Quantum Thermopower of Metallic Atomic-Size Contacts at Room Temperature

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ABSTRACT: We report conductance and thermopower measurements of metallic atomic-size contacts, namely gold and platinum, using a scanning tunneling microscope (STM) at room temperature. We find that few-atom gold contacts have an average negative thermopower, whereas platinum contacts present a positive thermopower, showing that for both metals, the sign of the thermopower in the nanoscale differs from that of bulk wires. We also find that the magnitude of the thermopower exhibits minima at the maxima of the conductance histogram in the case of gold nanocontacts while for platinum it presents large fluctuations. Tight-binding calculations and Green’s function techniques, together with molecular dynamics simulations, show that these observations can be understood in the context of the Landauer–Büttiker picture of coherent transport in atomic-scale wires. In particular, we show that the differences in the thermopower between these two metals are due to the fact that the elastic transport is dominated by the 6s orbitals in the case of gold and by the 5d orbitals in the case of platinum.

KEYWORDS: Quantum thermopower, quantum conductance, atomic-size metallic contacts, Landauer approach, molecular dynamics simulations

Thermoelectric devices hold the promise for helping to solve key problems related to energy conversion and refrigeration.1 The discovery that nanostructured materials may enhance their efficiency2 underlines the need to understand the mechanisms that govern thermoelectricity at the nanoscale. Although notable progress has been made in this respect,3−5 there remain basic open problems. Thus, for instance, it is still unclear what determines the thermoelectricity in a metallic atomic-size contact,6 a system that has become the test bed for nanoelectronics and mesoscopic physics.7 Here we report room-temperature thermopower measurements of gold and platinum atomic-size contacts that show that even its sign differs from that of bulk wires. We find that gold few-atom contacts exhibit a negative thermopower whose magnitude is determined by the sign of the conductance histogram, whereas platinum contacts have an average positive thermopower with large fluctuations. We show that these observations can be understood within the picture of coherent electron transport and explain the differences between metals in terms of their distinct electronic structure. Our results illustrate that thermoelectricity at the nanoscale differs substantially from the macroscopic limit.

If a temperature difference ΔT is applied across a metallic junction, an electric potential difference ΔV appears across the junction, which is defined as S = −ΔV/ΔT. In macroscopic metallic wires, the thermopower has two contributions due to both electron diffusion and phonon drag.8 The phonon drag contribution plays a very important role at low temperatures (lower than the Debye temperature). However, the thermopower at room temperature in metals is dominated by the diffusion contribution,9 which is qualitatively understood since the pioneering work of Sir N. F. Mott.9 Thus, for
instance, the relatively large magnitude and negative sign of the thermopower of transition metals (like Ni, Pd, or Pt) is attributed to the increasing relaxation time with energy due to their characteristic density of states. This is clearly at variance with noble metals (Cu, Ag, and Au), which exhibit a smaller and positive thermopower.6 This picture is valid only in the case of bulk metals and, as we shall show below, a different picture emerges at the nanoscale due to quantum effects.

The advent of experimental techniques like the scanning tunneling microscope (STM) and the mechanically controllable break junctions (MCBJs) has allowed investigating the transport properties of metallic atomic-size contacts.7 These atomic wires have turned out to be ideal systems where quantum theories of charge and energy transport have been thoroughly tested.7 However, thermoelectricity in these contacts has received little attention so far due to experimental challenges. The first measurements of the thermopower of an atomic-size contact were reported using gold MCBJs at 12 K.6 The thermopower was found to be different in each experimental realization and to have a very small average value, while its fluctuations were explained in terms of interference effects due to the presence of impurities near the contact region. However, in very recent experiments10 the room-temperature thermopower of gold atomic-size contacts has been shown to have a nonzero average value and to exhibit oscillations as a function of the contact size that were attributed to quantum confinement. This apparent contradiction has renewed the interest in the basic question of how the thermopower of atomic-scale metallic wires depends on the material, the size of the contacts, and their geometry.

