Density of states and magnetoconductance of disordered Au point contacts

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(Dated: November 19, 2018)

We report the first low temperature magnetotransport measurements on electrochemically fabricated atomic scale gold nanojunctions. As $T \to 0$, the junctions exhibit nonperturbatively large zero bias anomalies (ZBAs) in their differential conductance. We consider several explanations and find that the ZBAs are consistent with a reduced local density of states (LDOS) in the disordered metal. We suggest that this is a result of Coulomb interactions in a granular metal with moderate intergrain coupling. Magnetoconductance of atomic scale junctions also differs significantly from that of less geometrically constrained devices, and supports this explanation.

PACS numbers:

At low temperatures disordered metals exhibit a reduced local density of states (LDOS) at the Fermi level, seen as a zero bias anomaly (ZBA) in tunneling spectroscopy (e.g.). This is the result of disorder-enhanced electron-electron interactions. Granular metals with large intergrain conductances ($g \equiv \langle G_{i,j} \rangle/(2e^2/h) \gg 1$) are predicted to have LDOS suppressions approaching the perturbative result for weakly disordered films. With strong disorder and geometric constraint, the ZBA in metal films can approach $100\%$, ascribed to a correlation gap due to strong Coulomb interactions.

Similarly, weakly coupled granular metals ($g << 1$) should act as arrays of tunnel junctions, with an exponentially suppressed tunneling LDOS as $T \to 0$.

Metallic nanojunctions (MNJs) are tools to examine geometrically constrained, disordered metals on the nanometer scale. While clean break junctions made in ultrahigh vacuum (UHV) have been studied extensively, nanojunctions between highly disordered metals are comparatively unexplored.

We present the first low temperature measurements of atomic scale metal junctions made by electrochemical deposition, a method proposed for molecular electronics investigations. Such metals may be disordered by grain boundaries, ionic impurities, and surface adsorbates. As we reported elsewhere, in “large” junctions ($G(300 \text{ K}) \gg G_0 \equiv 2e^2/h$), small ZBAs are consistent with the perturbative theory of Altshuler, Aronov and Lee (AAL). When $G(300 \text{ K}) \sim 2e^2/h$, however, low $T$ conductance suppression approaches $100\%$. Here we consider several models and show that these junctions are atomic scale probes of the LDOS of the disordered metal leads, which exhibit non-perturbative, temperature-dependent LDOS corrections. We give a phenomenological description of the LDOS suppression, and argue that its likely origin is the granular character of the electrodeposited material. Finally, these junctions exhibit nontrivial weak localization magnetoconductances, consistent with junction size and the hypothesis of granularity.

The MNJs are prepared by electrochemistry starting from electrodes defined by e-beam lithography. The details of sample fabrication are available elsewhere. Gold electrodes 25 nm thick with separations of $\sim 20 \text{ nm}$ are prepared on p+ silicon substrates coated with $200 \text{ nm}$ of thermal oxide. Electrode configurations are shown in Fig. 1. Lumped capacitance between each electrode and the substrate is estimated to be $\sim 50 \text{ pF}$. The electrodes are covered by 20 nm $\text{Al}_2\text{O}_3$ during evaporation, limiting electrochemistry to the electrode edges. The evaporated Au has a typical resistivity of $5 \mu\text{O}\text{-cm}$.

Additional gold is deposited using a buffered aqueous solution of potassium cyanurate, while interelectrode conductance is monitored with standard lock-in techniques. Discrete conductance steps on the order of $G_0$ are observed during junction formation, corresponding to atomic reconfigurations. The MNJ is grown to a specified conductance, rinsed in deionized water, and dried with dry nitrogen. Through measurements on test structures, we find that the average resistivity of the electrodeposited gold is $\sim 35 \mu\text{O}\text{-cm}$ at $4.2 \text{ K}$, corresponding to an elastic mean free path of $\sim 2.5 \text{ nm}$, much shorter than that of the evaporated Au.

Spontaneous conductance switching and its strong suppression as $T$ is lowered suggest that the junctions consist of a small number of atoms that can diffuse readily at room temperature. Surviving junctions with $G \sim$
The conductance then continues to decrease upon cooling. At 15 K, $T < G_0$, an intergrain conductance on the order of 50 nanojunctions are Ohmic up to 200 mV at 300 K. We interpret this ZBA and its scaling with bias voltage as consistent with the AAL perturbative DOS suppression. An analysis of the Coulomb interaction with a single coherent scatterer can quantitatively explain this phenomenon. The form of the dependence is nonactivated. Solid lines are fits: (A) $0.61 \exp(1.91T^{-0.5})$; (B) $0.91 \exp(8.06T^{-0.8})$; (C) $1.65 \exp(3.61T^{-0.56})$.

