MAGNETOTHERMOELECTRIC PROPERTIES OF SINGLE-CRYSTAL WIRES AND FILMS BASED ON Bi–3at%Sb

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Abstract

Results of a study of the magnetothermoelectric properties and the Shubnikov–de Haas effect in single-crystal wires of various diameters and films based on $Bi_{1-x}Sb_x$ semimetal alloys have been described. According to the Shubnikov–de Haas oscillations, it has been calculated that the overlap of the *L* and *T* bands in the Bi–3at%Sb semimetal wires decreases more than twofold owing to an increase in the antimony concentration. Thermoelectric gap ΔE, the dependence of the gap on wire diameter *d*, and the temperature dependence of power factor $\alpha^2\sigma(T)$ as a function of diameter and magnetic field have been calculated. It has been found that a decrease in wire diameter *d* leads to a semimetal–semiconductor transition at $d < 1.2$ μm, which is more than an order of magnitude higher than in pure Bi wires and 1.5 times higher than in wires of Bi–2at%Sb alloys. It has been shown that thermal gap ΔE increases with decreasing wire diameter *d* in accordance with a law close to $1/d$, which is consistent with theoretical calculations based on the occurrence of the quantum size effect in semimetals. A switching effect in the magnetothermopower has been found; the dependence of this effect on wire diameter *d* and temperature has been determined. It has been shown that, in a weak magnetic field, the magnetothermopower anisotropy in Bi–3at%Sb wires and films increases with decreasing temperature; this feature can be used in anisotropic thermoelectric energy converters.

1. Introduction

Bismuth and antimony form a continuous series of substitutional solid solutions; that is, during the alloying with bismuth, a Sb atom occupies the place of a Bi atom in the crystallographic structure. In this case, the symmetry of the unit cell is preserved, and the unit cell parameters vary only slightly; therefore, the addition of antimony provides a gradual rearrangement of the band spectrum of bismuth.

In $Bi_{1-x}Sb_x$ alloys, a smooth transition from the semimetallic state to the gapless state and then to the semiconductor state is observed at $x > 6$ at % Sb [1, 2].

In a concentration range of $0 < x < 4$ at % Sb, $Bi_{1-x}Sb_x$ alloys are semimetals in which the band overlap decreases with increasing antimony concentration; the process is accompanied by a decrease in the electron and hole Fermi surfaces.

The undying interest in $Bi_{1-x}Sb_x$ alloys is attributed to the fact that this alloy is, on the one hand, a promising low-temperature ($T < 200$ K) thermo- and magnetothermoelectric material [3, 4] and, on the other hand, a model material in solid state physics owing to the high sensitivity of this alloy to composition, sizes, and the effect of external factors, such as temperature, deformation, and magnetic field [5, 6].

In recent years, interest in low-dimensional structures based on $Bi_{1-x}Sb_x$ has abruptly increased owing to the prediction of Prof. M. Dresselhaus that thermoelectric figure of merit

$$ZT = \frac{\alpha^2 \sigma}{\chi_e + \chi_L} T$$

(σ is the electric efficiency, α is the thermoelectric power, χ_e and χ_L are the points of lattice and electronic heat conductivity) in $Bi_{1-x}Sb_x$ semimetal alloys increases owing to the occurrence and implementation of a quantum size effect (QSE) [7–10]. Typically, the QSE is implemented at low temperatures.

Single-crystal samples are required for the occurrence of the QSE. A decrease in the overlap of the L and T bands in $Bi_{1-x}Sb_x$ semimetal alloys ($x < 5$ at %) can lead to an increase in the temperature or the thickness at which the QSE is implemented.

The aim of this study was to develop a technology for the preparation of single-crystal films and glass-insulated wires based on Bi–3.5at%Sb and Bi–3at%Sb semimetal alloys and determine their anisotropy and magnetothermoelectric properties as a function of diameter, temperature, and magnetic field in a temperature range of 80–300 K.

2. Experimental

Samples of $Bi_{1-x}Sb_x$ film single crystals were grown by zone melting under a protective layer [11, 12]. A finely dispersed film of the respective composition was deposited on mica by thermal evaporation in a vacuum.