To address these questions, we have studied the thermopower of Au–Au and Pt–Pt atomic-size contacts, using a modified STM setup.11 The gold (single crystal, 99.999% purity) and platinum (99.999% purity) surfaces are flame annealed. In addition, Pt is chemically etched with aqua regia (HNO3/HCl 1:3). We use mechanically cut Au and Pt tips and the contacts are formed by controlled indentation of the substrate with the STM tip and subsequent separation.12,13 The STM tip is heated with a resistive element while keeping the substrate at room temperature, and a voltage bias \( V_{\text{bias}} \) is applied to the substrate. We measure with temperature differences between the tip and the substrate of 20 and 40 K. This temperature difference \( \Delta T \) gives rise to a thermovoltage \( V_{\text{th}} \) which consists of a contribution from the contact \( S\Delta T \) and a contribution from the tip-connecting lead \( S_{\text{lead}}(-\Delta T) \), where \( S \) and \( S_{\text{lead}} \) are the thermopower of the contact and the lead, respectively. The current between the tip and substrate is given by

\[
I = G(V_{\text{bias}} - V_{\text{th}}) = G(V_{\text{bias}} + S_{\text{lead}}\Delta T - S\Delta T)
\]

where \( G \) is the conductance of the contact (see Figure 1a). Taking into account that for \( V_{\text{bias}} = V_{\text{th}} \) the current vanishes, by measuring an \( I-V \) curve we can obtain simultaneously the thermopower and the conductance: the zero crossing yields \( V_{\text{th}} \) (and hence \( S \)) and the slope gives \( G \) (see Supporting Information for more details).

In Figure 1b–d, we show some characteristic examples of the simultaneous measurements of the conductance \( G \) and thermopower \( S \) in the last stages of the breaking of Au wires. As it is well-known for Au contacts,14 the conductance decreases in a steplike manner due to atomic rearrangements in the contact15,16 with a tendency to exhibit plateaus close to multiples of the conductance quantum, \( G_0 = 2e^2/h \), where \( e \) is the absolute value of the electron charge and \( h \) is the Planck constant. The thermopower also presents plateaus separated by abrupt variations in response to atomic rearrangements but evolves in a more complicated fashion exhibiting predominantly negative values but also positive ones (see Figure 1b–d). In particular, we observe that in the quantized conductance plateaus, the thermopower tends to be partially suppressed. This is particularly clear for junctions with \( G \approx G_0 \) which correspond to single-atom contacts or short atomic chains17 (see Figure 1b).

Figure 1. Simultaneous measurement of the conductance and thermopower of metallic atomic-size contacts. (a) Schematic representation of the setup used to measure simultaneously conductance and thermopower in metallic atomic-size contacts. The tip is heated to a temperature \( T_{\text{th}} \) while the substrate is kept at room temperature \( T_c \). A temperature gradient \( \Delta T = T_{\text{th}} - T_c \) is established across the junction and along the tip-connecting lead. (b–d) Three characteristic examples of the conductance (blue curves) and thermopower (red curves) in the last stages of the breaking of an Au wire at room temperature. Both conductance and thermopower are very sensitive to atomic rearrangements at the junction. In some cases, an atomic rearrangement that produces just a small change in the conductance results in a huge change in the thermopower, as illustrated in panel c.
To establish the characteristic behavior of the thermopower we have carried out a systematic statistical analysis collecting the data of a few hundreds of contact breakings. As we show in the density plot of Figure 2a, starting from very large contacts (up to $10^8$–$10^9 G_0$) of 134 breakings of Au (a) and 263 of Pt contacts (d). Red thick lines show the fit that describes the transition between atomic contacts and bulk-like wires. The values used in the fit are the following: for Au, $S_b = -0.75 \mu V/K$ and $S_M = 1.94 \mu V/K$; for Pt, $S_b = +1.1 \mu V/K$ and $S_M = -5.3 \mu V/K$. (b,e) Thermopower density plots as a function of the conductance for small contacts up to $10G_0$, of 674 and 385 breakings of Au (b) and Pt (e) contacts, respectively. Thick black lines show the average thermopower value and the black thin lines the region around the average value within the standard deviation. The mean value of thermopower is negative for Au and positive for Pt. The sign of the mean thermopower changes from negative (positive) for small atomic contacts of Au (Pt) to positive (negative) for large contacts. (cf) Conductance histogram (blue) and average thermopower (red) for few atom contacts ($G < 4G_0$) of 909 breaking curves on Au (c) and 216 breaking curves on Pt (f). The magnitude of the thermopower of Au exhibits minima coinciding with the maxima of the conductance histogram, while for Pt there is not any pronounced feature. See Supporting Information Figure S4 for the corresponding density plots.

