Effect of Weak and High Magnetic Fields in Longitudinal and Transverse Configurations on Magneto-Thermoelectric Properties of Quantum Bi wires

A. Nikolaeva, L. Konopko, T. E. Huber, Gh. Para, and A. Tsurkan

INTRODUCTION

The electrical transport and magneto-thermoelectric properties of single crystal Bi nanowires have attracted considerable attention because of the quantum size effect (QSE). In a semimetal, the QSE causes the conduction band and the valence band to break up into subbands whose numbers correspond to discrete values of the wave vector along the “quantizing” dimension. By introducing a quantum confinement, a semimetal – semiconductor transition can be achieved [1]. Due to a long electron mean free path (m.f.p.) \(l_e\) (\(\sim 100\) nm at room temperature) and a very large Fermi wavelength \(\lambda\) (40–60 nm), material Bi is the best candidate to study the classical and quantum size effects for the object size comparable to \(l_e\) and \(\lambda\) [1–9].

In [10, 11] a significant increase in thermoelectric efficiency \(Z\) was predicted in quantum Bi-wires at the semimetal – semiconductor transition due to the QSE. In the thermoelectric figure of merit \(ZT = \frac{\alpha^2 \sigma}{k}\), \(\sigma\) is the electrical conductivity, \(\alpha\) is the Seebeck coefficient (thermopower), \(\chi = -k_e + k_i\) is the thermal conductivity \((k_e, k_i\) are the electron and lattice contributions, \(T\) is the absolute temperature).

An approach to increase \(Z\) is to increase the density of states near the Fermi level at the size quantized and to decrease thermal conductivity due to an additional strong phonon scattering on the surface of quantum Bi nanowire walls [1, 10, 11]. Single-crystal wires are required so as to observe the QSE.

The galvanomagnetic size effect (GMSE) was studied theoretically and experimentally in bismuth wires with \(d > 200\) nm, prepared by various methods [3, 6–10]; in particular, its occurrence in \(\rho(H), (H)l\) is in fairly good agreement for both individual Bi wires and nanowire arrays.

As for the thermoelectric power, the available experimental results obtained in most cases on Bi nanowire arrays embedded in a porous Al\(_2\)O\(_3\) dielectric matrix are very contradictory [12–14] and differ not only quantitatively but also qualitatively. This is probably due to some variation in the diameter of nanowire arrays, filling of pores Al\(_2\)O\(_3\) as well as to the presence of uncontrolled structural defects, especially in establishing contacts, because the length of the nanowire arrays is less than 200 \(\mu\)m.

The most suitable material to study the QSE and GMSE is strictly cylindrical single-crystal Bi wires, die-cast from the liquid phase in a glass envelope with a length of a few \(mm\) [6, 8, 9].

In this paper we report the dimensional features in the magneto-field dependences of resistance and thermopower in longitudinal and transverse magnetic fields up to 14T for single crystal Bi wires with diameters of 250 nm and 75 nm (at the semimetal – semiconductor transition due to the QSE).

In weak magnetic fields, \(R_{\text{max}}\), the maximum in the longitudinal magneto-resistance (LMR) \(R(H)\),
corresponds to the “cutoff” magnetic field of SdH oscillations at 4.2 K. With decreasing diameter of the wires ($d < 80$ nm) this maximum disappears and magneto thermopower achieves the maximum positive value at 20–30 K.

It is for the first time that the effect of the negative magneto-resistance in a transverse magnetic field (TMR) due to the QSE has been observed. The power factor $\alpha^2\sigma$ and its dependence on the diameter, magnetic field and temperature were calculated from the experimental data.

SAMPLES AND EXPERIMENT

Individual glass-coated Bi wires with the diameter < 100 nm were prepared by the high frequency liquid phase casting (the improved Ulitovsky-Taylor method) [6, 8, 9].

The orientation of the wires was verified by the X-Ray diffraction. Studies on the Diffractometer Xcalibur-E reveal that the investigated wires are single crystals and have the $\langle 110\rangle$ orientation along the wire axis (Fig. 1, inset). In this orientation the wire axis makes an angle of 19.5° with the bisector axis $C_1$ in the bisector-trigonal plane. The trigonal axis $C_3$ is inclined to the wire axis at the angle of 70°, and one of the binary axes $C_2$ is perpendicular to it (Fig. 1, inset).

