Thermoelectric Properties of Bi microwires at Low Temperatures

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***Abstract* — The thermopower of single crystalline Bi microwires with diameters ranging from 0.1 to 14 μm were measured in the temperature range 4 – 300 K. Cylindrical crystals with glass coating were prepared by the high frequency liquid phase casting in a glass capillary. The peaks are the dominant features of the temperature dependences of thermopower at temperatures below 12 K. This peak is a manifestation of the phonon drag effect. We observe that the phonon-drag thermopower depends on the wire diameter and increases with increasing diameter of the sample. We have studied the dependence of the phonon drag thermopower on transverse magnetic field and transverse electric field. Effect of transverse magnetic field (B=0.4 T) of various orientation to the phonon drag thermopower is negligible for Bi microwires $d<0.6$ μm but quickly arise for Bi microwires $d>1.5$ μm. This means that in fine Bi microwires at low temperatures mobility of electrons are much smaller than holes (due to strong surface scattering of electrons on surface roughnesses). Influence of transverse electric field to the phonon drag thermopower of Bi microwires is very small.A possible explanation of these experimental results is presented.**

***Index Terms* — bismuth, magnetic field, microwire, phonon drag effect, thermopower.**

I. INTRODUCTION

Over the past ten years there has been considerable interest in the thermoelectric power of bismuth. The goal of these investigations is to understand the peculiar behavior of the thermopower in this semimetal and to find out the conditions of the highest thermoelectric figure of merit of bismuth, the criterion which determines the usefulness of the material for possible applications in thermoelectric energy conversion devices. Recently, Heremans *et al.*[1] studied the the Seebeck coefficient (S) of ~10 nm diameter Bi nanowire composites; they report that the composites have a very large thermoelectric power. These results are interpreted in terms of the quantum confinement theory by Dresselhaus *et al.,*[2,3] that predicts an enhancement of the thermoelectric power for fine wires. This enhancement is significant because it can enable a technology of solid state thermoelectrics based on the utilization of Bi nanowires for thermoelectric applications.

It is well known that the thermoelectric power contains two main contributions, namely, the diffusion thermoelectric power and the contribution due to phonon drag. Carriers of diffusion thermoelectric effects are associated with the difference in broadening of the Fermi distributions of electrons and holes as temperature vary across the sample. It is assumed that the the phonons are in thermal equilibrium. This is true when the relaxation time τ_p for the scattering of phonons by boundaries, other phonons and defects is very short compared to the phonon-carrier relaxation time. The diffusion thermopower is proportional to temperature for T< 50 K and it is around 1 μV/K at 4 K. However, experimental study of bulk bismuth samples at low temperatures clearly demonstrates [4-8] that the thermopower exceeds by at least an order of magnitude this value. Such large thermopower are commonly attributed to a phonon drag mechanism. At low temperatures the contribution of the phonon drag is usually greater than the diffusion thermopower, but strongly depends on sample size, presumably because of the relative contributions of various phonon scattering processes. Theory of phonon drag effect proposed by Gurevich [9] and Herring [10] was refined by Korenblit [11] for the anisotropic carrier spectrum in bismuth. In 1971 Kozlov and Nagaev [12] described new two-step phonon drag for large high-quality bismuth samples.

The purpose of this work was to investigate of phonon drag thermopower of thin monocrystal bismuth wires under influence of transverse magnetic and transverse electric fields and analyze the carrier-phonon scattering in these wires.

II. EXPERIMENTAL

The cylindrical Bi crystals ranging in size from 0.19 to 3 μm with glass coating were prepared by the liquid phase casting in a glass capillary (Ulitovsky method) [13]. The Bi in the microwires can be viewed as cylindrical single crystals with the (10$\underline{1}$1) orientation along the wire axis. In this orientation the wire axis makes an angle of 19.5° with the bisector axis C_3 in the bisector-trigonal plane also, the trigonal axis C_3 is inclined to the wire axis at an angle of 70°, and one of the binary axes C_2 is perpendicular to it. A low magnification scanning electron microscope image of a 240 nm Bi microwire is shown in Fig. 1. Fig. 2 shows the orientation of our microwires with respect to the Fermi surface. The electron pockets *LB* and *LC* are located symmetrically with respect to the wire direction. To verify that the microwire is a single crystal, we studied x-ray Laue diffraction patterns obtained using a cylindrical film camera (spindle was not rotating) and a monochromatic x-ray source.