After that, in a vacuum, the material of the coating (KBr) was deposited onto the resulting polycrystalline film of a bismuth–antimony solid solution to eliminate the contraction of the molten film into droplets during the subsequent zone recrystallization. The melting point of the material of the coating should be higher than the melting point of the original film.

The zone recrystallization of the film was implemented on a special setup at a zone passage velocity of 1 mm/h. The zone recrystallization process was run in an argon atmosphere.

After zone recrystallization, the sample was placed in a solvent. In the case of using KBr as the protective coating, distilled water was used to remove it.

Using the proposed method, single-crystal films of a bismuth–antimony solid solution with a uniform distribution of components throughout the volume on a mica substrate were prepared. The uniform distribution of components throughout the volume and the monocrystallinity of the structure were confirmed by experimental studies of the prepared thin films by X-ray diffraction analysis according to the width of the 5th order peak.

Thus, homogeneous single-crystal films of Bi–3.5at%Sb alloys with a thickness of 0.2–3 μm and the orientation of C_3 perpendicular to the film plane on a mica substrate were prepared.

Single-crystal Bi–3at%Sb wires of various diameters were prepared by liquid-phase casting by the Ulitovsky method [13–15]. Diameters were controlled under a BIOLAM-12 optical microscope and by test measurements on a scanning electron microscope. The monocrystallinity of the samples was determined by X-ray diffraction studies and confirmed by transverse magnetoresistance rotation diagrams (TMRDs) and Shubnikov–de Haas (SdH) oscillations. The studied Bi–3at%Sb wires, as pure Bi wires (prepared by liquid-phase casting), have almost the same crystallographic orientation in the entire thickness range: the wire axis lies in the bisector–trigonal plane and forms an angle of ≈20° with the C_1 bisector axis (orientation 1011).

The resistance and magnetoresistance of the films were measured by the four-probe method (Fig. 1a); the thermopower was determined by the two-probe method. Studies of the wires were conducted by the two-probe method using an InGa eutectics to form ohmic contacts [14, 15].

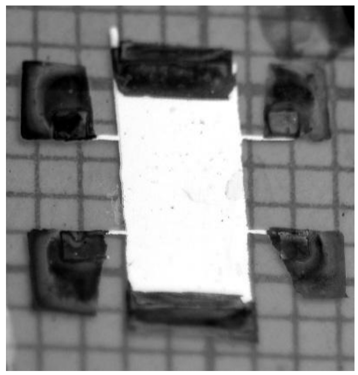

Fig. 1. Sample of the Bi–3.5at%Sb film single crystal on mica with four sprayed silver contacts.

Shubnikov–de Haas oscillations were measured at the International Laboratory of Strong Magnetic Fields and Low Temperatures (Wroclaw, Poland) in a superconducting solenoid at a temperature of 4.2 K in magnetic fields of up to 14 T.

3. Results and Discussion

3.1. Shubnikov–de Haas effect

Using Bi–3at%Sb wires (d = 1 μm), the SdH effect on longitudinal magnetoresistance $R(H)$ ($H \parallel I$) was studied. Figure 2 shows the dependences of reduced longitudinal magnetoresistance $\Delta R/R(H)$ ($H \parallel I$) of the Bi–3at%Sb wire and the pure Bi wire with d = 1 μm at 4.2 K. As in pure Bi wires, a maximum is formed in the initial portion of the $R(H)$ curves; the position of the maximum and the $\Delta R/R$ value significantly depend on wire diameter d [13, 16]. In the Bi–3at%Sb wires, the increase in $\Delta R/R$ at the maximum and the position of H_{max} at 4.2 K are 4 times higher than the respective parameters in the pure Bi wires of the same diameter.

The initial increase in resistance in a weak magnetic field $R(H)$ is attributed to both the anisotropy of the material and the occurrence of a galvanomagnetic size effect (GMSE). In a weak magnetic field, the curvature of the electron trajectory by the magnetic field leads to a decrease in the charge carrier mobility owing to an increase in the contribution of surface scattering.