Figure 2. Thermopower of Au and Pt atomic-size contacts. (a,d) Density plots of the thermopower versus conductance for very large contacts (up to $10^8$–$10^9 G_0$) of 134 breakings of Au (a) and 263 of Pt contacts (d). Red thick lines show the fit that describes the transition between atomic contacts and bulk-like wires. The values used in the fit are the following: for Au, $S_b = -0.75 \mu V/K$ and $S_M = 1.94 \mu V/K$; for Pt, $S_b = +1.1 \mu V/K$ and $S_M = -5.3 \mu V/K$. (b,e) Thermopower density plots as a function of the conductance for small contacts up to $10G_0$, of 674 and 385 breakings of Au (b) and Pt (e) contacts, respectively. Thick black lines show the average thermopower value and the black thin lines the region around the average value within the standard deviation. The mean value of thermopower is negative for Au and positive for Pt. The sign of the mean thermopower changes from negative (positive) for small atomic contacts of Au (Pt) to positive (negative) for large contacts. (cf) Conductance histogram (blue) and average thermopower (red) for few atom contacts ($G < 4G_0$) of 909 breaking curves on Au (c) and 216 breaking curves on Pt (f). The magnitude of the thermopower of Au exhibits minima coinciding with the maxima of the conductance histogram, while for Pt there is not any pronounced feature. See Supporting Information Figure S4 for the corresponding density plots.

with $G > 10^6 G_0$, where $S \approx +1 \mu V/K$ in fair agreement with bulk measurements, we observe a crossover to negative values as the contact size is reduced. Focusing on few-atom contacts with $G < 10^6 G_0$, see Figure 2b, we find that the thermopower fluctuates from contact to contact, but its average value is negative independently of the conductance. Moreover, for the smallest contacts ($G < 4G_0$), the thermopower magnitude exhibits minima coinciding with the maxima of the conductance histogram (see Figure 2c), which are close to multiples of $G_0$.

Turning now to the results for Pt contacts, we observe that the thermopower changes from large negative values of $S \approx +1 \mu V/K$, close to the known bulk result, to positive values as the contact size diminishes (see Figure 2d). As one can see in Figure 2e, Pt few-atom contacts exhibit an average positive thermopower with fluctuations that are several times larger than for Au. Finally, for the smallest contacts there is not a simple correlation between the thermopower and the conductance (see Figure 2f).

To elucidate the origin of the behavior of the thermopower of atomic-size contacts we computed the transport properties of these nanowires within the Landauer–Büttiker approach to coherent transport. In this approach, the conductance and the thermopower are expressed in terms of the energy-dependent transmission function $\tau(E)$ as

$$G = G_0 K_0(T) \quad \text{and} \quad S = -\frac{K_0(T)}{eTK_0(T)}$$

with $K_0(T) = \int dE (E-E_F)^n \tau(E)[-\delta_K f(E,T)]$. Here, $E_F$ is the Fermi energy and $f(E,T)$ is the Fermi function. At low temperatures, these expressions reduce to $G = G_0 \tau(E_F)$ and $S = -[(4\pi^2k_B T/3e)] [\delta_K \ln \tau(E)]_{E=E_F}$, where $k_B$ is the Boltzmann constant. The total transmission can be resolved into the transmission coefficients of the conduction eigenchannels, $\tau_n$, as $\tau(E) = \sum \tau_n(E)$. Thus, within this approach the technical task is the calculation of the energy dependence of the transmission. For this purpose, we first carried out classical molecular dynamics (MD) simulations to describe the formation of the atomic contacts. These simulations were performed with the code LAMMPS within the embedded atom method. Then, once the geometries of the atomic wires were determined, we computed the transmission coefficients by combining a tight-binding model for the electronic structure and Green’s function techniques (see Supporting Information).

