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THERMOELECTRIC PROPERTIES OF QUANTUM Bi WIRE DOPED WITH Sn AT ELECTRON TOPOLOGICAL TRANSITIONS INDUCED BY STRETCH AND DOPING

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Abstract. The work is devoted to investigation of thermopower and magneto-thermopower in the longitudinal magnetic field in wires of pure Bi and Bi<Sn> alloys with concentrations of *T*-holes at 4.2K up to $3 \cdot 10^{18}$ cm^{-3}. The diameters of wires change from 100 nm to 10^3 nm. Bi and Bi<Sn> wires (in glass cower) were fabricated by casting method from liquid phase. All wires had the same orientation – wire axis make up and angle of 20° with the bisector axis C_S in the bisector trigonal plane.

Peculiarities of thermopower and resistance behavior caused by electron topological transitions (ETT) induced by stretch and doping are found. ETT were fixed by change of the Fermi surface cross-section detected by the ShdH oscillations on both resistance and thermopower.

It is shown that the positive peak in the temperature dependence thermoelectric power α and power factor P.f.$=\alpha^2\sigma$ in nanowires of pure Bi, observed at ~40K, is shifted in area of higher temperatures with growing Sn concentration. At low temperatures the singularities in the thermopower and resistance at ETT induced by extension are significantly different for the cases, when the Fermi level ε_F is located in the conduction band or in the valence band of light L holes. Thus, in the first case the electron input increases with extension, but in the second case the hole one increases, i.e. the positive thermopower value becomes greater.

1. INTRODUCTION

In bulk tin-doped bismuth samples the thermoelectic effects have been investigated in works [1, 2, 3]. It was shown [4], that in the temperature range from 10 to 300K the thermoelectric power α has the positive maximum not exceeding +40 μV/K for all studied concentrations, and only in phonon drag area thermopower has sharp peak +85 μV/K in the bisectix direction near 4K. Such a large value α is more typical for a nondegenerate semiconductor than for a degenerate semimetal [4, 5].

The theoretical studies of low dimensional system have predicted that Bi- nanowires are a good candidate for n-type leg for the thermoelectric devices. According to [6] Bi-nanowires become semiconductors when the diameter is decreased below 50 nm due to the carrier energy spectrum size quantization. The diverging density of states at the extrema of 1D bands leads to high value of thermopower α and the thermoelectric efficiency ZT (Z – thermoelectric figure of merit: $Z=\alpha^2\sigma/\kappa$, α – thermoelectric power, σ – electrical conductivity, κ – thermal conductivity).

In previous theoretical modeling studies [7] on enhancement of the thermoelectric performance with $Z_{10}T>1$ was predicted for n and p-type Bi nanowires. The p-type nanowires are of a special interest, while the material for n-type legs at 77K ($Bi_{1-x}Sb_x$) is good known.

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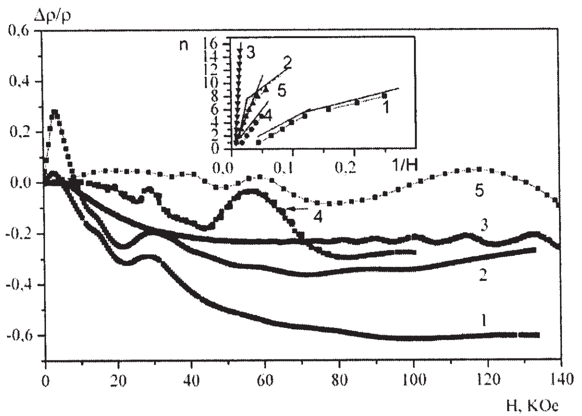

Fig. 1. Dependence of the longitudinal magnetoresistance $\Delta R(H)$ on field in single crystal wires of bismuth and its alloys with Sn at T=4.2 K. 1. Bi, d=0.48μm, 2. Bi-0.01at%Sn, d=0.9μm, 3. Bi-0.02at%Sn, d=0.5 μm, 4. Bi-0.05at%Sn, d=0.23 μm, 5. Bi-0.07at%Sn, d=0.3 μm. Insert dependences of quantum number n- ShdH oscillations vs H^{-1}.