Since the anisotropy of the Bi–3at%Sb wires is higher than that of pure bismuth and the charge carrier mobility increases while approaching a gapless state, an increase in $\Delta R/R$ at the maximum point and a shift of H_{max} to the region of stronger magnetic fields in the Bi–3at%Sb alloy wires compared with the pure Bi wires of the same diameter are obvious.

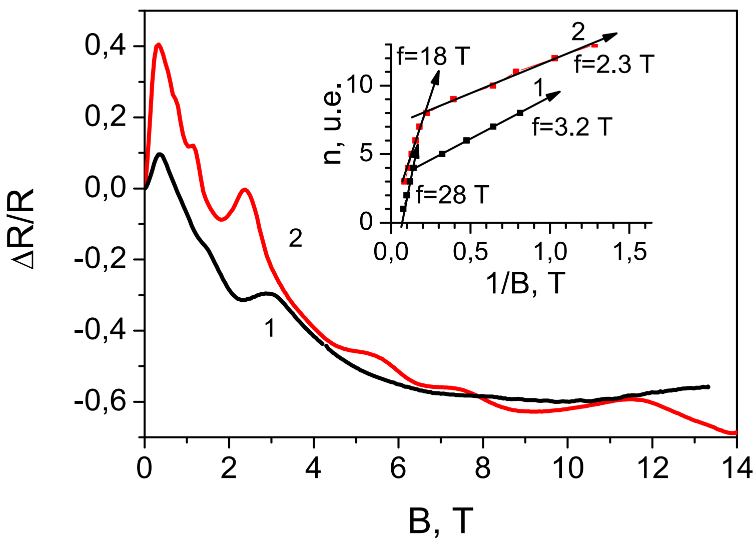

Fig. 2. Shubnikov–de Haas effect on longitudinal magnetoresistance $\Delta R/R(H)$ ($H \parallel I$) at 4.2 K: (curve *1*) the Bi–3at%Sb wire with d = 1 μm and (curve *2*) the pure Bi wire with d = 1 μm.

In the region where Larmor radius r_L is equal to wire diameter d ($r = d$), the role of the surface is excluded, and the resistance decreases tending to saturation in the region of strong magnetic fields ($\mu H >> 1$) for both the pure Bi and Bi–3at%Sb wires (Fig. 2).

The frequency of ShdH oscillations in a strong magnetic field from a *T*-hole ellipsoid $\Delta(1/H)$ decreases 1.5-fold compared with that for pure bismuth; this fact indicates a significant decrease in the cross section of the Fermi surface of *T*-holes and, together with a decrease in the volume of electron ellipsoids, proves a more than twofold decrease in the overlap of the *L* and *T* bands in the Bi–3at%Sb alloy wires, as in bulk samples of the respective composition.

3.2 Magnetothermoelectric properties

Figure 3a shows temperature dependences of relative resistance $\Delta R/R(T)$ of the Bi–3at%Sb wires with different diameters (curves *1*–*5*) and the Bi–3at%Sb single-crystal film with t = 1 μm (curve *6*).

It is evident from Fig. 3a that the $R(T)$ dependence exhibits a metallic behavior only in the wires with d > 1.2 μm.

The $R(T)$ dependences for the wires with d < 1.2 μm and films with t < 1.2 μm can be approximated by the expression

$$\rho = \rho_0 * exp\left(\frac{\Delta E}{2\kappa T}\right). \quad (1)$$

The $\rho(10^3/T)$ dependences were used to determine thermal gap ΔE formed owing to the occurrence of the QSE and the dependence of the gap on wire diameter d. It was found that the gap increases from ΔE = 6 meV for the wires with d = 1.2 μm to ΔE = 24 meV for the wires with d = 0.3 μm. For the Bi–3.5at%Sb single-crystal films with t = 1 μm, the gap was 4.5 meV.

