Surprising lack of magnetism in the conductance channels of Pt atomic chains

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Pt is known to show spontaneous formation of chains of metal atoms upon breaking a metallic contact. From model calculations these have been predicted to be spin polarized, which is reasonable in view of the Stoner enhanced susceptibility of bulk Pt and the increased density of states due to the reduced dimensionality. Here, we demonstrate that shot noise reveals information on the magnetic state of Pt atomic chains. Against all predictions, we find clear evidence for a non-magnetic ground state for the conductance channels of Pt atomic chains.

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At nanometer size scales one often finds unexpected behavior of matter. A particularly appealing example is the spontaneous formation of chains of metal atoms upon breaking a metallic contact [1, 2]. Pt is a metal with a modestly Stoner-enhanced magnetic susceptibility, indicating proximity to a ferromagnetic state. A transition to ferromagnetism can be induced by reducing dimensions, as evidenced by recent work on Pt clusters [3]. For these reasons, the ferromagnetic order predicted from model calculations for atomic chains [4–8] was not fully unexpected. Experimentally, it is very hard to design a probe that can directly measure the magnetism of atomic chains. Here, we demonstrate that shot noise, the intrinsic noise due to the discrete character of the electronic charge, reveals information on the magnetic state of Pt atomic chains. We find clear evidence for a non-magnetic ground state for the conductance channels of Pt atomic chains.

Shot noise was first discussed for vacuum diodes by Schottky [9], who showed that this current noise is independent of frequency (white noise) up to very high frequencies, and its power spectrum has a value of $\text{N}S_o e^2$ per electron charge, and $T$ the average current. In nanoscale conductors, for which the system size is much smaller than the electron scattering length, this noise can be understood as partition noise. In these systems the number of transmission channels available for electrons to cross a conductor is limited and the transmission through each one of the channels is set by the properties of the conductor. When the transmission probability is smaller than 1 the conductor can be viewed as an effective bottleneck causing a random sequence of electron backscattering events, which is observed as current fluctuations or noise. The theory has been elaborated by several groups and has been thoroughly reviewed by Blanter and Büttiker [10]. For a nanoscale conductor with $N$ conductance channels, each characterized by a transmission probability $\tau_n$, the current noise power at an applied bias voltage $V$ is given by,

$$S_I = 2eV \coth \left( \frac{eV}{2k_B T} \right) \frac{e^2}{h} \sum_{n=1}^{N} \tau_n(1-\tau_n) + 4k_BT \frac{e^2}{h} \sum_{n=1}^{N} \tau_n^2. \tag{1}$$

where $k_B$ is Boltzmann’s constant, and $T$ is the temperature of the nanoscale conductor. Anticipating spin splitting of the conductance channels we treat conductance channels for each spin direction separately. In equilibrium (at $V = 0$) equation (1) reduces to the Johnson-Nyquist thermal noise, $4k_BT$, describing the current fluctuations that are driven only by the thermal motion of electrons. $G = (e^2/h) \sum \tau_n$ is the conductance. Again, in the expression for $G$ we take the conductance quantum as $e^2/h$ and sum over spin states. In the low-temperature limit, $k_BT \ll eV$, equation (1) reduces to $S_I = 2eT F$, where the Fano factor $F$ measures the quantum suppression of Schottky’s classical result,

$$F = \frac{\sum_n \tau_n(1-\tau_n)}{\sum_n \tau_n}. \tag{2}$$

From this analysis it is apparent that one may obtain information on the transmission probabilities of the conductance channels by measurement of the noise power, and in favorable cases it is even possible to determine the number of conductance channels [11]. The Fano factor reduces to zero when all conductance channels are either fully blocked ($\tau_n = 0$), or fully open ($\tau_n = 1$). For a nanowire with a given conductance $G = (e^2/h) \sum \tau_n$ the noise has a lower bound that is obtained by taking all open channels to have perfect transmission, except for one that takes the remaining fraction of the conductance. This minimum will sensitively depend on whether the spin channels are restricted to be degenerate. It is
FIG. 1: (Color online) Schematics of the circuit used for measuring conductance and noise on an atomic junction formed by the MCBJ technique. Noise is measured by using two sets of low-noise amplifiers, with a total amplification factor of $10^5$, and by taking the cross spectrum of the two channels in a frequency range between 250Hz and 100kHz. After averaging of $10^5$ spectra the uncorrelated noise of the preamplifiers is strongly suppressed.

this property that we exploit when investigating the magnetic state of Pt atomic chains.

