GALVANOMAGNETIC EFFECTS IN STRONGLY DOPED p-Bi$_2$Te$_3$:Sn CRYSTALS

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ABSTRACT

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Magnetic field dependencies of Hall coefficient and magnetoresistivity are investigated in classical and quantizing magnetic fields in p-Bi₂Te₃ crystals heavily doped with Sn grown by Czochralsky method. Magnetic field was parallel to the trigonal axis C₃. Shubnikov-de Haas effect and quantum oscillations of the Hall coefficient were measured at temperatures 4.2 K and 11 K. On the basis of the magnetic field dependence of the Hall coefficient a method of estimation of the Hall factor and Hall mobility using the Drabble-Wolf six ellipsoid model is proposed. Shubnikov-de Haas effect and quantum oscillations of the Hall coefficient were observed at 4.2 K and 11 K. New evidence for the existence of the narrow band of Sn impurity states was shown. This band is partly filled by electrons and it is overlapping with the valence states of the light holes. Parameters of the impurity states, their energy $E_{Sn} \approx 15$ meV, band broadening $\Gamma \ll k_0 T$ and localization radius of the impurity state $R \approx 30$ Å were obtained.
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Denis Dvornik
Publications

Experimental results have been published in following article and seminar.

1. *Quasi-local states of Sn in Bi$_2$Te$_3$ according to the studies of galvanomagnetic effects in classical and quantizing magnetic fields.* Semiconductors. Vol. 41, 5, pp. 546-549.

2. *Galvanomagnetic effects in strongly doped p-Bi$_2$Te$_3$:Sn crystals in classical magnetic fields.* 14$^{th}$ of November 2006 during X Intergovernmental Seminar "Thermoelectrics", IPTI, Saint-Petersburg, Russia.
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Symbols and abbreviations

\[ SdH \quad \text{Shubnikov-de Haas} \]
\[ DW \quad \text{Drabble-Wolfe} \]
\[ LL \quad \text{Landau levels} \]
\[ \rho_{xx} \quad \text{magnetoresistance} \]
\[ R_{\text{Hall}} \quad \text{the Hall coefficient} \]
\[ B \quad \text{magnetic field (inductance)} \]
\[ I \quad \text{electric current} \]
\[ U \quad \text{voltage} \]
\[ e \quad \text{electron charge} \]
\[ h \quad \text{Plank constant} \]
\[ T \quad \text{temperature} \]
\[ \mu \quad \text{hole mobility} \]
\[ f_{||} \quad \text{Hall factor} \]
\[ k_B \quad \text{Boltzmann constant} \]
\[ \omega_c \quad \text{cyclotron frequency} \]
\[ T_D \quad \text{Dingle temperature} \]
\[ E_F \quad \text{Fermi level} \]
\[ E_a \quad \text{impurity level} \]
\[ m_c \quad \text{cyclotron mass} \]
\[ J \quad \text{electric current density} \]
\[ p \quad \text{hole concentration} \]
\[ \Delta_{sdl} \quad \text{period of Shubnikov-de Haas oscillations} \]
1. Introduction

Thermoelectricity is widely used in modern technics. Searching for high-efficient thermoelectric materials remains an actual problem nowadays. Among many of thermoelectric materials one of the most popular is bismuth telluride and solid solutions on its base. Doping with Sn extensively increases the electrical homogeneity of Bi$_2$Te$_3$ crystals with explanation in various interpretations of resonance states model (V.A. Kulbachinskii, M.K. Zhitinskaya).

This work is devoted to the experimental test of these models. Investigation of galvanomagnetic effects in classical and quantizing magnetic fields has been chosen. The results obtained strongly confirm the existence of the resonance quasi-local impurity states in p-Bi$_2$Te$_3$:Sn.
1.1. Physicochemical properties of bismuth telluride

1.1.1. Crystal structure of bismuth telluride

Bismuth telluride (Bi₂Te₃) has trigonal crystal structure with spatial group $D_{3d}^5(R\overline{3}m)$ [1]. Parameters of rhombohedral elementary cell at 300 K are given [2] (see Fig.1.1 and Appendix 1)

$$a_R = 10.477 \, \text{Å}, \quad \alpha_R = 24^\circ 9' 32''$$ (1.1)

The Bi₂Te₃ structure is described using hexagonal low-level cell, but in the case of the simple hexagonal Bravais lattice the hexagonal close-packed crystal structure has to be used (see Figs.1.2, 1.3 and 1.4). Parameters of this structure are connected to $a_R$ and $\alpha_R$ by

$$a = 2a_R \sin \frac{\alpha_R}{2} = 4.3835 \, \text{Å}$$ (1.2)

$$c = \sqrt{3}a_R (1 + 2 \cos \alpha_R)^{1/2} = 30.487 \, \text{Å}.$$ (1.3)

Fig 1.1 Rhombohedral elementary cell [3].
Fig. 1.2 The simple hexagonal Bravais lattice [4].

Fig. 1.3 The hexagonal close-packed crystal structure [4].
Fig. 1.4. Crystal structure of Bi$_2$Te$_3$ [5].
1.1.2. Crystal structure of Bi₂Te₃

Structure of Bi₂Te₃ can be presented in the form of complex layers, with name quintets, which are perpendicular to triad axis (axis $C_3$ in hexagonal lattice). In hexagonal unit cell exist three quintets (the number of atoms in low-level hexagonal cell is equal to fifteen). Each quintet consists of five primitive layers (Fig. 1.5).

Fig. 1.5. Atomic arrangement in the lattice quintet [3]

Atoms in one layer are identical and form hexagonal lattice in plane. Layers compose the sequence $\text{Te}^{(1)}-\text{Bi}-\text{Te}^{(2)}-\text{Bi}-\text{Te}^{(1)}$. The atoms of each subsequent layer are located above the centers of the triangles formed by the atoms of the previous layer (the hexagonal close packing).

Layer-like Bi₂Te₃ structure lead to easy chip off along the planes (0001). Te$^{(2)}$ atoms have as the nearest neighbors six Bi atoms (three from each adjoining a layer). On one hand the Te$^{(1)}$ atoms are connected with three Bi atoms and on another hand - with three Te$^{(1)}$ atoms. As a result, two completely different places for tellurium atoms are available in the lattice. Atoms of Bi have three neighboring Te$^{(2)}$ and three Te$^{(1)}$ atoms, correspondingly.

The bond length and angles between the bonds is presented in the Table 1.1 and in Fig. 1.6 [6].
The atoms of Te\textsuperscript{(2)} are surrounded by atoms of Bi by almost regular octahedral. The angles between these bonds differ approximately on 4.5° from the angles inherent to the right octahedral symmetry. Atoms of Bi are coordinated in a lattice approximately in the octahedral order while coordination of Te\textsuperscript{(1)} atoms remains asymmetrical.