We simulated 100 stretching events for Au and Pt wires at 300 K oriented in the <100> direction to obtain a reliable statistics. Our main results for the thermopower and the conductance of Au and Pt contacts are summarized in Figure 3. Let us remark that while the low-temperature approximation for the conductance gives excellent results (with 1% errors), we found it necessary to employ the full formula of eq 2 to get accurate results for the thermopower. As one can see in Figure 3a,b, the thermopower changes from realization to realization with a negative average value for Au and a positive one for Pt, irrespective of the conductance value. Moreover, for Au contacts the magnitude of the thermopower exhibits minima correlated with the conductance maxima (Figure 3b) and in particular it is largely suppressed close to $1G_0$. The analysis of the transmission coefficients (see Figure 3c) shows that this suppression is due to the fact that the transport is dominated by a single fully open conduction channel due to the Au 6s orbitals. Thus, the transmission reaches a maximum at the Fermi energy, which leads to a very small thermopower value at $1G_0$. Similarly, the other minima in the thermopower magnitude are due to the saturation of the transmission of other channels when the conductance is a multiple of $G_0$. In the case of Pt, there is no noticeable structure in the thermopower related to the main peak in the conductance histogram ($\sim 1.9G_0$, see Figure 3e) and in general the fluctuations are several times larger than in Au contacts. We attribute these features to the fact that the transport in Pt contacts is dominated by the 5d orbitals. This implies that several partially open channels contribute to the transport even in single-atom contacts, see Figure 3f. Thus, the transmission does not reach an extremum at the Fermi energy and the thermopower is not suppressed. Moreover, the d orbitals are...
anisotropic and thus much more sensitive to local disorder than the s orbitals, which leads to larger fluctuations in the thermopower for Pt. Overall, these results are in very good qualitative agreement with our experimental findings.

Let us now shed some more light on the origin of the sign of the thermopower. According to eq 2, this sign is determined by the electron–hole asymmetry in the transmission function. In Figure 4a,c, we show the total transmission as a function of energy for Au and Pt few-atom contacts obtained from the same stretching simulation. Notice that while the slope around the Fermi energy, $E_F$, is dominated by a single fully open channel, (d–f) the same as in panels a–c but for Pt. Notice that the average thermopower is positive. The conductance histogram exhibits a peak at around $1.9G_0$, which corresponds to single-atom contacts and short atomic chains. This conductance region is dominated on average by four conduction channels.
case of Pt, which results in a positive thermopower. This
different behavior can be traced back to the different electronic
structure of these two metals. In the case of Au, $E_F$ lies on a
region dominated by the 6s orbitals with smaller contributions
from the 6p bands. The density of states (DOS) for these
orbitals, which are responsible for the transport, tends to
slightly increase with energy. This is illustrated in Figure 4b
where we show the local DOS projected onto the different
orbitals of a central atom in a two-atom contact. On the
contrary, for Pt, $E_F$ lies close to the edge of the 5d bands, a
region where the transmission typically diminishes with
increasing energy. This reflects in turn the typical behavior of
the local DOS, as we show in Figure 4d for a single-atom
contact.

Let us now compare with previous results. For Au, our results
are in qualitative agreement with those recently reported in ref
10, while the interpretation is clearly at variance. To explain
their results, the authors of ref 10 invoked simple free-electron
models meant to describe ballistic quantum point
contacts.28–30 However, these models only predict a negative
sign for the thermopower and they are thus unable to explain
the appearance of positive values in some Au contacts or the
typical behavior of the Pt contacts. This shows that our results
cannot be simply explained in terms of quantum confinement.
On the other hand, the claim in ref 6 that the thermopower of
Au contacts vanishes on average is because those experiments
were performed at a much lower temperature (12 K) and thus,
the thermopower is expected to be around 30 times smaller
than in our case.25 Moreover, the role of the impurities
advocated in that work to explain the behavior of the
thermopower fluctuations is certainly important, but in our
simulations the origin of thermopower fluctuations can be
 traced back to local disorder, underlining the importance of the
detailed atomic arrangement at the contact. In contrast, the
average behavior and in particular the characteristic sign of the
thermopower is determined by the intrinsic electronic structure
of the metal.

