicate that the electronic conductivity of these compounds has a property known as cones Dirac.

Priority experimental studies of the quantum size effect in the conductivity of thin films of bismuth, antimony and their alloys have been carried out, and the possibility of separating the contributions of the effects of weak localization and interaction has been shown. The relationship between the strong spin-orbit interaction and the potential gradient near the metal surface is revealed.

A number of experimental works indicated that both donor and acceptor impurities in (Bi-Sb) alloys are ionized even at the lowest temperatures, and impurity charge carriers simply fill the corresponding bands. However, this model contradicts the discovered nonmonotonic dependence of the resistance in compensated Bi crystals and the temperature dependence of the coefficient of carrier recoil by the impurity. Studies of the effect of dopants, which are often used to improve the parameters of devices, for example, refrigerators based on the Nerist-Ettingshausen effect, are also relevant. It should be noted that for the study in the case of bismuth materials, the scattering of electrons in the overlying valleys, and even more so the advancement of the Fermi level in them with an increase in the degree of doping, is most noticeable in galvanomagnetic studies. Therefore, it is very important to study the effects in n-$Bi_{1-x}Sb_x$ to reveal the role of additional energy valleys of electrons by the galvanomagnetic method.

Analysis of publications of theoretical and experimental works devoted to the study of Bi, Sb and Bi-Sb alloys, doped or not with impurities, made it possible to formulate the goal and objectives of this dissertation work.

Purpose and objectives of the study. The main purpose of the dissertation consists of studying the characteristics of the electronic structure and the process of scattering of charge carriers in single crystals of proper and doped (Sn, Te) homogeneous bismuth-antimony solid solutions and determining the effect of crystal structure distortion on luminescence spectra.

The following tasks were set to achieve this goal:

- Synthesis of homogeneous composition and perfect single crystals of $Bi_{1-x}Sb_x$ alloys;
- Synthesis of homogeneous composition and perfect single crystals of $Bi_{1-x}Sb_x$ alloys uniformly doped with tellurium and tin.
- Study of temperature dependences ($77K \leq T \leq 300K$) of galvanomagnetic effects of synthesized $Bi_{1-x}Sb_x$: Te, Sn solid solutions
- Study of photoluminescence spectra of synthesized $Bi_{1-x}Sb_x$: Te, Sn solid solutions

Research objects and methods: The following samples were taken as the object of research:

- $Bi_{1-x}Sb_x$ (x=0; 0.6; 0.8; 0.12; 0.16; 0.18; 0.20; 0.22; 0.25) single crystals;
- $Bi_{1-x}Sb_x$ single crystals doped with Sn,Te;

As research methods were used X-ray phase analysis, DSC method, LS-55 luminescence spectrometer and galvanomagnetic coefficient measuring device.

Main provisions for the defense.

1. In all compositions of solid solutions $Bi_{1-x}Sb_x$, in case $x \leq 15$at%, the electron density is concentrated in three ellipsoids, and for all alloys with x> 15at%, - in six ellipsoids of the Brillouin zone;
2. Electronic density, corresponding to the concentration of the hole, the maximum in the T and Γ-T valleys of the Brillouin zone;
3. The surface of the Fermi hole in $Bi_{1-x}Sb_x$ with $0,16 \leq x \leq 0,25$ represents the tremor of ellipsoids of the general type, presumably located at the point Σ Brillouin zone.
4. The angle of inclination of electronic ellipsoids decreases with increasing content of antimony in the composition of $0 \leq x \leq 0,25$ $Bi_{1-x}Sb_x$ alloys;
5. Ellipsoid holes in alloys $Bi_{1-x}Sb_x$ with $0,16 \leq x \leq 0,25$ are less anisotropic than ellipsoid holes in alloys with $0 \leq x \leq 0,16$.

6. Temperature dependence of electron concentrations, light and heavy holes, as well as energy levels Fermi in solid solutions $Bi_{1-x}Sb_x$, due to the redistribution of the hole between the zones of heavy and light holes, the zoning of the holes, the closing of the holes zones in the conduction zone.
7. Spectra of excitation and luminescence $Bi_{1-x}Sb_x$ of all compositions indicate on them in the vibrating structure corresponding to the cooperative effect of Yana-Teller

The scientific novelty of the research:

1. In all compositions of solid solutions $Bi_{1-x}Sb_x$, in case $x \leq 15$at%, the electron density is concentrated in three ellipsoids, and for all alloys with $x > 15$at%, - in six ellipsoids of the Brillouin zone;
2. Electronic density, corresponding to the concentration of the hole, the maximum in the T and Γ-T valleys of the Brillouin zone;
3. The angle of inclination of electronic ellipsoids decreases with increasing x in $0 \leq x \leq 0{,}25$ $Bi_{1-x}Sb_x$ alloys;
4. temperature dependence of electron concentrations, light and heavy holes, as well as Fermi level energy, conditioned by redistribution of the hole between the zones of heavy and light holes, overlaps of the hole T-zones with the electron zone, and also with heat flushes carriers from the valence zone to the conduction zone;
5. Spectra of excitation and luminescence in the visible and ultraviolet regions of the spectrum, cooperative pseudo-effect of Jahn-Teller.

The theoretical and practical significance of the research: Establishing the nature of the thermodynamic stability and behavior of the physical properties of a number of Bi-Sb metal systems, unalloyed and doped with tellurium and tin, is extremely important for increasing the thermoelectric efficiency of alloys of the bismuth-antimony system, including those doped with tellurium and tin impurities, which are already used in practical applications.