Table 1.1. Bond length and angles between bonds in Bi\textsubscript{2}Te\textsubscript{3} [3]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance, Å</th>
<th>Angles between bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi — Te\textsuperscript{(2)}</td>
<td>3.22</td>
<td>85°30'</td>
</tr>
<tr>
<td>Bi — Te\textsuperscript{(1)}</td>
<td>3.12</td>
<td>89°20'</td>
</tr>
<tr>
<td>Te\textsuperscript{(1)} — Te\textsuperscript{(1)}</td>
<td>3.57</td>
<td>75°42'</td>
</tr>
</tbody>
</table>

The symmetry group of bismuth telluride \(D_{3d}\) contains following symmetry elements:

1) one of triad axis \(C_3\) (in a direction of the longest main diagonal of the rhombohedral cell);
2) three reflecting plane \(\sigma_y\) containing the triad axis;
3) three twofold axis, perpendicular to triad axis, having angle to the reflecting plane \(\sigma_y\);
4) the center of inversion \(I\).
1.1.3. Energy band structure of Bi$_2$Te$_3$

Information about the band structure of semiconductors is important for full explanation of physical properties of materials and also for direct practical applications, for example designing of semiconductor devices and improvement of their properties. Our understanding of physical properties of bismuth telluride and solid solutions on its basis, despite of the intensive studying during last years, has not reached the level of germanium, silicon or A$^{III}$B$^V$ compounds. Reasons for that are as following:

1) The complex lattice of these compounds leads to big anisotropy of their physical properties. This makes the understanding and interpretation of experimental results complicated.

2) Because of mechanical weakness of crystals in the direction of the triad axis it is very difficult to obtain big single crystals. This limits the number of experimental data.

Up to now the problem of growing crystals with low concentration of charge carriers has not been solved. However, despite of difficulties listed above, nowadays there is a certain progress in the understanding of the energy band structure of bismuth telluride.

Strong anisotropy of the Hall effect and electric conductivity, together with the big longitudinal magnetoresistance, point out that the Fermi surfaces of charge carriers Bi$_2$Te$_3$ are not spheres. The total contribution of all valleys to the transport phenomena should reflect full symmetry of a crystal though the separate extremum may have lower symmetry. The theory for the transport phenomena for the multivalley models is in progress and is done for Bi$_2$Te$_3$ on the base of a model of a spherical Fermi surface.

It comes out from the group theory, that in crystals with symmetry $D_{3d}$ the various energy bands (with different dependence $E(\vec{K})$) do not cross each other. Therefore energy in the vicinity to the extremums of Brillouin zone can be spread out on degrees of small size $(K_i - K_{0i})$.
\( \varepsilon(\mathbf{K}) = \varepsilon(\mathbf{K}_0) + \frac{1}{2} \sum_{ij} \left( \frac{\partial^2 \varepsilon}{\partial K_i \partial K_j} \right)_{K=K_0} (K_i - K_0)(K_j - K_0) + \ldots, \quad (1.4) \)

where \( i \) and \( j \) independently get values 1, 2, 3 (x, y, z) [3]. Decomposition is limited by second order from \((K_i - K_0)\). Linear terms are equal to zero in the extreme case

\[
\left( \frac{\partial \varepsilon}{\partial K_i} \right)_{K=K_0} = 0.
\]

If \( \mathbf{K} \) is counted from \( \mathbf{K}_0 \) (1.4) it is possible to write

\[
\varepsilon(\mathbf{K}) = \frac{\hbar^2}{2m_0} \alpha_{ij} K_i K_j, \quad (1.5)
\]

where \( \varepsilon(\mathbf{K}) \) is energy counted from \( \varepsilon(\mathbf{K}_0) \), \( \alpha_{ij} = \frac{m_0}{\hbar} \left( \frac{\partial^2 \varepsilon}{\partial K_i \partial K_j} \right)_{K=K_0} \) is symmetry tensor of the second order (\( \frac{\alpha_{ij}}{m_0} \) is tensor of reciprocal effective mass) [3]. In quadratic approximation for \( \mathbf{K} \) (1.5) the surfaces of constant energy in the vicinity of the extremums points of the Brillouin zone are ellipsoids, which parameters are characterized by their dimensions \( \alpha_{ij} \).

The tensor \( \alpha_{ij} \) does not vary during the symmetry transformations of the vector \( \mathbf{K}_0 \). That is ellipsoid is combined with itself, and transformations of crystal symmetry are not included into the group of vector \( \mathbf{K}_0 \) transfer point \( \mathbf{K}_0 \) to the equivalent points of Brillouin zone in such array, that the Fermi surface reflects the symmetry of the crystal as a hole.

Spherical Fermi surface approach does not explain the majority of experimental data, especially transport properties. Interesting feature of bismuth telluride single crystals is the dependence of their physical properties on the crystal orientation. For example at 300 K the values of electric conductivity along and across the cleavage plane differ 3 - 6 times [7-15], the Hall effect differ twice [7-15], and transverse Nernst-Ettingshausen effect differ in 2 - 4 times [8]. Hence, physical properties of Bi\(_2\)Te\(_3\) cannot be explained within the simple spherical models of the Fermi surfaces.

Drabble and Wolf [16] proposed for Bi\(_2\)Te\(_3\) valence and conductivity bands 6-ellipsoid Fermi surface model with the centers of ellipsoids in mirror planes (Fig. 1.7.b). The axis of the main ellipsoid \( e_3 \) (Fig. 1.7.a) should be symmetric in a mirror plane \((e_2 \perp xz)\) and
two others \(e_1\) and \(e_3\) have angle \(\theta\) to crystal axes \(x\) and \(z\). The dispersion law for the main ellipsoid in crystal axes is

\[
e(\mathbf{K}) = \frac{\hbar^2}{2m_0} (\alpha_{11} K_1^2 + \alpha_{22} K_2^2 + \alpha_{33} K_3^2 + 2\alpha_{13} K_1 K_3) \tag{1.6}
\]

and in elliptic coordinates

\[
e(\mathbf{K}') = \frac{\hbar^2}{2m_0} (\alpha_{11} K_1'^2 + \alpha_{22} K_2'^2 + \alpha_{33} K_3'^2) . \tag{1.7}
\]

Fig. 1.7. The six ellipsoids Drabble-Wolfe (DW) model for Bi\(_2\)Te\(_3\) structure of the Fermi surface [17]

a) Orientation of the constant energy ellipsoids in a reflection plane, ellipsoids are connected by inversion operation.

b) Model (DW), a kind on axis Z (C\(_3\)), a dotted line is designated ellipsoids under a figure plane, mn. is main ellipsoid, 1p, 2p are collateral or equivalent ellipsoids connected with the main symmetry operation of C\(_3\).

Relation between \(\alpha_{ij}\) also \(\alpha_i\) is

\[
\begin{align*}
\alpha_{11} &= \alpha_1 \cos^2 \theta + \alpha_3 \sin^2 \theta \\
\alpha_{22} &= \alpha_2 \\
\alpha_{33} &= \alpha_1 \sin^2 \theta + \alpha_3 \cos^2 \theta \\
\alpha_{13} &= (\alpha_1 - \alpha_3) \cos \theta \cdot \sin \theta,
\end{align*}
\]

where \(\theta\) is the angle of rotation of ellipsoid’s axes in a mirror plane relatively to the crystal axes and \(\alpha_i\) is anisotropy factor in Drabble–Wolfe model.

Such model allows explaining anisotropy of physical properties of bismuth telluride single crystals.
1.1.4. The width of forbidden gap in Bi$_2$Te$_3$

Band gap $E_g$ is one of main parameters of the semiconductor and plenty of investigations is devoted to estimation of $E_g$ in Bi$_2$Te$_3$. In [10, 18 - 22] $E_{g0}$, the width of the forbidden gap at $T = 0$ K, was defined from changes of electrical conductivity and the Hall effect in the range of the intrinsic conductivity. The $E_{g0}$ value is between 0.16 - 0.21 eV.

