

THERMOELECTRIC PROPERTIES OF WIRES Bi-6at%Sb AND Bi-8at%Sb UNDER ELASTIC STRETCHES

I.A. Popov

*Institute of Applied Physics, Academy of Sciences of Republic of Moldova,
Academiei str., 5, Chisinau, Republic of Moldova*

Thin $\text{Bi}_{1-x}\text{Sb}_x$ wires with stibium concentration of 6 and 8at% in the free state and under elastic stretches are studied. Under 6-8% stretches the electron topological transition semiconductor-semimetal is found. The power factor is calculated.

It is known that $\text{Bi}_{1-x}\text{Sb}_x$ alloys, being substitutional solid solutions in the whole x interval, are the best thermoelectric material for n-type branches of thermoelements. Thermoelectric properties of the material considerably depend on the value of the energy gap ΔE_g [1]. In bulk single crystals of bismuth, one of the methods of the band gap change is doping with stibium. In this case there occurs reconstruction of the substance band structure accompanied by the transition semimetal-semiconductor at $x \approx 0,07$ due to removal of overlapping of the conduction and valence bands. When stibium concentration achieves twenty two percent an inverse transition takes place. Thus, $\text{Bi}_{1-x}\text{Sb}_x$ alloys in the x interval from 0,07 to 0,22 are narrow band semiconductors with the maximal value of the band gap about 25 meV [2]. Stibium concentration whereat ΔE_g achieves its maximal value corresponds to 12-16 percent according to different authors [3-5].

Additional possibilities to reconstruct zone spectrum of BiSb alloys are given by thin wires obtained by the liquid phase casting. First, appearance of the classical size effect may lead to the gap increasing, second, bismuth wires sustain significant elastic deformations, which influence the band gap too.

This paper is devoted to investigation of thermoelectric and magnetoelectric properties of single crystal nanowires BiSb (6 and 8at%Sb) in a glass cover. Measurement were carried out in the temperature range $4,2 \div 300$ K and partially in the range $77 \div 300$ K. Field dependences of the resistance were studied in Wroclaw in strong magnetic fields up to 14T. The samples were investigated both in the free, undeformed state and under elastic stretches ($\xi = \Delta l / l$, where Δl is the sample elongation) up to 2,5%. The wire diameter was varied from $0,2 \mu\text{m}$ to $3 \mu\text{m}$.

Thin Bi wires and BiSb alloys with different stibium concentration were obtained by the liquid phase casting by the Ulitovsky method [6]. Weighings of the corresponding composition were placed in an ampule made of pyrex or molybdenum glass and were melted under the high-frequency inductor action. The material in its turn melted the ampule bottom, which subsequently was stretched into a capillary. Due to a good adhesion the weighing material was consecutively dragged into the obtained capillary. The possibility to change the velocity of the microwire stretching allowed us to obtain samples with the diameter $\geq 0,2 \mu\text{m}$.

Temperature dependences of the resistivity of BiSb wires of both compositions were investigated (Fig. 1,2). The measurements were carried out in the temperature range $77 \div 300$ K. It is obvious that bismuth nanowires with six and eight percent stibium impurity in the free, undeformed state are semiconductors. This is confirmed by distinct exponential sections on the obtained resistivity curves on the inverse temperature on the logarithmic scale. By the value of inclination of the exponential sections the band gap for every sample was calculated

(insert in Fig.1, 2). For sufficiently thick wires with diameter $\geq 8 \mu\text{m}$, ΔE_g was about 10-15 meV (Fig. 1,2). These results qualitatively agree with the data on bulk [2] and film single crystals [7].

