We report measurements of thermopower oscillations vs magnetic field in a diffusive Andreev interferometer. Upon the increase of the dc current applied to the heater electrodes, the amplitude of these oscillations first increases then goes to zero as one would expect. Surprisingly, the oscillations reappear at yet higher heater currents with their phase being π-shifted compared to low current values. From direct measurements of the temperature gradient we estimate the amplitude of the oscillations to be orders of magnitude smaller than predicted by theory.

In a nonuniformly heated conductor there arises an electric field, \( E \), proportional to the temperature gradient \( E = QVT \), where \( Q \) is known as thermopower. In metals \( Q \) is determined by a derivative of the logarithm of conductivity \( \sigma \) with respect to energy \( \varepsilon \) taken at the Fermi level

\[
Q = \frac{\pi^2 k_B^2 T}{3 e} \left\{ \frac{\partial \ln \sigma}{\partial \varepsilon} \right\}_{\varepsilon=\varepsilon_F},
\]

where \( k_B \) is Boltzman constant and \( e \) is electron charge. In normal metals with diffusive electron transport the conductivity changes very little with energy and the thermopower has the following order of magnitude

\[
Q = C \frac{k_B T}{\varepsilon_F},
\]

where \( C \) is a constant of the order of unity depending on the topology of Fermi surface and the energy dependence of scattering time.

The thermoelectric properties of a normal metal \( (N) \) in contact with a superconductor \( (S) \) are strongly modified by the proximity effect. First, the electrical conductivity has a much stronger energy dependence, so that the thermopower can be orders of magnitude larger than predicted by Eq. (2) \( 2 \). In the geometry of Andreev interferometer, when the normal part is connected to the superconducting loop, the thermopower will oscillate as a function of the magnetic flux \( \Phi \) through the loop, with a period equal to the flux quantum \( \Phi_0 = \hbar c/2e \). It was shown that these oscillations can be symmetric or antisymmetric with respect to \( \Phi \) depending on the sample topology in contrast to the conductance oscillations which are always symmetric \( 3 \). Second, the voltage between \( N \) and \( S \) circuits may appear due to nonequilibrium branch imbalance in the \( N \) film created by temperature gradient \( 3 \). The thermopower associated with this effect is predicted to be giant compared with Eq. (2) as it does not contain small factor \( k_B T/\varepsilon_F \). The thermopower oscillations are predicted to be close to antisymmetric in this case \( 3 \).

Recently, the oscillating thermovoltage of mesoscopic (Au/Al) Andreev interferometer has been discovered in a pioneering experiment by Chandrasekhar’s group \( 4 \). The value of \( Q \) was estimated to be consistent with theoretical predictions \( 2 \). For various geometries of Andreev interferometer, both symmetric and antisymmetric oscillations were observed. Later experiments by the same group with direct measurements of temperature gradients proved that the thermopower was indeed orders of magnitude larger than (2) \( 5 \). The origin of the phase of thermopower oscillations for different geometries is still unclear.

In this Letter we report measurements of thermopower oscillations vs magnetic field in a \( (\text{Sb/Al}) \) Andreev interferometer. As a function of heater current the amplitude of oscillations first increases then goes to zero similar to that in Ref. 4. However, we have discovered a novel effect: at higher heater currents the oscillations reappear with their phase shifted by \( \pi \) compared to low current ones. In our case the amplitude of oscillations was of the order of (2), as extrapolated from the value of \( Q \) for Sb at \( T = 273K \), although classical thermopower was not observed.

The structures were made by multi-layer electron-beam lithography as shown in the scanning electron micrograph (Fig. 1). The first layer was 40 nm thick Sb (semimetal) followed by second layer of 60nm thick Al (superconductor). Prior to the deposition of the second layer, \( \text{in-situ} \) Ar+ etching was used to clean the interface. Two hybrid loops form two Andreev interferometers which we will call "top interferometer" (TI) with interfaces to superconductor situated on the current lines of \( N \)-part and "bottom interferometer" (BI) with the interfaces being off current lines. TI has \( S \)-contacts (S1 and S2) and \( N \)-contacts (N1, N2, N3, N4, H1, H2). BI has \( S \)-contact S3 and \( N \)-contacts N5, N6, N7, N8, H1, H2 (see Fig. 1). The geometry of the sample allowed us to measure the temperature gradient across an interferometer, so that the absolute value of thermopower could be determined.