Based on measurements of electrical conductivity, thermoelectric power and thermal conductivity, in the impurity and the mixed conductivity range in n- and p- types with concentration of carriers $6 \cdot 10^{18}$ cm$^{-3}$ and $1.1 \cdot 10^{17}$ cm$^{-3}$ at 77 K the value of forbidden band $E_g$ of Bi$_2$Te$_3$ was estimated in temperature interval 300 - 420 K. At $T = 420$ K $E_g = 0.145$ eV and increases with decreasing of temperature as $\frac{\partial E_g}{\partial T} = -0.9 \cdot 10^{-4}$ eV/deg. The method of $E_g$ estimation described in [23], is convenient for bismuth telluride because if all measurements are performed along one of the crystal axes, knowledge of concentration of the impurity carriers is not needed. This makes the situation easier because the definition of the impurity by carriers concentration in Bi$_2$Te$_3$ is complicated due to anisotropy of Hall effect.
1.1.5. Valence band

The valence band of bismuth telluride has multivalley structure and consists of the upper valence band (UVB, in which there are “light” holes) and the lower valence band (LVB, in which there are “heavy” holes). Both valence bands are sixellipsoids centered on mirror planes and turned around the binary axis $C_2$. The band gap (energy difference between the top of the valence band and the bottom of the conduction band) $E_g$ in $\text{Bi}_2\text{Te}_3$ is indirect and equal to approximately $E_g \approx 0.20 \text{ meV}$ at a room temperature, increasing up to $0.25 \text{ meV}$ at 4.2 K [24].

The size of energy gap $\Delta E_V$ between bands is approximately 20 meV [25]. The schematic structure of $\text{Bi}_2\text{Te}_3$ valence band top is presented in Fig.1.8.

![Fig. 1.8. Structure of valence band in $\text{Bi}_2\text{Te}_3$. LVB is lower valence band; UVB is upper valence band; $E_F$ is Fermi level and $E_a$ is impurity band.](image)

Holes appear in the lower valence band when the hole concentration exceeds critical value $p_c \approx 5 \cdot 10^{18} \text{ cm}^{-3}$. Essential is big difference of effective masses in the upper and lower valence bands: in the upper valence band cyclotron mass $m^*_c \approx 0.08 m_e$, while in the lower valence band $m^*_c \approx 0.16 m_e$ [25]. Doping of bismuth telluride with tin results in appearance of impurity band located above the top of the lower valence band and is lower than the top of the upper valence band [26].
1.3. Defects of crystal structure in Bi$_2$Te$_3$

Defects of crystal structure are inevitable, because of wide homogeneity area of Bi$_2$Te$_3$. The main interests attract dot defects: vacancies of bismuth and tellurium; atoms of these elements in interstice; antistructural defects (atoms Bi on places Te and on the contrary) and more complex formations, thereby in Bi$_2$Te$_3$ crystal there is a lot of various defects. The antisite defects are electrically active and are the reason of high hole concentration ($p \sim 10^{19}$ cm$^{-3}$). This strongly complicates control of physical properties of these materials. The energy of formation of antisite defect is 0.4 eV and formation of Te vacancy is 1.2 eV, i.e. formation of antisite defect is easier [27].

Layered structure and peculiarities of the phase diagram of Bi$_2$Te$_3$ are the reason for existence of at least two kinds of inhomogeneities in these crystals. One of them is various dot defects. These are connected to the non-uniform distribution of atoms in layers (see Fig.1.9.a). Second is inhomogeneities inside the layer (see Fig.1.9.b). It is obvious, that presence of defects and inhomogeneities in crystals influence on their electrical properties and on opportunity of correct definition of their energy spectrum parameters. Studies of the influence of various impurities on thermoelectric efficiency of Bi$_2$Te$_3$ in this case are complicated.

Figures (1.9.a) and (1.9.b) shows the electronic density in the single crystalline samples grown by Czochralsky method. It is seen the presence of inhomogeneities.

Fig.1.9. Density distribution of electros obtained by means of the scanning tunnel microscope [28]. (a) is with non-uniform distribution of atoms in layers, (b) is with inhomogeneities inside the layer.
Influence of crystals perfection on electrophysical properties and the parameters of a power spectrum of Bi$_2$Te$_3$ [3, 29] were not discussed in literature. It is natural, that the most reliable information about energy spectrum of charge carriers can be obtained from the most perfect monocrystals. Traditionally are used two methods for growth of Bi$_2$Te$_3$ crystals: Czochralski method [30], allowing to obtain individual monocrystals with high degree of perfection, and directed crystallization method in which single and block crystals are obtained. Fist is laboratory method and second is industrial method.
1.4. Hall effect in weak magnetic fields

Hall effect refers to the appearance of potential difference (Hall voltage) on the opposite sides of an electrical conductor in an applied magnetic field when electric current is flowing.

Hall coefficient is the Hall voltage divided by current value, magnetic field and the conductor's thickness. Hall coefficient is a characteristic of the material of the conductor. In Fig. 1.10.A, the Hall element creates on a negative charge on the top edge (symbolised by the blue color) and positive at the lower edge (red color). In "B" and "C", either the electric current or the magnetic field is reversed, causing the reversing of polarization. Reversing both current and magnetic field (drawing "D") causes the Hall element again to assume a negative charge at the upper edge.

Reason for the Hall effect is the nature of the current flow in the conductor. Current consists of charge-carrying particles (typically electrons) which experience a force (called the Lorentz force) in the presence of a magnetic field. When magnetic field is absent, there is no Lorentz force and the charge follows an approximate 'line of sight' path. When a perpendicular magnetic field is applied, the path is curved perpendicular to the magnetic field due to the Lorentz force. The result is an asymmetric distribution of charge density across the Hall element perpendicular to the 'line of sight' path the electrons would follow in the absence of the magnetic field. As a result, an electric potential is generated between the two ends.
Let us denote by $J$ the current density, by $B$ the inductance of magnetic field, by $E_H$ the strength of the electric field produced in the $y$ direction, by $R_H$ the Hall constant (characteristic of the material of which the element is composed). Hall effect give electric field

$$
\tilde{E}_H = R_H \cdot [\tilde{J} \times \tilde{B}],
$$

(1.9)

where $E_H = \frac{U_H}{w}$ and $J = \frac{I}{S} = \frac{I}{w \cdot d}$. Here $U_H$ is Hall voltage, $I$ is electric current flowing through the sample, $S$ is area of sample's cross-section, $w$ is width, $d$ is thickness, Fig. 1.11.
Fig. 1.11. Hall effect circuit.

It the angle between $\vec{J}$ and $\vec{B}$ is $90^\circ$ we can replace $[\vec{J} \times \vec{B}]$ by $J_x \cdot B_z$.

$$\frac{U_H}{w} = R_H \cdot \frac{I_x}{wd} \cdot B_z \implies U_H = R_H \cdot \frac{I_x}{d} \cdot B_z.$$  \hspace{1cm} (1.10)

It can be seen that Hall voltage increases linearly with magnetic field.

The Hall coefficient is estimated as

$$R_H = \frac{U_H \cdot d}{I_x B_z}.$$  \hspace{1cm} (1.11)

The current in conductor (or semiconductor) is the charge carrier flow and the Hall constant is equal to $R_H = \frac{1}{q n}$, where $n$ is concentration of free charge carriers and $q$ is the charge of these particles. Measurements of Hall coefficient give opportunity to estimate concentration of the free charge carriers.
1.5. Magnetoresistance in weak magnetic fields

Magnetoresistance (magnetoresistivity effect) is the changing of material’s electrical resistivity in a magnetic field. In semiconductors the relative change of electrical resistivity is bigger than in metals and can achieve hundreds of percents.