The samples for the measurements were cut from long wires and were from 10 mm down to 0.8 mm in length and were mounted on special foil-clad fiber-glass plastic holders. Electrical contact to the copper foil was made with In-Ga or Ga solder. The main sample parameters are given in Table 1.

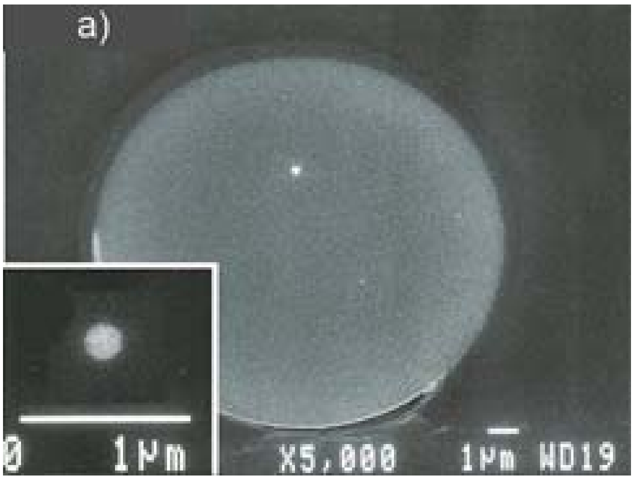

Fig. 1. Scanning electron microscope cross sections of the 240 nm Bi wire in its glass coating.

The sample's thermopower was measured in a closed-cycle refrigerator operating in a temperature range of 4 to 300 K**.** The differential thermopower between the samples and copper is defined as S = V/($T_H - T_C$), where $T_H - T_C$ is the temperature difference established and V is the potential difference generated between the ends of the sample. $T_H - T_C$ was fixed at approximately 0.5 K at T< 15 K and slowly increased up to 3 K in the temperature range 15 K < T<300 K. We employed the arrangement which consists of two copper blocks; the heater is mounted on one of them. A Cu-Cu(0.01at% Fe) thermocouple is in thermal contact but electrically insulated from each copper block. To eliminate the heat flow through the thermocouple the thermocouple's wires are thin (diameter = 60 μm) and the leads are thermally anchored to the copper blocks. Contact thermal resistance between the copper blocks and sample holders is minimized by employing a low-melting-temperature InGa eutectic solder.

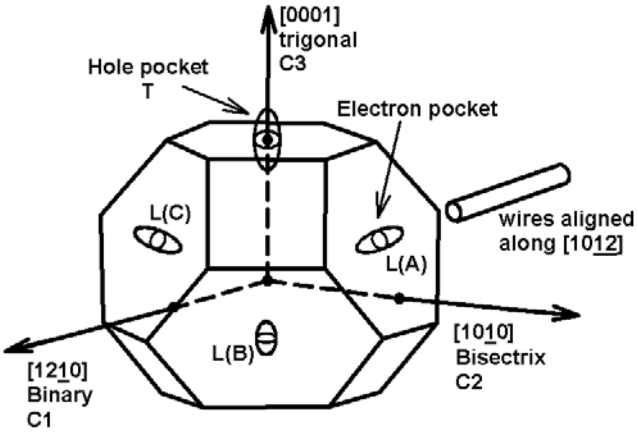

Fig. 2 The Brillouin zone for Bi, showing symmetry lines, which are indexed in the hexagonal system, and planes showing the orientation of the wires in the present study. The three Fermi surface electron pockets (*LA*, *LB*, and *LC)* and the *T* hole pocket are also represented.

The thermopower of the samples was measured in a closed-cycle refrigerator operating in a temperature range from 300 K down to 4 K**.** The magnetic measurements were made using two permanent Nd magnets. For thermopower measurements in transverse electric fields the gate electrodes were prepared by painting the surfaces of glass coating of the samples with liquid Ga.

TABLE I. EXPERIMENTAL PARAMETERS FOR THE SAMPLES

Sample	***d*, μm**	***L*, mm**	**$R_{300}/R_{4.2}$**	**S_{Drag}, μV/K**
1	0.19	2.5	1.9	5
2	0.32	2.5	8.2	8
3	0.54	2.5	10.3	8
4	0.74	3.7	11	9
5	1	8.4	18	12
6	1.7	3.6	18.1	13
7	2.5	4.2	18.7	10.5
20	0.23	4.6	5.6	7
21	0.56	3.7	3.7	11
22	6.5	4.8	6	8

Note: *d*, *L*, S_{Drag} are the sample's diameter, the sample's length, the maximum value of the phonon drag thermopower.