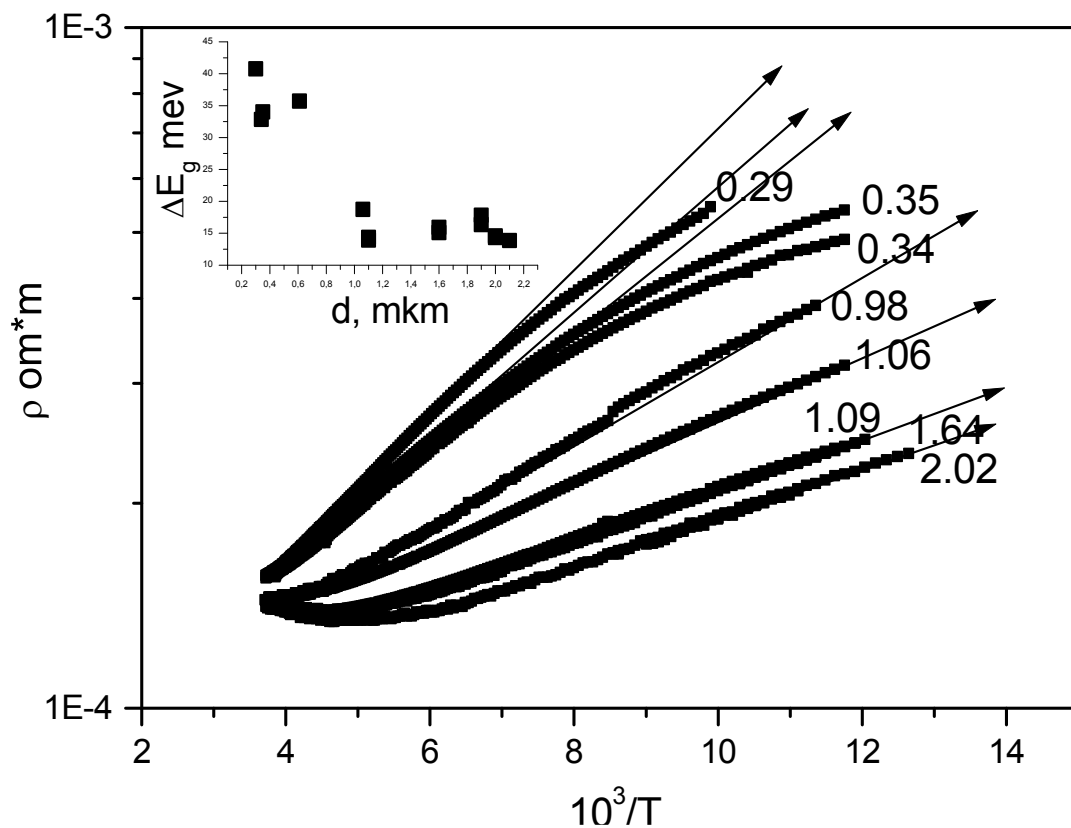


Fig.1 The resistivity dependence on the inverse temperature of $\text{Bi}_{0.92}\text{Sb}_{0.08}$ and the band gap of $\text{Bi}_{0.92}\text{Sb}_{0.08}$ on diameter

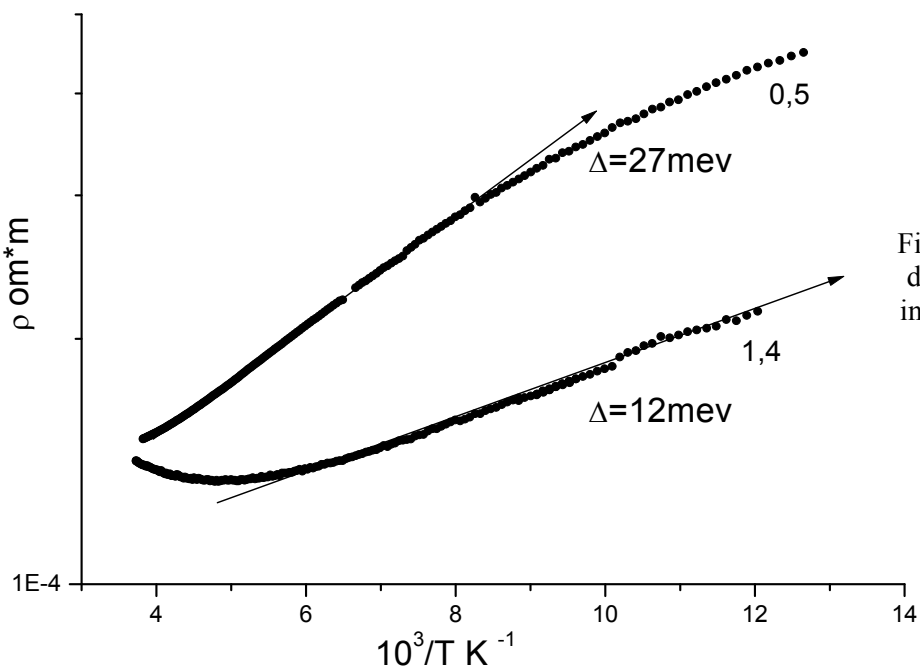


Fig.2 The resistivity dependence on the inverse temperature of $\text{Bi}_{0.94}\text{Sb}_{0.06}$

However, for wires with diameter $\leq 0,6 \mu\text{m}$ a significant increase of the band gap is observed. This may be due to the classical size effect influence, and it should be noted that for thinner samples the linear section shifts into the region of higher temperatures. Thus, at $d \approx 0,5 \mu\text{m}$ the curve becomes straight at the temperatures $200 \div 125 \text{ K}$. Respectively, the temperature range of the linear section of these samples ($\Delta T \approx 75 \text{ K}$) is smaller than for thicker ones ($\Delta T \approx 90$). This leads to less accuracy of calculation of ΔE_g of thin samples.