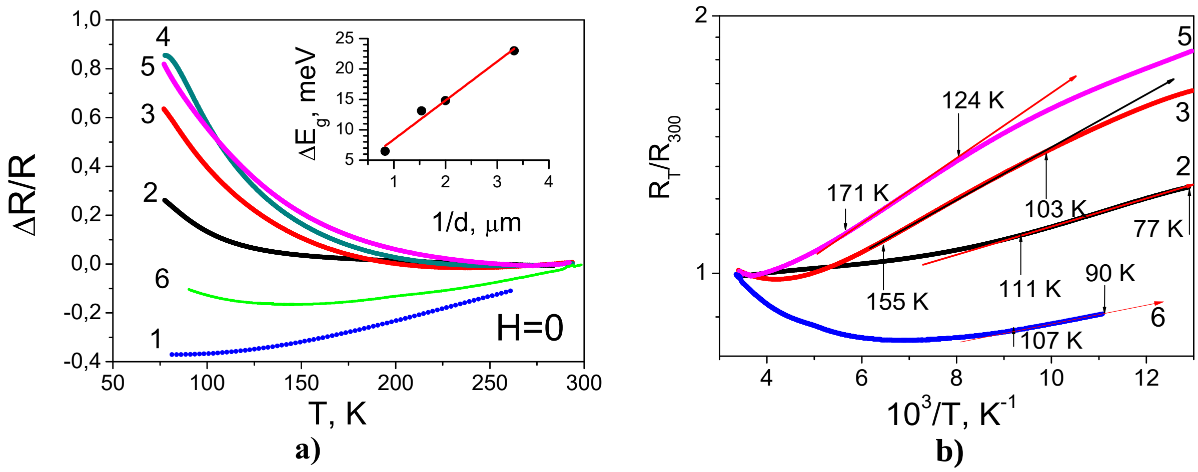

Fig. 3. (a) Temperature dependences of reduced resistance $\Delta R/R(T)$ of $Bi_{0.97}Sb_{0.03}$ thin wires and (b) R_T/R_{300} dependences on the reciprocal of temperature $10^3/T$: d = (*1*) 3.3, (*2*) 1.2, (*3*) 0.6, (*4*) 0.5, and (*5*) 0.3 μm; (*6*) the $Bi_{0.965}Sb_{0.035}$ film single crystal with t = 1 μm..

Note that the maximum gap value of ΔE = 15 and 20 meV in the pure Bi wires is achieved for diameters of 75 and 50 nm, respectively [14, 17]; in the Bi–3at%Sb wires, ΔE = 6 and 24 meV takes place for d = 300 nm; this fact suggests that the addition of antimony to bismuth leads to a decrease in the overlap of the *L* and *T* bands E_o; therefore, the QSE can be observed for thicknesses of ≈1 μm. Figure 3a (inset) shows the dependence of the thermal gap on the reciprocal of wire diameter $\Delta E(1/d)$. It is evident from the figure that the dependence is close to linear; this finding is consistent with the theoretical predictions of [7, 16] and indicates the formation of a gap of *L* carriers in the Bi–3at%Sb semimetal wires during the implementation of the QSE.

The magnetothermoelectric properties of the wires and single-crystal films were studied in a temperature range of 300–77 K in a magnetic field of 0.4 T ($H \perp I$).

To provide the orientation of the magnetic field ($H \perp I$, $\perp \Delta T$) in respective crystallographic directions, TMRDs $\Delta R/R(\theta)$ and thermopower $\alpha(\theta)$ were recorded, while rotating the magnetic field in the trigonal–bisector plane.

Figure 4 shows TMRDs $\Delta R/R(\theta)$ of the Bi–3.5at%Sb film with t = 1 μm at temperatures of 300 and 77 K and the Bi–3at%Sb wires with d = 6 and 0.3 μm (Fig. 8b, insert) in a magnetic field of 0.4 T.

It is evident from Fig. 4 that, at 300 K, the TMRDs $\Delta R/R(\theta)$ are symmetric with respect to the rotation axis for both the films and the wires and correspond to analogous dependences of the bulk samples at the orientation of the principal axis of the crystal along the C_1 bisector axis and in the case of magnetic field rotation in the trigonal–bisector plane.

