Phonon Drag Effect in Bi Microwires

D.Gitsu[1], T.Huber[2], L.Konopko[1], and A.Nikolaeva[1]
[1]Institute of Applied. Physics, Academy of Sciences of Moldova, Chisinau, MD-2028, Moldova
[2]Department of Chemistry, Howard University, 525 College St. N.W. Washington, DC 20059
email: konopko@lises.asm.md (L.Konopko), phone: +37322-737072, fax: +37322-738149

Abstract

The temperature dependencies (4.2 – 300 K) of thermopower of thin Bi wires were investigated. The cylindrical Bi crystals ranging in size from 0.1 to 3 μm with glass coating were prepared by the high frequency liquid phase casting in a glass capillary and represented cylindrical single crystals with the (1011) orientation along the wire axis. At the temperatures below 12 K the thermopower is dominated by phonon drag and a maximum is observed near 6K. The position of this maximum and its value depends on the wire's diameter and the length of the samples. At the temperature range 8 – 11K the phonon drag contribution follows an exponential temperature dependence characteristic of a two-stage mechanism. The positive thermopower maxima of the order of 10 μVK^{-1} are explained in terms of the phonon drag of holes. Several mechanism, which may account for the data, are discussed.

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. Bi is a material with near-ideal properties for thermoelectric applications at ~100 K. Bi has a very small effective mass, resulting in a long Fermi wavelength (~60 nm), which eases the limitations on the fabrication of quantum wires. Bulk Bi is a semimetal whose three conduction band minima at the L-points overlap the valence band maximum at the T point by about 40 meV. 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 this results agree with the confinement theory by Dresselhaus *et al.*,[2,3]. This theory predicts that the maximum enhancement of the thermoelectric power increases with decreasing wire diameter, although the actual value of S depends upon the charge carrier density in the nanowires.

It is well known that the thermoelectric power contains two main contributions, namely, the diffusion thermoelectric power and the contribution due to phonon drag.

The diffusion thermoelectric power theory is normally deduced under the supposition that 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. Under these conditions the diffusion thermopower at liquid-helium temperatures must have a magnitude less than 1 mV/K. However, the investigations of bulk bismuth samples at low temperatures clearly demonstrate [4-8] that the thermopower exceeds by at least an order of 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 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 a large high-quality bismuth samples.

The purpose of this work was to extend the measurements of phonon drag thermopower to the low-dimensional objects like monocrystal bismuth wires and analyze the carrier-phonon scattering in these samples.

Experimental Procedure

The cylindrical Bi crystals ranging in size from 0.1 to 3 μm with glass coating were prepared by the high frequency liquid phase casting in a glass capillary and represented cylindrical single crystals with the (1011) orientation along the wire axis. In this orientation the wire axis made up an angle of 19.5° with the bisector axis C_3 in the bisector-trigonal plane. 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. The samples were cut from long wires and were from 10 mm down to 0.8 mm in length, and then they 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 listed in the table.

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. We employed the arrangement which consists of two copper blocks; the heater is mounted on one of them. A Cu-$CuFe_{0.01at.\%}$ 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.

Table1. Experimental parameters for Bi samples

Sample	d, μm	L, mm	$R_{300}/R_{4.2}$	θ, K	T_{max}, K	$S_{Drag,max}$, μV/K
1	0.19	2.5	1.9	50		>5
1s	0.19	1	2		7.2	1
2	0.32	2.5	8.15	50		>8
2s	0.32	0.8	7.7	64	7	2.5
3	0.54	2.5	10.3	60	5	8.1
3s	0.54	0.8	8.6	55	7	1.4
4	0.74	3.7	11	53	4.85	9.2
4s	0.74	1	12.2		6.8	0.6
5	1	8.4	18	55		>11.9
5s	1	0.5	15.5	47	5.5	5.5
6	1.7	3.6	18.1	73	4.8	13.3
6s	1.7	1	16.4	60	6.5	1.1
7	2.5	4.2	18.7	64	4.8	10.4
7s	2.5	0.8	11.4	64	6	3.7

Note: d, L, θ, T_{max}, $S_{Drag,max}$ are the sample's diameter, the sample's length, the characteristic temperature, the temperature corresponding to maximum of the phonon drag thermopower, the maximum value of the phonon drag thermopower.

Results and Discussion

The overall temperatuire dependence of the thermopower is illustrated in Fig.1. A broad maximum near 40 K is dominant feature of thin (d≤0.54 μm) samples. The general behaviour observed at low temperatures for all samples is as follows: deviation from linear temperature dependence at T< 12 K significantly depends on the diameter of the sample and its length. The value of this deviation defines the phonon drag thermopower.

