

# Temperature and magnetic dependence of the resistance and thermopower in the topological insulator $\text{Bi}_{1-x}\text{Sb}_x$ nanowires

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Received 6 June 2013, accepted 4 March 2014

Published online 15 April 2014

**Keywords** semiconductor nanowires, surface states, topological insulators

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We report on the electrical transport and thermoelectric properties of  $\text{Bi}_{1-x}\text{Sb}_x$  nanowires in the semiconductor region made of  $\text{Bi}_{1-x}\text{Sb}_x$ . Such alloys are classified as topological insulators. The individual Bi-17 at% Sb wires in a glass capillary with diameters ranging from 100 to 1000 nm were prepared by high-frequency liquid-phase casting in an argon atmosphere. They were cylindrical single crystals with (1011) orientation along the wire axis. For large-diameter wires we observed that the temperature-dependent resistance,  $R(T)$ , displays the temperature-activated dependence that is expected of semiconductors. We also found that small-diameter wires at low temperatures show a sharp deviation from the behavior of the resistance  $R(T)$ , characteristic of semiconductors. The

contrasting behavior of wires of different diameters can be interpreted in terms of the conductance of the surface states in BiSb where the surface states arise through a spin-orbital Rashba interaction in the surface of BiSb. The thermopower remains negative over the entire temperature range, but it is strongly temperature dependent. The longitudinal magnetoresistance  $R(H)$  at low temperature shows quantum Shubnikov-de Haas oscillations only in thin ( $d < 200$  nm) Bi-17 at% Sb nanowires. Only high-mobility carriers display SdH oscillations. Since we expect the electronic transport in the 200-nm semiconducting  $\text{Bi}_{1-x}\text{Sb}_x$  nanowires to be dominated by the surface, this indicates that the surface states have sufficiently high mobility to display SdH.

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**1 Introduction** A large number of studies on the band structure and the band parameters of Bi-Sb alloys have been reported [1–3]. The direct energy gap of the L-point in the Brillouin zone of  $\text{Bi}_{1-x}\text{Sb}_x$  decreases with increasing Sb concentration up to about  $x = 0.04$  [4]. The energy overlap between the conducting band at the L-point and the hole band at the T-point also decreases with increasing Sb concentration and it becomes zero at about  $x = 0.06$ – $0.07$  [5, 6].

At a concentration of Sb ( $0.08 < x < 0.2$ ) alloys  $\text{Bi}_{1-x}\text{Sb}_x$  are semiconductors with an inverted band spectrum [3]. In these semiconductors with the inverted spectrum, a topological insulator (TI) state occurs [7–9]. A topological insulator (TI) represents another class of states that are topologically distinct from band insulators. It is

known that  $\text{Bi}_{1-x}\text{Sb}_x$  alloys exhibit the topological nature of surface states [9–11]. However, the evidence is spectroscopic. There have been few studies of surface electronic transport. Taskin and Ando [12] interpreted SdH phenomena that they observed in bulk  $\text{Bi}_{0.91}\text{Sb}_{0.09}$  in terms of surface states.

The authors of Ref. [13] studied the transport properties of a TI nanowire under a magnetic field applied along its length. They predict that, with a strong surface disorder, a characteristic sign of the band topology is revealed in Aharonov–Bohm (AB) oscillations of conductivity. This is another motivation to study magnetotransport in nanowires.

The AB oscillations in quantum Bi wires with a period  $hc/e$  and  $hc/2e$  are observed in both longitudinal and

transverse magnetic fields and interpreted in terms of surface states [14, 15].

It has been predicted that the surface states of TI have large thermopower and ultrahigh mobilities [16, 17].

In the present work we measure the electric and thermoelectric properties and quantum oscillations in nominally insulating Bi-17 at%Sb nanowires with different diameters in the temperature range of 2–300 K in a magnetic field up to 14 T.

**2 Samples and experimental details** Individual Bi-17 at%Sb single-crystal nanowires in a glass capillary were prepared by the improved Ulitovsky methods [18, 19]. The technique described in Ref. [20], allows single-crystal wires in a glass cover with diameters from 100 nm to 10 μm to be prepared.

