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Kondo Effect in Electromigrated Gold Break Junctions

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ABSTRACT

We present gate-dependent transport measurements of Kondo impurities in bare gold break junctions, generated with high yield using an electromigration process that is actively controlled. Thirty percent of measured devices show zero-bias conductance peaks. Temperature dependence suggests Kondo temperatures ∼7 K. The peak splitting in magnetic field is consistent with theoretical predictions for $g = 2$, though in many devices the splitting is offset from $2g\mu_B B$ by a fixed energy. The Kondo resonances observed here may be due to atomic-scale metallic grains formed during electromigration.

The physics of many-particle entangled spin states has attracted recent interest in a variety of systems. The correlation that may form at low temperature between a localized electron spin and a surrounding Fermi sea is one of the most carefully studied of these states. This correlation gives rise to the Kondo effect, originally observed in the 1930s as an enhanced low-temperature resistance in magnetically doped metals.[1] Several decades later a new manifestation of the same physics was discovered in systems where a charge trap is positioned between two electrical leads.[2−6]

During transport, electrons tunnel from one lead onto the trap and off to the other lead. In general, transport is allowed only when two charge states are degenerate, an effect known as Coulomb blockade. If the trap binds an unpaired electron, high-order tunneling processes may give rise to an enhanced conductance at zero bias despite Coulomb blockade. Metal tunnel junctions containing paramagnetic impurities were the first systems to show the narrow zero-bias peak characteristic of this effect.[2−6] The peak splits in magnetic field and is suppressed above the Kondo temperature, T_K.

The Kondo temperature corresponds to the energy of formation of the many-body spin state; it depends exponentially on the binding energy of the trap, ϵ_0, and the coupling to the leads, Γ: $T_K \propto e^{-\pi|\epsilon_0|/2\Gamma}$.[6] An electrostatic gate can be used to control T_K by tuning ϵ_0 and can even turn off the Kondo resonance by changing the number of bound electrons. A gateable Kondo effect was first observed in lithographically defined quantum dots,[7,8] where the primary difficulty was achieving a Kondo temperature high enough to be experimentally accessible.

Larger Kondo temperatures can be found in much smaller systems consisting of an atomic-scale charge trap between two metallic leads. However, fabrication of such leads in a gateable geometry is a formidable lithographic challenge. One successful approach is to break a single wire into an electrode pair using electromigration,[9] the process by which an electric current causes the atoms in a conductor to move.[10] Both Coulomb blockade and the Kondo effect have been observed in electromigrated gold junctions with organic molecules deposited on the surface as charge traps.[11−13]

In this paper we show that localized states giving rise to the Kondo effect may be found even in the gated gold junction itself. Active control over the electromigration process gives a high yield (up to 30%) of devices showing zero-bias peaks that are suppressed at finite temperature and split with magnetic field. For most devices, T_K fell in the range 5−10 K. Above $g\mu_B B \sim 0.5k_B T_K$ the splitting was linear in field with slope $g = 2$, but the absolute magnitude of the splitting varied from device to device for reasons that are not yet understood. We discuss possible sources of the Kondo resonance in bare junctions, focusing on atomic-scale metallic grains. Grains consisting of 18−22 atoms, formed in electromigrated junctions, have been shown to possess novel optical properties;[14] the transport properties presented here offer a further glimpse of the rich physics in this system.

The devices (Figure 1a inset) are patterned on a GaAs substrate using a combination of optical and electron beam lithography and a resist/liftoff process. A 12 nm thick aluminum back gate is deposited by evaporation with the substrate held at 77 K. The surface is oxidized for 10 min in ozone under a UV lamp. Gold wires (15 nm thick) are deposited on the gate at room temperature; each tapers to a