Platinum atomic junctions were formed at liquid helium temperatures using mechanically controllable break junctions (MCBJ, for more details see Refs. 12–14). The electronic circuit for the measurement is shown schematically in Fig. 1. The Pt contact was first characterized by recording a conductance histogram 13,15. The conductance histogram shows a first peak at a conductance of about $1.5 \cdot (2e^2/h)$ with very few conductance counts below $1 \cdot (2e^2/h)$, as expected for clean Pt point contacts: Pt being an s-d metal has up to 12 conductance channels due to the six s and d orbitals, and spin. Each of these channels has a finite transmission probability and they sum up to a total of about $1.5 \cdot (2e^2/h)$, in agreement with calculations 16,17. The strong peak at $1.5 \cdot (2e^2/h)$ reflects the frequent formation of atomic chains in the contact. Chain formation can be demonstrated more explicitly by recording a histogram of the length of the conductance plateaux with conductances in the range of the first conductance peak, between 1.2 and 2 times $(2e^2/h)$ 13,17,18.

After this preliminary characterization of the junction an atomic chain was made by pulling, starting from a large contact until the conductance drops to a value near $1.8 \cdot (2e^2/h)$. Measurements of conductance and noise were taken at several points of subsequent stretching starting from here. The corresponding piezo voltages were recorded in order to identify the length in terms of the mean number of atoms forming the chain. The zero-bias differential conductance, $dI/dV$, was recorded, which is needed in combination with the noise for the analysis of the conductance channels. The accuracy of the ac conductance measurement is better than 1%, as verified by tests on standard resistors. Fig. 2 shows an example of noise spectra taken in the window from 1kHz to 100kHz for a series of current settings, and illustrates how the noise power is obtained from the data. First, the thermal noise is recorded at zero bias, and after taking noise spectra at several bias settings the zero bias noise is recorded once more (labelled as $0\mu A$) in order to verify that the junction has remained stable. The low-frequency upturn at larger currents is due to 1/f-like noise. At high frequencies there is a roll-off due to the transfer characteristics of the circuit. The thermal noise level corresponds to a temperature of 6.3 K, which agrees within the accuracy of the temperature measurement with a reading of 6.1 K, as obtained from a ruthenium oxide 10k resistance thermometer. For several junction settings conductance measurements were repeated after the shot noise bias sequence in order to detect possible changes in the conductance. Typical changes observed were smaller than 2%. Fig. 2(b) shows that the spectra become white above 10kHz after correction for the roll-off with a single RC time constant. The thermal noise (at zero bias) is subtracted, which explains the negative values in the data fluctuations for the lowest currents. The data points are projected in the form of a histogram, shown at the right, and the level of white noise is obtained from the center of the histogram for each voltage bias. The bullets
and error bars at the right indicate the position and accuracy of the noise power as determined from a gaussian fit to the histograms.

Since shot noise and thermal noise are of comparable magnitude in these experiments it is useful to represent the data such that the expected dependence on the applied bias in Eq. (1) is apparent. The voltage dependence in Eq. (1) can be lumped into a single variable \( X = x \coth x \), with \( x = eV / 2k_BT \). The reduced excess noise is then defined as,

\[
Y = \frac{S_I(V) - S_I(0)}{S_I(0)},
\]

where \( S_I(V) \) is the noise at finite bias, and \( S_I(0) \) is the thermal noise, at zero bias. The reduced excess noise is now expected to depend linearly on the control parameter, \( Y = (X - 1)F \), from which the Fano factor \( F \) can be easily obtained.

Figure 3 shows a series of measurements on a Pt atomic chain with a conductance of \( G = 1.425 \pm 0.01(2e^2/h) \) at a short length of 2 atoms in the chain, for 26 settings of the bias voltage in the range from 0mV to 16.6mV (0 to 1.83\( \mu \)A). The slope of the plot gives a Fano factor \( F = 0.269 \pm 0.009 \). The accuracy for each of the points is 3%, as obtained by a fit to the power spectrum after correction for the roll-off as in Fig. 2. The measurement required about 50 minutes, illustrating the long-term stability of the atomic chains. It shows a very nice agreement with the expected dependence, and the scatter around the linear slope is within the data point accuracy.