Let the current $j$ to flow in the sample along axis $x$. In the absence of magnetic field the charge carriers are moving along straight lines and between two collisions they pass the distance defined as free path $\lambda$. In external magnetic field $B$ their trajectories look like a part of cycloid in infinite large specimen. On the free path $\lambda$ along the electric field $E$ the particle will move the way shorter than $\lambda$, namely

$$\lambda_x \approx \lambda \cos \phi \approx \lambda \left(1 - \frac{\mu^2 B^2}{2}\right).$$

(1.12)

As long as for the time of free path $\tau$ the particle moves the shorter way along the electric field $E$. Then it is equivalent to the decreasing of drift velocity (or mobility) and, as a result, conductivity. By other words the resistivity will increase. Taking into account statistic dispersion of free path times (and lengths), one can write for relative resistivity change

$$\frac{\Delta \rho}{\rho} = \mu^2 B^2.$$

(1.13)

In finite limited sample the Hall field compensates the influence of magnetic field and, as a result, the charge carriers move along the straight lines, therefore magnetoresistance should not exist. However velocities of electrons and holes are different and magnetic field influences stronger than Hall field to the fast particles, but slow particles deviate under the influence of the Hall field. As a consequence, dispersion in particles’ velocities decrease the contribution in conductivity from fast due to magnetic field and slow due to Hall field charge carriers that lead to increasing of resistance.

If magnetic field is directed along $j$, in that case changing in resistance cannot take place. But in some cases the magnetoresistance is observed, that can be explained by complex shape of Fermi surfaces in certain materials.
1.6. Shubnikov-de Haas effect

Energy spectrum of charge carriers in the semiconductor with applying of strong magnetic field is quantized and density of states of charge carriers demonstrates oscillating behavior vs. energy.

Shubnikov – de Haas oscillations are oscillations of magnetoresistance in a magnetic field. Shubnikov – de Haas oscillations are the periodical changing of density of states of charge carriers on the Fermi level if the intensity of magnetic field is changed.

Landau described this phenomenon as quantum-mechanical [31], which presents the nature of quantization for charge carriers density of states within the bounds of isotropic quadratic law of dispersion for free electrons. Analysis shows that energy in magnetic field can be described by expression (see Fig.1.12):

\[
\varepsilon_{n\text{m}K_yK_z} = (N_m + 1/2)\hbar\omega_c + \frac{\hbar^2 k_z}{2m}
\]  

(1.14)

where \(\omega_c = eB/m_e\); \(m_e\) is cyclotron mass of electron, \(N_m\) is integer, \(k_z\) is electron’s wave vector component along the axis \(\hat{z}\), magnetic field is parallel to axis \(\hat{z}\). The first term in (1.14) is discrete energy variable of electron motion in the plane perpendicular to magnetic field direction. Second term is the energy of continuous electron motion along \(\hat{z}\) – axis. Thus, three-dimensional zone in \(k\) – space with quasicontinuous energy levels distribution splits to a member of one dimensional magnetic sub bands or Landau level (LL). This resulting in energy quantization of charge carriers orbital motion in the plane perpendicular to direction of magnetic field. The distance between energy sub bands is equal to cyclotron energy \(\hbar\omega_c\). The level with \(N_m = 0\) is situated on \(\frac{\hbar\omega_c}{2}\) above the conduction band without magnetic field (see Fig. 1.12).
Fig. 1.12. Electron’s energy sub bands in magnetic field $B = B_z$.

Charge carriers density of states distribution $\rho(E)$ in quantizing magnetic field starts to depend on the magnetic field:

$$
\rho(E) = \frac{m^{3/2}}{\sqrt{2\pi^2\hbar^3}} \frac{\hbar\omega_c}{2} \sum_{N_m=0}^{N_m} [E - (N_m + 1/2)\hbar\omega_c]^{-1/2}
$$

Discontinuous character of function $\rho(E)$ close to points $E = (N_m + 1/2)\hbar\omega_c$ lead to the nonmonotonic transport properties in magnetoresistance because density of states is infinite in the vicinity of the bottom of each Landau sub bands (Fig. 1.13).
Fig. 1.13. Distribution of density of electron states $\rho(E)$ in magnetic field. Hatch line shows density of states without magnetic field.

Fermi energy $E_F$ changes in magnetic field and is connected to Fermi energy without magnetic field $E_{F_0} = \left(\frac{\hbar^2}{2m}(3\pi^2n)^{2/3}\right)$ by

$$E_F = \frac{2}{3} \left(\frac{E_{F_0}}{\hbar \omega_c}\right) \sum_{N_m=0}^{N_m} [E - (N_m + 1/2)\hbar \omega_c]^{-\frac{1}{2}}.$$  \hspace{1cm} (1.16)

Dependence $E_F(B)$ should be taken into account only for small values of $N_m$ ($N_m \leq 3$), where ratio $E/\hbar \omega_c$ is small that follows from (1.16).

Observation of Shubnikov – de Haas oscillations requires the following conditions:

$$\omega_c \tau >> 1$$ \hspace{1cm} (1.17)

$$\hbar \omega_c >> k_B T$$ \hspace{1cm} (1.18)

$$E_{F_0} > \hbar \omega_c$$ \hspace{1cm} (1.19)

Condition (1.17) means that distance between Landau levels must be bigger than broadening of each level $\hbar / \tau$ (or $\mu B >> I$). From (1.18) follows that distance between LL must be bigger than their thermal broadening. Condition (1.19) shows the highest limit of magnetic field when the oscillations disappear. For observing Shubnikov – de Haas oscillations is needed degeneration of electron gas ($E_{F_0} >> k_B T$, see (1.18), (1.19)).

Expression for Shubnikov – de Haas oscillations for longitudinal conductivity $\sigma_{zz}$ at $\vec{B}$

$(0, 0, B_z), \vec{j}(0, 0, j_z)$ if charge carriers dissipate on the acoustical phonons [32]
\[ \frac{\sigma_z}{\sigma_0} = 1 - x \left( \frac{\hbar \omega_c}{2E_f} \right)^{1/2} \sum_{M=1}^{\infty} \frac{(-1)^M M^{1/2}}{\text{sh}(Mx)} \exp \left( - \frac{2\pi M}{\omega_c \tau'} \right) \cos \left( \frac{2\pi ME_f}{\hbar \omega_c} - \frac{\pi}{4} \right), \]  

(1.20)

where \( x = 2\pi^2 k_BT/\hbar \omega_c \), \( \text{sh} x = \left( e^x - e^{-x} \right)/2 \); \( M \) is a natural number and \( \tau' \) is relaxation time, which characterizes nonthermal broadening of the LL.

Nonthermal broadening of the LL can be determined by heterogeneity of analyzing samples and dispersion of charge carriers on the defects of crystal structure. In some cases it is convenient instead of relaxation time to use effective temperature \( T_D = h/\pi k_BT' \), named Dingle temperature.

Estimation of cyclotron mass of charge carriers, which take part in SdH oscillations, is done using (1.21). Here is used temperature dependence of amplitude of SdH oscillations with approximation that \( T_D \) is independent from temperature [33]. The ratio of SdH oscillations amplitudes at two temperatures \( T_1 \) and \( T_2 \) corresponds to the equation

\[ \frac{A_{T_1}}{A_{T_2}} = \frac{x_1/\text{sh} x_1}{x_2/\text{sh} x_2}, \]  

(1.21)

where \( A_{T_i} \) are amplitudes of SdH oscillations at temperature \( T_i \), and

\[ x_i = 14.68 m_i T_i / m_0 B. \]  

(1.22)

By solving (1.21) it is possible to find the cyclotron mass of charge carriers, which take part in SdH oscillations. For \((\text{Bi}_{0.99}\text{Sn}_{0.001})_2\text{Te}_3\) crystal one gets \( m_c = 0.12m_0 \).