Measurements were performed in a He\(^3\) cryostat in temperatures from 0.28K to 6K with a magnetic field (j 5T) applied perpendicular to the substrate. Resistivity, \( \rho \), of Sb film was 60µΩcm and that of Al film was 1.2µΩcm, with diffusion constants, \( D \), 133cm\(^2\)/s and 223cm\(^2\)/s, respectively. The resistance of interface be-
tween the two films in normal state was 8Ω for the interface area 150x150nm².

Figure 2 shows the resistance and thermovoltage oscillations for both interferometers as a function of the magnetic field, with a period corresponding to the flux quantum through the superconducting loop. Magnetoresistance measurements were performed using conventional ac bridge technique. For thermopower measurements a heating current, $I_h$, was a sum of dc and small ac currents. Thermovoltage, $V_{th}$, was measured using lock-in amplifier on the frequency of ac signal.

The polarity of the connection of $S$ and $N$ electrodes to the voltmeter was the same for both TI and BI. Yet, the phase of thermovoltage oscillations is opposite for TI and BI. If we assume some heat escape through the $NS$ interfaces into superconductor, then for BI the closest to the $N$ reservoir $NS$ contact will have higher temperature, contrary to TI. Thus, the temperature gradient will be opposite for BI and TI, resulting in opposite phase of thermopower oscillations for BI and TI. However, for quasiparticle energies below superconducting gap there should be no heat transfer into the $S$ contact (neglecting phonon heat conductivity at $T \approx 0.28K$). In this case, there is no temperature gradient between the $NS$ contacts for BI and the reason for the opposite phase for BI and TI remains unclear. In our experiment the oscillations of the thermopower for the BI with NS interfaces off classical current lines between the $N$ reservoirs (corresponding to the house structure of Ref. 4) were π/2-shifted from magnetoresistance oscillations (as opposed to the two being in phase in Ref. 4). This fact can probably be attributed to the noticeable asymmetry in the position of $NS$ contacts of BI with respect to the "hot" point (see Fig. 1).

Figure 3 shows $V_{th}$ vs magnetic field oscillations of the TI for four different dc current, $I_h$. With increasing $I_h$ the oscillations first disappear, and then remarkably reappear at a higher $I_h$ with a π phase shift compared to low $I_h$ measurements. The phase of the thermopower oscillations at each $I_h$ was checked against that of the magnetoresistance, which remained the same for all temperatures and currents. Note magnetic field independent $V_{th}$ resulting in a vertical shift of the curves in Fig. 3 with increasing $I_h$. This is not due to classical thermopower in Sb as control Sb structures of exactly the same geometry of the heater but with all normal electrodes (no superconductors) showed no such a shift. In Fig. 4 we show the amplitude of thermovoltage oscillations for both our interferometers. Note that the amplitude of the thermovoltage oscillations for BI and TI is about the same. For both interferometers no noticeable oscillations were detected for $I_h$ in the range from 3 to 8 $\mu$A.

We have also performed similar measurements of the thermopower on the structures with extra normal electrodes connected to the Andreev interferometer. This allows us to compare the thermovoltage arising between two normal electrodes with that arising between a normal and a superconducting electrode. We found the amplitude of the thermovoltage oscillations being approximately the same for both cases, contrary to the prediction of Ref. 3. The disagreement probably originates from the condition $h/\varepsilon \tau_\alpha \ll 1$ (here $h$ is Plank’s constant, $\varepsilon$ is a characteristic energy of quasiparticles and $\tau_\alpha$ is the energy relaxation time) at which the results of Ref. 3 were calculated. In our experiment it was $h/\varepsilon \tau_\alpha \sim 1$.