III. RESULTS AND DISCUSSION

The universal temperature dependences of the thermopower for all samples are illustrated in Fig. 3. A broad maximum near 40 K is dominant feature of thin (*d*≤0.54 μm) Bi samples. This maximum is due to interaction between bulk and boundary contributions to the mobility of majority carriers in Bi microwires [14].

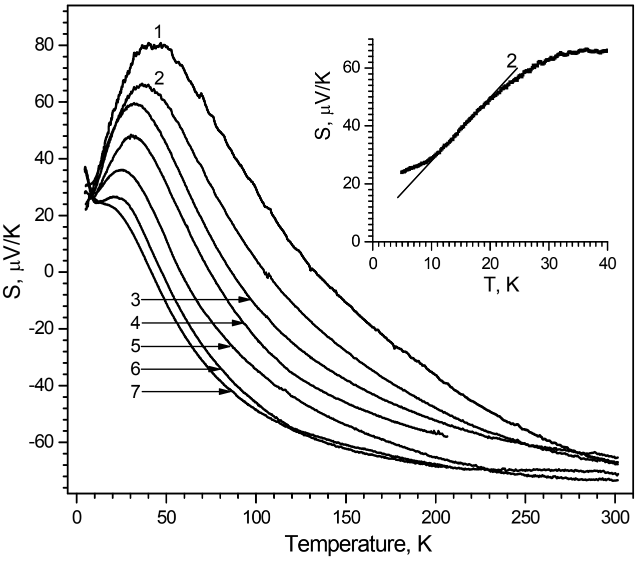

Fig. 3. The temperature dependences of the thermopower for Bi microwires. Insert: The temperature dependences of the thermopower for Bi microwire, *d*=0.32 μm. Solid straight line passes through the experimental diffusion thermopower values from 18 K down to 12 K and are extrapolated to low temperatures. All numbers refer to samples described in Table 1.

The thermopower of Bi microwires deviates from linearity below T ≈ 12 K. As an example, these thermopower deviations for bismuth sample with diameter *d*=0.32 μm is shown in the inset in Fig. 3. Straight line which passed through the experimental thermopower points from 18 K down to 12 K and is extrapolated to low temperatures is the diffusion component of the thermopower. The difference between the experimental thermopower values at $T < 12$ K and the diffusion thermopower is attributed to the phonon drag component of the thermopower. It should be noted that it is quite difficult to exactly determine the temperature range for which phonon drag effect has considerable contribution. The temperature dependences of the phonon drag components of the thermopower for all samples are shown in Fig. 4, these dependences were obtained by subtracting the diffusion thermopowers from the total experimental values.

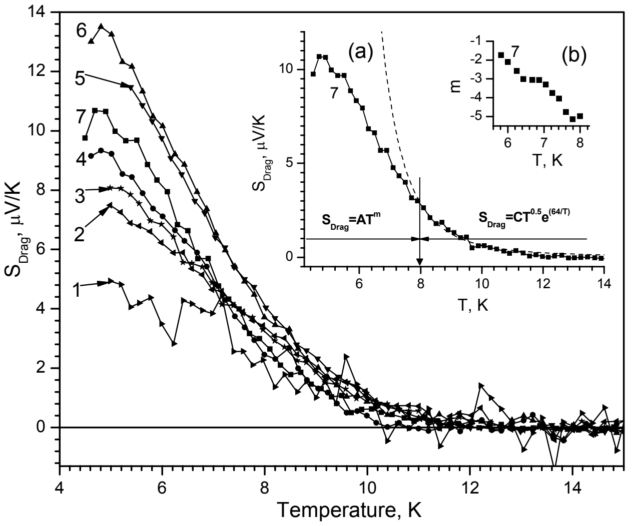

Fig. 4. Temperature dependences of the phonon drag component of the thermopower for Bi microwires. Inset (a): The temperature dependences of the phonon-drag thermopower for Bi sample, d=2.5 μm. Fit of the phonon-drag thermopower to an expression of the form CT^{n-1} $\exp(\theta/T)$ is shown by dashed line. Insert (b): Changes of the power m for power law fitting of the form AT^m for Bi sample, d= 2.5 μm. All numbers refer to samples described in Table 1.