Approbation and implementation:

The main results of dissertation work were discussed at the following national and international conferences and seminars:

- İnternational conference “Large scale research projects-2012 Materials science and informatics for high tecnologies”Baku-09-12 November 2012;
- Materials of the VII Republican scientific conference "Actual problems of physics" Baku-November 26, 2012;
- University Science: Topical Issues, Achievements and Innovations, International Scientific and Practical Conference "Penza-30 September 2020;

Publications: The main results obtained in the dissertation were published in 13 articles (2 of them are inlcuded SCI list with impact factor) and in 3 conference materials

Name of the organization the Dissertation has been performed: The dissertation was carried out in the Laboratory of “Resonance spectroscopy of ferromagnetic substances” at the Institute of Physics named after H.M. Abdullayev of the National Academy of Sciences of Azerbaijan.

Volume, structure and the main content of the dissertation: The dissertation consists of 231552 symbols, including introduction, four chapters, 14 tables, 50 pictures and 190 references.

CONTENT OF WORK

In the introduction the importance of the dissertation subject was substantiated, the purpose of the work and main claims in the defence, and the scientific novelty and practical significance of the results were explained.

First chapter: In the first chapter was given description of the technology for the production of $Bi_{1-x}Sb_x$ alloys, which makes it possible to obtain from a solid-fed melt single crystals that are perfect in structure and homogeneous in composition, possessing significant segregation of components, as well as a technique for uniform doping of single crystals of Bi-Sb solid solutions with tellurium and tin in the process synthesis.

Second chapter: This chapter mainly focuses on the description of brief review and analysis of theoretical and experimental publications on the structure of electron shells, the Brillouin zone, electronic spectra and their features, their reflection in galvanomagnetic effects in $Bi_{1-x}Sb_x$ alloys, the role of the mechanism of scattering of charge carriers under all-round compression and temperature conditions.

A technique for measuring the temperature dependence of the galvanomagnetic properties of $Bi_{1-x}Sb_x$ alloys is described, and the results of measurements of galvanomagnetic coefficients with an antimony content of 0 - 0.25 at.% In the temperature range 77 - 300 K are presented, and the calculated and experimental results obtained are analyzed in detail. A technique for measuring the temperature dependence of the galvanomagnetic properties of $Bi_{1-x}Sb_x$ alloys was described, and the results of measurements of galvanomagnetic coefficients with an antimony content of 0 – 0,25 at.% in the temperature range 77 - 300 K are presented, and the calculated and experimental results are analyzed in detail.

At the beginning of the chapter, was considered the methodology for determining the twelve galvanomagnetic coefficients in a weak magnetic field depending on the relative orientation of the sample.

The calculation of the parameters of the energy spectrum of charge carriers in the alloys $Bi_{1-x}Sb_x$ was carried out within the framework of the model, teaching the results of galvanomagnetic experiments, as well as analysis of known publications, representing the surface of Fermi electrons in the form of three transitioning to another when turning on 120^0 ellipsoids of general type L- electron ellipsoids, slightly inclined in relation to the trigonal axis (L-electrons) and the surface of the Fermi hole - in the form of three ellipsoids L-hole, three ellipsoids Σ-hole and ellipsoids rotation T-hole. Within the framework of this model, assuming the independence of the deposits in the general current carriers of different grades, the components of the galvanomagnetic coefficients are determined by three components of the mobility of electrons (μ_1, μ_2, μ_3), three components of the mobility of holes (ν_1, ν_2, ν_3), the angle of inclination of electrons and hole ellipsoids φ_e, φ_d respectively, and the concentration of N_e, N_d, and finally, the two components of the mobility of the T-hole and their concentration $N_d^{'}$.

Within the framework of the selected model, the relationship between the parameters of the energy spectrum and galvanomagnetic coefficients has the following species:

$$\delta_{11,0} = \frac{N_{e\cdot e}}{2}(\mu_{1+}\alpha_1^2\mu_2 + \beta_1^2\mu_3) + \frac{N_{g\cdot e}}{2}(\nu_1 + \alpha_2^2\nu_2 + \beta_2^2\nu_3) + N_{g\cdot e}^{`}\nu_1^{`}$$

$$\delta_{33,0} = N_{e\cdot e}(\beta_1^2\mu_2 + \alpha_1^2\mu_3) + N_{g\cdot e}(\beta_2^2\nu_2 + \alpha_2^2\nu_3) + N_{g\cdot e}^{`}\nu_3^{`}$$

$$-\delta_{231} = -\frac{N_{e\cdot e}}{2c}[\mu_2\mu_3 + \mu_1(\beta_1^2\mu_2 + \alpha_1^2\mu_3)] + \frac{N_{g\cdot e}}{2c}[\nu_2\nu_3 + \nu_1(\beta_2^2\nu_2 + \alpha_2^2\nu_3)] +$$

$$+\frac{N_{g\cdot e}^{`}}{c}\nu_1^{`}\nu_3^{`}$$

$$-\delta_{123} = -\frac{N_{e\cdot e}}{c}[\mu_1(\alpha_1^2\mu_2 + \beta_1^2\mu_3)] + \frac{N_{g\cdot e}}{c}[\nu_1(\alpha_2^2\nu_2 + \beta_2^2\nu_3)] + \frac{N_{g\cdot e}^{`}}{c}\nu_1^{`2}$$