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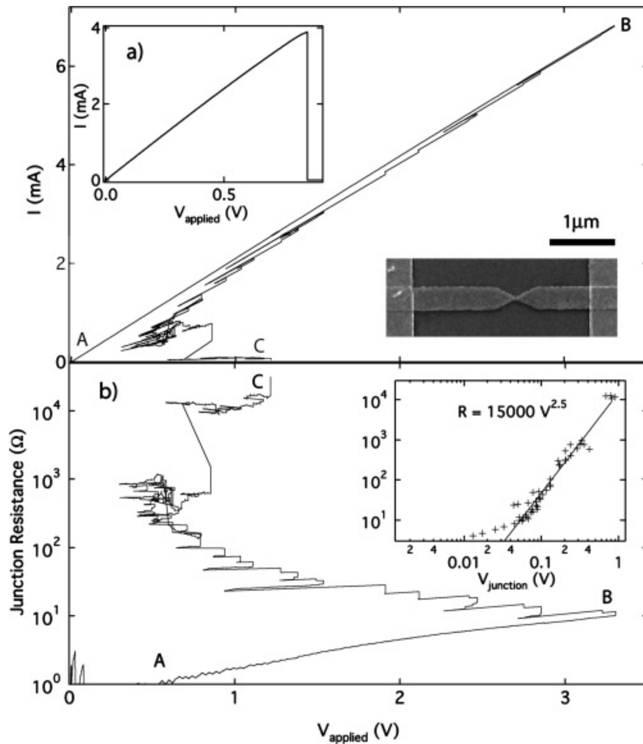

Figure 1. Two views of controlled electromigration. (a) Current−voltage ($I-V$) curve for a characteristic break. Insets show scanning electron micrograph of device, and $I-V$ curve of uncontrolled electromigration for comparison. (b) Same data, after subtracting lead resistance. Voltage dropped in leads is also subtracted in inset. Two distinct phases of breaking can be seen: the initial voltage ramp in which no breaking occurs (A to B) and controlled electromigration (B to C). The entire process takes ∼10 min for each wire. Solid line in inset of part b shows fit of B−C section to power law; extracted exponents for all devices suggest $R \propto V^{2\pm0.5}$.

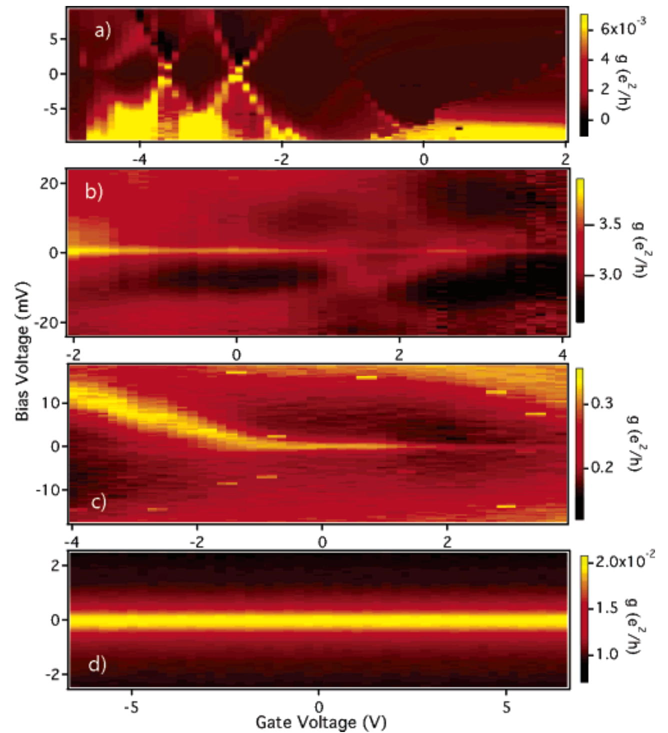

Figure 2. Differential conductance maps for four devices at 250 mK. (a) Coulomb blockade. (b) Superposition of a broad Coulomb blockade diamond (centered around gate voltage 1.8 V) and the Kondo effect. (c) Transition from Kondo resonance to Coulomb diamond. The absence of conductance features at negative bias may be due to an asymmetric lead coupling. (d) Gate-independent Kondo effect. (c) Numerical derivative of dc measurements; others measured with 50 μV ac bias at 47 Hz.

