Observation of a Parity Oscillation in the Conductance of Atomic Wires

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(Received 4 March 2003; published 15 August 2003)

Using a scanning tunnel microscope or mechanically controllable break junctions atomic contacts for Au, Pt, and Ir are pulled to form chains of atoms. We have recorded traces of conductance during the pulling process and averaged these for a large number of contacts. An oscillatory evolution of conductance is observed during the formation of the monoatomic chain suggesting a dependence on the numbers of atoms forming the chain being even or odd. This behavior is not only observed for the monovalent metal Au, as was predicted, but is also found for the other chain-forming metals, suggesting it to be a universal feature of atomic wires.

DOI: 10.1103/PhysRevLett.91.076805 PACS numbers: 73.23.–b, 73.21.–b, 73.22.–f, 73.40.Cg

Wires of one-atom thick and several atoms long (chains of atoms) connecting two macroscopic electrodes can be formed when pulling atomic contacts using a scanning tunneling microscope (STM) or mechanically controllable break junctions (MCBJ) [1]. Chains of atoms have also been formed using a transmission electron microscope (TEM) where the edges of two holes in a thin film meet, just before their coalescence [2–4]. Recently it has been shown that the formation of such structures depends on the metal and that for clean environments they can only be formed with Au, Pt, and Ir [5,6].

The atomic chains constitute a unique metallic structure where one-dimensional properties of matter can be tested. Although they have been realized only recently, atomic wires have been textbook examples and toy models for a long time because of their simplicity. Moreover, they are the ultimate limit in the miniaturization of electronics, being the simplest object to be connected into a circuit. This has stimulated numerical simulations of their transport properties well before their experimental observation. Various groups [7–12] have found oscillations in the conductance as a function of the number of atoms for calculations of sodium atomic chains, where this metal was selected because it has the simplest electronic structure. Sim *et al.* [8], using first-principles calculations and exploiting the Friedel sum rule, found that the conductance for an odd number of atoms is equal to the quantum unit of conductance $G_0(= 2e^2/h)$, independent of the geometry of the metallic banks, as long as they are symmetric for the left and right connections. On the other hand, the conductance is generally smaller than G_0 and sensitive to the lead structure for an even number of atoms. The odd-even behavior follows from a charge neutrality condition imposed for monovalent-atom wires. The parity oscillations survive when including electron-electron interactions [9], which can even amplify the oscillations [13]. While most authors predict perfect transmission for chains composed of an odd number of atoms and a transmission smaller than unity for an even number, some groups find the opposite [7,11]. This anomalous phase shift of the oscillations can likely be attributed to the artificial interface introduced in going from the Na atoms to jellium leads as used by those groups [12].

Here we present an experimental investigation of the parity effect by measuring the changes of conductance in the process of pulling atomic chains of Au, Pt, and Ir. We make a statistical analysis in order to remove the influence of different electrode configurations and thus uncover the effects which are intrinsic to the atomic chain. The experiments were performed using MCBJ and were reproduced for Au with a low-temperature STM. The Au, Pt, and Ir wires have a purity of 99.998%, 99.998%, and 99.98%, respectively. In MCBJ the wires are notched and glued on a substrate that can be bent by use of a piezo element. Once the sample is at 4.2 K inside a cryogenic vacuum the notch is broken by bending the substrate resulting in the separation of the wire into two electrodes with fresh surfaces. The relative displacement of the two resulting electrodes can be controlled with a resolution better than a picometer.

When pulling apart two electrodes in contact, the conductance decreases in a stepwise fashion following the atomic rearrangements in a succession of elastic and plastic stages [14,15] (Fig. 1). The successive values of conductance are related to the sizes of the contacts between the two electrodes. The last plateau of conductance before rupture is in general due to a single atom contact. The formation of an atomic wire results from further pulling of this one-atom contact, and its length can be estimated from the length of the last conductance plateau [1,5,16]. A histogram made of those lengths (filled curves in Fig. 2) shows peaks separated by distances equal to the interatomic spacing in the chain. These peaks correspond to the lengths of stretching at which the atomic chain breaks, since at that point the strain to incorporate a new atom is higher than the one needed to break the chain