$$\delta_{11,11} = \frac{N_{e\cdot e}}{8c^2}[\beta_1^2\mu_2(\mu_1 - \mu_3)^2 + \alpha_1^2\mu_3(\mu_1 - \mu_2)^2 + 3\alpha_1^2\beta_1^2\mu_1(\mu_2 - \mu_3)^2] +$$

$$+\frac{N_{g\cdot e}}{8c^2}[\beta_2^2\nu_2(\nu_1 - \nu_3)^2 + \alpha_2^2\nu_3(\nu_1 - \nu_2)^2 + 3\alpha_2^2\beta_2^2\nu_1(\nu_2 - \nu_3)^2]$$

$$\delta_{11,22} = \frac{N_{e\cdot e}}{8c^2}[3\beta_1^2\mu_2(\mu_1^2 + \mu_3^2) + 3\alpha_1^2\mu_3(\mu_1^2 + \mu_2^2) + \alpha_1^2\beta_1^2\mu_1(\mu_2 - \mu_3)^2$$

$$+ 2\mu_1\mu_2\mu_3] +$$

$$+\frac{N_{g\cdot e}}{8c^2}[3\beta_2^2\nu_2(\nu_1^2 + \nu_3^2) + 3\alpha_2^2\nu_3(\nu_1^2 + \nu_2^2) + \alpha_2^2\beta_2^2\nu_1(\nu_2 - \nu_3)^2 +$$

$$2\nu_1\nu_2\nu_3] + \frac{N_{g\cdot e}^{`}}{c^2}\nu_1^{`2}\nu_3^{`}$$

$$\delta_{11,33} = \frac{N_{e\cdot e}}{2c^2}[(\mu_1 + \alpha_1^2\mu_2 + \beta_1^2\mu_3)\mu_1(\alpha_1^2\mu_2 + \beta_1^2\mu_3)] +$$
$$+\frac{N_{g\cdot e}}{2c^2}[(\nu_1 + \alpha_2^2\nu_2 + \beta_2^2\nu_3)\nu_1(\alpha_2^2\nu_2 + \beta_2^2\nu_3)] + \frac{\grave{N_{g\cdot e}}}{c^2}\grave{\nu_1}^3$$
$$\delta_{33,11} = \frac{N_{e\cdot e}}{2c^2}(\beta_1^2\mu_2 + \alpha_1^2\mu_3)[\mu_2\mu_3 + \mu_1(\beta_1^2\mu_2 + \alpha_1^2\mu_3)] +$$
$$+\frac{N_{g\cdot e}}{2c^2}(\beta_2^2\nu_2 + \alpha_2^2\nu_3)[\nu_2\nu_3 + \nu_1(\beta_2^2\nu_2 + \alpha_2^2\nu_3)] + \frac{\grave{N_{g\cdot e}}}{c^2}\grave{\nu_1}\grave{\nu_3}^2$$
$$\delta_{33,33} = \frac{N_{e\cdot e}}{c^2}\alpha_1^2\beta_1^2\mu_1(\mu_2 - \mu_3)^2 + \frac{N_{g\cdot e}}{c^2}\alpha_2^2\beta_2^2\nu_1(\nu_1 - \nu_3)^2$$
$$-\delta_{23,23} = \frac{N_{e\cdot e}}{2c^2}(\beta_1^2\mu_2 + \alpha_1^2\mu_3)[\mu_1(\alpha_1^2\mu_2 + \beta_1^2\mu_3)] +$$
$$+\frac{N_{g\cdot e}}{2c^2}(\beta_2^2\nu_2 + \alpha_2^2\nu_3)[\nu_1(\alpha_2^2\nu_2 + \beta_2^2\nu_3)] + \frac{\grave{N_{g\cdot e}}}{2c^2}\grave{\nu_1}^2\grave{\nu_3}$$
$$\delta_{22,23} = \frac{N_{e\cdot e}}{4c^2}\alpha_1\beta_1\mu_1(\mu_2 - \mu_3)(-\mu_1 + \alpha_1^2\mu_2 + \beta_1^2\mu_3) + \frac{N_{g\cdot e}}{4c^2}\alpha_2\beta_2\nu_1(\nu_2 - \nu_3)$$
$$(-\nu_1 + \alpha_2^2\nu_2 + \beta_2^2\nu_3)$$
$$\delta_{23,22} = \frac{N_{e\cdot e}}{4c^2}\alpha_1\beta_1(\mu_2 - \mu_3)[\mu_2\mu_3 - \mu_1(\beta_1^2\mu_2 + \alpha_1^2\mu_3)] +$$
$$+\frac{N_{g\cdot e}}{4c^2}\alpha_2\beta_2(\nu_2 - \nu_3)[\nu_2\nu_3 - \nu_1(\beta_2^2\nu_2 + \alpha_2^2\nu_3)]$$

where N-concentration of charge carriers, μ_i and ν_i -corresponding tensor components of the mobility of electrons and holes; α_1 ,β_1 and α_2 , β_2 cosines and sines angles of inclination of electrons and hole ellipsoids, respectively.

The selected model was used to interpret the results of the measurements of the dependence of the anisotropy of magneto-resistance in the weak and intermediate magnetic fields in the weak and intermediate magnetic fields.

Determining η from the equivalence of electron neutrality and comparing the results with the results of the calculations were obtained temperature dependence of the Hall coefficient, the temperature dependence of the Fermi ξ_F level, the concentration of electrons, lightp_L and heavy p_T holes and mass ratio.