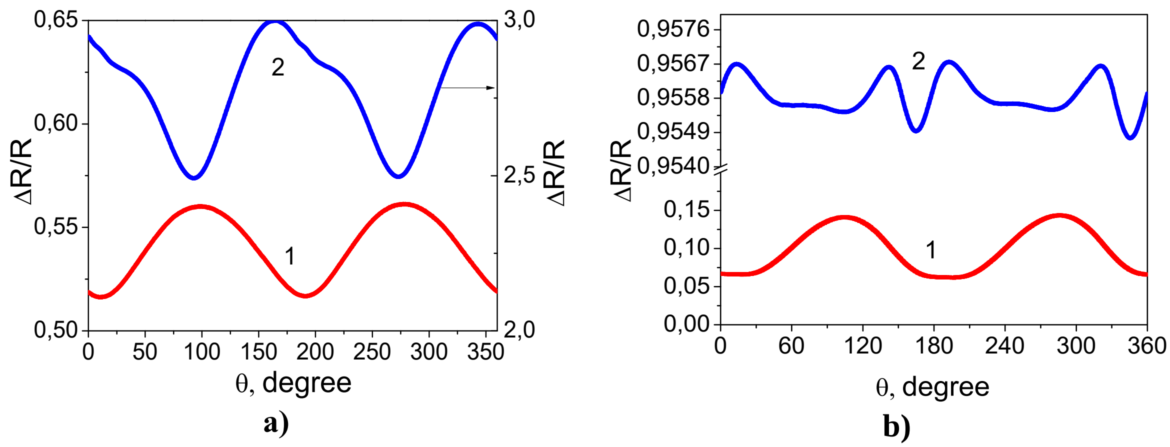

Fig. 4. TMRDs $\Delta R/R(\theta)$ ($H_T = 0.4$ T, $H \perp \Delta T$) of (a) the $Bi_{0.965}Sb_{0.035}$ film single crystal with t= 1 μm and (b) Bi–3at%Sb wire with d = 6 μm: (*1*) 300 and (*2*) 77 K.

With a decrease in temperature to 77 K, a decrease in anisotropy and a complication of the TMRDs $\Delta R/R(\theta)$ are observed. The slight asymmetry is associated with the deviation of the C_2 axis from the wire axis by 20° (according to X-ray diffraction studies of the single-crystal wires) [13–15].

Figure 5 shows the transverse thermopower rotation diagrams of (a) the $Bi_{0.965}Sb_{0.035}$ film and (b) the Bi–3at%Sb wire at temperatures of 300 and 80 K.

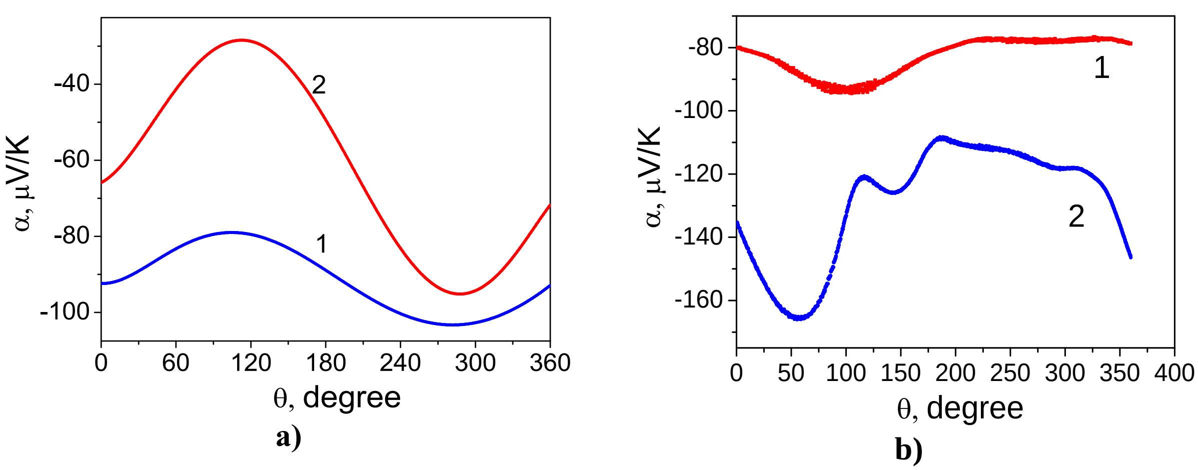

Fig. 5. Transverse magnetothermopower rotation diagrams $\alpha(\theta)$ (($H_\perp$ = 0.4 T) of (a) the $Bi_{0.965}Sb_{0.035}$ film single crystal with t = 1 μm and (b) the Bi–3at%Sb wire with d = 6 μm: (*1*) 300 and (*2*) 77 K.