The diffusion thermopower for degenerate electron gas is linear in temperature and can be derived from the expansion in terms of the parameter T/ε_F, where T is the temperature and ε_F is the Fermi energy. The thermopower of thin Bi wires deviates from linearity below T = 12 K. By way of example, these thermopower deviations for long and short bismuth samples with diameters d =0.32 and 1 μm are shown in Fig. 2. The experimental thermopower values at T < 12 K exceed the diffusion thermopower, which is linearly continued in Fig. 2 from the temperature T~ 18 K to the lower temperatures. This difference is attributed to the phonon thermopower component. The temperature dependences of the phonon thermopower components are shown in the inset in Fig. 2; these dependences were obtained by subtracting the diffusion thermopowers from the total experimental values.

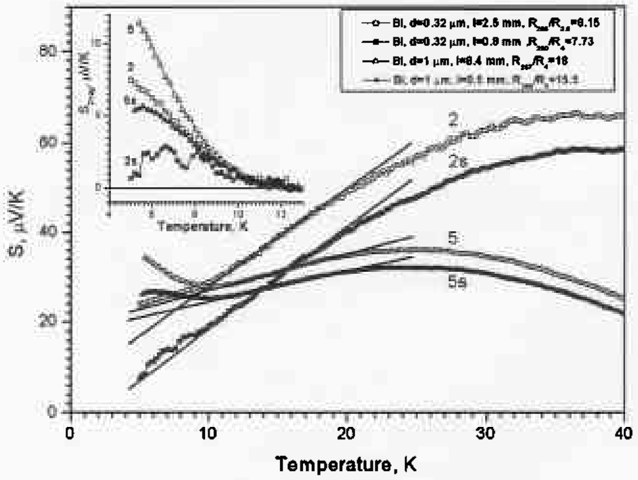

Fig.2.The temperature dependences of the thermopower for Bi wires. Numbers refer to samples described in table 1. Solid straight lines pass through the experimental diffusion thermopower values from 18 K down to 12 K and are extrapolated to low temperatures. The same dependences for the phonon drag component are shown in the inset.

The temperatuire dependence of the phonon drag thermopower for all samples are shown in Fig.3. At is seen from the figure the magnitude of the phonon drag thermopower and position of maximum attained by the thermopower hump strongly depends on the wire's diameter and the length of the samples. In thin Bi samples with d<1

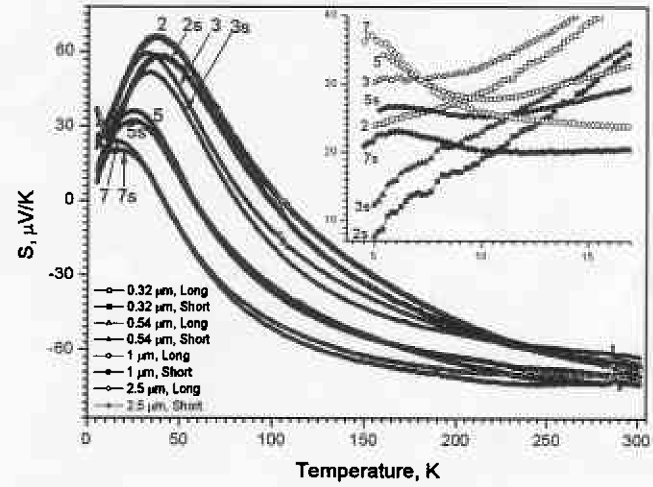

Fig.1.The temperature dependences of the thermopower for Bi wires. Numbers refer to samples described in table 1. The low temperature parts of these dependences are shown in the inset.

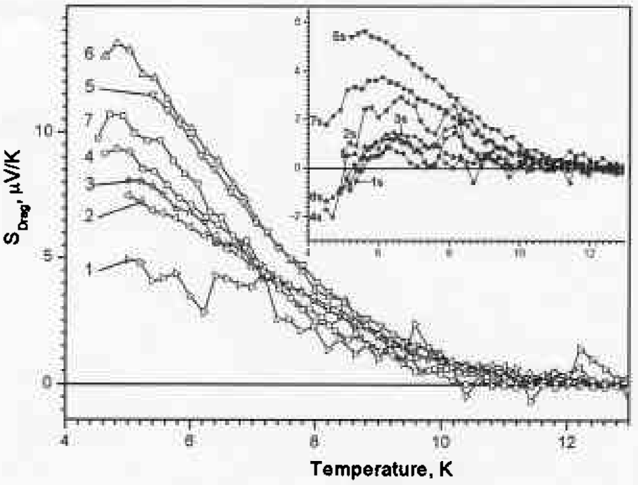

Fig.3.The temperature dependences of the phonon drag thermopower for long Bi samples. The temperature dependences of the phonon drag thermopower for short Bi samples are shown in the inset. Numbers refer to samples described in table 1.