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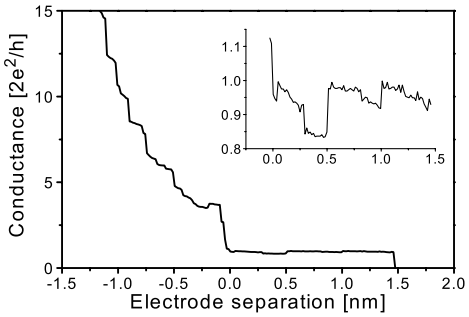

FIG. 1. Evolution of the conductance while pulling a contact between two gold electrodes. In the inset, an enlargement of the plateau of conductance at $\sim 1\,G_0$ is shown. Variations to lower conductance and back up by about 10–15% can be noticed when the atomic chain is stretched.

[17]. This implies that a chain of atoms with a length between the position of the nth and $(n + 1)$th peak consists typically of $n + 1$ atoms.

The valence of the metal determines the number of electronic channels through the chain, and each channel contributes a conductance with a maximum of the quantum unit, G_0 [18]. For gold, a monovalent metal, both the one-atom contact and the chain have a conductance of about $1\,G_0$ with only small deviations from this value (see Fig. 1) suggesting that the single channel has a nearly perfect coupling to the banks. The small changes of conductance during the pulling of the wire shown in the inset in Fig. 1 are suggestive of an odd-even oscillation. The jumps result from changes in the connection between the chain and the banks when new atoms are being pulled into the atomic wire. In order to uncover possible patterns hiding in these changes we have averaged many plateaus of conductance starting from the moment that an atomic contact is formed (defined here as a conductance dropping below $1.2G_0$) until the wire is broken (conductance dropping below $0.5G_0$). In the upper panel of Fig. 2 it can be seen that the thus obtained average plateau shows an oscillatory dependence of the conductance with the length of the wire. The amplitude of the oscillation is small and differs slightly between experiments. Figure 3 shows three further examples of similar measurements for Au out of about a dozen independent experiments. It shows that the period and phase are quite reproducible.

We have repeated the same procedure with the other two metals forming chains of atoms, namely, Pt and Ir. These metals have s and d orbitals giving rise to five channels of conductance. Each of the channels may have different transmissions that can be affected by the details of the contact and therefore the average plateau conductance is expected to show a more complicated behavior. A one-atom Pt contact has a conductance of about $2G_0$ while for a Pt atomic chain it is slightly smaller, $\sim 1.5\,G_0$ [19] with variations during the pulling process that can be as large as $0.5G_0$. We observe oscillations similar to those for Au, which we compare to the peak

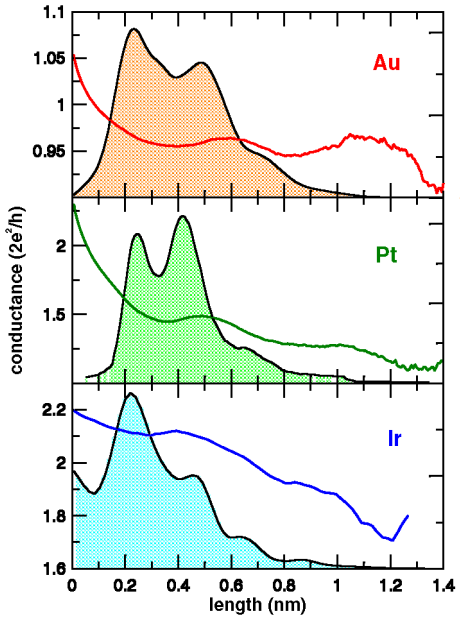

FIG. 2 (color online). Averaged plateaus of conductance for chains of atoms of the three metals investigated: Au, Pt, and Ir. Each of the curves are made by the average of individual traces of conductance while pulling atomic contacts or chains. Histograms of the plateau lengths for the three metals obtained from the the same set of data are shown by the filled curves. They compare well to those in Ref. [5].

spacing in the length histogram in Fig. 2. The latter is obtained by taking as a starting point of the chain a conductance dropping below $2.4G_0$, following Ref. [5]. Ir shows a similar behavior although somewhat less pronounced and it is more difficult to obtain good length histograms.