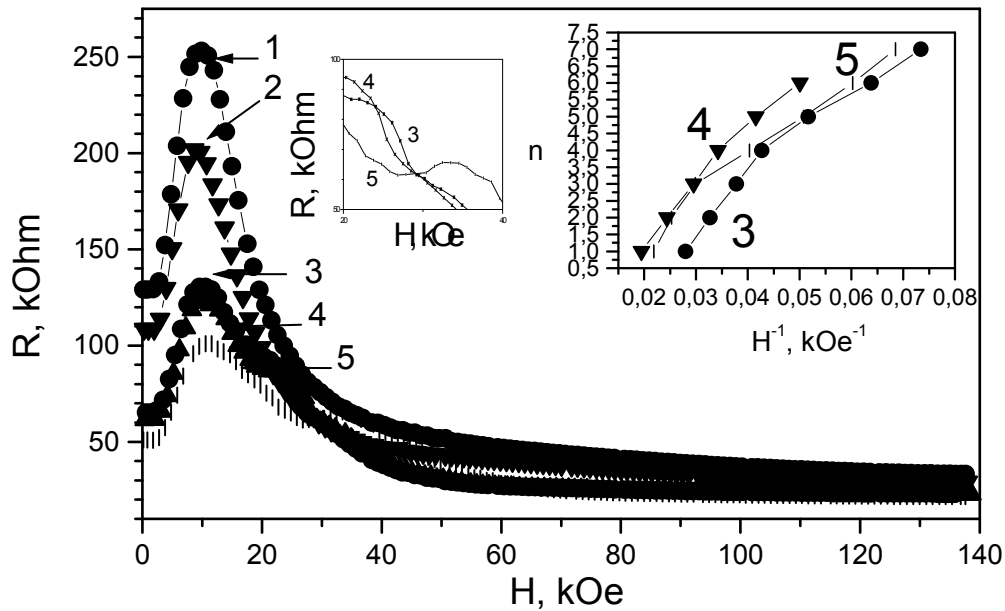


Fig.3 Field dependences of the longitudinal magnetoresistance of $\text{Bi}_{0.94}\text{Sb}_{0.06}$ at $T=4,2 \text{ K}$, where ξ values are the following: 1-0%; 2-0,59%; 3-0,87%; 4-1,19%; 5-1,35%

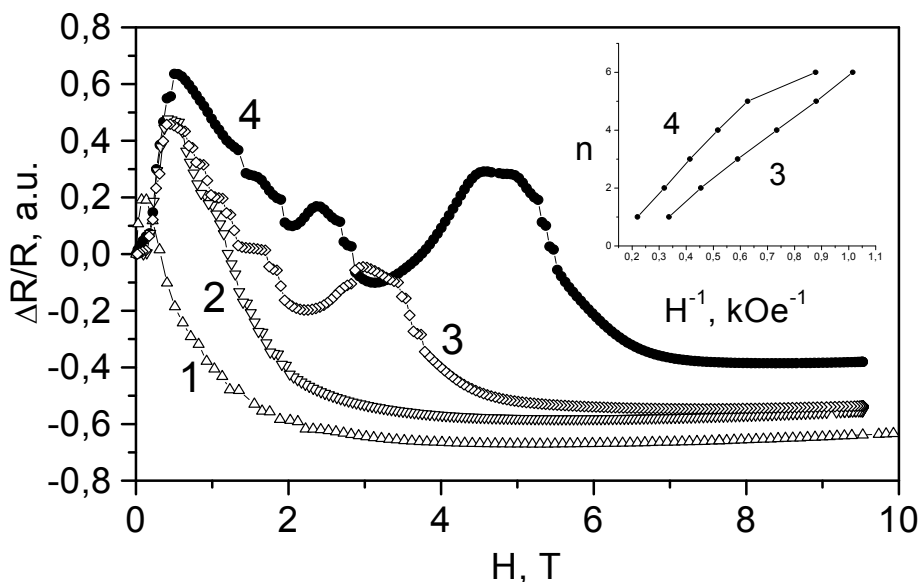


Fig.4 Field dependences of the longitudinal magnetoresistance of $\text{Bi}_{0.92}\text{Sb}_{0.08}$ at $T=4,2 \text{ K}$, where ξ values are the following: 1-0%; 2-0,7%; 3-1,1%; 4-1,6%