We have successfully measured ten nanojunctions with room temperature conductances ranging from 0.5 to 200 $G_0$ in a variable temperature cryostat. Using standard quasi-4-terminal lock-in techniques we have measured nanojunction differential conductance $G(V,T) = dI/dV$ and differential resistance as a function of temperature, dc bias voltage, gate voltage, and magnetic field. All nanojunctions are Ohmic up to 200 mV at 300 K.

As discussed elsewhere, high conductance junctions ($e.g.$ $G(300 K) \sim 30 G_0$) typically exhibit a small (15%) at 1.8 K) ZBA, logarithmic in temperature below 30 K. We interpret this ZBA and its scaling with bias voltage as consistent with the AAL perturbative DOS suppression. An analysis of the Coulomb interaction with a single coherent scatterer can quantitatively explain this data, provided the disordered metal is granular, with an intergrain conductance on the order of 50 $G_0$; such an analysis is only applicable for systems with $G \gg G_0$.

In atomic scale junctions prepared as above with $G(300 K) \sim 1G_0$, we find ZBAs approaching 100% conductance suppression as $T \rightarrow 0$. Such deep ZBAs are never seen in the larger junctions and are present in both differential conductance and resistance measurements. The only difference between large and atomic scale junctions is a brief amount of electrodeposition time; the microstructure of the deposited material is identical. Figure 2 shows the zero bias resistance vs. $T$ on Arrhenius-style axes for three of these samples.

We now present evidence that these large ZBAs are caused by nonperturbative low temperature corrections to the LDOS of the electrodeposited material. Figure 3 (left inset) shows $G(V = 0,T)$ for sample A ($G(T=300K)=1G_0$) as a function of temperature cycling. During initial cooling (trace 1), $G$ varies little until $T < 50$ K, when the zero bias suppression begins. At 15 K, $G$ spontaneously increases by about 0.6 $G_0$. The conductance then continues to decrease upon cooling. When the nanojunction is warmed (trace 2), the high temperature conductance appears to be $\sim 2G_0$. At 220 K, however, $G$ spontaneously decreases by about 0.85 $G_0$, returning near its original value. Repeated thermal cycling and LED illumination at 2 K result in other branches of $G$ vs. $T$ (traces 3,4,5). All these $G(V = 0,T)$ curves collapse onto one curve when each branch of $G(T)$ is multiplied by a non-integer constant.

The discrete changes in $G$ strongly support the idea that this junction’s low room temperature conductance ($\sim G_0$) is due to the junction’s atomic scale. The addition of a single partially transmitting channel upon cooling occurs as thermal contraction slightly decreases the interelectrode distance. Thermal expansion on warming stretches the junction, and the additional channel is lost, just as in hysteresis seen in mechanical break junction measurements. These serial rearrangements indicate that this junction was in a fortuitous regime of stability. In the other samples, when rearrangements took place the junctions either broke completely or coalesced to a high conductance state.

For each conductance branch, the ZBA is measured at several temperatures. Figure 4 shows the conductance versus bias voltage at 2 K, 10 K, and 20 K for this nanojunction in one of its configurations. The same factors used to collapse the $G(V = 0,T)$ branches also collapse the bias sweep data onto a single set of curves. It is clear that $G(V,T)$ is only multiplicatively scaled by discrete atomic rearrangements of the small number of conducting channels.

We now consider possible origins of such a nonperturbative ZBA. A successful explanation must be consistent with: (a) the temperature dependence of the zero bias conductance; (b) the functional form of the ZBA vs. bias voltage and temperature; and (c) the scaling of the ZBA data with junction conductance as shown in Fig. 4.

Coulomb blockade in an array of grains weakly coupled by tunnel junctions can produce a ZBA. However, the
Another candidate is environmental Coulomb blockade (ECB)\textsuperscript{17}. Conduction through a single junction in series with an environmental impedance is suppressed at low $T$ and $V$ because tunneling electrons excite electromagnetic modes of the environment, reducing the phase space for tunneling\textsuperscript{18}. The IV characteristics are determined by $P(E)$, the probability of a tunneling electron to excite an environmental mode of energy $E$. The form of $P(E)$ depends on the impedance of the environment, which typically must be well controlled to observe ECB in single junctions.

ECB has been seen\textsuperscript{19} in clean point contacts made using mechanical break junctions. The environmental impedance was modeled as the junction capacitance in parallel with the lead resistance\textsuperscript{19}. Our voltage and temperature scales would imply a charging energy $10^2 \times$ that in Ref.\textsuperscript{19}. This seems unlikely given our similar geometry and greater stray capacitance. Furthermore, in atomic scale junctions the ECB suppression scales with a geometry and greater stray capacitance. Additionally, different branches are equivalent to probing the same LDOS suppression using tunnel junctions of various sizes.