The homogenization of Bi<sub>1-x</sub>Sb<sub>x</sub> nanowires was achieved by multiple zone recrystallization at a very low rate (~0.1 mm h<sup>-1</sup>). According to X-ray diffraction all Bi-17 at%Sb wires were cylindrical single crystals, with the (1011) orientation along the wire axis. The trigonal C<sub>3</sub>-axis was inclined at an angle of ~70° to the wire axis. Contacts to the microwires were made using liquid (at 300 K) eutectic InGa.

The contacts were found to be Ohmic in all the temperature range 2.1–300 K. The fact that the Bi-17 at%Sb wires with different diameters have the same orientation was verified by the diagrams of rotation of transverse magnetoresistance (Fig. 1). It is seen that with decreasing diameter of the nanowires the anisotropy of the transverse magnetoresistance decreases.

The wires were held in special holders and inserted in a cryostat for low-temperature measurements.

Measurements of the Shubnikov–de Haas oscillations were carried out in a longitudinal magnetic field up to 14 T (*H* || *I*) in a superconducting solenoid at *T* = 2–4.2 K in the

International Laboratory of High Magnetic Fields and Low Temperatures, Wrocław, Poland.

**3 Results and discussion** Figure 2 shows the temperature dependences of the normalized electrical resistance  $\Delta R/R_{300}$  where  $\Delta R = R_T - R_{300}$ , of the Bi-17 at%Sb wires with different diameters in the 1.5–300 K region. It is seen that in the room temperature region the difference in the resistivities of the wires with various diameters is small.

For all the wires with different diameters, the resistance *R*(*T*) tends to increase with decreasing temperature and all the curves log  $\rho$ (1/*T*) were selectable linear sections indicating that these wires are semiconductors having narrow bandgaps (Fig. 2, inset).

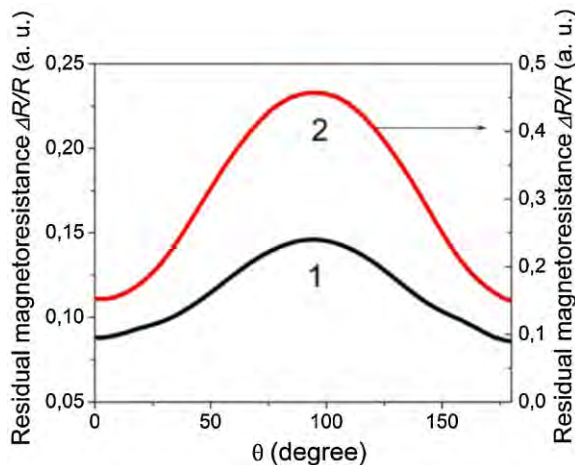
Above 160 K a plot of log  $\rho$  versus 1/*T* gives a straight line. This indicates that above 150 K the variation of  $\rho$  with temperature is exponential.

Semiconductor Bi<sub>1-x</sub>Sb<sub>x</sub> alloys with 0.09 ≤ *x* ≤ 0.17 are direct-gap semiconductor with a gap at the point *L*, since that of the dependencies log  $\rho = F(1/T)$  in these alloys is practically determined by the value of the parameter gap  $E_g^L$ .

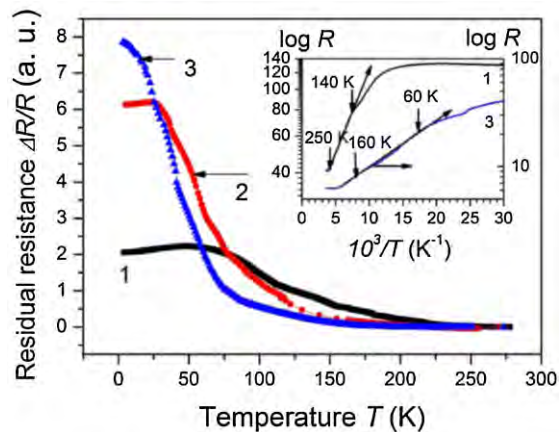
We have calculated the thermal energy gaps  $E_g^L$  from the temperature dependence of resistivity  $\rho$  with an assumption that the resistivity follows an exponential law:

$$\rho = \rho_0 \exp\left(\frac{E_g}{2kT}\right), \quad (1)$$

where resistivity  $\rho_0$  is a const, and  $E_g^L$  is the bandgap. The results are shown in Fig. 2 (inset). The present data indicates that  $E_g^L \approx 20 \pm 3$  meV for wires with *d* = 1000 and 600 nm, and  $E_g^L \approx 28 \pm 3$  meV for *d* = 200-nm wires. Note that the exponential dependence  $\rho(T)$  realize in the region 150 K < *T* < 250 K in 200-nm nanowires, while for 600- and 1000-nm wires this exponential  $\rho(T)$  dependence occurs at 160 K < *T* < 90 K.