At is seen from Fig. 4 the magnitude of the phonon-drag thermopower and position of the maximum attained by the thermopower hump depends strongly on the wire diameter. In thin Bi samples with $d < 0.5$ μm values of phonon-drag thermopower are very small. A common behavior of the phonon-drag thermopower for Bi microwires is as follows: as the wire diameter d increases, the thermopower increases in magnitude and the peak gradually shifts towards lower temperatures.

In large single crystals of excellent quality in the case of very weak phonon–phonon Umklapp interactions a two-step phonon-drag mechanism, first proposed by Kozlov and Nagaev [12], can exist. In this case long-wavelength phonons which drag the carriers can gain an additional momentum from the thermal phonons by interacting with them via N processes. The two-stage partial phonon-drag thermopower was described by the equation [8] $S_{Drag}=CT^{n-1}exp(\theta/T)$, where C is a constant and θ a characteristic temperature. We obtain good fits for pure Bi samples over the range 8-12 K to the phonon drag thermopower yielding values of θ between 47 K and 73 K for various samples (n=1.5, the value of n between 1 and 2 is suggested by the electrical resistivity of Bi [8]). A typical fit of our experimental data for Bi sample with d=2.5 μm is shown in the inset (a) in Fig. 4. Fitting our data below 8 K to power law of the form $S_{Drag}=AT^m$ give us the monotonic dependences m versus T (Fig. 4, insert (b)). The dependence of the power exponent m on temperature and Te doping level has been also observed in bulk Bi samples [15] and was explained by various phonon scattering mechanisms.

Phonon mean free path for normal N processes, l^N can be found from the equation $l^N=0.4\ T^{-4}$ [cm] [17]. We assume that this formula obtained for the bulk Bi samples can be used for our Bi microwires. For samples 1 (d=0.19 μm) $l^N > d$ at T < 12 K and for samples 7 (d=2.5 μm) $l^N > d$ at T < 6.3 K. This means the phonon will be strongly scattered by the surface of the thick samples (d=2.5 μm) when T<6.3 K but by the surface of the thin sample (d=0.19 μm) when T<12 K. This consideration may explain qualitatively the size dependence (from diameter of the sample) of the thermopower at low temperatures. $S_{Drag,max}$ shows a tendency to saturation at about 12 μV/K for thick samples. Similar qualitative dependences of the phonon drag thermopowers, versus diameter d were observed in bulk Bi monocrystals with the characteristic dimensions 0.15 cm<d <0.6 cm and length l≈6 cm [16].

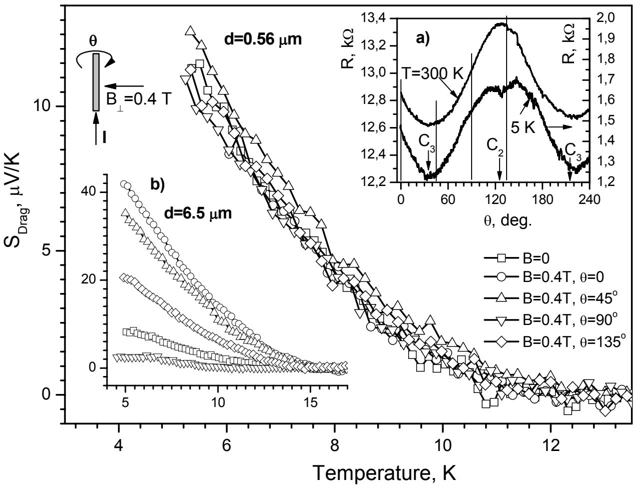

Fig. 5. Temperature dependences of the phonon drag thermopower of the Bi samples d=0.56 μm and d=6.5 μm (insert (b)) in transverse magnetic field $B_\perp = 0.4T$ various orientations (including the case of B=0). Insert (a): angular diagrams of transverse magnetoresistance for sample d=0.56 μm obtained at T=300 K and 5 K.