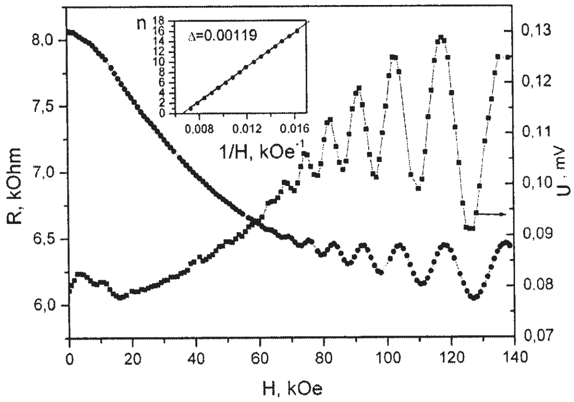

Fig. 2. ShdH oscillation on magnetoresistance and thermopower Bi-0.025at%Sn (H II I) d=400nm. Insert dependences of quantum number n- ShdH oscillations vs H^{-1}. U – the signal of thermopower with constant gradient.

We used the elastic elongation of the nanowires as an additional parameter to the Sn alloying effect and quantum confinement effect.

Proceeding from the above-said we have studied the resistance (ρ_{ii}) and thermopower (α_{ii}) of thin single crystal wires of bismuth doped with tin in the temperature range 4.2–300K at elastic deformation up 2.5% and magnetic field up 14 T.

2. SAMPLES

The single crystal wires of Bi and its alloys with Sn in a glass sheath were obtained by the liquid phase casting. The alloys with low content of the impurity were obtained by bismuth dissolution of preliminarily synthesized bulk crystals of alloys Bi<Sn> of a given composition. In order to avoid the alloy oxidation, especially of Sn impurity the process of the wire preparation was performed in Ar atmosphere. Due to intensive stirring of the alloy melted drop by the high-frequency electromagnetic filed (~880 kHz), high velocity of the wire crystallization process (~600 m/min) a uniform distribution of the impurity along the whole stretched wire was achieved. The crystal wire diameter was varied in the limits of $100<d<10^3$ μm. [8].

All the measured crystals had the same orientation. One of the bisector axes C_s made up with the wire axis an angle φ ~ 19.5° in corresponding specular plane of the crystals so that one of the binary axes is perpendicular to it and the third order axis C_3 in inclined to the wire at an angle of ≈70 °. This orientation corresponds to the natural direction of the bismuth crystal growth.

The perfection and orientation of the samples were verified with the help of roentgenograms of rotation, and magnetoresistance by quality and structure of the ShdH oscillations at H II I. The magnetic field-dependent resistance $R(H)$, was measured in the temperature range 4.2-300K, and for magnetic fields of up to 14 T, in a Bitter-type magnet and in a superconducting solenoid in the International High Magnetic Field Laboratory (Wroclaw, Poland).

For studying of kinetic effects under the influence of strong elastic deformation a displacement transformer was used [9], having pitch. This allowed to measure the resistance, Seebeck coefficient, magnetoresistance both in the continuous and discrete regimes.

3. RESULTS AND DISCUSSION

To evaluate the Fermy level (FL) location in wires with different Sn concentrations the ShdH oscillations have been measured in the longitudinal magnetic field (H || I) (Fig. 1).

The most pronounced oscillations have been observed in the thermomagnetic power (Fig. 2). In wires Bi-0.01at%Sn the ShdH oscillations from both electrons in L and holes in T are observed. In the