**Figure 1** Rotation angular diagrams of the residual transverse magnetoresistance  $\Delta R/R(\theta)$  for Bi-17 at%Sb wires at *T* = 77 K, *H*<sub>⊥</sub> = 0.4 T: (1) *d* = 200 nm, (2) *d* = 900 nm.



**Figure 2** Temperature dependences of residual resistance  $\Delta R/R(T)$  for Bi-17 at%Sb wires with different diameters: (1) *d* = 200 nm, (2) *d* = 600 nm, (3) *d* = 900 nm. Inset: the dependence log *R* versus 10<sup>3</sup>/*T*.

The increase in the gap for 200-nm wires may be related to the manifestation of the quantum size effect and partly to increased surface scattering in the wires, resulting in an increase in resistance.

However, the behavior of the resistance  $R(T)$  in the range  $T < 100$  K is different for wires with different diameters. At low temperatures in thin wires  $d = 200$  and  $600$  nm (Fig. 2, curves 1 and 2) a sharp deviation from exponential temperature behavior of the resistance  $R(T)$  is observed. With decreasing diameter of the wires the temperature  $T_d$  at which there is a deviation from the exponential dependence of  $R(T)$  and saturation with the formation of the plateau of the residual resistance at low temperatures shift to higher temperatures ( $T_d = 40$  K for the wires with  $d = 600$  nm and  $T_d = 90$  K for the wires  $d = 200$  nm) (Fig. 2, curves 1 and 2).

For the wire Bi-17 at% Sb with  $d = 200$  nm the dependence  $R(T)$  was similar to semimetallic Bi wires with  $d < 100$  nm [19]. In order to explain the experimental results of  $R(T)$  shown in Fig. 2, we need to take the surface state into account. According to this, the deviation correspond to a considerable influence of a metalized well conducting near-surface layer formed from the surface states arising through a spin-orbital Rashba interaction in nanowires.

As mentioned in the introduction according to the work [12] in the semiconductor  $\text{Bi}_{1-x}\text{Sb}_x$  alloys showing properties of topological insulator, the field dependence of the magnetoresistance  $R(H)$  at 4.2 K, exhibits quantum SdH oscillations of the surface states.

On the other hand, in Ref. [13] oscillations of the Aharonov–Bohm have been predicted in semiconducting  $\text{Bi}_{1-x}\text{Sb}_x$  alloys connected to the band topology and a surface-curvature-induced Berry phase, characteristic of topological insulator surfaces.

We investigated the field dependence of the magnetoresistance  $R(H)$  ( $H \parallel I$ ) at temperatures in the range 1.5–4.2 K for Bi-17 at% Sb wires with three different diameters.

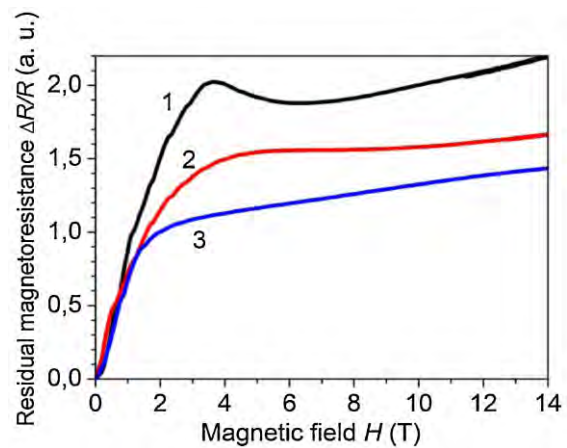
An example of the field magnetoresistance dependences  $R(H)$  ( $H \parallel I$ ) measured at 2.1 K at different diameters is shown in Fig. 3. The SdH oscillations on  $\delta R/\delta H(H)$  are clearly seen only on thinner wires (Fig. 4). The oscillation period was  $\Delta(1/H) = 0.5 \times 10^{-5} \text{Oe}^{-1}$ . This fact indicates an essential contribution of surface states to the electron transport in semiconducting  $\text{Bi}_{1-x}\text{Sb}_x$  nanowires.