To estimate the absolute value of thermopower we need to know temperature gradient across the interferometer. We have used proximity effect in the TI as a thermometer. Figure 5 shows the amplitude of magnetoresistance oscillations of the TI as a function of temperature and dc current, $I_h$. From this we can roughly estimate the temperature, $T_m$, in the middle of the normal part of the TI (Fig. 6, inset). Figure 6 shows the correspondence of the temperature to the heating current extracted from Fig. 5. The solid line in Fig. 6 shows the best fit of $T_m$ by the formula $\sqrt{T_m^2 + \Delta T^2}$, obtained from a solution of Nagaev’s equation neglecting electron-phonon scattering at low temperatures, where $\alpha$ is a sample-specific constant, which we used as a fitting parameter. We will use the solid line on Fig. 6 to obtain $T_m$ at a given heating current. Broken lines on Fig. 6 show error in finding $T_m$ due to data scattering. The thermopower of Andreev interferometer, $Q_A$, can be estimated as $Q_A = V_{th}/\Delta T$, where $V_{th}$ is voltage measured between $S$ and $N$ and $\Delta T \approx T_m - T_0$ is temperature difference across the interferometer. Measurements on the N6-N7 part of the structure confirmed that the temperature of this part does not deviate from the base temperature at low ($I_h \leq 1\mu A$) heater currents.

The reliable estimation of the temperature using this method can be done only at small currents when the corresponding temperature is far away from the critical temperature of the superconducting transition. This is because close to the superconducting transition the temperature dependence of the proximity effect is governed by the temperature dependence of the gap rather than actual electron temperature. For $I_h = 1\mu A$ we have $T_m \approx 0.36 \pm 0.02 K$, so that $\Delta T \approx 80mK$. This gives the value of $Q_A \approx 50nV/K$. It is interesting to compare this value with the classical thermopower of Sb, $Q_d$. Using table value of $Q_d = 36\mu V/K$ for Sb at $T = 273K$ we can expect the value of the order of $36nV/K$ at $T = 0.28K$. Thus, in our experiment the ratio $\varepsilon_F/k_BT$ seems to be orders of magnitude larger than $Q_A/Q_d$. However, the fact that we did not observe classical thermovoltage down to the level of about 0.1nV, which corresponds to the thermopower of about 1nV/K at $I_h = 1\mu A$, suggests that the classical thermopower is also at least two orders of magnitude smaller than one would expect from free electron model. Unfortunately, the thermopower measurements at these temperatures are very difficult, because one needs a small temperature gradient, resulting in a small thermovoltage. The reference data for Sb thermopower at these low temperatures is also lacking.

At low heater currents our results are in general in line
with earlier experiment of Ref. [1]. In terms of thermovoltage our results are of the same order as in [1] but in terms of thermopower we find our values of 50 - 100 nV/K to be smaller than 4µV/K reported in [1] and than theoretical prediction of few µV/K [2].

Main discovery made in this work is reappearance of thermopower at higher heating currents with the π-shift in the phase of the thermopower oscillations. We emphasize that our result is different from the reversal of Josephson current observed in Ref. 11, because we don’t see any anomalies in magnetoresistance oscillations (see Fig. 5) with their phase being exactly the same throughout the whole range of temperatures and currents.

In real metals with anisotropic Fermi surface and scattering times (2) will be no longer valid. Instead, we must add up contributions from all different parts of the Fermi surface, some having opposite sign. Sb is a highly anisotropic semimetal with the concentration of electrons and holes being nearly equal and with effective masses differing by a factor of 10 for different directions. Contributions to the proximity-effect correction to conductivity from these different types of carriers will have different energy dependence. Therefore, it is possible that at some temperature these contributions may cancel each other and the thermopower will change sign in the way observed on the experiment.

The other mechanism that strongly affects the thermopower of metals at low temperatures and may also result in giant thermopower and a change in the sign of thermopower is a phonon drag [12]. However, at the base temperature of our experiment, \( T = 0.28K \), phonon effects should be minimal. To our knowledge the phonon drag has never been studied with regard to superconducting proximity effect.

In conclusion, we have observed the reversal of the phase-dependent thermopower of diffusive Andreev interferometer at low temperatures. The magnetic-field independent Andreev thermopower was observed, while classical thermopower was smaller than the experimental noise level. The amplitude of both Andreev and classical thermopower was orders of magnitude smaller than that predicted by theory. We believe that the full theoretical treatment of the problem including the topology of real Fermi surface is needed for complete understanding of the observed effects.

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$A_{th}$, nV

$T = 0.28$K
\[ \frac{A_{\text{MR}}}{A_{\text{MR}}(0)} \]

\[ I_{\text{mod}} = 0.75 \, \mu A \]

\[ I_h = 0 \]

\[ T = 0.28 \, \text{K} \]
\[ T_m = \sqrt{T_0^2 - T_{ih}^2} \]