Analysis of the obtained results allows to assume the following:

- The initial area of dependence ξ_F (T) is due to the redistribution of the hole between the zones of heavy and light holes. Then the level of Fermi grows with the increase of the overlap of the T-zone with the electron zone. Further

reduction is associated with an increase in the width of the restricted zone.

- In the area of the hole coverage of the hole T-zone with the electron zone, the concentration of electrons grows with the increase of their coverage at the initial section of the growth temperature. With further increase in temperature, the removal of the hole zone from the electron occurs. The further increase in the concentration of electrons is associated with the usual heat transfer of valence electrons in the conduction band.
- The concentration of light holes initially increases in the temperature range, where the gap at point L decreases. Then it falls due to the removal of the hole zone from the electron. The farthest growth concentration is caused by the heat transfer of electrons from the valence band into the conduction band.
- The concentration of heavy holes first grows with the increase of the overlap of the T-zone with the electron. Then it falls due to separation of electronic and hole zones. The farthest growth occurs due to the usual heat dissipation of electrons of the valence band to the conduction band.

Thus, in $Bi_{1-x}Sb_x$ (x = 0.06; 0.12) quantitative calculations of the temperature dependence of the Holl coefficient allowed to establish the mechanism of growth of charge carriers concentrations and the temperature dependence of ratio of their effective masses.

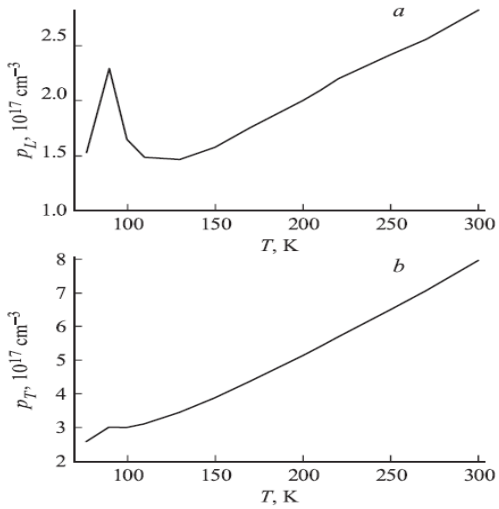

Figure 1.Temperatures dependence of concentrations of light (a) and heavy (b) holes in $Bi_{0,94}Sb_{0,06}$[1]

Third chapter: This chapter was dedicated to the results of the study of galvanomagnetic coefficients in $Bi_{1-x}Sb_x$ alloys doped with tin and tellurium in the temperature range of 77÷300K and the results obtained from calculations and experiments which analyzed in detail. The temperature dependences of the Hall coefficient and the specific resistance are established in $Bi_{0.88}Sb_{0.12}$-0,1at. % Sn, $Bi_{0.88}Sb_{0.12}$-0,01at. %Sn alloys.

In contrast to the non alloyed samples the dependence of specific resistance, and the Hall coefficient, carry a non-monotonous character. Such dependencies are also characteristic for ordinary proper semiconductors. At the low temperatures, the main role in conduction played by the holes, the concentration of which remains practically constant, and the mobility decreases with temperature. This is accompanied by an increase in specific resistance to a certain temperature. With a further increase in temperature, the generation of

[1] Таиров, Б.А., Гасанова, Х.А., Селим– Заде, Р.С. Температурная зависимость коэффициента Холла в системе $Bi_{1-x}Sb_x$ (x=0.06, 0.12) //–Россия: Физика и Техника Полупроводников,–2016. т.50, №8,–с.1016–1020.

electrons and holes begins, while in the semi-metal, in contrast to the semiconductor, there is an simultaneous increase in the overlap of the zone.A change in the concentration and especially the generation of light electrons leads to a decrease in the resistivity. The maximum on the resistivity dependences shifts towards higher temperatures, with increasing in the concentration of impurities, similar to the shift of the intrinsic conductivity region in semiconductors. Here, as before, it should be noted that from the change in the resistivity with temperature, it is impossible to determine the band gap like conventional semiconductors, since it is a function of temperature. The temperature change in the Hall coefficient is explained in a similar way. At low temperatures, the Hall coefficient is determined by holes and has a positive sign; as the temperature rises, electrons with higher mobility come into play, and as their concentration increases, the Hall coefficient decreases.

As with p-type semiconductors, before a specific region has yet been reached,

$$n_e\mu_e^2 = n_d\mu_d^2$$

when this condition is satisfied, the Hall coefficient becomes zero. Then, with the further increase in temperature already in its own area, the Holl coefficient achieves the maximum negative value corresponding to the ratio of electrons to the hole, which, of course, increases the concentration of growth, account of the increase in the relative share of electronic investment. At low temperatures up to 100K, the Hall coefficient grows with temperature, which is explained by the presence of holes in the two varieties. However, the above explanation remains in force and in that case, if under the vision of the hole to understand their average value for two zones.

Comparison of the data shows that with an increase in the tin content, all the components of the magnetoresistance strongly decrease, which, naturally, is explained by an increase in the scattering of charge carriers and a change in their effective masses upon doping and a corresponding decrease in mobilities, which, is known, as determine the magnitude of the magnetoresistance. Note that, nevertheless, the electrical conductivity changes much less,

which is associated with a simultaneous increase in the concentration of charge carriers.