We have recorded similar plots for over 500 configurations of Pt atomic chains of various length, for which we took 7 bias voltage points between 0 and 0.44\( \mu \)A. When the scatter in the plot of the reduced excess noise was larger than 3%, or the thermal noise at start and end of the measurement differed by more than 2%, we rejected the data. The scatter is mostly due to a large 1/f component in the noise spectrum and the contribution of the residual amplifier noise correlations to the spectra. After this selection 119 configurations remain. Figure 4 shows the Fano factors determined from these 119 sets of shot noise measurements.

The bold red curve shows the minimum noise curve when spin degeneracy is imposed. Relaxing spin degeneracy results in a minimum noise curve shown by the thin black curve. The inset illustrates the principle of the break junction experiment.
of this Letter, is that all Fano factors for the Pt chain configurations fall on, or well above, the curve describing the minimum noise for spin-degenerate channels. More than 15% of the measured points are even found to coincide within the error bars with the minimum-Fano curve for spin-degenerate channels, and none of the points are found significantly below it. For spin-split conductance channels the limiting curve is represented by the thin curve in Fig. 4. This provides strong evidence that the conductance channels in the Pt atomic chains formed in the experiment are spin degenerate, at variance with results from DFT calculations [4–8]. Most points in Fig. 4 are measured for Pt chains of 3 to 4 atoms in length, occasionally 5 or 6 atoms. We do not find any systematic evolution of the Fano factor with stretching of the chain. While increasing the length of the chain in steps the Fano factor may be seen to jump towards the minimum noise curve, but then it jumps away from the curve to higher values at next steps in increasing the chain length (see [13]).

A second remarkable observation is the fact that there is a group of 18 points that coincide with the curve describing the minimum noise power for spin-degenerate channels. This is quite unexpected. Whether spin degenerate or spin polarized, all calculations predict that at least six spin channels are involved, and no mechanism is known that would lead to unit transmission for the dominant channels [5, 6, 16, 17]. The most complete calculations [6], fully relativistic Density Functional Theory for realistic chain sizes, show that a magnetic moment above 0.4μB per atom already appears for a chain only three atoms in length, at equilibrium interatomic distance.

It has been argued [21, 22] that the zero bias anomalies observed in the differential conductance for Pt atomic chains provide evidence for local magnetic order. Indeed, the differential conductance often shows a pronounced structure near V = 0 (see [13]). However, this structure is very irregular and may have any sign or structure, which hampers a straight-forward interpretation. If any magnetic order is present for a consistent interpretation we would have to assume such moments would be formed by states that do not participate in the conductance.

In conclusion, we find strong evidence for an absence of magnetic order in the conductance channels for Pt atomic chains. The fact that this observation disagrees with many DFT-based computations suggests that effects beyond the present models, such as electron-electron correlations, may need to be considered.

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Supplementary Information

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I. EXPERIMENTAL PROCEDURE

Platinum atomic junctions were formed at liquid helium temperatures using mechanically controllable break junctions (MCBJ). The sample chamber was pumped to $\sim 10^{-5}$ mbar before cooling down in liquid helium. The chamber was fitted with active charcoal for cryogenic pumping such that the pressure in the chamber drops below measurable values at liquid He temperature. Once cold and under vacuum the Pt sample wire was first broken by mechanical bending of the substrate. By relaxing the bending the broken wire ends can be rejoined and the size of the contact can be adjusted with sub-atomic precision by means of a piezo-electric actuator.

Conductance was measured dc, or ac by means of a small modulation voltage (2mV and 2.3kHz) and a lock-in amplifier. This circuit can be decoupled from the sample during shot noise measurement using a switch at room temperature. Noise was measured by using two sets of low-noise amplifiers, with a total amplification factor of $10^5$, and by taking the cross spectrum of the two channels in a frequency range between 250Hz and 100kHz. After averaging of $10^4$ spectra the uncorrelated noise of the preamplifiers is strongly suppressed. The cryostat along with all amplifiers for both conductance measurement and shot noise measurement were placed in a Faraday cage that also provides acoustic shielding. During the shot noise measurements the conductance circuit was disconnected in order to eliminate external noise sources.