In fig. 5 the phonon drag thermopower of the Bi samples d=0.56 μm and d=6.5 μm (insert (b)) in transverse magnetic field $B_\perp = 0.4T$ various orientations (including the case of B=0) is plotted against temperature T. Angular diagrams of transverse magnetoresistance for sample d=0.56 μm obtained at T=300 K and 5 K are shown in the insert (a). As opposed to thick sample d=6.5 mm where phonon drag thermopower strongly depend on magnetic field (Fig. 5, insert (b)) in thin sample d=0.56 μm phonon drag thermopower has no dependence on magnetic field. In theoretical and experimental papers of Korenblit [5, 11] have been shown that in bulk Bi samples phonon drag thermopower does not depend on magnetic field only in samples with one group of carriers (electrons in Bi exist as 3 different groups of carriers). In the experimental work that sample was Bi-0.1 at% Sn. This means that in our fine Bi microwires at low temperatures mobility of electrons are much smaller than holes (due to strong surface scattering of electrons on surface roughnesses [18]) and a broad positive maximum near 40 K (Fig. 3.) can be attributed to this mobility differences.

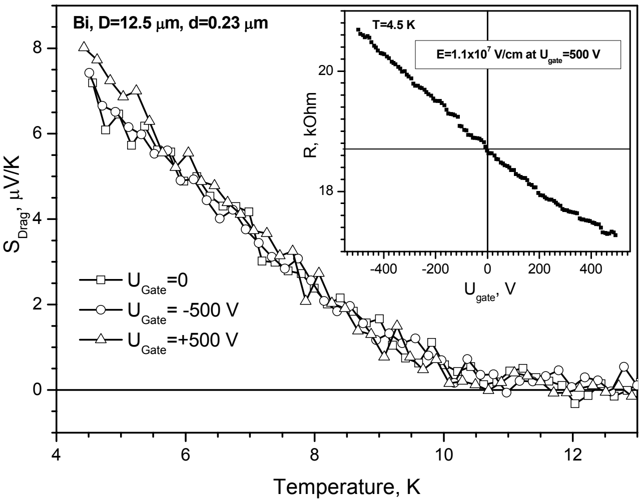

Fig. 6. Temperature dependences of the phonon drag thermopower of the Bi microwire *d*=0.23 μm in transverse electric field. Resistance of the sample as function of potential on gate electrode is shown in the insert, T=4.5 K.

Fig. 6 shows the temperature dependence of the phonon drag thermopowers of the thin Bi wire d=0.23 mm on transverse electric field. Due to coaxial geometry of the sample we can get very big electric field intensity on the sample's surface without breaking of the sample. 500 V applied to the gate electrode of the sample relative to Bi core induce the electric field on the sample's surface E=1.1x10^7 V/cm. This electric field modulates the resistance of the sample (insert in Fig. 6). According to the theory of electric field effect for semimetals [19] this curve correspond to the case when surface hole mobility is bigger than surface electron mobility. The penetration depth of the electric field into the semimetallic microwire (the Debye screening length, L_e) is much smaller than diameter d of the wire; in this case the conditions of carriers-phonons interactions in Bi core are not changed. Therefore phonon drag thermopower does not depend on transverse electric field.

IV. CONCLUSION

The dominant feature of the thermopower of Bi microwires at temperatures below 12 K is a peak, which is due to phonon drag. In the temperature range of 8 K<T<12 K the phonon drag contribution fits into an exponential temperature dependence. This suggests that the two stage phonon drag is an important transport mechanism in Bi microwires. The phonon-drag thermopower depends on the wire diameter and increases with increasing diameter of the sample, which is qualitatively explained by the suppression of two-step phonon processes in the finer wires due to the shortening of the phonon mean free path for normal (momentum conserving) processes due to diffusive wall scattering. The positive thermopower maxima of the order of 10 μVK^{-1} are explained in terms of the phonon drag of carriers. Effect of transverse magnetic field (B=0.4 T) of various orientation to the phonon drag thermopower is negligible for Bi microwires *d*<0.6 μm but quickly arise for Bi microwires *d*>1.5 μm. This means that in fine Bi microwires at low temperatures mobility of electrons are much smaller than holes (due to strong surface scattering of electrons on surface roughnesses). Influence of transverse electric field to the phonon drag thermopower of Bi microwires is very small.

ACKNOWLEDGMENTS

This work was supported by the Academy of Sciences of Moldova Grant No 09.808.05.02A.

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