The values of the components of mobilities and concentrations of charge carriers for three La, Ls, T bands, according to the models of the Fermi surface for $Bi_{0.88}$ $Sb_{0.12}$ single crystals, doped with tin to varying degrees. When analyzing the obtained values of the kinetic parameters, first of all, it should be noted that even with the maximum doping with tin, the "single-band" state is not achieved. Note that with a tin content of 0.3 at.%, the electron concentration is more than three orders of magnitude lower than the hole concentration. However, due to the relative increase in their mobility, even this number of electrons plays an essential role in galvanomagnetic phenomena. Thus, without taking into account the electronic component, it is impossible to explain the significant relative values of the magnetoresistance components.

The next interesting fact is that, like undoped alloys, in alloys with different tin contents, the concentration of holes at the extremum T remains 8-10 times higher than the concentration of holes at the extremum L, despite the fact that, according to the scheme for changing the energy spectrum in alloys, bismuth - antimony, the level of the extremum L lies higher on the energy scale than the level of the extremum T. Thus, the transition to the state of "single-band" in $Bi_{0.88}$ $Sb_{0.12}$ alloys, by alloying this alloy with tin, turns out to be even less accessible than in bismuth. From the scheme of rearrangement of the energy spectrum of charge carriers of the Bi_{1-x} Sb_x alloy on the concentration of antimony for semiconductor alloys with a composition of $0.15<x<0.22$, it follows that the minimum energy gap is determined by the terms L_a and Σ. However, in undoped alloys, the contribution of La electrons to galvanomagnetic effects is so great that it is impossible to study the structure of the valence band. Therefore, by selecting the antimony content from the above range and the concentration of the tin dopant, one can obtain "single-band" Bi_{1-x} Sb_x alloys, in which only holes in the Σ band in the impurity conduction region are charge carriers.

The next interesting fact is that, like undoped alloys, in alloys with different tin contents, the concentration of holes at the extremum

T remains 8-10 times higher than the concentration of holes at the extremum L, despite the fact that, according to the scheme for changing the energy spectrum in alloys, bismuth -antimony, the level of the extremum L lies higher on the energy scale than the level of the extremum T. Thus, the transition to the state of "single-band" in $Bi_{0.88}$ $Sb_{0.12}$ alloys, by alloying this alloy with tin, turns out to be even less accessible than in bismuth. From the scheme of rearrangement of the energy spectrum of charge carriers of the Bi_{1-x} Sb_x alloy on the concentration of antimony for semiconductor alloys with a composition of $0.15<x<0.22$, it follows that the minimum energy gap is determined by the terms La and Σ. However, in undoped alloys, the contribution of La electrons to galvanomagnetic effects is so great that it is impossible to study the structure of the valence band. Therefore, by selecting the antimony content from the above range and the concentration of the tin dopant, one can obtain "single-band" Bi_{1-x} Sb_x alloys, in which only holes in the Σ band in the impurity conduction region are charge carriers.

Have seted the temperature dependence of specific resistance, Holl coefficients and magnetoresistance coefficients for alloys $Bi_{0,88}Sb_{0,12}$, alloyed with tellurium. For alloys $Bi_{0,88}Sb_{0,12}$ -0,01 at.% Te the resistance of the alloy grows monotonically with temperature, and the temperature dependence of the coefficients and m magnetoresistance has a maximum, corresponding to 190K, uniform for the coefficient. In the alloy $Bi_{0,88}Sb_{0,12}$-0,2 at.% Te these coefficients grow monotonically with temperature.[2] Compositions containing more than 0.1 at.% have one type of charge carriers in the entire temperature range. Of particular interest is the unusual movement of the coefficients of Hall and magnetoresistance. Analogous temperature dependence R was observed in other semiconductors with n-type conductors. In the case of the presence of quasi-local levels located in the conduction zone, they, beginning with a certain temperature, play the role of traps for charge carriers. At this concentration of carriers with growth the temperature decreases, R and $\Delta\rho/H^2$ grow with temperature, and when

[2] Гасанова, Х.А., Таиров, Б.А. Факторы Холла и магнитосапративление многокристалического сплава $Bi_{0,88}Sb_{0,12}$ легированным Te // Физика низких температур, –2015. т.41, №4, –с.389–392.

achieving energy, sufficient for ionization of these quasilocallic states, the concentration grows again, and, consequently, R and $\Delta\rho/H^2$ increase. A characteristic feature of quasilocal impurity levels is that when the Fermi level reaches an energy corresponding to quasilocal levels or a band of quasilocal states, the concentration should stabilize, i.e. further introduction of impurities or an increase in temperature should lead to an increase in the concentration of free electrons, and the Fermi level should stabilize near the quasi-local level. However, in our experiments, the electron concentration varies in a wide range (10^{16}-10^{20} sm^{-3}). Therefore, to explain the temperature dependences of the Hall coefficients and magnetoresistance, it is necessary to take into account the influence of the overlying subband. In the presence of an overlying subband, with increasing concentration, when the Fermi level reaches the value of the energy gap between the minima of the conduction band, i.e. falls into the overlying subband, in which the carriers have a large effective mass and, therefore, a lower mobility, heavy electrons make a relatively small contribution to ρ_{ijk}və $\rho_{ij,kl}$, and, as the electrons move to the second zone, the effective concentration decreases, and the Hall coefficients and the magnetoresistance increases.