Figures 3 and 4 show the dependences of the longitudinal magnetoresistance of nanowires $\text{Bi}_{0.94}\text{Sb}_{0.06}$ and $\text{Bi}_{0.92}\text{Sb}_{0.08}$ at $T=4,2$ K both in the elastic stretch conditions and without them. In all the cases the general form of the curve remains unchanged. Beginning with small values of the field $R(H)$ increases, then it achieves its maximum at certain value $H=H_{\text{max}}$. All along the resistance curve on the magnetic field at $\xi=0$ monotonous course is observed.

Table 1

Composition	Diameter d , μm	Stretch ξ , % rel.un.	Period T
$\text{Bi}_{0.94}\text{Sb}_{0.06}$	0.5	0.87	0.02046
$\text{Bi}_{0.94}\text{Sb}_{0.06}$	0.5	0.87	0.01
$\text{Bi}_{0.94}\text{Sb}_{0.06}$	0.5	1.19	0.01932
$\text{Bi}_{0.94}\text{Sb}_{0.06}$	0.5	1.19	0.00987
$\text{Bi}_{0.94}\text{Sb}_{0.06}$	0.5	1.35	0.01548
$\text{Bi}_{0.94}\text{Sb}_{0.06}$	0.5	1.35	0.008
$\text{Bi}_{0.92}\text{Sb}_{0.08}$	0.5		0.202
$\text{Bi}_{0.92}\text{Sb}_{0.08}$	0.5		0.272

Under loading of BiSn nanowires (6 and 8at%Sb) the band gap decreases. When elongation achieves 0,6-0,8%, Lifshits $21/2$ electron topological transition semiconductor-semimetal takes place. This is confirmed by appearance of the Shubnikov-de Haas oscillations on the longitudinal magnetoresistance curves (insert of Fig.3, Fig.4) for different ξ well observed against the background of the monotonous course. According to the obtained data the dependences of quantum number n on the inverse field ($1/2$) of the Shubnikov-de Haas oscillations were plotted (see the inserts) and values of the oscillation periods were calculated (see Table 1). When the loading (stretch) increases, the period of the Shubnikov-de Haas oscillations decreases, this confirming increase of the appeared Fermi surface cross-section.

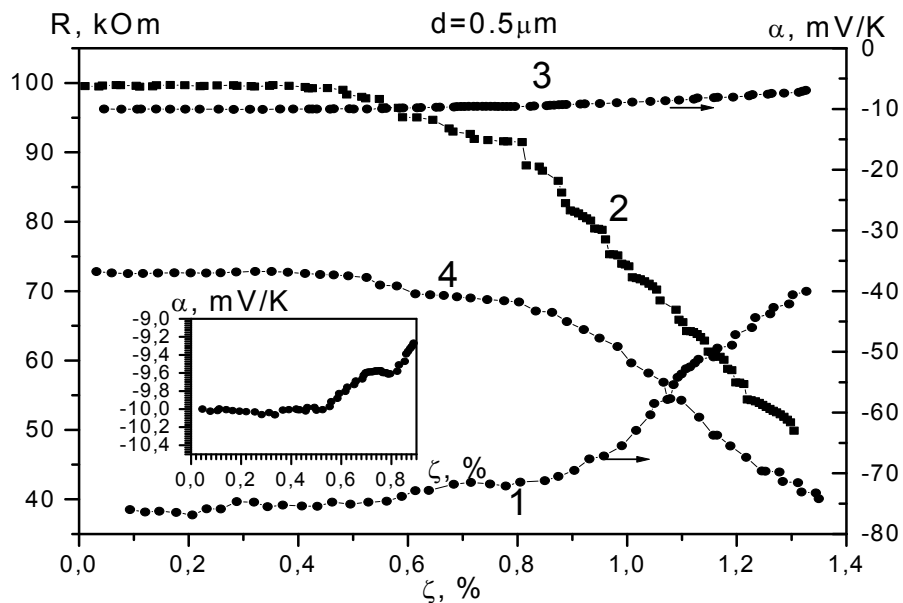


Fig.5. Dependence of thermopower and resistance of Bi-6at%Sn nanowire on stretch ($d=0,5$ μm) at the temperature of 5 K (1,2) and 45 K (3,4).