Amplitude of SdH oscillations is described by

\[ A \approx x \cdot \exp \left( -2\pi^2 k_BT_D \gamma \cdot \hbar \omega_c \right) \frac{(BE_f)^{1/2} \cdot \text{sh}(x)}{\left(1/B_m^* \right) - \left(1/B^*_\text{sh} \right)}, \]  

(1.23)

where \( \gamma = \frac{\left(1/B_m^* \right) - \left(1/B^*_\text{sh} \right)}{\Delta_{\text{sh}}} \) describes contribution of the spin splitting of LL. Therefore, it is possible to find Dingle temperature from the inclination of the dependence \( \ln \left[ A(BE_f)^{1/2} \text{sh}(x)/x \right] \) vs. \( 1/B \). Comparison of the Dingle temperature value calculated from Hall mobility \( \mu = R_0\sigma_0 \) [4]

\[ T_{D\mu} = \frac{he}{\pi k_B m \mu}, \]  

(1.24)
and $T_D$ shows if the dispersion is a dominant reason in nonthermal broadening of Landau levels.

Finally it is possible to make a conclusion that experimental investigation of Shubnikov – de Haas effect is an efficient method for analysis of energy band structure of semiconductors. This method allows to study the topology of Fermi surface in the material and to estimate such important parameters as tensor components of effective mass, $g$ – factor, effective mass of density of states and, moreover, to evaluate the perfection degree of the grown crystal.
1.7. Crystal growth (Czochralski method)

Thermoelectric materials based on bismuth telluride have intermediate position between the high-resistance semiconductors for radio electronics (germanium, silicon), and metal alloys. High concentration of charge carriers in these materials permit lower requirements to their purity and crystal structure in comparison with high-resistance semiconductors. A big number of thermoelements used in powerful thermoelectric devices, industry require methods of mass production.

It is possible to distinguish two technological directions: growing of samples for basic research and industrial manufacturing of thermoelements. In the first case are applied laboratory methods of growing of single crystals from melt (method of Bridgman, zone melting, and Czochralsky method). In the second case it is necessary to achieve big productivity and to use cheaper primary materials to decrease the costs of production.

This is a method for growing of bulk crystals and is widely used in modern electronics to grow crystals of the big diameter: Si, GaAs, etc. [33]. This process is named after Yan Czochralsky who discovered the method in 1916 while investigating the crystallization rates of metals. The scheme of the method is shown on Fig.1.14.

Fig. 1.14. Czochralsky method. 1 is growth rod bar; 2 is crucible; 3 is safety flux; 4 is thermoelectric material flux; 5 is heater and 6 is crucible holder.
In crucible 2 is the material in melt, above which is boric anhydride layer for protection against evaporation. The crucible is in the special holder 6, which rotates the crucible. A graphite heater 5 provides necessary temperature in crucible. Seed for crystal is fixed in a holder, which rises upwards with necessary speed after the contact with the melt. The holder is simultaneously rotating in opposite direction in comparison to the crucible. All the listed elements are in the hermetic chamber filled with inert gas.

To increase the homogeneity of the grown crystal some additional equipment is used. For example, floating crucible with narrow hole through which it is contacted with the flux.
1.8. Topic of investigations

Experimental investigations of quantum oscillations on p-Bi$_2$Te$_3$ crystals with Sn impurity, grown by Bridgman method, show quantizing of Hall component of resistance tensor $\rho_{xy}$. This can be connected with existence of impurity states of Sn in the valence band, fixing position of a Fermi level $E_F$.

This conclusion is ambiguous, because holes concentration in the investigated samples is close to critical. In Bi$_2$Te$_3$ critical holes concentration is $p_c \approx 3 \times 10^{18}$ cm$^{-3}$ in which filling with heavy-hole band [6] begins. Quantizing of the Hall effect was observed in p-Bi$_2$Te$_3$ crystals doped with also Ag which does not create any impurity states and was attributed to the influence of heavy-hole band.

Temperature and concentration dependences of the main kinetic coefficients (electrical conductivity and Hall $R$, Seebeck $S$, and Nernst–Ettingshausen $Q$ coefficients) of the $p$-Bi$_2$Te$_3$ crystals doped with Sn exhibit features that can be interpreted as manifestations of impurity Sn states in the valence band. In turn, the data of photoelectron spectroscopy indicate that the electron density of states increases in the vicinity of the Fermi level in the Bi$_2$Te$_3$:Sn crystals.

Thus, significant amount of experimental data can be connected with the existence of the impurity states of Sn in Bi$_2$Te$_3$ valence band.

The main target of the present work is the experimental testing of validity of quasilocal impurity states model of tin in bismuth telluride by measurements of galvanomagnetic effects in classical and quantizing magnetic fields.
2. Experimental technique

2.1. Measuring equipment

Investigations of transport properties were performed by means of the automatic setup. The installation consists of measuring system, superconducting magnetic system, cryostat, power supply, indicator of liquid helium level, and computer-based system for temperature control. The block scheme of the setup used is presented in Fig. 2.1.

![Block scheme of measuring equipment](image)

Fig. 2.1. Block scheme of measuring equipment.

Three \((\text{Bi}_{1-x}\text{Sn}_x)\text{Te}_3\) samples, with x=0.005; x=0.007 and x=0.01 were investigated. All samples were single crystals orientated by x-ray and were grown by the Czochralski technique with filling of the melt from a liquid phase. Because of the complex crystal structure of \(\text{Bi}_2\text{Te}_3\), some special approach concerning the choice of parameters growing (pulling rate, seed and crucible rotation rates, temperature gradient at the growth front, etc.) was developed to provide the production of perfect crystals. The single crystals were grown in the [1010] direction normal to the main crystallographic axis \(\bar{N}\) in He atmosphere under an excess pressure of \(0.5\times10^5\) Pa. The starting seed was prepared from 99.9999% pure Bi, Te and Sn. The tin content was determined by plasma atomic-absorption spectroscopy. The quality of single crystals was monitored by X-ray
diffraction topography (Schulz, Berg-Barrett and Lang techniques) [34]. Orientation of crystals was made by a radiographic method. The impurity was added under the assumption, that Sn atoms replace bismuth in its sublattice.

The samples in the form of a rectangular prism were cut by cutting device presented in Fig.2.2. The geometry of samples meets the requirements of experiment (length is longer than width).

Fig.2.2. Cutting device for samples.

The size of the largest sample is 10.9x7.05x4.95 mm. The samples were etched after cutting. Contacts were soldered by fusible solder, 80 % of tin as an alloy in 20 % of bismuth, on standard six-probe scheme (see Fig.2.3).
Contacts were soldered under microscope Reichert by microsoldering-iron WECP-20 with a temperature control.

Measuring wires were wounded in pairs with the purpose of decreasing the induction in a measuring circuit when sweeping of a magnetic field. The experimental sample is presented in Fig.2.4. The sample is fastened on the special holder (see Fig.2.5) and placed into the cryomagnetic system (see Fig.2.6).
Fig. 2.6. Experimental setup.
Experimental data was processed by LabView program, which in a real-time mode perform measurements. Data are collected using three voltmeters HP 34401A Multimeter, the temperature was controlled by LakeShore 330 Autotuning Temperature controller (see Fig.2.7).

Fig.2.7 Complex of instrumentation.

Parameters of cryomagnetic system is presented in Table 2.1:
Table 2.1. Main parameters of cryomagnetic system.