The large ZBAs in the atomic scale junctions, reminiscent of correlation gaps in highly disordered metal films\textsuperscript{1-5}, imply a nonperturbative LDOS suppression. Efetov and Tscherich\textsuperscript{3} consider the LDOS in granular metals having a dimensionless intergrain conductance $g$. They derive expressions for the LDOS in the limit $g >> 1$ ($g << 1$), but the calculated $T$-dependence is too gradual (steep) to fit our data. This suggests that our samples fall between these extremes, into the intermediate range of $g$ for which there is currently no analytic expression.

A generalized treatment of corrections to electron tunneling\textsuperscript{22} accounts nonperturbatively for both intra-electrode Coulomb effects (the AAL LDOS correction) and interelectrode Coulomb interactions in the presence of an electromagnetic environment ($P(E)$ theory). Effective tunneling densities of states have been calculated that agree well with experiments on spatially extended tunnel junctions\textsuperscript{22}. One would expect some form of this generalized theory to apply in the granular metal case. We introduce an ansatz for the functional form of $\delta \nu(\epsilon, T)$:

$$\delta \nu(\epsilon, T) = \nu_0 \left(1 - \text{erf} \left( \frac{-e \Gamma}{\sqrt{\epsilon^2 + (a + b T)^2}} \right) \right)$$

where $\Gamma$, $a$, and $b$ are sample-specific, temperature independent parameters. This model LDOS is able to describe empirically the ZBA data over a broad temperature and voltage range. The $T = 0$ version of this form is derived\textsuperscript{22} for 1d tunnel junctions, and is also equivalent to ECB in an ultrasmall junction connected to an $RC$ transmission line\textsuperscript{13, 22}. However, the Fano factors discussed above for ECB in point contacts make this interpretation difficult to reconcile with the observed scaling. The solid lines in Figs.\textsuperscript{3} and\textsuperscript{4} are fits using Eqn.\textsuperscript{1}. The relevant parameters are shown in Table\textsuperscript{I}.

| Sample | $G_b \ [2e^2/h]$ | $e \Gamma \ [J]$ | $a \ [J]$ | $b \ [J/K]$ |
|--------|------------------|----------------|----------|----------|
| A      | 1.51*            | 2.96 $\times 10^{-22}$ | 2.33 $\times 10^{-22}$ | 1.43 $\times 10^{-22}$ |
| B      | 1.29             | 5.11 $\times 10^{-21}$ | 1.70 $\times 10^{-22}$ | 6.94 $\times 10^{-22}$ |
| C      | 0.57**           | 6.07 $\times 10^{-22}$ | 1.87 $\times 10^{-23}$ | 1.57 $\times 10^{-22}$ |

TABLE I: Model parameters from Eqn.\textsuperscript{1} used to reproduce the ZBA data for the samples shown in Fig.\textsuperscript{2}. *For sample A, data from branch number 3 from Fig.\textsuperscript{8} were used for the fits. **For sample C, a slight junction rearrangement led us to use $G_b = 0.62$ to fit data at 2 K, with the other parameters unchanged.

We also observe magnetoconductance (MC) in atomic scale junctions that differs from that in larger, cleaner
We find that the ratio \( \frac{L_\phi}{L_{SO}} \) is comparable with \( \tau_{SO} \) but \( \tau_{SO} \) is temperature independent, \( \tau_{\phi} \) typically increases with decreasing \( T \), and \( \tau_{\phi} > \tau_{SO} \) for \( T > \sim 6 \text{ K} \).

Quantitative analysis is difficult because the coherent volume around the constriction is of uncertain dimensionality with respect to diffusion and quantum coherence. As a qualitative guide, solid curves are fits using 1D weak localization, assuming 3D diffusion, an effective width of 3 nm (roughly sets the field scale) and an effective length of 5 microns (essentially a fixed numerical factor to scale the conductance axis), and allowing \( L_\phi \) and \( L_{SO} \) to vary at each temperature. A natural explanation for a varying \( L_{SO} \) would be a fixed \( \tau_{SO} \) but a temperature-dependent diffusion constant, \( D(T) \), that decreases as \( T \to 0 \). Such a dependence supports the granular model, where \( D(T) \) would vary as intergrain interactions become important with decreasing \( T \). We find that the ratio \( \frac{L_\phi}{L_{SO}} \) increases with decreasing \( T \) roughly like \( 1/T \).

The fact that \( \tau_{\phi}/\tau_{SO} \approx 1 \) here suggests that \( \tau_{\phi} \) is shorter here than in larger junctions.

These first low-\( T \) studies of electrochemically made atomic scale Au nanojunctions have revealed significant departures from the properties seen in larger and cleaner Au structures. Atomic scale junctions locally probe a suppressed density of states in the disordered leads. We provide an expression that describes the data phenomenologically, and suggest an underlying physical origin for the effect consistent with magnetoconductance data. Further studies are required to determine conclusively the physics behind the gap observed in the LDOS and the nontrivial MC properties of this system when examined at the atomic scale.

The authors gratefully acknowledge the support of the Robert A. Welch Foundation and the Research Corporation.

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