Noteworthy is the fact that the magnetoresistance anisotropy is extremely low both at 300 and 77 K for wires with the different diameters (d = 6 and 0.3 μm), whereas the thermopower anisotropy significantly increases with a decrease in temperature to 80 K for both the wires with

d = 3.4 μm and the Bi–3.5at%Sb film with t = 1 μm.

Thermomagnetic effects are more sensitive to the features of the band structure, the charge carrier mobility, and the scattering process than galvanomagnetic effects; this factor leads to the occurrence of the switching effect [18–20]. The switching effect, i.e. the manifestation of the dependence of thermoelectric coefficient α(θ) on a change in the magnetic field direction α(–) and α(+) is associated with the presence of electrons and holes with different symmetries of energy extreme localization points and the slope of the isoenergetic surface relative to the crystallographic axes [18].

This effect was particularly pronounced in bulk Bi samples when the temperature gradient did not coincide with the principal axes of the crystal [21]. A decrease in the temperature and an increase in the magnetic field (>1 T) lead to a significant enhancement of the switching effect.

It is known that, in Bi and $Bi_{1-x}Sb_x$ wires, the wire axis is deflected from the bisector axis by approximately 20° in the bisector–trigonal plane and temperature gradient ΔT does not coincide with the C_2 bisector axis. Therefore, the occurrence of the switching effect in the Bi–3at%Sb wires with d = 6 μm and the Bi–3.5at%Sb films with t = 1 μm is obvious.

The occurrence of anisotropy of 60 μV/K at 77 K in the Bi–3at%Sb wires and films can be used in anisotropic thermoelectric converters at low temperatures.

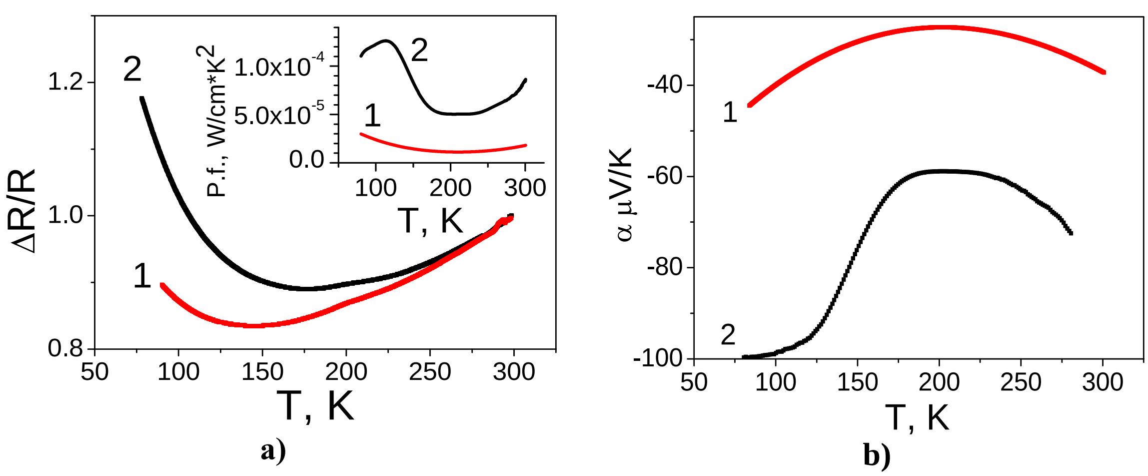

Fig. 6. Temperature dependences of (a) the reduced resistance of the film single crystal and (b) the thermopower of the $Bi_{0.965}Sb_{0.035}$ sample at H = (*1*) 0 and (*2*) 0.4 T ($H \perp I$, $H \parallel C_3$); the sample thickness is t = 1 μm. Inset: calculated values of the power factor as a function of temperature P.f.(T).