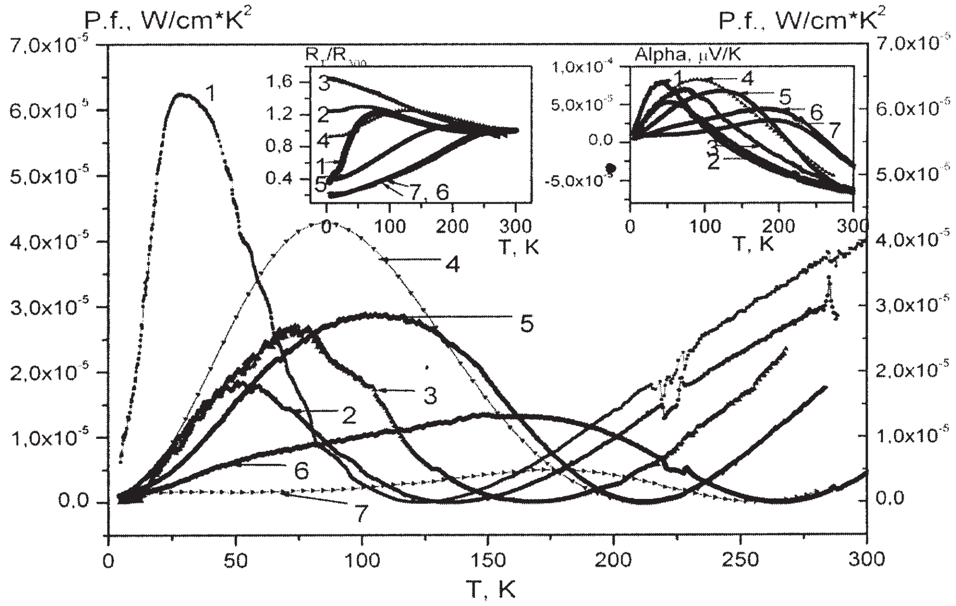

Fig. 3. The temperature dependence of the thermopower $\alpha(T)$ and (insert on the right) residual resistance R_T/R_{300} (insert on the left) and P.f. = a^2s of Bi – doped Sn wires. 1- Bi, d=0.23μm; 2. Bi-0.01at%Sn, d=0.3μm; 3. Bi-0.02at%Sn, d=0.5μm; 4. Bi-0.02at%Sn, d=0.2μm; 5. Bi-0.025at%Sn, d=0.4μm; 6. Bi-0.05at%Sn, d=0.32μm; 7. Bi-0.07at%Sn, d=0.35μm.

wires Bi-0.02at%Sn only oscillations from T- holes were well seen at magnetic field up to 14T. This together with the absence of the magnetoresistance in the weak magnetic field indicates that the Fermi level is in the band-gap in L-point of the Brillouin zone and conductivity at 4.2K is realized only by T-holes. The ShdH oscillations observed in wires Bi-0.05at%Sn and Bi-0.07at%Sn contain frequencies $\Delta(H^{-1})$ relating only to L-holes. High concentration of T-holes shifts the region of its observation in stronger magnetic fields.

Estimation of position of the Fermi level of T-holes ε_F^T in the frames of the two-band Kein model was calculated by the expression:

$$\varepsilon_F^T = E_{par} - \frac{1}{2}\varepsilon_g^T + \left[\varepsilon_{par}^2 + \left(\frac{1}{2}\varepsilon_{gT}\right)^2\right]^{\frac{1}{2}}, \qquad (1)$$

where $E_{par} = \dfrac{S_T}{2\pi m_{cT}} = \dfrac{eh}{2\pi c}\cdot\dfrac{\Delta_T^{-1}}{m_c^T}$, E_{par} is the energy in the approximation of parabolic band, ε_F^T is the energy of holes in T calculated from the top of T-band downwards, ΔE_F^{-1} is the frequency of oscillations from the minimal cross-section of T-holes, ε_{gT}=200 meV according to [11]. In the case when the oscillations from T-holes were not observed (curves 4.5 in Fig.1) the value of ε_F^T was estimated from the dependence of the quasi-classical frequency Δ_b^{-1} from small cross-section S_b of ellipsoids (H||C$_2$) from the Fermi energy ε_F^T of holes in T obtained in [11]. At the calculation it was taken into account that at H II I as in the pure Bi- wires of the same crystallographic orientation the period of SdH oscillation from light L-holes (b ellipsoid) differs from the small cross-section at (H||C$_2$) by 1.9 times [8, 9].

Thus, we have studied single wires where the Fermi level is in the conductivity band of electrons (Bi, Bi-0.01at%Sn), in the band-gap ε_g^e (Bi-0.02at%Sn), in the hole L-band (Bi-0.025at%Sn, Bi-0.05at%Sn, Bi-0.07at%Sn). Values of the energy ε_F^T are given in Table 1. The dependences of the residual resistance R_T/R_{300} and the thermopower $\alpha(T)$, P.f. vs. temperature in Bi wires with different Sn concentrations are shown in Fig. 3.

As it is seen from Fig.3, the positive maximum $\alpha_{ii}(T)$ is shifted to higher temperatures at Sn doping. Near T=80K there is the maximum value P.f.=4.2·10^{-5}W/cm·K^2 (for Bi-0.02at%Sn, d=200nm), however it is less than in pure bismuth due to monotonous increase of $\rho_{ii}(T)$.

