Spectroscopic Measurements of Discrete Electronic States in Single Metal Particles

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We have made tunnel junctions containing one Al particle of diameter <10 nm. Tunneling via discrete electronic states in the particle produces steps in the current-voltage (I-V) curve, providing, for the first time, a spectroscopic measurement of the electronic energy levels in a metal particle. With superconducting leads, the I-V contribution from each discrete state has the form of the BCS density of states. We can determine the parity of the electron number in the particle’s ground state through the effects of an applied magnetic field on the I-V curve.

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Because of spatial confinement, the spectrum of electronic eigenstates in a nanometer-scale metal particle consists of discrete, well-separated levels at low temperature. This is predicted to change dramatically the superconducting, magnetic, and optical properties, relative to bulk metal [1]. In the past, direct study of these eigenstates has been impossible because no technique could resolve states in single particles. We accomplished this goal by fabricating devices consisting of one Al particle, with diameter <10 nm, connected by tunnel junctions to two separate metal leads. The current-voltage (I-V) curve consists of discrete steps due to tunneling via individual electronic states in the particle, providing the first spectroscopic measurement of these states.

Our studies of electronic levels in metal particles are analogous in many respects to previous experiments on semiconductor “artificial atoms” [2]. By using metal devices, however, we are able to examine several new phenomena. We find that the tunneling current via a single electronic state in contact with a superconducting lead reflects the superconducting density of states in the lead. Studies with increasing bias voltage allow measurement of relaxation times for nonequilibrium electronic excitations on a metal particle. The dependence of the I-V curve on the magnetic field provides a means to determine whether a particle possesses an even or an odd number of electrons in its ground state.

A schematic diagram of our devices is shown in the inset to Fig. 1(a). We use electron-beam lithography and reactive-ion etching to fabricate a bowl-shaped hole in an insulating Si₃N₄ membrane, with the opening on the lower edge having diameter 3–10 nm [3]. We make one electrode by evaporating Al on the top side so as to fill the bowl, and oxidize for 3 min in 50 mtorr O₂ to form a tunnel barrier near the lower edge of the Si₃N₄ membrane. We then evaporate 2 nm of Al on the reverse side to form a layer of electrically isolated particles [4]. Following a second oxidation, we deposit a second Al electrode to cover the particles. We study selected devices in which electron transport between the leads occurs by tunneling via only one particle.

Figure 1 displays the I-V curve and dI/dV vs V for one sample at 4.2 K, a temperature high enough that discrete states are not resolved. The existence of a single set of equally spaced “Coulomb-staircase” [5] peaks in dI/dV provides the first indication that current in this device is due to tunneling through a single metal particle. (Further conclusive evidence is discussed below.) We define R_A, C_A, R_B, and C_B as the resistances and capacitances of the two tunnel barriers, and Q₀ as the polarization charge on the particle [5]. The data of Fig. 1(b) (solid curve) can be fitted well by the theory of single-electron tunneling [5] (dashed curve), to determine C_A = 4.9 ± 0.5 aF, C_B = 8 ± 1 aF, R_A/R_B = 8 ± 2, R_A + R_B = 9 ± 1 MΩ, and Q₀/e = 0.20 ± 0.03 [6]. The charging energy, E_C = e²/[2(C_A + C_B)] ~ 6 meV. (We measured E_C as large as 40 meV in another single-particle sample.)

Based on C_B = 8 aF, we can estimate the particle size and the expected energy-level spacing for the device in Fig. 1. Our group has made larger tunnel junctions, ≈70 × 70 nm², by a similar oxidation procedure, which have C per unit area ~70–80 fF/μm². The area of FIG. 1. (a) I vs V and (b) (solid curve) dI/dV vs V for tunneling via a single particle at 4.2 K and H = 0. (b) Dashed curve: Theoretical fit discussed in the text, offset 100 GΩ⁻¹. Inset: Schematic diagram of device.