The most surprising result is that we observe SdH oscillations (periodic in  $1/B$ ) and did not observe AB oscillations that are periodic in  $B$ . The SdH that we observe and is presented in Fig. 4 compares favorably with the results by Taskin and Ando [12]. Unfortunately, the character of the SdH oscillations at  $T = 4.2$  and  $2.4$  K did not allow us to calculate the cyclotron mass.

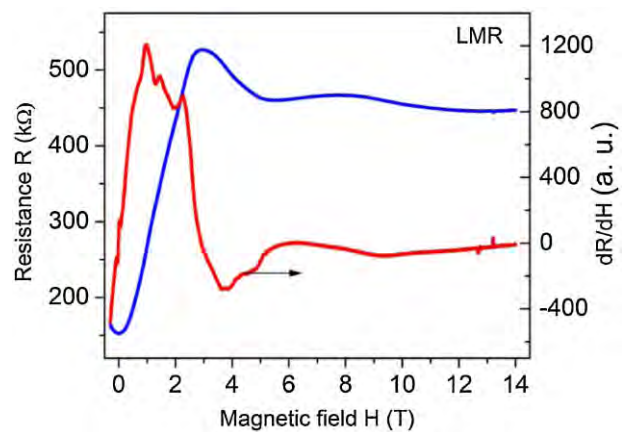
We also investigated the temperature dependence of the Seebeck coefficient  $\alpha(T)$  in the range 4.2–300 K.

The Seebeck coefficients (thermopower) of Bi-17 at% Sb wires along the wire axis are shown as a function of temperature in Fig. 5.

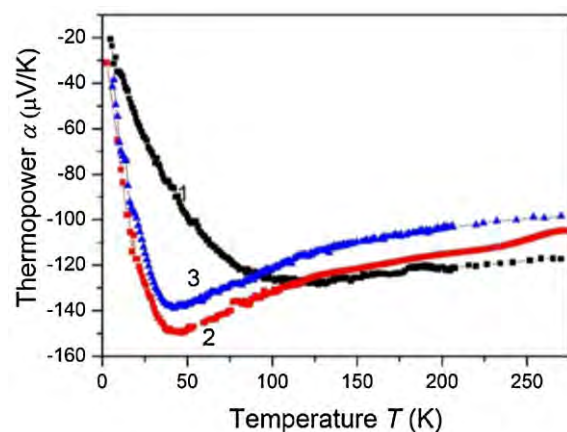
For all wires the thermopowers are negative in all temperature regions. It may be seen that the absolute value



**Figure 3** Field dependences of residual longitudinal magneto-resistance  $\Delta R/R(H)$ ,  $H \parallel I$  for Bi-17 at% Sb wires with different diameters: (1)  $d = 200$  nm, (2)  $d = 600$  nm, (3)  $d = 900$  nm.



**Figure 4** The magnetic-field dependences of the resistance  $R(H)$  and  $\delta R/\delta H(H)$  at 1.5–4.2 K shows quantum oscillations in thin 200-nm Bi-17 at% Sb wires.



**Figure 5** Temperature dependences of thermopower  $\alpha(T)$  of Bi-17 at% Sb wires with different diameters: (1)  $d = 200$  nm, (2)  $d = 600$  nm, (3)  $d = 900$  nm.

of the thermopower  $\alpha$  increases with decreasing temperature from  $100 \mu\text{V K}^{-1}$  to about  $\sim 150 \mu\text{V K}^{-1}$  in the range 40–120 K and then decreases again with decreasing temperature up to 4.2 K. By contrast, the thin Bi and semimetal  $\text{Bi}_{1-x}\text{Sb}_x$  wires change their sign from negative to positive, forming the positive polarity peak at low temperatures (20–50 K) [13, 14].