Further doping of Bi nanowires with tin up to 0.05at%Sn and 0.07at%Sn, where the Fermi level considerably shifts into the region of the valence band of L-holes and degeneration of both L-holes

Table 1.

N	at%Sn	ε_F^T, mV	α_{max}, μV/K	T^{max}, K	P.f. max, W/cm·K^{-2}
1	Bi	32	86	39	$6.2 \cdot 10^{-5}$
2	Bi-0.01	36	70	75	$2.7 \cdot 10^{-5}$
3	Bi-0.02	45	80	90	$4.3 \cdot 10^{-5}$
4	Bi-0.025	58	70	130	$3 \cdot 10^{-5}$
5	Bi-0.05	102	49	165	$1.75 \cdot 10^{-5}$
6	Bi-0.07	115	27	180	$4 \cdot 10^{-6}$

and *T*-holes increases. This leads to the positive maximum shift on the thermopower temperature dependence into the region of higher temperatures and to the decrease of its positive value.

As it is seen from Fig.3 the value of the P.f. in the measured samples Bi-0.05at%Sn are not big, but their maximal values lie in a wide temperature range of 80-130 K. The Seebeck coefficient $\alpha_{ii}(T)$ in the wire Bi-0.07at%Sn with d=0.23 μm becomes negative at T>250K.

Earlier it was shown by us [10] that sign inversion of the thermopower in Bi nanowires is due not only to the change of the ratio μ_e/ν_e, where μ_e is the mobility of electrons, ν_e is the mobility of holes due to the surface scattering of the carriers, but also due to change of the partial value of the thermopower of electrons and holes. In the first place this is explained by the fact that the scattering factor *r* having the value 0.5 for bulk Bi differs from *r* Bi- wires. When the temperature decreases (< 40K) the degeneration increases. The increase of the degeneration leads to the thermopower decrease.

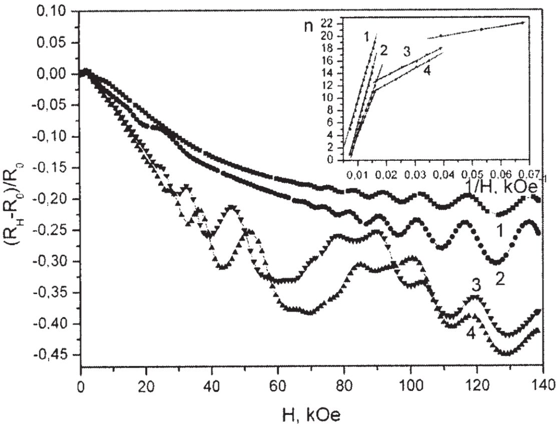

Fig. 4. ShdH oscillations LMR Bi-0.025at%Sn – wire at different deformations 1. ξ=0; 2. ξ=1,4%; 3. ξ=2.1%; 4. ξ=2.4%, T=4.2K, H II l. Insert dependences of quantum number n- ShdH oscillations vs H^{-1}.

At Sn doping the degeneration of *T*-holes responsible for positive value of α increases, and thus the thermopower maximum must shift into the region of higher temperatures, this being observed in the experiment.

Influence of the size effect consisting in this case in the increase of α_{max} value with the diameter d decreasing is most brightly shown in the wires with concentrations close to pure Bi. In the wires with concentrations Sn-0.05at% and especially 0.07at%Sn the size effect is shown more weakly. Increase of the impurity scattering leads to a decrease of the free path length of the carriers, this in its turn results in weakening of influence of the sample sizes on kinetic characteristics. The temperature dependences $\alpha(T)$ and $R(T)$ of wires Bi-0.07at%Sn are close to analogous dependences of bulk material. Thus, for observation of influence of the wire sizes on R and α, wires being thinner than in pure Bi – wires are necessary.

The peculiarity of Bi-0.02at%Sn, Bi-0.025at%Sn wires is that the FL position changes from 42 to 58 meV, i.e. the FL may be located either near the conduction band bottom or near the valence band top in the point L. Thus, the ETT may be produced at the elastic extension, i.e. the Fermi surface appears above the FL (when the ε_F ~ 45-40 meV) or under the FL (ε_F ~ 50 -55 meV).