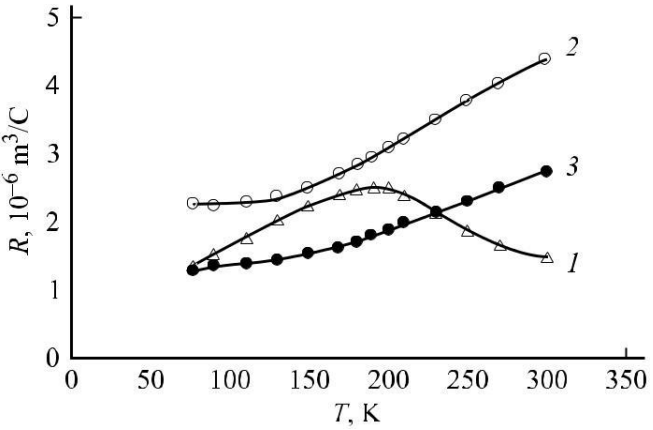

Figure 2. Temperature dependences of the Hall coefficient *1* — $Bi_{0.88}Sb_{0.12}$+0.01 at% Te, *2* — $Bi_{0.88}Sb_{0.12}$+0.1 at% Te, *3* — $Bi_{0.88}Sb_{0.12}$+0.2 at% Te.

Chapter 4 The fourth chapter of the dissertation was devoted to the results of studies of $Bi_{1-x}Sb_x$ luminescence, analysis of features and interpretation of luminescence spectra, based on models that take into account the distortion of the crystal lattice along the trigonal axis, the cooperative pseudo-Jahn-Teller effect and vibronic interaction.

The photoluminescence spectra of $Bi_{0.97}Sb_{0.03}$, $Bi_{0.88}Sb_{0.12}$ and $Bi_{0.85}Sb_{0.15}$ alloys were presented at the temperature of 300 K in the range from 250 nm to 650 nm of the spectrum. The analysis of the spectra is carried out by decomposition into Lorentz Gaussian components. Photoluminescence spectra were studied on LS-55 spectrometer (Perkin-Elmler) at room temperature in the wavelength range 300–700 nm at excitation from radiation 150W xenon source: 237 nm (5.23 eV), 285 nm (4.35 eV), 298 nm (4.16eV), 337nm (3.678eV), 377nm (3.288eV), 423nm (2.93eV). The accuracy of setting the wavelength is ± 1.0 nm, the reproducibility of the setting of the wavelength is ± 0.5 nm.

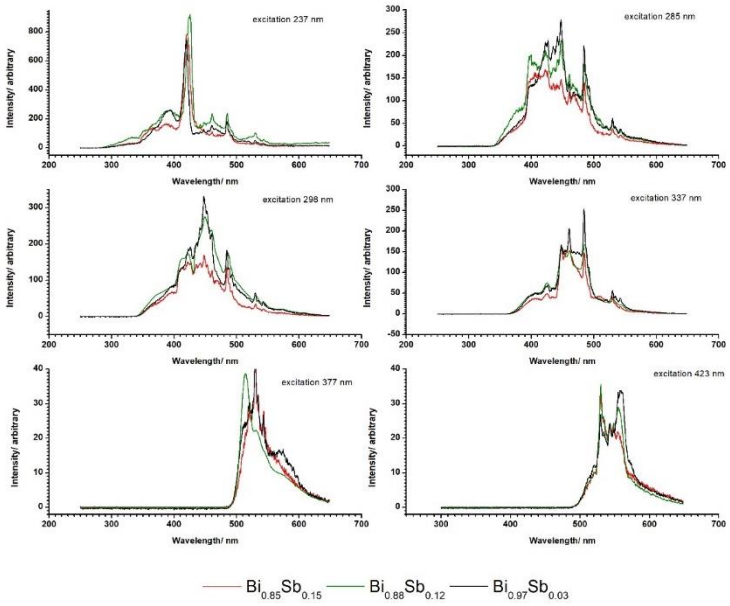

Figure 3. Luminescence spectra of $Bi_{1-x}Sb_x$ alloys

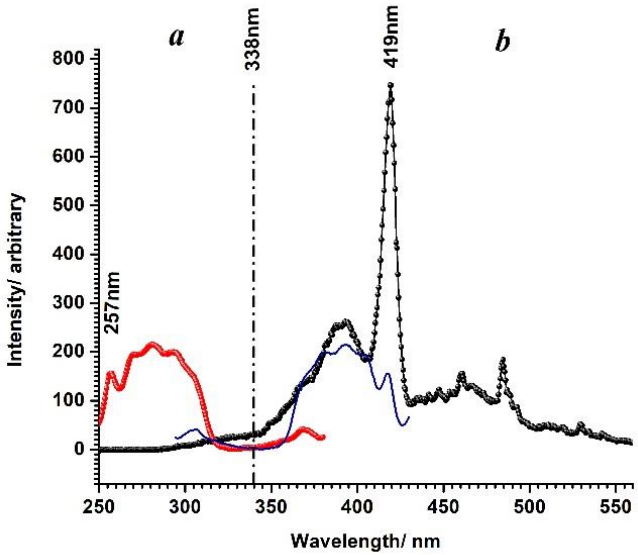

Figure 4. Spectrum of excitement (a) and luminescence (b) of $Bi_{0.97}Sb_{0.03}$ compound (semi-metallic state)

We must note that the formation of spectral bands, indicating the phase transition to the semi-metallic behavior for elementary Bi and Sb, and their compounds are different. Experimental studies of bismuth-containing materials have shown that blue luminescence (≈400-500nm) arise in an electronic transition of $^3P_1 \rightarrow {}^1S_0$ between energy levels of Bi^{3+} ions. However, the formation of red luminescence is associated with the Bi^{2+} ion and the $^2P_{3/2}(1) \rightarrow {}^2P_{1/2}$ transition.