For unambiguous interpretation of the observed SdH oscillations more research is needed on  $R(H)$  in a transverse magnetic field in the general crystallographic directions, and observe the change the period of SdH oscillations of the angle and estimate the cyclotron masses and their dependence on the crystallographic orientation.

**4 Summary** Thin semiconductor single-crystal  $\text{Bi}_{1-x}\text{Sb}_x$  nanowires displayed a sharp deviation from the exponential temperature behavior resistance  $R(T)$  characteristic of bulk and thin semiconductor  $\text{Bi}_{1-x}\text{Sb}_x$  wires. This deviation corresponds to a considerable influence of a metalized well-conducting near-surface layer, presumably formed from the surface states arising through a spin-orbital Rashba interaction in nanowires.

Our studies of the longitudinal magnetoresistance are intriguing. We did not observe AB oscillations. Instead, we observe SdH oscillations. This suggests that the surface states do not form as a thin, two-dimensional sheet, a nanotube, on the surface of the nanowire but instead are three-dimensional and fill a substantial portion of the volume of the nanowire.

**Acknowledgement** This work was supported STCU 5373 and US National Science Foundation PREM.

## References

- [1] E. J. Tichovolski and J. G. Mavrodies, *Solid State Commun.* **7**(13), 427 (1969).

- [2] Yi-Han Kao, R. D. Brown, and R. L. Hartman, *Phys. Rev. A* **136**, 858 (1964).
- [3] G. A. Mironova, M. V. Sudakova, and Ya. G. Ponomarev, *JETP* **51**(5), 918 (1980).
- [4] S. Golin, *Phys. Rev.* **176**, 830 (1968).
- [5] N. B. Brandt, S. M. Chudinov, and V. G. Karavaev, *JETP* **34**(2), 368 (1972).
- [6] N. B. Brandt, M. V. Semenov, and L. A. Falkovsky, *J. Low Temp. Phys.* **27**(1–2), 75 (1977).
- [7] H.-J. Zhang, C.-X. Liu, X.-L. Qi, X.-Y. Deng, X. Dai, S.-C. Zhang, and Z. Fang, *Phys. Rev. B* **80**, 085307 (2009).
- [8] J. C. Y. Teo, L. Fu, and C. L. Kane, *Phys. Rev. B* **78**, 045428 (2008).
- [9] J. C. Y. Teo, L. Fu, and C. L. Kane, *Phys. Rev. B* **78**, 045426 (2008).
- [10] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. A. Hasan, *Nature (London)* **452**, 970 (2008).
- [11] D. Hsieh, Y. Xia, L. Wray, D. Qian, A. Pal, J. H. Dil, J. Osterwalder, F. Meier, G. Bihlmayer, C. L. Kane, Y. S. Hor, R. J. Cava, and M. Z. A. Hasan, *Science* **323**, 919 (2009).
- [12] A. A. Taskin and Y. Ando, *Phys. Rev. B* **80**, 085303 (2009).
- [13] Yi. Zhang and A. Vishwanath, *Phys. Rev. Lett.* **105**, 206601 (2010).
- [14] T. E. Huber, A. Adeyeye, A. Nikolaeva, L. Konopko, R. C. Johnson, and M. J. Graf, *Phys. Rev. B* **83**, 235414 (2011).
- [15] L. A. Konopko, T. E. Huber, A. A. Nikolaeva, and L. A. Burceacov, *J. Low Temp. Phys.* **171**(5–6), 677 (2013).
- [16] R. Takahashi and S. Murakami, *Phys. Rev. B* **81**, 161302 (R) (2010).
- [17] P. Ghaemi, R. S. K. Mong, and J. E. Moore, *Phys. Rev. Lett.* **105**, 166603 (2010).
- [18] N. B. Brand, D. V. Gitsu, A. A. Nikolaeva, and Ya. G. Ponomarev, *JETP* **45**, 1226 (1977).
- [19] D. Gitsu, L. Konopko, A. Nikolaeva, and T. Huber, *Appl. Phys. Lett.* **86**, 10210 (2005).
- [20] A. A. Nikolaeva, L. A. Konopko, A. K. Tsurkan, and T. E. Huber, *J. Thermoelectr.* **3**, 41 (2009).