Figures 6 and 7 show the temperature dependences of the magnetoresistance ΔR/R(T) ($H \perp I$) and magnetothermopower α(T) ($H \perp \Delta T$, $H_\perp$ = 0.4 T) of the single-crystal film (Figs. 7, 8) with a thickness of t = 1 μm and the wires with diameters of 3.3 and 0.3 μm (Fig. 7). The magnetic field of 0.4 T ($H \perp \Delta T$) was directed along the C_3 axis (point 0 in the TMRDs) and along the C_2 axis (θ = 90°).

In wires with d > 1 μm and films with t > 1 μm, a magnetic field of 0.4 T ($H \perp \Delta T$) leads to an increase in the absolute value of thermopower with a decrease in temperature to 80 K; in the wires with d = 6 μm, the thermopower increases to –180 μV/K (Fig. 7b, curve *2*).

In thin Bi–3at%Sb wires (d = 0.3 μm), the absolute value of thermopower decreases at 80 K (Fig. 7b, 8b, curve *1*). A significant decrease in the absolute value of thermopower with a decrease in wire diameter d up to the sign reversal from (–) to (+) was observed in thin Bi wires [22] and theoretically substantiated in studies where a theoretical calculation of the thermopower in quantum bismuth wires was conducted taking into account the scattering of electrons and holes by long-wave acoustic vibrations and a rough surface (in the form of a delta-like surface fluctuation).

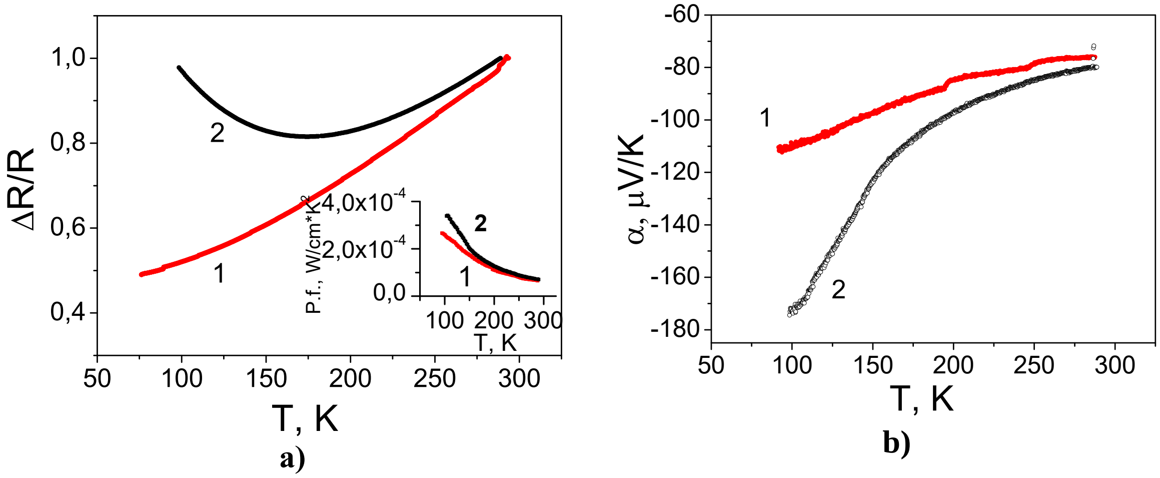

Fig. 7. Temperature dependences of (a) reduced resistance ΔR/R(T) of Bi–3at%Sb wire with d = 6 μm and (b) thermopower α(T) at H = (*1*) 0 and (*2*) 0.4 T. Inset: calculated values of the power factor as a function of temperature P.f.(T).