Comparing to our previous theoretical work the technical
approach is essentially identical. Main changes concern the
number of atoms in the central wire (563 here as compared to
112 there) and the electronic and phononic temperatures of
300 K, as compared to 12 and 4.2 K in ref 25, respectively.
Because of the lower temperatures, our theoretical results in ref
25 were indeed in agreement with those of ref 6. Upon close
inspection, the statistically averaged thermopower of Au in
Figure 4 of ref 25 is negative and shows a suppression at a
conductance of 1$G_0$ while for the Pt contacts in contrast it is
indeed slightly positive. Let us point out that due to the smaller
contact size in ref 25, only junctions with rather low
conductance values up to 2–3$G_0$ are not affected by the
starting configurations in our MD simulations. The larger
contacts used here allow us to discuss the thermopower reliably
up to much higher conductances, reproducing the oscillations
and the nonzero offset of the thermopower.

Let us now consider in more detail the variation of the
thermopower from the bulk value to the atomic contact value.
In Figure 2a,d, the thermopower is plotted as a function of the
conductance of the contact, which is related to the contact
radius, $a$. For radii smaller than the inelastic electron mean free
path $l$, the electron traverses the contact coherently
(ballistically) and the conductance is given by Sharvin’s
expression: \[ G = G_0(k_Fa/2)^2 \]
where $k_F$ is the Fermi wavenumber. For $a \gg l$, the electrons move through the
contact diffusively and Maxwell’s expression for the spreading
conductance must be used: \[ G = 2a/\rho \]
in which $\rho$ is the resistivity. The transition from the coherent
(ballistic) regime to the diffusive regime may be described by a simple formula as
\[ G = xG_0 + (1 - x)G_M \]
where $x$ goes from a value of one for an
atomic contact to zero for a contact larger than the electron
mean free path. We may choose a simple form like $x = e^{-a/l}$. A
similar formula should be valid for the variation of the
thermopower with contact size because, as discussed above, in
this range of temperatures phonon drag effects are negligible in
bulk and only electron diffusion needs to be considered. Thus,
we write $S = xS_0 + (1 - x)S_M$, where $S_0$ is the thermopower in
the atomic scale and $S_M$ is the corresponding bulk value. Using $l$ as a free parameter for the fit of the average thermopower, we
obtain the red solid lines in Figure 2a,d. The best fit is obtained
for values of $l$ of 37 and 14 nm for Au and Pt, respectively,
which are in good agreement with the inelastic mean free path
obtained from the resistivity (38 nm for Au and 8 nm for Pt).
The fact that this simple analytical expression describes so well
the transition between atomic contacts and bulk wires clearly
suggests that this crossover is indeed determined by the ratio $a/l$ and it originates from the change in the dominant transport
mechanism.

In summary, we have shown that metallic contacts offer the
unique possibility of investigating how thermoelectricity is
continuously modified from bulklike devices all the way down
to the atomic scale. Moreover, we have shown that the change
in the dominant transport mechanism from incoherent
transport in bulk samples to coherent one in atomic-scale
wires leads to a qualitative modification of the thermopower, a
very important lesson for the fields of thermoelectrics and
nanoelectronics.

**ASSOCIATED CONTENT**

3 Supporting Information
Experimental technique; thermal circuit; thermovoltage cal-
ibration; density plots of few-atom contacts ($G < 4G_0$);
simultaneous measurement of conductance and thermopower
of Pt atomic-size contacts; and theoretical modeling: molecular
dynamics simulations and transport calculations. This material
is available free of charge via the Internet at http://pubs.acs.org.

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**Author Contributions**
C.E. and L.R.-G. performed the experiments and M.M. carried
out the MD simulations and the thermopower calculations.
C.E. performed the calibration of the setup for the ther-
mos power measurements. F.P., P.N., J.C.C., G.R.-B., and N.A.
planned the project and advised the students. J.C.C. and N.A.
wrote the manuscript with contributions from all the authors.

**Notes**
The authors declare no competing financial interest.

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