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the larger junction for the sample of Fig. 1 is therefore $\approx 100 \text{ nm}^2$. We can roughly estimate the volume $V$ of the particle by assuming it is a hemisphere with a curved surface of area $100 \text{ nm}^2$; this gives $V \approx 130 \text{ nm}^3$. The mean spacing of independent-electron spin-degenerate energy levels can then be predicted as $\delta E \approx 2\pi^2 \hbar^2/[mk_F V]$, where $m$ is the electron mass, and $k_F$ is the Fermi wave vector ($1.75 \times 10^8 \text{ cm}^{-1}$ for Al) [7]. Using $V = 130 \text{ nm}^3$, we expect $\delta E \approx 0.7 \text{ meV}$ for the particle of Fig. 1. Individual levels should be resolvable by tunneling for $T \lesssim \delta E/(3.5k_B)$ [2,8], or $T \approx 2 \text{ K}$ for this particle.

Figure 2(a) displays part of the $I$-$V$ curve at $T = 320 \text{ mK}$ for the same sample as in Fig. 1, for a range of $V$ just beyond the Coulomb-blockade threshold. When a small magnetic field is applied to suppress superconductivity in the Al leads (lower curve) [9], the current consists of well-resolved discrete steps, just as predicted for tunneling via electronic levels on the particle [8]. We cooled seven samples to 320 mK or below, and all have shown similar $I$-$V$ curves, with varying sequences of steps. In order to determine the level spacing on the particle from Fig. 2(a), one must multiply the measured spacing in $V$ by $eC_B/(C_A + C_B) = 0.6$ to account for capacitive division of the applied $V$ across the two tunnel junctions [10]. The seven current steps between 5.6 and 10.2 mV in Fig. 2(a) correspond to a mean level spacing of roughly 0.5 meV, in good agreement with the estimate based on particle size.

Current flow via an electronic level is predicted [5,8] to occur by means of incoherent sequential tunneling through the particle’s two tunnel barriers. The initial tunneling step will involve either adding or subtracting one electron to or from the particle, to achieve an excited electronic state. The voltage threshold for current flow is determined by the energy of the excited state, including a Coulomb charging energy. After the second tunneling step (which returns the electron number on the particle to the ground-state number $n_0$), it is energetically allowed that the electrons on the particle may be left in an excited $n_0$-electron state, with possibly a different total spin than the ground state. The $I$-$V$ curve will therefore be sensitive to the rates of energy and spin relaxation ($\Gamma_\epsilon$, $\Gamma_\sigma$) relative to the rate of electron tunneling ($1/e$). As long as $\min(\Gamma_\epsilon, \Gamma_\sigma) \gg 1/e$, observed current steps will be due only to the addition or subtraction of electrons to or from the $n_0$-electron ground state; otherwise, additional steps may occur due to transitions starting from excited $n_0$-electron levels [8].

The $I$-$V$ curve changes dramatically if the Al leads are superconducting (S) [9], as occurs when no magnetic field is applied. Each current step is shifted to higher $V$, relative to the N-lead data, and takes the form of a spike, with a region of negative $dI/dV$ [upper curve, Fig. 2(a)]. These effects are explained by a simple golden-rule argument. For the data of Fig. 2(a) the rate-limiting step for current flow via a single eigenstate is the slow initial tunneling event which surmounts the charging energy barrier [11]. The rate of this process is proportional to the density of electronic levels in the lead which are degenerate with the eigenstate. Therefore the current via a single eigenstate (not $dI/dV$ as for a conventional tunnel junction) directly reflects the singularity in the BCS density of states in the superconducting lead.

The shift in $V$ between signals for $S$ and $N$ leads is a consequence of the energy difference $\Delta$ (the superconducting gap) between the $N$-state Fermi level and the threshold for quasiparticle states in the $S$ leads [9]. Because of capacitive division of $V$ across the two tunnel junctions, two values of $V$ shift should be observed among different current steps: $(C_A + C_B)\Delta/(eC_B)$ for thresholds involving an initial tunneling step across junction $A$, and $(C_A + C_B)\Delta/(eC_A)$ for junction $B$. If both $V$ shifts are observed for the same sign of bias, they distinguish the separate spectra for the addition and subtraction of an electron to or from the particle. In Figs. 2(b) and 2(c) we plot $dI/dV$ vs $V$ for both $N$ and $S$ leads, with the $S$ curves shifted in $V$ so as to align a majority of the peaks. For the range of positive bias displayed, the values of $C_A/C_B$ and $Q_0$ are such that the Coulomb barrier can only be sur-