70 nm constriction. A 50 nm gold layer connects the narrow wires to optical lithography. The pressure during evaporation was $\sim 2 \times 10^{-7}$ mbar. The devices are cleaned with acetone and methanol, followed by oxygen plasma to remove any residual organic materials. Electromigration is performed in a ^{3}He refrigerator containing 1 mbar of ^{3}He exchange gas. The sample is then cooled immediately and measured.

An active control algorithm differentiates the electromigration performed here from previous work. When junctions are created without using feedback, the yield showing even weak tunneling is low (5−10%) and there is little control over final resistance. For better control we monitor the resistance of the entire electromigration circuit and adjust the voltage to maintain a constant break rate, measured as $(1/R)(\partial R/\partial t)$, where R is the resistance of the circuit after subtracting a lead resistance. Break rate is extracted from 20 resistance measurements at fixed voltage, taken over 200 ms.

Figure 1 shows the two stages of a typical break. In the first (A to B), the break rate is negligible as the voltage is ramped up. Once the break rate exceeds a target (0.01−0.1 s^{-1}), the voltage is actively adjusted to maintain that rate (B to C). When the resistance exceeds 50 kΩ, the voltage is reduced to zero at 1 V/s. There is remarkable consistency from device to device; extracted power laws indicate that constant power is dissipated in the break region for the B−C stage (see Figure 1b inset).

We present results for electromigration of 167 wires, of which 118 broke to a room-temperature resistance between 10 kΩ and 5 MΩ. We cooled 72 of these to 250 mK and measured differential conductance as a function of gate voltage and dc bias.[15] No conductance, or only weakly nonlinear conductance, was visible in 31 devices. Three showed a gate-independent conductance dip at zero bias suggesting transport through metallic grains in good contact with the leads.[16]

The remaining 38 showed transport through charge traps: Coulomb blockade or a Kondo resonance (see Figure 2). The binding energy of these traps is primarily determined by the energy, E_C, needed to add or remove an electron from a trap. No device that showed a Kondo resonance also showed two charge degeneracy points, necessary for accurate measurement of E_C; in many the conductance was featureless up to hundreds of millivolts. However, multiple Coulomb diamonds were occasionally observed in devices without Kondo resonances, giving values as low as $E_C \sim 5$ mV in these (e.g., Figure 2a).

A zero-bias conductance peak was observed in 30 devices. We measured the temperature and field dependence of a representative subset, including one device that showed both a zero bias peak and Coulomb blockade. One signature of the Kondo effect is a suppression of the peak conductance