Figure 1 shows the rotation angular diagram of the transverse magneto-resistance (ADTMR) $R(\theta)$ Bi wires with $d = 75$ nm and $d = 250$ nm at 100K. The curves qualitatively correspond to the similar ADBMR for bulk single crystal Bi samples for the case where the current is directed along the bisector axis [15]. In weak magnetic fields ADBMR curves have a simple bell-shape with a periodicity of 180°. The maximum on the $R(\theta)$ ($\theta = 90°$) corresponds to $H||C_2$ and the minimum ($\theta = 0° = 180°$) corresponds to the situation when the wire axis, the crystallographic $C_3$ axis and the vector $\vec{H}$ are in one plane, and the angle $\angle HC_3 \approx 20°$.

The SdH oscillations are periodic in $1/H$, with a period of $\Delta(1/H) = 2\pi\hbar e/cS$, which is inversely proportional to the extreme cross-section $S$ of the Fermi surface in the plane normal to the magnetic field $H$.

In the longitudinal magnetic field ($H||I$), there are three different extreme cross sections $S$ (cross-hatched in Fig. 1, inset) and three respective SdH oscillation periods: $1 - \Delta_1 = 7 \cdot 10^5$ Oe$^{-1}$ from one
Fig. 3. Magnetic field dependences of longitudinal residual MR \( \Delta R/R(H) \) for 250 nm Bi wire at different temperatures (temperatures indicated). Vertical bars indicate maximum position on \( \Delta R/R(H) \). Inset: Peak position \( H_{\text{max}} \) as function of temperature. 

Fig. 4. Longitudinal thermopower (HFAT) as function of magnetic field at various temperatures (temperatures indicated) Bi wire, \( d = 250 \) nm. Inset: Magnetic field dependences (HF) of P.f. = \( \alpha \sigma(H) \) for various temperatures calculated from Figs. 3, 4 of Bi wire, \( d = 250 \) nm. 1 – \( T = 13 \) K; 2 – \( T = 25 \) K; 3 – \( T = 98 \) K. 

Fig. 5. Magnetic field dependences of longitudinal residual MR \( \Delta R/R(H) \) Bi wire \( d = 75 \) nm at different temperatures (temperature indicated). Inset: Peak position \( H_{\text{max}} \) as function of temperature. 

Fig. 6. Longitudinal thermopower (HFAT) as function of magnetic field at various temperatures (temperatures indicated in Fig. 5) Bi wire, \( d = 75 \) nm. Inset on the right: Peak position \( H_{\text{max}} \) as function of temperature. Inset down: Magnetic field dependences (HFAT) of P.f. = \( \alpha \sigma(H) \) for various temperatures calculated from Figs. 5, 6 of Bi wire \( d = 75 \) nm. 1 – \( T = 5 \) K; 2 – \( T = 10 \) K; 3 – \( T = 20 \) K; 4 – \( T = 57 \) K; 5 – \( T = 100 \) K. 

The Dingle temperature was determined from the dependences of the SdH oscillation amplitude versus the magnetic field at 2.1K. The Dingle temperature \( T_D = \hbar / \kappa_B \tau \), where \( \tau = 1/\nu_F = em/\hbar \kappa_F \) is the carrier relaxation time. In our 250 nm Bi wire \( T_D \approx 1 \) K [6]. This suggests that the investigated single Bi wires have very high structural perfection. 

Figure 2 shows temperature dependences of the residual resistance \( \Delta R/R(T = T_0) = R_R - R_{T_0} / R_{T_0} \) of Bi wires with \( d = 250 \) nm and \( d = 75 \) nm. For wires with \( d = 75 \) nm, a semiconducting behavior of \( R(T) \) is observed; it indicates the semimetal-semiconductor transition due to the QSE. The temperature dependence \( \Delta R/R(T) \) for the wire with \( d = 250 \) nm characterizes the transition from bulk bismuth to size-dimensional wires [6, 9]. 