The noise spectra were recorded for a window from 250Hz to 100kHz. An example of such spectra is given in Fig. 2 of the main text. At the low-frequency end of the spectrum one observes an increase in the spectrum above the white noise level due to a $1/f$-like noise contribution, the amplitude of which varies between different junction settings, which has been attributed to defect fluctuations in the leads [1]. This part of the spectrum is ignored for the analysis, but it influences the accuracy of the determination of the white noise power. At the high-frequency end of the spectrum a roll-off is seen, with a characteristic frequency of about $50$kHz that is due to the RC time constant of the stray capacitance of the leads in combination with the junction resistance. Finally, a slight upturn in the spectra at the highest frequencies is due to residual correlations in the noise of the two amplifiers. The analysis presented below eliminates the roll-off, but is sensitive to the residual correlations and the $1/f$ noise, which limit the accuracy in determination of the Fano factor.

II. CONDUCTANCE HISTOGRAM

Before starting shot noise measurements the Pt contact was first characterized by recording a conductance histogram, Fig. S1. The conductance histogram for a clean Pt contact at liquid helium temperatures is recorded by combining one thousand conductance breaking traces. Contacts are repeatedly made and broken, controlled by the piezo voltage that regulates the substrate bending of the mechanically controllable break junction device, at a fixed bias voltage setting of 80mV. The points of the digitized traces of conductance are collected into a histogram and the counts are plotted as a function of the conductance. The first peak at $\sim 1.5 \cdot (2e^2/h)$ represents the average conductance of a contact of a single Pt atom in cross section. Below this peak the count drops to very low numbers, indicating that the contact finally breaks to a clean vacuum tunnel junction. Note that we use units of $2e^2/h$ here for reasons of comparing to earlier work, but that the conductance units per spin, $e^2/h$, are used throughout the text. The arrows indicate the boundaries used for recording
III. LENGTH HISTOGRAM

Figure S2 shows a length histogram obtained for a clean Pt junction at low temperatures. This is used to verify chain formation and for calibrating the displacement. The histogram in Fig S2 is obtained by combining 4500 traces and recording the length of the conductance plateaux with conductances between 1.2 and 2 times \((2e^2/h)\), i.e. in the range of the first conductance peak in Fig. S1. The length axis is given in units of the voltage on the piezo element, where the proportionality constant is 0.25 V/Å. The histogram is consistent with the earlier work of Untiedt et al. [2]. The first three peaks can be interpreted as the lengths corresponding to chains of 2, 3, and 4 atoms.

IV. STRETCHING SEQUENCES OF THE FANO FACTOR

Figure S3 shows two examples of the evolution of conductance \(G\) and Fano factor \(F\) when a Pt atomic chain is stepwise elongated. The stretching sequence has a length of 3.0V (~12Å, solid arrows and filled symbols) and 3.52V (~14Å, dashed arrows and open symbols), corresponding to 5 or 6 atoms final length, respectively. These two examples are chosen to illustrate that there does not appear to be a systematic evolution towards the minimum noise curve for longer chains, although points at the curve are more frequently found for longer chains.
V. ZERO-BIAS ANOMALY

Figure S5 shows four examples of differential conductance characteristics of Pt atomic chain junctions. A zero-bias anomaly is typically observed, that resembles a Kondo anomaly. This feature has been remarked before, but an unambiguous identification of its origin was not made. It does not show a regular peak structure expected for a Kondo anomaly, and its shape varies strongly between chain configurations, appearing sometimes as a peak, sometimes as a dip. Moreover, similar structure is also found for single-atom contacts and even for much larger contacts. Zero-bias anomalies may arise from various excitations, including two-level atomic configurations and low-lying vibrational modes. While a magnetic origin cannot be excluded, the related magnetic moment does not appear to be associated with the conductance channels of the atomic chain, as evidenced by the shot noise measurements presented in this work.

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FIG. 3: Examples of the evolution of conductance $G$ and Fano factor $F$ when a Pt atomic chain is stepwise elongated.
FIG. 4: Four examples of differential conductance characteristics of Pt atomic chain junctions.