<table>
<thead>
<tr>
<th>The name of a parameter</th>
<th>Value of a parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic induction, T</td>
<td>13</td>
</tr>
<tr>
<td>Operating time of cryostat with one filling by liquid helium in a mode of short-circuited current CMC, hour, not less</td>
<td>40</td>
</tr>
<tr>
<td>Nominal output current of the power supply, A</td>
<td>200</td>
</tr>
</tbody>
</table>

During measurements were kept all necessary requirements of the safety engineering. Only persons acquainted with service regulations for cryomagnetic systems and electrical devices were allowed to work.
2.2. Accuracy of measurements

Experimental results of transport effects were analyzed using formulas of the isothermal conditions of experiment. The experiment can be considered isothermal with high accuracy and $T = \text{const}$ during the time of measurement.

Uncontrolled heating of the sample is possible only with strong measuring current because only in this case temperature of the sample can differ from cryogenic liquid because of formation of a gas bubble around the sample. The bubble of helium gas is formed, if the heat dissipation in the sample exceeds as a rule 0.1 W/cm$^2$. The maximum current value through the sample was defined when a deviation from linearity in voltage-current characteristic appears. Measurements were performing using half of the maximum current. This excluded thermal heating.

Kinetic coefficients were calculated from the experimental data by the standard formulas. Specific conductivity $\sigma$

$$\sigma = \frac{J \cdot l}{U \cdot S} \quad (\Omega^{-1} \text{m}^{-1}) \quad (2.1)$$

the Hall constant $R_{\text{Hall}}$

$$R = \frac{U \cdot d}{J \cdot B} \quad (\text{m}^3 \text{C}^{-1}) \quad (2.2)$$

Changing of resistance in a magnetic field

$$\frac{\Delta \rho}{\rho_0} = \frac{\rho_H - \rho_0}{\rho_0} \quad (\%) \quad (2.3)$$

where $d$ is height of the sample, m

$l$ is distance between contacts, m

$S$ is area of cross-section of the sample, m$^2$

$J$ is current through the sample, A

$B$ is induction of magnetic field, T

$U$ is values of appropriate measurements, V
Accuracy of temperature of samples is better than ± 0.03 K. Error in the magnetic field induction is not more than 0.5%. The geometrical sizes of samples were measured by means of the microscope WECP-20 within the accuracy ± 0.05 mm. Orientation of samples in a magnetic field was within 1°. Voltage and current measurements were done within 0.05 %.
3. Results and discussion

We studied experimentally and theoretically magnetic field and temperature dependence of transverse magnetoresistance and Hall-factor for bismuth telluride with magnetic field orientation $\vec{B}$ parallel to the axis $C_3$. Measurements were performed in magnetic fields up to 12 T at temperatures 4.2 and 11 K. Investigated samples demonstrated quantum oscillations of transverse magnetoresistance $\rho_{xx}$ and Hall component $\rho_{xy}$ at both temperatures. This gives evidence for high quality of crystals.

Table 3.1. Hole concentration $p$ and Hall voltage $U_H$ of samples $(\text{Bi}_{1-x}\text{Sn}_x)\text{Te}_3$.

<table>
<thead>
<tr>
<th>Nº samples</th>
<th>$x_{\text{Sn}}$, at.%</th>
<th>$p_{4.2, K}$, $\times 10^{18}$ cm$^{-3}$</th>
<th>$R\sigma = U_H$ cm$^2$/V·s</th>
</tr>
</thead>
<tbody>
<tr>
<td>S90</td>
<td>0.5</td>
<td>6.2</td>
<td>3900</td>
</tr>
<tr>
<td>S101</td>
<td>0.7</td>
<td>3.1</td>
<td>3460</td>
</tr>
<tr>
<td>S91</td>
<td>1</td>
<td>2.7</td>
<td>2790</td>
</tr>
</tbody>
</table>

Main experimental data are shown in Figs. 3.1-3.12. The magnetic field $B$ was oriented along trigonal axis $C_3$, while electric current flows in perpendicular plane, $j \perp C_3$.

Contrary to undoped p-Bi$_2$Te$_3$ crystals [3, 35], the magnetic-field dependences of the transverse magnetoresistance $\rho_{ax}(B)$ and Hall coefficient $R_{123}(B)$ exhibit saturation at 4.2 K and exhibit a clear tendency towards saturation at 11 K, Figs. 3.1 - 3.8. Bi$_2$Te$_3$ single crystals doped with tin demonstrated clear Shubnikov-de Haas quantum oscillations (SdH) and, unexpectedly, the Hall coefficient.

Only one period of SdH and Hall coefficient oscillations is observed and oscillations $\rho_{xx}$ and $R_{123}$ are in the opposite phase, Figs. 3.9 - 3.11.
Fig. 3.1. Magnetic field dependence of the transverse $(\mathbf{B} \perp \mathbf{j})$ magnetoresistance $\rho_{xx}$ for $(\text{Bi}_{1-x}\text{Sn}_x)_2\text{Te}_3$ crystal for $B_{||C_3}$ at $T = 4.2$ K and $x = 0.005$. 
Fig 3.2. Magnetic field dependence of the Hall coefficient $R_{123}$ for (Bi$_{1-x}$Sn$_x$)$_2$Te$_3$ crystal for $B \parallel C_3$ at $T = 4.2$ K and $x = 0.005$. 
Fig. 3.3. Magnetic field dependence of the transverse $\left(\vec{B} \perp \vec{j}\right)$ resistivity $\rho_{xx}$ for $(\text{Bi}_{1-x}\text{Sn}_x)\text{Te}_3$ crystal $B\parallel C_3$ at $T = 11$ K and $x = 0.005$. 
Fig. 3.4. Magnetic field dependence of the Hall coefficient $R_{123}$ for $(Bi_{1-x}Sn_x)Te_3$ crystal $B||C_3$ at $T = 11$ K and $x = 0.005$. 
Fig. 3.5. Magnetic field dependences of the transverse $(\bar{B} \perp \bar{j})$ resistivity $\rho_{xx}$ for $(\text{Bi}_{1-x}\text{Sn}_x)_2\text{Te}_3$ crystal $B\parallel C_3$ at $T = 4.2$ K and $x = 0.007$. 

**Bi$_2$Te$_3$:Sn**
0.7 at. %
$T = 4.2$ K
Fig. 3.6. Magnetic field dependences of the Hall coefficient $R_{123}$ for $(\text{Bi}_{1-x}\text{Sn}_x)\text{Te}_3$ crystal $\mathbf{B}\parallel C_3$ at $T = 4.2$ K and $x = 0.007$. 

$\text{Bi}_2\text{Te}_3\text{Sn}$

0.7 at.

$T = 4.2$ K
Fig. 3.7. Magnetic field dependences of the transverse $(\vec{B} \perp \vec{j})$ resistivity $\rho_{xx}$ for $(\text{Bi}_{1-x}\text{Sn}_x)_2\text{Te}_3$ crystal $B\parallel C_3$ at $T = 11$ K and $x = 0.007$. 