Comparison of the energies of electronic transitions obtained from experimental photoluminescence spectra for the $Bi_{0.97}Sb_{0.03}$, $Bi_{0.88}Sb_{0.12}$ and $Bi_{0.85}Sb_{0.15}$ alloys at a temperature of 300K in the range from 250nm to 650nm and theoretical calculations of the band structure by the pseudopotential method, in which, In order to establish reliable energy spectra, the fitting of the Bi and Sb pseudopotentials to the experimentally investigated optical absorption spectra was used, showed, in the first approximation, good agreement between them.

In most studies of the luminescence of inorganic compounds doped with bismuth impurities, the main attention was paid to intraconfigurational d-d transitions with charge transfer. Intraconfigurational p-p junctions have hardly been studied due to the absence of stable ions with a partially filled p shell. The luminescence of dopants $6s^26p^1$ Tl^0, Pb^+, and Bi^{2+} was explained by the p-p transition. Due to the spin-orbit coupling, there are two states in the $6s^26p^1$ (Bi^{2+}) electronic configuration: the ground state $^2P_{1/2}$ and the excited state $^2P_{3/2}$. The excited state is divided into two energy levels: $^2P_{3/2}$ (1) and $^2P_{3/2}$ (2), if the ion is in a place with low symmetry coordination. Since the spin-orbit coupling strongly increases with the atomic number, p-p junctions in heavy elements are in the visible and near infrared regions of the spectrum.

In Table 1, the luminescence maxima corresponding to the pseudopotential calculations of the band structures of bismuth and antimony are highlighted in red. However, as expected, the photoluminescence spectra of $Bi_{0.97}Sb_{0.03}$, $Bi_{0.88}Sb_{0.12}$ and $Bi_{0.85}Sb_{0.15}$ have a more complex picture of transitions, luminescence related to the "blue" (400-500) nm and "red" (590-640) nm spectral bands, as well as their overlaps.[3] The observed picture of electronic transitions is significantly complicated by the fact that bismuth and antimony belong to the series of heavy p-elements, like Sn, Pb and Te, which exhibit in some of their compounds (for example, $Bi_{1-x}Sb_x$) a valence two units less than the group number. This phenomenon, called the effect of inert pairs, is structurally observed in the distortions of the coordination environment of metal ions. The trivalent ions Bi^{3+} and Sb^{3+} have electronic coordination [Xe] 4f145d106s2 and [Kr] 4d105s2, that is, the 6s2 pair becomes "stereochemically active" due to the fact that it is not in a spherical orbital, displaces asymmetrically relative to the center of the ion (similar to what happens when the formation of a hybridized sp-orbital). As a result, various types of structure distortions may occur. On the other hand, the analysis of data on the radii of antimony and bismuth ions, it is easy to notice a big difference between them.

[3] Mehdiyev, T.R., Gasanova, Kh. A. Absorption and luminescence in $Bi_{1-x}Sb_x$ alloys // –Baku:Azerbaijan Journal of Physics, –2019, 25(4), –p.14–21

As a consequence, the resulting geometric distortions of the structure of the $Bi_{1-x}Sb_x$ compositions relative to the pure initial components should lead to a decrease in symmetry, splitting of degenerate states, that is, to the Jahn-Teller effect, or the need to take into account vibronic interactions. Note that a complete classification of possible point groups of crystals subjected to Jahn-Teller deformations is given in the work. To describe the Jahn-Teller (or vibronic) interactions of electrons with nuclei, one often resorts to the formalism of potential energy surfaces.

In fig. 4 shows the excitation (a) and luminescence (b) spectra of $Bi_{0.97}Sb_{0.03}$ (semi-metallic state). The maximum of the 257 nm spectral line of the excitation spectrum, according to the Levshin mirror symmetry principle, corresponds to the maximum of 419 nm luminescence relative to the 338 nm mark. Mirror-inverted relative to the mark, the excitation spectrum (indicated in blue) is aligned with the luminescence spectrum. If we assume that the maximum at 257 nm (4.82 eV) corresponds to the $^1S_0 \rightarrow {}^1P_1$ transition in Bi^{3+}, then the $^3P_1 \rightarrow {}^1S_0$ transition, corresponding in this case to the maximum at 419 nm (2.96 eV) of the luminescence spectrum, should, according to pseudopotential calculations of the band structure of bismuth, occur on the line symmetry $L_s \rightarrow L_a$. The observed Stokes shift is 261 nm. Note, however, that the $^3P_1 \rightarrow {}^1S_0$ transition is observed not only in all $Bi_{1-x}Sb_x$ compositions, but also in the luminescence spectra upon excitation by 298nm (4.16eV) and 337nm (3.678eV) radiation. The latter turns out to be explainable, since the luminescence spectrum of $Bi_{0.97}Sb_{0.03}$ exhibits similar but low-intensity structures, which are confirmed by excitation at 285nm (4.35eV), 298nm (4.16eV), and 337nm (3.678eV). (see fig.4a). The sequence of their arrangement from each other corresponds to: 190 meV between 1-2 spectra; 80 meV between 2-3 spectra (or 270 meV between 1-3 spectra), which are close in terms of vibrational frequencies, and may well indicate the presence of cooperative PJT, the Jones-Peierls transition. A similar structure is observed in the spectra of $Bi_{1-x}Sb_x$ at excitations of 377nm and 423nm, and the luminescence spectra for all investigated compositions are outwardly similar. In the luminescence spectra of $Bi_{1-x}Sb_x$, it is easy to see how the overlap of the luminescence spectra of Bi and Sb changes.