![FIG. 2. Signals due to the same device as Fig. 1, at 320 mK. (a) $I$ vs $V$ for superconducting and normal leads. The S-lead curve has been displaced 10 pA in $I$. (b) and (c) $dI/dV$ vs $V$ for positive and negative bias, with the S-lead data shifted in $V$, as labeled, so as to align the maxima of $dI/dV$ with the N-lead data. For ease of comparison, the amplitude of the S-lead data is reduced by a factor of 2 and offset on the $dI/dV$ axis in (b) and (c).](image-url)
mounted by initial tunneling across junction A, so only one V shift is observed, 0.283 ± 0.008 mV. For negative bias, between −9 and −12 mV, the initial tunneling step occurs through junction B, so a second shift, 0.524 ± 0.015 mV, is measured. The junction A V shift, 0.28 mV, applies to the signals between −12 and −15 mV. The fact that we observe only these two values of the V shift confirms that all the current steps are due to tunneling via states on the same metal particle. From the measured V shifts, we determine \( C_A/C_B = 0.56 \pm 0.03 \), in agreement with the large-scale Coulomb-staircase value determined independently, and \( \Delta = 0.18 \pm 0.01 \) meV. For Al, a weak-coupling superconductor, this corresponds to a critical temperature \( T_c = \Delta/(1.764k_B) = 1.18 \pm 0.07 \) K, which agrees with the measured film \( T_c = 1.21 \) K.

Comparison of positive- and negative-bias signals provides a measure of the relaxation rates for electronic excitations on the particle. Tunneling via the same eigenstates can be observed in both bias directions, with the relative positions of the signals determined by \( C_A/C_B = 0.56 \). The N-lead peaks at 5.6 and −9.7 mV are due to the same state, and features at 6.0 and −10.9 mV are due to another. However, signals exist between −9.7 and −10.9 mV with no corresponding peaks at positive bias. We ascribe this additional structure to transitions originating from excited n₀-electron states, which have non-negligible occupation because the high current level at negative bias does not allow time for excited states to relax to the ground state between tunneling transitions. The current at −10 mV is approximately 100 pA, so we estimate that \( \text{min}(\Gamma_S, \Gamma_E) \sim (100 \text{ pA})/e \sim 10^9 \text{ s}^{-1} \) for relaxation of the excited n₀-electron states in this particle.

Over most of the temperature range we studied, the full width at half maximum (FWHM) of the \( dI/dV \) peaks with N state leads is approximately 3.5\( k_B T \) (after correcting for capacitive division of \( V \)), expected from the FWHM of the derivative of the Fermi function in the lead (inset, Fig. 3). At sufficiently low \( T \), however, all peaks exhibit residual broadening exceeding the thermal value. At 30 mK, the first peaks beyond the Coulomb-blockade threshold have widths (3.5\( k_B T_{\text{eff}} \)) in the range \( T_{\text{eff}} = 50 \) to 100 mK, with peaks at higher \( V \) increasingly broad. Currently we cannot judge whether these limiting widths are due to the intrinsic lifetimes of the excited states or due to extrinsic effects such as heating.

The current at 30 mK due to a single state for both \( N \) and \( S \) leads is shown in Fig. 3. We assume that for the low current level in this device (≤ 50 pA), effects of nonequilibrium occupation of n₀-electron states are minimal. The predicted current then reduces to a simple sequential tunneling form [8,12]

\[ I = e\Gamma_1\Gamma_2/\left(\Gamma_1 + \Gamma_2\right), \]

where \( \Gamma_1 \) is the rate of the initial tunneling step (across junction A), and \( \Gamma_2 \) is the rate of the second step. Because \( \Gamma_1 \) is limited by charging while \( \Gamma_2 \) is not,

and because \( R_A/R_B = 4.0 \pm 0.5 > 1 \) for this device, we expect \( \Gamma_2/\Gamma_1 \gg 1 \), so that \( I \approx e\Gamma_1 \). In fitting to the data, however, we use the full form of Eq. (1). As we discussed previously, for voltages greater than the threshold for current flow with S-state leads (\( V_S \)), Fermi’s golden rule predicts the value of \( \Gamma_1 \) with S-state leads (\( \Gamma_{1S} \)) to be proportional to the BCS density of states (DOS):}