Figures 3–6 show field dependences of LMR \( \Delta R/R(H) \) and longitudinal magneto-thermopower (LMTP) \( \alpha(H) \) of Bi wires with \( d = 250 \) nm (Fig. 3, 4) and \( d = 75 \) nm (Fig. 5, 6) in a temperature range of 1.5–100K. A specific feature of LMR in Bi wires is the presence of a maximum in \( R(H) \) in weak magnetic fields, which depends on the wire diameter and negative magneto-resistance in strong magnetic fields. Magnetic fields change the trajectory of the carriers, which leads to a change in the electrical conductivity of metals placed in an external magnetic field. The nature of the electron motion in weak and strong magnetic fields is very different. In a weak magnetic field, the Larmor radius \( r_L \) of the electron orbit \( r_L = p_\perp c / eH \) is superior to the mean free path \( r_L > 1 \), \( (p_\perp \) is the component of the Fermi momentum vector perpendicular to the magnetic
field \( H \), m.p.f. evaluated in our paper [9]) and, between the successive acts of scattering, an electron moves along a short arc trajectory. In this case, the electron motion under the influence of an applied electric field is the same as in the absence of a magnetic field. Electrons, due to the curvature of the trajectory in the magnetic field, can reach the surface and be additionally scattered on the surface. In a strong magnetic field (\( \mu H >> 1 \)), the electron has time to make several complete cycles of motion without scattering, and in this case \( r_1 < 1 \).

As mentioned previously [3, 4, 6] in the wires with \( 200 \text{ nm} < d < 1 \text{ \( \mu \)m}, the dependence of \( H_{\text{max}} \sim d^{-1} \). The Fermi momentum \( P_F \) was calculated from the dependence

\[
H_{\text{max}} = \frac{2P_F e}{\mu d},
\]

(1)

In the redistribution of the measurement, an error of \( P_F \) calculated from (1) coincides with the value of \( P_F \), obtained from SdH oscillations from the two electron ellipsoids \( L_2, 3 \) symmetrically arranged with respect to the wire axis (inset in Fig. 1). The presence of the maximum \( H_{\text{max}} \) in weak magnetic fields and negative magneto-resistance in strong magnetic fields testify to the occurrence of the GMSE in Bi wires. Later Dresselhaus [10] observed a similar behavior on Bi nanowire arrays.

In the wires with \( d = 75 \text{ nm} \), the maximum of the longitudinal magneto-resistance at 4.2K was absent (Fig. 5, curve 1), indicating that there is a very small contribution to the conductivity of the \( L \) carrier, or none at all, due to the absence or reduction of the overlap of \( L \) and \( T \) bands because of the QSE. However, with increasing the temperature to a certain \( T \) value, depending on the wire diameter \( d \) (in this case, \( T \approx 13K \)) in weak magnetic fields, \( R(H) \) exhibits the maximum, the behavior of which with a further rise in temperature \( T \) is similar to the behavior of \( H_{\text{max}}(T) \) in the Bi wires with \( d = 250 \text{ nm} \). At \( T > 40K \), \( H_{\text{max}} \) is shifted towards higher temperatures according to the law close to linear (inset in Fig. 5). Apparently, an increase in temperature results in the diminishing of the forbidden band for semiconductors or of a band overlapping for semimetal proportionally \( kT \), promoting the appearance of \( L \) carriers and increasing their contribution to the conductivity.

As shown in [2] and subsequently widely used in [17], especially at high temperatures, in order to explain the anomalous peak of the LMR in wires and films at higher temperatures, the following expression should be used:

\[
H_{\text{max}} = \frac{2P_F}{e\mu d \text{l}}
\]

(2)

where \( l \) is m.p.f., i.e. in the maximum m.f.p. \( l = d \). In this case, the temperature dependence of \( H_{\text{max}} \) at \( R(H) (H \parallel I) \) becomes clear. In fact, it represents the temperature of a carrier mobility \( \mu \) in Bi wires, and the maximum of \( R(H) \) separates strong and weak magnetic fields (\( \mu H < 1 \) and \( \mu H > 1 \)).

In the longitudinal configuration, the magneto-thermopower \( \alpha(H) \) also exhibits its maximum in low magnetic fields (Fig. 6) and generally shows the same trends as the \( H_{\text{max}} \) on \( R(H) \).

In the wires with \( d < 100 \text{ nm} \), the dependence of the maximum \( H_{\text{max}}(T) \) on the longitudinal thermopower \( \alpha(H) (H \parallel \Delta T) \) is nonmonotonic (inset in Fig. 7). At \( T > 20K \), the maximum is shifted to the area of strong magnetic fields under the law close to linear, as in the wires with \( d = 250 \text{ nm} \).