The periodicity p of the oscillation in the conductance for the three metals is about twice the interpeak distance d of their corresponding plateau-length histogram as is shown in Table I. This behavior agrees with the expected

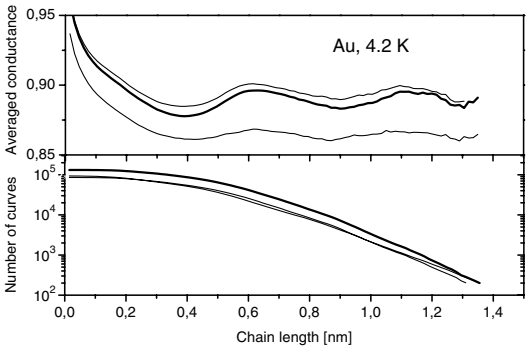

FIG. 3. Three further examples of measurements of the averaged conductance plateau for Au at 4.2 K (top panel). The lower panel shows the number of points used in obtaining the average and illustrates the rapid decrease in the number of plateaus for longer lengths, which explains the increase in noise to the right in the top panel.

TABLE I. Values obtained from the data in Fig. 2 for the interpeak distance d and the oscillation period of conductance p, which is divided by 2 to facilitate comparison. The period p was obtained from the distance between the maxima (minima) after subtracting a linear slope.

Metal	Peak distance d (nm)	Half period $p/2$ (nm)
Au	0.25 ± 0.02	0.24 ± 0.02
Pt	0.23 ± 0.02	0.25 ± 0.03
Ir	0.22 ± 0.02	0.23 ± 0.04

alternating odd-even evolution of the conductance with the number of atoms. The phase of this evolution also agrees with predictions [8–10,12] that chains having an odd number of atoms should have a higher conductance than even-numbered chains.

This odd-even behavior is essentially an interference effect and can be easily understood in the frame of a simplified one-dimensional free-electron model. Consider an atomic wire of a length $L = na$ connected to two one-dimensional (1D) reservoirs, where n is the number of atoms and a the interatomic distance. The reservoirs are characterized by a Fermi wave vector k_1, and k_2 is the equivalent for the 1D channel inside the chain. The transmission of an electron at the Fermi energy can be obtained from matching of the wave functions and can be written as

$$T = \frac{16\gamma^2}{(1+\gamma)^4 + (1-\gamma)^4 - 2(1+\gamma)^2(1-\gamma)^2\cos(2k_2L)},$$

where $\gamma = k_2/k_1$. The connection between wire and reservoirs is represented by a mismatch in Fermi wave vector and interference of partial waves scattering from the two contact points gives rise to the oscillatory term in the denominator. It is essential to note that k_2 is fixed by charge neutrality inside the wire. An isolated wire of finite length will have a limited set of accessible states $k_2^i = \frac{\pi}{a}\frac{i}{n}$ for $i = 1, \ldots, n$, that can couple to the reservoirs when the wire is contacted. The number of electrons will fix the Fermi energy and the corresponding Fermi wave vector, which in the case of a monovalent metal has a value $k_2 = (\pi/2a)(n+1)/n$. After coupling to the reservoirs the Fermi energy may adjust somewhat, but as chain and reservoir are composed of the same metal there will be very little charge transfer. Therefore we obtain $2k_2L = \pi(n+1)$ that, when substituted in the expression for T above, gives a transmission $T = 1$ for the case of an odd number of atoms n, and $T = 4\gamma^2/(1+\gamma^2)^2$ for n even. We find that for an odd number of atoms in a chain of a monovalent metal the conductance is G_0, in agreement with Refs. [8–10;12]. The conductance for the even-numbered chain is smaller than $1\,G_0$ (since $\gamma < 1$) and is sensitive to the interface geometry, here modeled by γ.

Such oscillatory behavior of the conductance is therefore expected for chains of a monovalent metal such as gold and explains the observed oscillation and its period and phase. In the averaged curves of the experiment (Figs. 2 and 3) the conductance does not quite reach a maximum of $1\,G_0$. This is largely due to the averaging procedure, where for a given length there are contributions from n and $(n+1)$-numbered chains and only the relative weight of these varies. In individual traces (Fig. 1) the maxima come much closer to full transmission. Further suppression of the maximum conductance may result from asymmetries in the connections to the leads. The relatively small amplitude of the oscillations is consistent with the fact that the average conductance is close to unity, implying that the contact between the chain and the banks is nearly adiabatic (γ is close to 1 in our model). The rise above $1G_0$ for short lengths in Figs. 2 and 3 can be attributed to tunneling contributions of additional channels.