However, if the presence of "blue" luminescence in $Bi_{1-x}Sb_x$ was not in doubt, then the presence of a weak "red" luminescence is possible only when Bi or Sb are in bivalent states. Of course, one can assume the existence of low concentrations of defect or impurity centers of bivalent ions Bi^{2+} and Sb^{2+}, especially since, as can be seen from Table 1, for this one can choose the appropriate transitions. However, the purpose of these studies was only the task of detecting the cooperative effect of PJT in $Bi_{1-x}Sb_x$. Oddly enough, but in scientific publications information on the luminescence associated with electronic transitions in the ultraviolet and visible spectra of $Bi_{1-x}Sb_x$ alloys is practically absent. Table 1 lists all the electron transitions experimentally observed in the luminescence spectra.

Comparison of electronic transitions found in the spectra of luminescence alloys $Bi_{0.85}Sb_{0.15}$,$Bi_{0.97}Sb_{0.03}$, $Bi_{0.88}Sb_{0.12}$ at the temperature of 300K in the range from 250nm to 650nm with theoretical calculations by pseudo-method

Accounting		$Bi_{0.85}Sb_{0.15}$	$Bi_{0.88}Sb_{0.12}$	$Bi_{0.97}Sb_{0.03}$
[4]	[5]	624,6		
		603,7	606,2	
		587,7	597,2	
		571,9	571,7	573,2
		565,4		568,2
		553,7		558,2
		549		549,0
		543,3	543,9	542,7
		534,8		534,6
		530,2	530,8	530
		519,6	519,8	520,3
		512,6	513,5	513,6
498,6	496,6	503	502,3	
492,7		491,6	491,9	491,9
		484,7	485,3	485,4
		469,1	466,8	467,6
		460,9	460,9	460,9
		446,6	448,4	447,8
		439,4	442,2	435,8
		428,9	425,5	426
420,6		421,4	423,3	419,3
	417,8	410,6	408,5	409,3
		397,2	395,5	396
387,7	371,4	382,2	377,5	384,9
362,7	362,7	364,4	366,4	372,7
343,5	346,4	349,6	353,5	350,0
			334,5	332,6

[4] Абрикосов А.А., Фальковский Л.А. Теория электронного энергетического спектра металла с решеткой висмута // ЖЭТФ, 1962, т.43, с.1089-1101

[5] Абрикосов А.А. Диэлектрическая проницаемость металлов типа висмута в инфракрасной области // ЖЭТФ, 1963, т.44, №6, с.2039-2057

MAIN RESULTS PRESENTED FOR DEFENCE

1. In all compositions of $Bi_{1-x}Sb_x$ solid solutions, in which $x \leq 15$at%, the electron density is concentrated in three ellipsoids, and for all alloys with x> 15at%, - in the six ellipsoids of the Brillouin zone. Electronic density corresponding to the hole concentration, maximum in the T and Γ-T valleys of the Brillouin zone;
2. The surface of the Fermi hole in $Bi_{1-x}Sb_x$ with $0{,}16 \leq x \leq 0{,}25$ represents with the ellipsoids of the general type, presumably located at the point Σ Brillouin zone. The angle of inclination of electronic ellipsoids decreases with an increase in the content of antimony in the composition of $0 \leq x \leq 0{,}25$ $Bi_{1-x}Sb_x$ alloys. Ellipsoid holes in alloys $Bi_{1-x}Sb_x$ with $0{,}16 \leq x \leq 0{,}25$ are less anisotropic than ellipsoid holes in alloys with $0 \leq x \leq 0{,}16$.
3. Temperature dependence of electron concentrations in light and heavy holes, as well as Fermi energy levels in solid solutions of $Bi_{1-x}Sb_x$, is due to the redistribution of the hole between the zones of heavy and light holes, conductivity zone.
4. The initial area of dependence ξ_F (T) is due to the redistribution of the hole between the zones of heavy (T-point ZB) and light (L-point ZB) hole. With the increase in the coverage of the T-zone with the electronic zone, the level of Fermi grows. The maximum recovery is associated with the competitive process of increasing the width of the restricted zone.
5. At the initial section of the growth temperature, in the area of the overlap of the hole T-zone with the electron zone, the concentration of electrons grows. Further, as the temperature of the hole zone increases, the electron is removed, and finally, an increase in the concentration of electrons will occur as a result of the usual heat transfer of valence electrons in the conduction band.
6. At the initial point of growth, the temperature, the concentration of light holes increases, the gap at point L

decreases, and then falls due to the removal of the hole from the electron zone. The farthest growth of the concentration caused by the heat transfer of electrons from the valence band into the conduction band.

7. The effect of distortion of the crystalline structure of homogeneous Bi-Sb solid solutions is observed in the spectra of luminescence mixing of maxima and cleavage, which is the result of detailed research and use of the device.
8. The mixing of the luminescence spectra occurs on the other side of the lower energy, which corresponds to an increase in the concentration of Bi^{+2} ions.
9. Spectra of excitation and luminescence of $Bi_{1-x}Sb_x$ of all compositions indicate on their vibrational structure corresponding to the cooperative effect of Jahn-Teller

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