For the sample of Bi-6at%Sb nanowire with the diameter 0,5 μm , the dependences of the thermopower and resistance on stretch were plotted (Fig.5). The measurements were carried out at the temperature of 5 K (curves 1,2) and of 45 K (curves 3,4). Initially, up to 0,4% stretching, both thermopower and resistance depend very weakly on deformation. However, at $\xi \approx 0,8\%$ the resistance behaviour changes, it begins to fall with increasing loading and twice reduces. For the thermopower another type of behaviour is characteristic, besides, on the curve $\alpha(\xi)$ at corresponding values of elongation a peculiarity is observed (insert of Fig.5). This confirms the presence of the transition semiconductor-semimetal.

Fig.6 shows the temperature dependences of thermopower and resistance for two BiSb samples with stibium concentration 6at%. On the basis of the obtained results the temperature dependence of the power factor ($\alpha^2\sigma$) was calculated and plotted. Diameters of the studied wires were 1 and 0,5 μm (curves 2 and 1, respectively). If on curves $\alpha(T)$ there is no big difference, the resistance of the sample with $d=0,5 \mu\text{m}$ increases more rapidly with the temperature lowering. Near helium both curves meet again, because the thermopower values decrease by modulus and tend to zero. As a result, the curve $\alpha^2\sigma(T)$ of sample with the diameter 1 μm is located above in the temperature range 50-250 K.

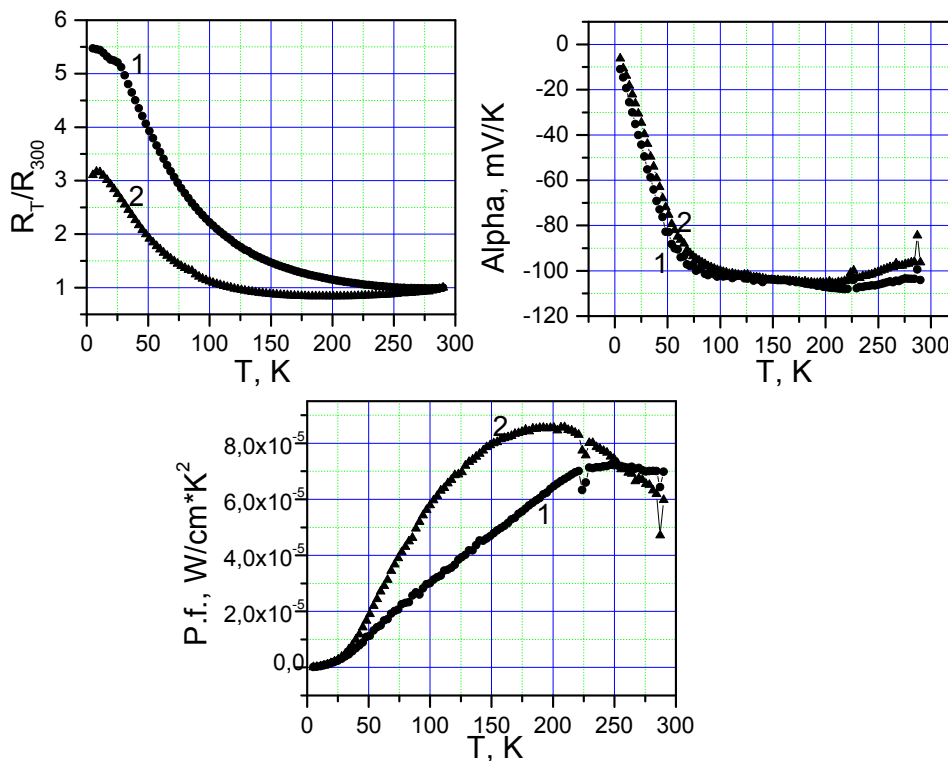


Fig.6. Temperature dependences of the resistance, thermopower and power factor of $\text{Bi}_{0.94}\text{Sb}_{0.06}$.

In the present work thermoelectric properties of BiSb wires (6 and 8at%) were studied. It was found that both compounds are semiconductors. The band gap value is 10÷15 meV when the sample thickness is $\geq 8 \mu\text{m}$. The electron topological transition semiconductor-semimetal under elastic stretch $\xi \approx 0,6-0,8\%$ was found. For Bi-6at%Sb by the temperature dependences $\alpha(T)$ and $R(T)$ the power factor was calculated. The maximal value $\alpha^2\sigma$ was $8 \cdot 10^{-5} \text{ w/smK}^2$ at the temperature 210-150 K.

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