The fact that similar behavior is also found for Pt and Ir is unexpected. The above arguments restricting the k vector in the chains do not apply for multivalent metals and one would expect contributions from several conductance channels. We have performed a further test in order to verify whether the oscillations in the conductance are due to interference in the wave functions. Here we make use of the curvature of the transmission T as a function of the applied bias voltage. For odd chains T is at a maximum and decreases for increasing bias, while the reverse applies for even chains and the transmission should increase with bias. Therefore, we have measured simultaneously the conductance and its second derivative using two parallel lock-in amplifiers tuned to the first and third harmonic of the applied bias voltage modulation to the contact, and averaged the signals for a large number of chains.

Figure 4 shows the results for Pt. The maxima (minima) in conductance are found to coincide with the minima (maxima) in the curvature of the conductance d^2G/dV^2, just as expected from the resonant behavior. Also the increase of the amplitude if d^2G/dV^2 with the length of the chain agrees with our simple free-electron model, which can be understood from the fact that the resonances become more closely spaced. This experiment provides additional evidence for the interpretation of the oscillations for Pt as an odd-even effect. For Au, because of the smaller amplitude of the odd-even features, no convincing d^2G/dV^2 signals have been obtained.

In addition to the oscillations for Pt and Ir in the mean conductance of the chains the measurements in Figs. 2 and 4 show an unexpected slope of about $(0.3–0.4)G_0/\text{nm}$. For a ballistic wire the conductance as a function of length is expected to be constant, apart from the oscillatory behavior discussed above. The fact that this decrease of conductance is found for the multivalent metals and not for Au suggests that partly open channels may play a major role. Probably the overlaps of the electronic states decrease for increasing numbers of atoms along the chain, which may suggest that only one or two channels

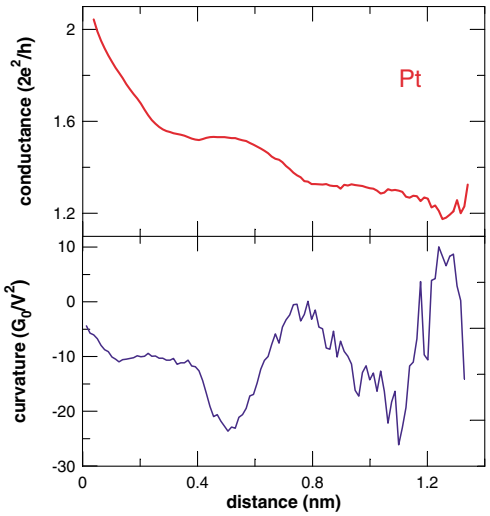

FIG. 4 (color online). Averaged conductance plateau for chains of Pt atoms (top panel), measured on a new sample illustrating the reproducibility of the measurements in Fig. 2. The bottom panel shows the mean value of the second derivative of the conductance d^2G/dV^2 measured simultaneously. The data have been obtained using a bias voltage modulation amplitude of 40 mV_{rms} at a frequency of 2.37 kHz and are averaged over 8000 scans.

survive for long chains. We would welcome numerical simulations to test this effect.

In summary, we have observed a parity oscillation of the conductance as a function of the number of atoms forming an atomic wire. We find this behavior not only for Au, as predicted, but also for the other two metals that form chains, Pt and Ir, suggesting that the effect may be universal for atomic wires, independent of the number of channels. In addition, Pt and Ir show a monotonic decrease of the conductance with the length of the wire on top of the oscillations which requires further explanation.

We thank J. C. Cuevas, N. Agraït, and S. Vieira for stimulating discussions and M. Polhkamp for assistance in the experiments. This work is part of the research program of the ''Stichting FOM.'' G. R. aknowledges suport of the Spanish DGI by the Project No. MAT 2001-1281. C. U. has been supported by the European Union under Contract No. HPMF-CT-2000-00724.

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