In Fig. 4 variations of SdH oscillations are shown for longitudinal magnetoresistance in Bi-0.025at%Sn at various values of the relative extension $\xi=\Delta l/l$ (l – is the initial sample length). At ξ=0 we observed only one period of ShdH oscillations from *T*-holes. The initial ε_F value in these wires is 59 meV (ac-

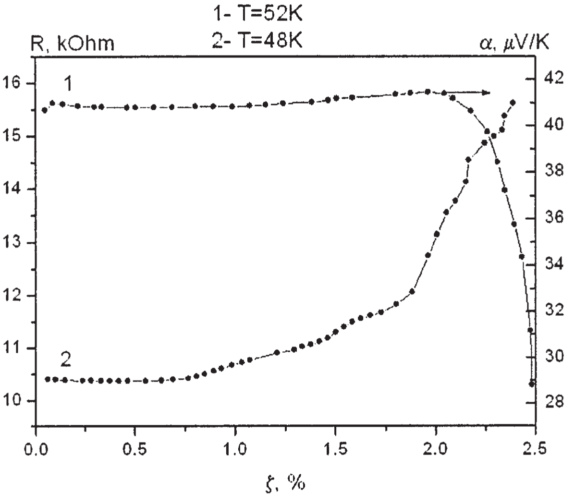

Fig. 5. Deformation dependences resistivity $R(\xi)$, T=48K (1) and thermopower $\alpha(\xi)$, T=52K, (2) Bi-0.025at%Sn - wire, d=350 nm.

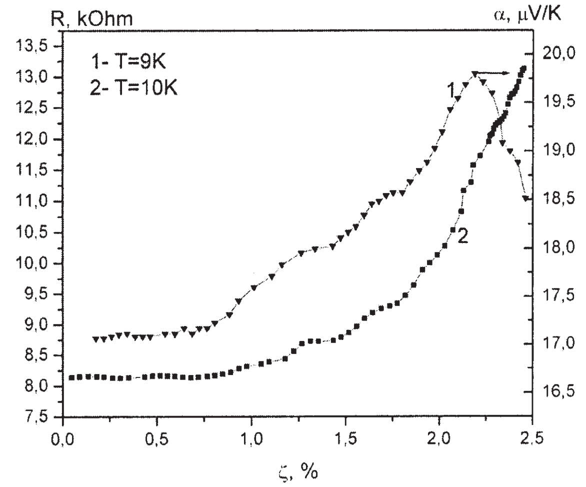

Fig. 6. Deformation dependences resistivity $R(\xi)$, T=10K (1) and thermopower $\alpha(\xi)$, T= 9K, (2) Bi-0.025at%Sn – wire, d=350 nm.

cording to (1)), i.e. ε_F is located just near the top of the band of light L holes. Under the elongation we can see clearly that the Fermi surface from L-light holes grows. The ETT accompanied by anomaly on $\alpha(\xi)$ at ξ=2.2% is probably connected to appearance of the Fermi surface of $L_{2,3}$ – electrons (Fig. 6).

The deformation dependences $R(\xi)$ and $\alpha(\xi)$ for Bi-0.025at.% Sn (ε_F = 58 meV) are shown in Fig. 5, 6. The $R(\xi)$ and $\alpha(\xi)$ behaviour at extension differs significantly for pure Bi wires and for Bi-0.01at%Sn wires. At it is seen from Fig. 6, the input of holes into thermopower increases with elongation at low temperatures and the positive value of thermopower grows. This is very important result for possible applications in thermoelectric conversion devices.

When the temperature increases to 100K, i.e. when the kT tailing is great (10 meV), that the FL encloses the conduction band, the deformation α dependences become similar to those in pure Bi wires: the electron input increases with extension and α becomes negative at T>150K (Fig. 4).

4. CONCLUSIONS

It is shown that in thin 0.1<d<1 μm single crystal wires of bismuth doped with tin at temperatures below T<200K it is possible to obtain structures for p-branch with parameters approaching the parameters for n-branch of bulk bismuth.

Changing the wire diameter and doping degree it is possible to shift the interval of the P.F. maximal value from 30-50K in pure bismuth wires to 130-220K in alloys Bi-0.07at%Sn.

At low temperatures the singularities in the thermopower and resistance at ETT induced by extension are significantly different for the cases, when the Fermi level ε_F is located in the conduction band or in the valence band of light L holes. Thus, in the first case the electron input increases with extension, but in the second case the hole one increases, i.e. the positive thermopower value becomes greater.

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