$\text{Bi}_2\text{Te}_3$:Sn
0.7 at.%
$T = 11$K
Fig. 3.8. Magnetic field dependences of the Hall coefficient $R_{123}$ for $(\text{Bi}_{1-x}\text{Sn}_x)\text{Te}_3$ crystal $B || C_3$ at $T = 11$ K and $x = 0.007$. 
Fig. 3.9. Magnetic field dependence of the transverse resistivity $\rho_{xx}$ and the Hall coefficient $R_H$ in $(\text{Bi}_{1-x}\text{Sn}_x)_2\text{Te}_3$ with $x = 0.01$ at $T = 4.2$ K.
Fig. 3.10. Magnetic field dependences of the transverse resistivity $\rho_{xx}$ and the Hall coefficient $R_H$ in $(\text{Bi}_{1-x}\text{Sn}_x)\text{Te}_3$ with $x = 0.01$ at $T = 11$ K.
Fig. 3.11. Magnetic field dependences of the transverse resistivity $\rho_{xx}$ and the Hall coefficient $R_H$ in (Bi$_{1-x}$Sn$_x$)$_2$Te$_3$ with $x = 0.01$ at $T = 38$ K.
3.1. Transport properties in weak magnetic fields

It is known that in majority of semiconductors with high crystal quality, including undoped Bi$_2$Te$_3$ single crystals, saturation of magnetoresistance is not observed in high magnetic fields [27, 35]. Usually, magnetoresistance still increases in the region of quantizing magnetic fields. Such behavior is related to various types of fluctuations of the concentrations of free charge carriers [36].

As can be seen from Figs. 3.1-3.8, the behavior of transverse magnetoresistance $\rho_{xx}$ and Hall coefficient $R_{Hall}$ in magnetic field in Bi$_2$Te$_3$ single crystals, doped with the Sn up to 0.5 and 0.7 at. %, follows the classical theory of kinetic phenomena in ideal semiconductors [37]. Kinetic coefficients $\rho_{xx}(B)$ and $R_{Hall}(B)$ increase according to the square law with magnetic field in weak magnetic fields, saturate in high magnetic fields at 4.2 K and tend to saturation at 11 K.

In accordance with [36], such behavior of kinetic coefficients in a magnetic field indicates higher spatial electrical homogeneity of Bi$_2$Te$_3$ crystals doped with Sn, in comparison with undoped bismuth telluride single crystals. The obtained data are confirmed by the results of microthermoprobe studies of similar Bi$_2$Te$_3$:Sn crystals [38]. The obtained data and give evidence for the existence of the band of quasi-local Sn states in the valence band of bismuth telluride.

Existence of partly occupied Sn states brings about the pinning of the Fermi level ($E_F$) and stabilization of the concentration of hole in valence band. As a result, the concentration fluctuation of electrically active intrinsic defects and impurity atoms becomes less important. At the same time increases spatial homogeneity of the crystal’s electrical characteristics increases.

During these studies were obtained following formulas for the quantitative analysis of the experimental data. These formulas describe the dependences of the Hall coefficient, $R_{123}(\vec{B})$, and transverse magnetoresistivity, $\rho_{xx}(\vec{B})$, on the magnetic field using the six-ellipsoid Drabble-Wolf model [39]. When $\vec{B} \parallel C_3$, the formulas have the simplest form. In particular, the magnetic field dependence of the Hall coefficient $R_{123}(\vec{B})$ and the transverse magnetoresistivity $\rho_{xx}(\vec{B})$ in the case of pronounced degeneracy of the charge-carrier gas have the same form in relative units. This means,
\[
\frac{R_{123}(B)}{R_0} = \frac{\rho_{xx}(B)}{\rho_0} = 1 + \frac{(R_0\sigma_0 B)^2/f_{||}}{1 + (R_0\sigma_0 B)^2}
\]

(3.1)

where: \(R_0 = R_{123}\) at \(B \to 0\), \(\rho_0 = \rho_t\) at \(B = 0\), \(\sigma_0 = \sigma_t\) at \(B = 0\) and \(f_{||}\) is the Hall factor related to the anisotropy of the components of the effective masses tensor and orientation of ellipsoids with respect to crystallographic axes [27,40]. These dependences can be linearized in the coordinates \(\frac{B^2}{\Delta R/R_0}\) vs \(B^2\) and \(\frac{B^2}{\Delta \rho_{xx}/\rho_0}\) vs \(B^2\) where \(\Delta R_{123} = R_{123}(B) - R_{123}(0)\), \(\Delta \rho_{xx} = \rho_{xx}(B) - \rho_{xx}(0)\):

\[
\frac{B^2}{\Delta R/R_0} = 1 + \frac{1}{(1/f_{||} - 1)(R_0\sigma_0)^2} + \frac{1}{(1/f_{||} - 1)} B^2
\]

(3.2)

Formula (3.2) makes it possible to calculate the Hall factor from the slope \(a\) of straight line: \(f_{||} = \frac{1}{(1/tg \alpha + 1)}\). Using the intercept on the vertical axis \(a = \frac{1}{(1/f_{||} - 1)(R_0\sigma_0)^2} = tg \alpha / (R_0^2 \sigma_0^2)\), and the obtained slope, one can calculate the Hall mobility of holes \((R_0\sigma_0)\) in perpendicular plane.

Thus, experimental magnetic field dependences of kinetic coefficients can be used to estimate independently the Hall factor and Hall mobility of charge carriers. This approach is especially important for polycrystalline samples. Equation (3.2) allows estimating the mobility of charge carriers in the grains (crystallites) of polycrystals. Formula (3.1) is valid also for cubic crystals with a multiple-ellipsoids model of the band structure in case of pronounced degeneracy if the magnetic field is oriented along the symmetry axis \((C_3\text{ or } C_4)\) of the Fermi surface.

Experimental dependences \(R(B)\) and \(\rho_{xx}(B)\) are linear for \(\text{Bi}_2\text{Te}_3:\text{Sn}\) single crystals, as shown in Fig. 3.12. The intercepts \(a_R\) and \(a_{\rho}\) and slopes of the straight line are close to each other \((a_R = 4.5\ T^2, a_{\rho} = 4.5\ T^2, tg a_R = 0.80, \ tg a_{\rho} = 0.53, \text{ correspondingly})\). The Hall factors calculated from these intercepts and slopes \((0.44\ and\ 0.35)\) are also close to the published data [27, 38-40], while the calculated Hall mobility \((3300\ cm^2/(V\cdot s))\) is close to the experimental value \((3460\ cm^2/(V\cdot s))\), see Appendix 2. These results indicate that there
is no significant influence of the tin impurity to the energy-band parameters of light holes in bismuth telluride.
Thus, we observe not only qualitative but also quantitative agreement of the experimental data with both Drabble-Wolf model and the notions of quasi-local impurity states of Sn in Bi$_2$Te$_3$. 
Fig. 3.12. Dependences $\frac{B^2}{\Delta R_{123}/R_0}$ (1) and $\frac{B^2}{\Delta \rho_{xx}/\rho_0}$ (2) for $B^2$ for (Bi$_{0.995}$Sn$_{0.005}$)$_2$Te$_3$ monocrystal at $T = 4.2$ K. Solid lines are fit with Eq. (3.2).
3.2. Transport properties in quantizing magnetic fields

Figs.3.1-3.8 shows that oscillations of the transverse magnetoresistance $\rho_{xx}$ and the Hall coefficient $R_{123}$ data exhibit only one period. This means, in both Bi$_2$Te$_3$:Sn crystals, that only one type of charge carries (“light” holes) make contribution to the quantum oscillations in magnetic field up to 12T. In fact, if a magnetic field is oriented along the C$_3$ axis, six ellipsoids of Fermi surface of holes (the Drabble-Wolf model, Fig. 1.7) are situated symmetrically vs. applied magnetic field. These ellipsoids have the same square of the external cross section by the plane perpendicular to the magnetic field. Therefore, the Shubnikov-de Haas oscillations of “light” holes should have a single period due to the Drabble-Wolf model.