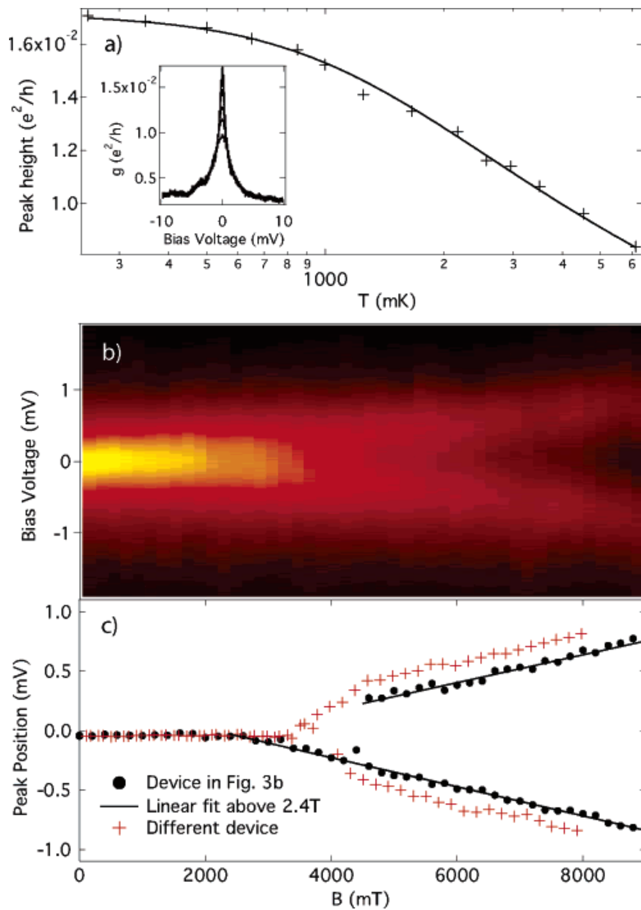

Figure 3. Signatures of the Kondo effect in a zero-bias conductance peak. (a) Suppression with temperature. Peak heights are extracted from raw data in inset. Fit to theoretical form (solid curve) gives $T_K = 6$ K for this device. (b) Splitting in magnetic field. (c) Extracted peak positions from the data in (b) (black circles) and from a different junction with the same Kondo temperature (red crosses). Solid black lines are linear fits to peak position. Splitting, defined as distance between peak positions, is linear for both devices (slope $2g\mu_B$ with $g = 2.1 \pm 0.05$) but extrapolates to zero at different fields.

with temperature: $G(T) \simeq G(0)/[1 + (2^{1/s} - 1)(T/T_K)^2]^s$, where $s = 0.22$ for spin-$^1/_2$ impurities.[17,18] We measured the temperature dependence of nine devices; all showed a good fit to this functional form; see, e.g., Figure 3a. The possibility of conductance pathways in parallel with the Kondo resonance (Figure 2b) prevents reliable determination of T_K from temperature dependence alone, so the width of the zero bias peak was used as confirmation. In most devices the peak width (defined as full width half-maximum) was $2k_BT_K$.[19] We consider T_K to be well-determined only in these devices. For most, $T_K \sim 7$ K; none showed $T_K < 4$ K, and only one $T_K > 15$ K.

Gate dependence of the Kondo resonance was evident in 26 of the 30 devices, but charge degeneracy points, identifiable by a Coulomb diamond and representing a change in the number of bound electrons, were accessible in only three. Many devices did not show clear Coulomb diamonds, presumably due to the large charging energies that are expected in such small grains as well as the strong screening of the electrostatic gate by the gold leads. In one, the zero-bias peak appears on only one side of the degeneracy point in gate voltage, as expected (see Figure 2c). In the other two devices, however, the zero-bias peaks continue through the edge of the diamonds (Figure 2b), leading us to suspect two parallel but independent conduction pathways.

Another identifying characteristic of the Kondo effect is the splitting of the zero-bias peak by $2g\mu_BB$ in magnetic field.[2] We measured the field dependence of 12 devices, and this signature was observed in all.[20] The splitting was visible only above a device-dependent critical field, B_c. Where T_K was well-determined, $g\mu B_c \sim 0.5k_BT_K$, consistent with theoretical predictions.[21]

Above B_c the splitting was linear; typical data are shown in Figure 3. In eight devices the slope of the splitting was consistent with $g = 2.1 \pm 0.1$. The other four showed g factors up to 4.5; these anomalously large values are not yet understood. In contrast, theoretical work predicts a *suppression* of the g factor, to between 1.3 and 1.7, for $g\mu_BB$ up to several times k_BT_K.[19,22]

The measurements in this paper cover the regime $g\mu_BB \sim k_BT_K$, where exact theoretical predictions for conductance have not been worked out. We find for the splitting of the zero bias peak a surprisingly simple functional form: $2g\mu_B(B - B_{ext})$, where B_{ext} is device dependent. Even devices with the same g factor and Kondo temperature show different values for B_{ext} (see, e.g., Figure 3c). A negative value, $B_{ext} = -2.5T$, was observed in one device, reminiscent of a recent observation in GaAs quantum dots.[23]