![Fig. 7. Magnetic field dependences of transverse MR \( (H \parallel I, H \parallel |C_i|) \) of Bi wire, \( d = 75 \text{ nm} \) for various temperatures (temperatures indicated). Inset: Magnetic field dependences \( R_{\text{H}/R_{\text{H}}(H)} \) in initial magnetic field.](image)

In a transverse magnetic field \( H \parallel I, \Delta T, H \parallel |C_i| \) (\( \theta = 0 \) point on curve 1 in Fig. 1) in Bi wires with \( d = 75 \text{ nm} \), we have been first to observe the effect of a negative magneto-resistance at \( T < 5K \) associated with the quantum size effect [18, 19], which occurs only in Bi wires with \( d < 80 \text{ nm} \). At the same time, the field dependence of the thermoelectric power \( \alpha(H) \) exhibits a maximum positive polarity, which decreases and shifts to the low magnetic field with increasing temperature (inset in Fig. 8). In strong magnetic fields, the thermoelectric power changes its sign from positive to negative and the point of the sign change is shifted in the region of weak magnetic fields according to the conclusions of the theory, taking into account the QSE [19].

Complex experimental studies of the resistance \( R(H) \) and thermopower \( \alpha(H) \) of Bi wires with \( d = 250 \text{ nm} \) and \( d = 75 \text{ nm} \) at different temperatures made it possible to calculate the Power factor \( P.f. = \alpha^2 \sigma \) and its dependence on the value and direction of the magnetic field at various temperatures.
Figures 4, 6 and 8 (insert) show the P.f. as a function of a magnetic field at various temperatures for wires with \( d = 250 \) nm and \( d = 75 \) nm. At the temperature of 100K, the maximum value of P.f. = \( 1 \times 10^{-4} \) W/cm-K² at \( H = 2 \) T is achieved for Bi wires with \( d = 250 \) nm. At \( T = 25K \), the maximum value P.f. = \( 8.0 \times 10^{-4} \) W/cm-K² at \( H = 5 \) T is observed. In the transverse field \( H \perp \Delta T \) indicated in Fig. 7).

It is known that in bulk Bi samples of trigonal orientation, in a temperature range of 100–150K, the thermopower has a negative value and increases 2-fold in magnetic fields \(< 1T\). The effect was used in the magneto-thermoelectric power converters.

It should be noted that in Bi wires \((d < 300 \) nm), the thermopower is positive at \( T < 100K \), which is an important factor for thermoelectric applications because for the \( n \)-branches of the thermoelectric energy converter alloys, Bi₁₋ₓSbₓ are usually used, and the creation of p branches at low temperatures is problematic.

CONCLUSIONS

Single-crystal wires in glass cover with diameters of 250 and 75 nm have been prepared and their magneto thermoelectric properties investigated. As a result, a semimetal-semiconductor transition has been observed due to size quantization of the energy spectrum. It is shown that field dependences of the longitudinal and transverse magneto-resistance and thermopower contain singular points characterizing the expression of the GMSE and the QSE, and contain information on the parameters of the energy spectrum and on the charge carrier mobility. It is for the first time effect of the negative magneto-


Received 07.06.13

Реферат

В работе приведены результаты измерений магнито-термоэлектрических свойств монокристаллических нанонитей Bi с диаметрами 75 нм и 250 нм в продольном и поперечном магнитном полях до 14 Т в интервале температур 1,5–300K. Цилиндрические нити Bi в стеклянной оболочке изготавливались литьем из жидкой фазы. Температурные зависимости сопротивления \( R(T) \) показывают переход от «металлической» к «полупроводниковой» зависимости благодаря проявлению квантового размерного эффекта (QSE) при уменьшении диаметра нитей Bi менее 80 нм. Впервые обнаружен эффект отрицательного магнитосопротивления в поперечном магнитном поле, связанный с проявлением квантового размерного эффекта в нитях с \( d < 75 \) нм. Термоэдс чувствительна к диаметру нитей \( d \) и значительно возрастает в слабом продольном магнитном поле. Полевые зависимости продольного и поперечного магнитосопротивления имеют особенности характеризующие проявление квантового и гальваномагнитного размерных эффектов, которые содержат информацию о параметрах энергетического спектра и подвижности носителей заряда. Обсуждается вопрос повышения термоэлектрической эффективности в нанонитях Bi. Из экспериментальных данных рассчитывался силовой фактор \( \alpha \sigma \) в зависимости от диаметра, нитей, магнитного поля и температуры.

Ключевые слова: нанонити висмута, термоэлектричество, квантовый размерный эффект.