It is observed that oscillations of transverse magnetoresistance and the Hall coefficient have opposite phase. This indicates that there is an additional reservoir for charge carriers with high density of states. This reservoir may be created either by an additional valence band extremum with higher density of states (so-called band of “heavy” holes; the effective mass of density of states of heavy holes $m_{d2} = 2.5m_0$, [41]), or by the band of intrinsic or impurity defects (Sn impurity states for instance). Since we do not detect any contribution of heavy holes to the quantum oscillations, and the concentration of introduced Sn exceeds significantly that of intrinsic defects, the phase shift of oscillations of $\rho_{xx}$ with respect to those of $R_{123}$ supports the existence of Sn impurity band inside the background states of the light-hole spectrum.
3.3. Impurity states of Sn

Experimental data of galvanomagnetic properties of the p-Bi$_2$Te$_3$ crystals doped heavily with Sn in classical and quantizing magnetic fields indicate existence of of Sn impurity band filled partially with electrons inside the valence band. This Sn impurity band stabilizes the position of the Fermi level in the system.

Stabilization of the Fermi level may be observed when (a) the impurity band is narrow (bandwidth $\Delta E_{i} < kT$, where $k$ is the Boltzmann constant) and (b) the impurity band is filled only partly by electrons.

If the Fermi level is pinned i.e. can not move, we can estimate the energy $E_{Sn}$ of the impurity states: $E_{Sn} \approx E_F$. Using the energy-band parameters of p-Bi$_2$Te$_3$ 

\[
E_F = \left( \frac{\hbar^2}{2m^*_e} \right)^{3/2} \left( \frac{3\pi^2 n}{\beta} \right)^{3/2}, [12],
\]

we obtain $E_{Sn} \approx 15$ meV.

Previously, quasi-local impurity states have been studied in lead chalcogenides doped with Group-III impurities [41, 42]. These states are of two types and include those weakly interacting with the Bloch band states of electrons in the crystals (for example, the In impurity states in PbTe and Pb$_{1-x}$Sn$_x$Te at $x < 0.28$ [41]) and those interacting strongly (for example, Tl in PbTe and In in SnTe [42, 43]).

Hole mobilities of (Bi$_{1-x}$Sn$_x$)$_2$Te$_3$ crystals are high (3900 cm$^2$/V·s at $x = 0.005$ and 3460 cm$^2$/V·s at $x = 0.007$, $T = 4.2$ K, see Appendix 2) and differ insignificantly in spite of the difference between impurity concentrations. We can conclude that scattering of holes by tin impurity atoms is not dominant and there is no significant resonance scattering of charge carriers to impurity states. This also means that the impurity states in Bi$_2$Te$_3$:Sn should be the quasi-local nonresonant levels. In accordance with the resonance-scattering theory developed in [9, 10], the absence of resonance scattering of holes in Bi$_2$Te$_3$:Sn means that broadening of $\Gamma$ state by Sn impurity state is small in comparison with thermal broadening $k_0T$ of the Fermi distribution function; i.e., $\Gamma \ll k_0T$ at 4.2 K.

The hole concentration in the samples of bismuth telluride under study decreases when the tin content $N_{Sn}$ increases; this decreasing of the hole concentration can be caused by the onset of interimpurity interaction. Taking this into account, we can estimate the localization radius (mean value of the distance between impurity atoms) for the impurity
state: \( R_{\text{Sn}} \approx \frac{1}{N_{\text{Sn}}^{\frac{1}{3}}} \approx 30 \, \text{Å} \). The obtained value of the radius for Sn impurity states indicates these states are highly localized within one or two low-level cells.
4. Conclusions

- We used the multiple-ellipsoid Fermi surface model to derive the formulas that describe Hall coefficient and transverse magnetoresistance in classical magnetic field in the case when this field is oriented along the symmetry axis of the Fermi surface. On the basis of these formulas, we suggested a method for determining the Hall factor $f_{||}$ (related to anisotropy of the isoenergy surface and orientation of the ellipsoids in reference to crystallographic axes) and the Hall mobility $R_o\sigma_0$ in the plane perpendicular to the symmetry axis. The opportunity to estimate the mobility in the grain of polycrystals from the magnetic field dependence of the Hall coefficient appears to be important. This makes possible to determine the mobility independently of measurements of electrical conductivity, which value is affected by the grain boundaries.

- Shubnikov–de Haas oscillations and the Hall coefficient at temperatures of 4.2 and 11 K were observed in the region of quantizing magnetic fields in the p-(Bi$_{1-x}$Sn$_x$)$_2$Te$_3$ single crystals grown by the Czochralski method with tin content of $x = 0.005$, 0.007 and 0.01. Quantum oscillations of $\rho_{xx}(B)$ and $R_{123}(B)$ have opposite phase. Analysis of experimental data obtained for classical and quantizing magnetic fields suggests that there is a narrow band of Sn states. This band is partially filled with electrons and is reason for the pinning of the Fermi level and for existence of the large-amplitude quantum oscillations of the Hall coefficient with phase opposite to SdH oscillations.

- The band of Sn impurity states is located approximately 15 meV below the top of the valence band. The data on the hole mobility indicate that there is no resonance scattering of holes to the Sn band at temperatures of 4.2 and 11 K and that the impurity band is very narrow, $\Gamma<<k_0T$.

- Investigations of Shubnikov-de Haas oscillations allowed to obtained the value of cyclotron mass for 1 at. % crystal: $m_c = 0.12m_0$.

- The localization radius for the impurity state $R \approx 30$ Å was obtained. This indicates that these states are highly localized within one-two low-level unit cells.
5. References


Table 1. Main parameters of Bi$_2$Te$_3$ [3]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters of hexagonal low-level unit cell, Å (300K)</td>
<td>$a=4.3835\pm0.0005$ $c=30.487\pm0.001$</td>
</tr>
<tr>
<td>Parameters of rhombohedral low-level unit cell, Å (300K)</td>
<td>$a_R=10.477$ $\alpha_R=24^\circ 9'32''$</td>
</tr>
<tr>
<td>Density, g/cm$^3$ (300 K)</td>
<td>7.8588</td>
</tr>
<tr>
<td>Specific heat of evaporation, kilocalorie/mole (298 K)</td>
<td>$\sim 18$</td>
</tr>
<tr>
<td>Coefficient of linear expansion, K$^{-1}$ (298K)</td>
<td>$\delta_\parallel = 12.9 \cdot 10^{-6}$ $\delta_\perp = 22.2 \cdot 10^{-6}$</td>
</tr>
<tr>
<td>Heat capacity $C_\vartheta$, calorie/g-atom·K (300 K)</td>
<td>5.7</td>
</tr>
<tr>
<td>Debye temperature, K</td>
<td>155.5</td>
</tr>
<tr>
<td>Number of ellipsoids: conducting band valance band</td>
<td>6 6</td>
</tr>
<tr>
<td>Effective mass of density of states (150K)</td>
<td>0.69$m_0$ 0.45$m_0$</td>
</tr>
</tbody>
</table>
### Appendix 2

Table 2. Experimental results

| № of samples | x_{Sn, at.\%} | t_g\alpha_p | t_g\alpha_R | a_p | a_R | f_|| | \( R\sigma \) cm^2/V·s |
|--------------|--------------|-----------|-----------|-----|-----|------|-------------------|
| S90          | 0.5          | 0.5       | 0.6       | 3   | 4   | 0.38 | 3900              |
| S101         | 0.7          | 0.53      | 0.80      | 4.5 | 4.5 | 0.44 | 3460              |
| S91          | 1            | 0.6       | 0.78      | 8   | 10  | 0.43 | 2790              |