A structure that consists simply of two gold electrodes above an electrostatic gate would not be expected to show either Coulomb blockade or the Kondo effect. The system must also contain one or more charge traps. While there are many candidates for charge traps in an electromigrated junction, the trends observed here may identify this additional component. Changes in the details of the electromigration procedure dramatically affect the yield of devices with zero-bias peaks, suggesting a strong dependence on the morphology of the gold. However, the range of T_K is surprisingly narrow given the inherent randomness of electromigration and the sensitivity of T_K to microscopic device parameters.[6]

Defects in the gate oxide are an unlikely candidate for the Kondo resonance here, though they have been shown to give rise to the Kondo effect in other systems.[2-6] Some devices were gate independent, suggesting that the Kondo impurities can be in a location screened by the gold leads. In addition, the location of defect sites relative to the leads would vary from device to device, giving a wide range of T_K.

Atomic or molecular adsorbates on the surface of the gold[24] are a more plausible, but still unlikely, source of Kondo impurities. The coupling between an adsorbed molecule and a lead would depend only weakly on junction geometry, consistent with our results. Oxygen has been cited as a source of Kondo impurities in metallic tunnel junctions.[25] This possibility, however, does not explain the observed sensitivity to electromigration parameters. In addition, we performed the same process on a small number of devices

in ultrahigh vacuum (with the walls of the vacuum chamber held at 4 K) and found similar device characteristics.

Isolated metal grains created during electromigration are the final possible Kondo impurity that we consider. Coulomb blockade in grains of size $\gtrsim$2 nm has been studied extensively[26] and observed occasionally in bare electromigrated junctions.[13] However, even over a wide range of lead−grain couplings,[27] no observation of the Kondo effect has been reported.

In principle a metal grain, if well-connected to the leads, could show a Kondo temperature as high as those reported here. However, even in the limit of nearly perfect lead−grain contact, one expects $T_K \propto \Delta^{3/2}/E_C^{1/2}$ for a grain with quantum level spacing Δ.[28] A rough geometric argument for a grain of radius r then gives $T_K \propto r^{-7/2}$;[26] even a modest range of sizes would result in a large range of T_K, in contrast with our observations. In addition, gold grains larger than a few nanometers would exhibit a g factor much less than 2 due to spin−orbit interactions.[29]

A more likely candidate for the Kondo impurity in these devices is an atomic-scale gold nanocluster of the type reported in ref 14. Those nanoclusters, formed during electromigration, contained 18−22 atoms.[14,30] This narrow range of sizes could explain the Kondo temperatures observed here, and the formation of these structures would depend strongly on the electromigration procedure. Atomic-scale nanoclusters are in many ways more similar to molecules than to larger gold grains and could display many of the physical effects expected in single-molecule transport. The electronic measurements of many-body spin correlations presented here, together with the recent demonstration of single photon generation in these nanoclusters,[14] show the promise that this system may hold for coherent electronics in the solid state.

Electromigrated gold junctions have been used by many groups to measure transport through single organic molecules. Control experiments on bare gold wires were used to distinguish between transport features due to the molecules and those native to the electrode system. The sensitivity of our results to the details of electromigration demonstrates the difficulty in interpreting these control experiments, as simply the presence of molecules deposited on the surface may change the morphology of the gold. This sensitivity can also be an advantage: we find that the yield of Kondo resonances in bare junctions can be dramatically reduced by briefly applying a large voltage (>1 V) across the junctions at room temperature. This large voltage is a natural result of more common electromigration procedures.

In summary, we have observed the Kondo effect in bare electromigrated gold junctions. The mere presence of Kondo resonances in this system is surprising and warrants further study. Careful analysis of the splitting at magnetic fields comparable to the Kondo temperature reveals a simple but unexpected functional form. Experiments are underway to better understand this behavior. The electromigration procedure outlined in this paper can also be extended to superconducting materials and offers an experimental platform to test emerging theoretical models of the interplay between the Kondo effect and superconductivity.

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