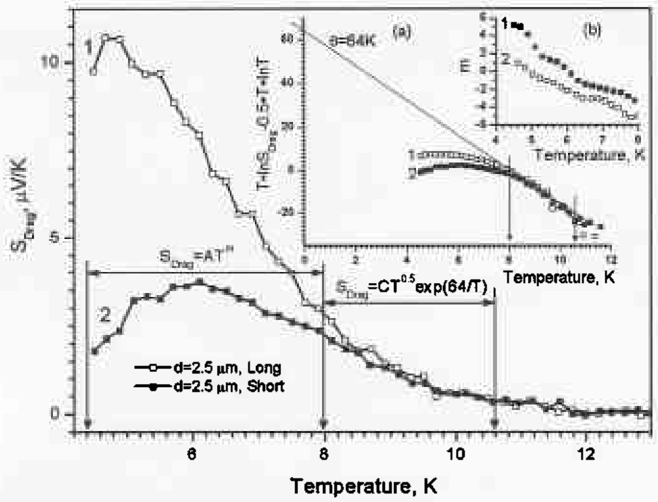

Fig.4. The temperature dependences of the phonon drag thermopower for Bi long and short samples, d=2.5 µm, 1- *L*=2.5 mm, 2– *L*=0.8 mm. A fits of the phonon-drag thermopower to an expression of the form $CT^{n-1}\exp(\theta/T)$ are shown in the insert (a). Characteristic temperature θ is determined from the intercept and is equal 64 K. Changes of the power *m* for power law fitting of the form AT^m are shown in the insert (b).

µm values of phonon drag thermopower is very small for short samples but quickly rise for long ones. A common behavior of the phonon drag thermopower 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 processes two-step phonon drag mechanism, first predicted by Kozlov and Nagaev [12], can exist. In this case long-wavelength phonons which drag the carriers can give 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]

$$S_{Drag} = CT^{n-1}\exp(\theta/T), \qquad (1)$$

where C is a constant and θ a characteristic temperature. We obtain a good fits over the range 8-10.5 K to the phonon drag thermopower yielding values of θ between 47 K and 73 K for various samples (n=1.5). A typical plots of $T\ln S_{Drag} - (n-1)T\ln T$ versus T for n=1.5 are shown in the inset (a) of Fig. 4. For Bi wire d=2.5 µm we define θ=64 K, which fits long and short samples. 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)), at T=7.8 K m=-5 for log sample and -4 for short sample. Change power m with temperature and Te doping level has been also observed in bulk Bi samples [13] and was explained by various phonon scattering mechanisms.

Fig.5 shows the dependences of the values of maxima of the phonon drag thermopowers, $S_{Drag,max}$ and temperatures of the maxima of the phonon drag thermopowers, T_{max} versus diameter *d*. The data are shown for long and short samples. As it is seen from figure $S_{Drag,max}$ for long samples shows a tendency to saturation at about 12 mV/K.

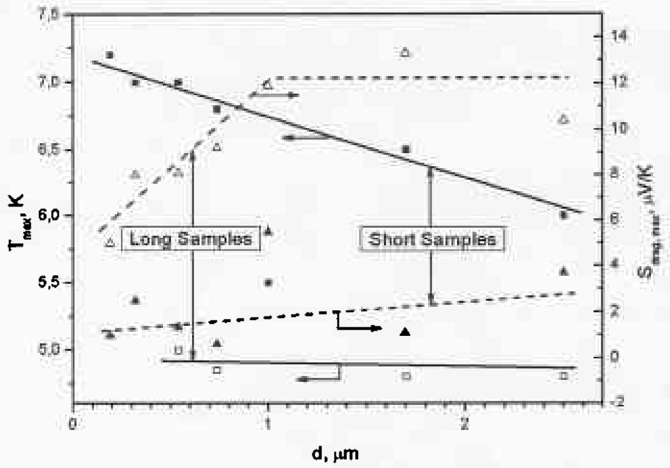

Fig.5. The dependences of the values of maxima of the phonon drag thermopowers, $S_{Drag,max}$ and temperatures of the maxima of the phonon drag thermopowers, T_{max} vs diameter *d* for Bi long and short samples. The solid lines represent linear fitting data for T_{max}, while the dashed lines are for $S_{Drag,max}$.

Conclusions

For the first time the phonon drag effect is observed in such low-sized objects like Bi microwires. The general behavior observed for all long samples (*L* ~ 2.5-8.4 mm) is as follows: as the temperature is lowered from 12 K the magnitude of the phonon drag part of thermopower increases and achieves its maximum at ~5 K. Modification of thermopower depends on the wire diameter and increases with increasing diameter of the sample. The effect strongly depends on the sample's length. Thus we are observed considerable decreasing of the phonon drag in the short samples when the length of the samples smaller than 1 mm. The positive thermopower maxima of the order of 10 μVK^{-1} are explained in terms of the phonon drag of holes.

Acknowledgments

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