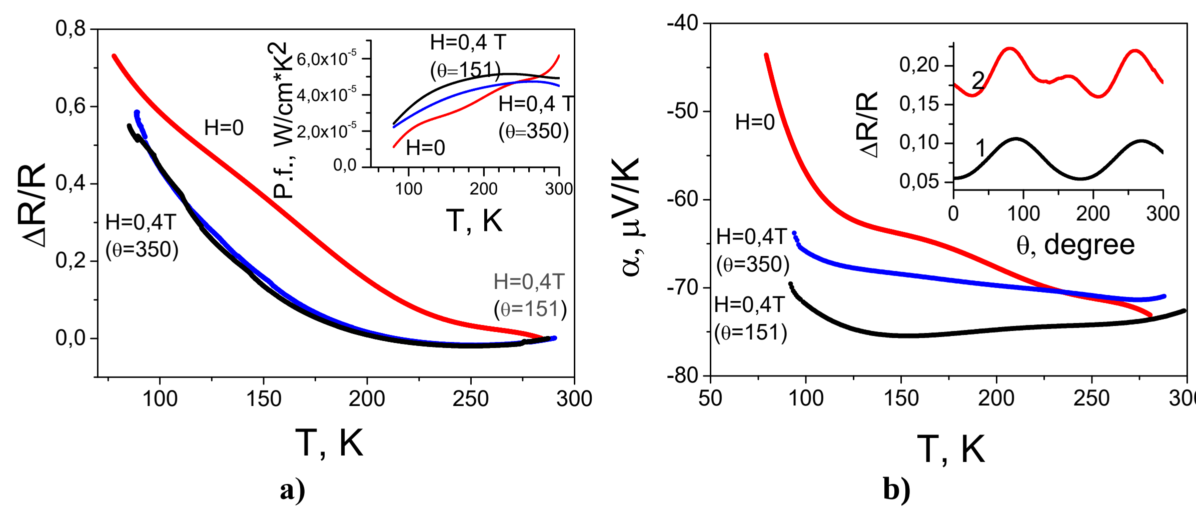

Fig. 8. Temperature dependences of (a) reduced resistance ΔR/R(T) of Bi–3at%Sb wire with d = 0.3 μm at H = (*1*) 0 and (*2*) 0.4 T and (b) thermopower α(T). Insets: (a) calculated values of the power factor as a function of temperature P.f.(T) and (b) TMRDs at T = (*1*) 300 and (*2*) 80 K.

The authors of [23–25] also indicated the possibility of occurrence of this mechanism. The weakening of the effect in Bi–3at%Sb wires is attributed to a decrease in the Fermi momentum of electrons. For large wire diameters, it is necessary to take into account a larger number of dimensionally quantized levels, which leads to a weakening of the effect.

According to the experimental results, power factor $\alpha^2\sigma$ was calculated for wires and films at H = 0 and $H_\perp$ = 0.4 T (Figs. 6a, 7a, 8a (insets)) and the temperature dependence of the power factor $\alpha^2\sigma$ (T) in a temperature range of 77–300 K was recorded.

It was found that power factor $\alpha^2\sigma$ achieves a maximum value of 3.5×10^{-4} W/(cm K^2) at 80 K in a magnetic field of 0.4 T ($H \perp \Delta T$); it is 3 times higher than the value obtained for the single-crystal film. A decrease in wire diameter d leads to a more than an order of magnitude decrease in the power factor in the Bi–3at%Sb alloys; this finding is primarily attributed to the fact that a decrease in wire diameter d (as in the pure Bi wires) leads to the thermopower sign reversal; that is, in the given ranges of temperatures and diameters, this factor leads to a decrease in the absolute value of thermopower, which in turn leads to a decrease in power factor $\alpha^2\sigma$ in thinner wires at low temperatures.

4. Conclusions

A technology for preparing single-crystal wires and films has been developed. Single-crystal wires and films based on Bi–3at%Sb semimetal alloys have been prepared.

The recorded dependences and SdH oscillations have revealed that, in the Bi–3at%Sb wires, the overlap of the L and T bands decreases more than twofold compared with that in pure Bi.

It has been found that, in Bi–3at%Sb wires, the QSE-induced semimetal–semiconductor transition occurs at diameters of $d < 1$ μm, which is more than an order of magnitude higher than in the pure Bi wires and 1.5 times higher than in Bi–2at%Sb.

It has been shown that, with a decrease in wire diameter d, the energy gap increases in accordance with a law close to $1/d$, which is consistent with theoretical calculations taking into account the quantum nature of conductivity.

It has been found that the maximum thermopower anisotropy is achieved at a temperature of ≈100 K; it is 60 μV in the single-crystal films with t = 1 μm and the Bi–3at%Sb wires with d = 6 μm, which is an important factor for designing anisotropic thermoelectric energy converters operating in a temperature range of 100–80 K.

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