\[ \Gamma_{1S}(V) = \Gamma_{1N} f \left[-E(V)/E(V)/[E(V)^2 - \Delta^2]^{1/2} \right], \]

where \( f \) is the Fermi function, \( E(V) = eC_B(V - V_N)/(C_A + C_B) \), and \( V_N \) is the voltage threshold for N-state leads. We assume that \( \Gamma_{2S} = \Gamma_{2N} \), independent of \( V \), since the second tunneling step does not involve resonance with the DOS singularity. All of the parameters except \( \Gamma_{2N}/\Gamma_{1N} \) can be measured using the N-lead data and the \( V \) shift between \( S \) and N-lead data. The fit shown in Fig. 3 determines \( \Gamma_{2N}/\Gamma_{1N} = 7 \pm 2 \). For voltages well above \( V_S \), agreement between the current and the BCS DOS is good. However, near the threshold, the measured current is broadened and reduced in amplitude, relative to the abrupt singularity of the simple BCS DOS. The broadening is greater than observed with conventional Al tunnel junctions [13]. The FWHM of the \( dI/dV \) peak for \( S \) leads is within 10% of the \( N \)-lead value, suggesting that the same broadening mechanism is at work.

From the effects of an applied magnetic field \( H \), we can, for the first time, determine the parity of n₀, the number of electrons in the \( V = 0 \) ground state, for a normal-state metal particle [9]. This parity has important consequences for magnetic [1] and superconducting [14] properties. For an even-n₀ particle, the many-electron wave function for the ground state will be a spin singlet, in order that the orbital energy is minimized [15].

Assuming time
reversal symmetry, the ground state of an odd-$n_0$ particle for $H = 0$ is necessarily degenerate—a Kramers doublet. Therefore, for an even-$n_0$ particle at small $H$, the lowest-lying tunneling excitations correspond to transitions from a singlet to the two states of a split Kramers doublet, so that the lowest-$V$ tunneling signal should exhibit Zeeman splitting in an applied field. On the other hand, for an odd-$n_0$ particle with $T \ll g \mu_B H / k_B$, the lowest-lying tunneling excitation will consist only of a single transition from the occupied lower-energy state of a split Kramers doublet to a spin singlet state, so that the first $dI/dV$ peak should not split into two as a function of $H$. We observed both behaviors in different particles. Figure 4(a) shows the lowest-voltage $dI/dV$ peaks for a particle with the signature of even $n_0$ [16], while Fig. 4(b) displays the first two $dI/dV$ peaks for a particle with the signature of odd $n_0$. We measured four even and three odd particles, and have never observed a change in parity at low temperature. The lack of splitting for both peaks in Fig. 4(b) indicates that the first two even-electron excited states for this particle are both spin singlets. There is, however, a small peak in Fig. 4(b) (visible below the second large $dI/dV$ peak), which moves to lower $V$ with increasing $H$, attributable to nonequilibrium occupation of the higher-energy level of the initial-state doublet. By measuring the difference in $V$ between Zeeman-split peaks, we determine $g = 1.87 \pm 0.04$ for the states in Fig. 4(a) and $g = 1.96 \pm 0.05$ for Fig. 4(b). The deviation from $g = 2$ is significant for Fig. 4(a), and is likely due to spin-orbit scattering from the surface or impurities [1,8].

In summary, we have, for the first time, measured the spectrum of energies for tunneling via discrete electronic levels on a single metal particle. For transport via a single level in contact with a superconducting lead, the superconducting density of states in the lead is reflected directly in the current, not in $dI/dV$ as for a conventional tunnel junction. The parity of the number of electrons in a normal-metal particle can be determined from the $H$ dependence of the lowest-energy tunneling excitation.

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[6] $Q_0/e = 0.2$ applies for $V < 15$ mV. At 15 mV there is a switch in $Q_0$ [as observed by C. T. Black, M. T. Tuominen, and M. Tinkham, Phys. Rev. B 50, 7888 (1994)], so that for $V > 15$ mV, $Q_0/e = 0.44$.
[9] We expect that our Al particles are effectively normal because $\delta E > \Delta$ for Al [P. W. Anderson, J. Phys. Chem. Solids 11, 26 (1959)]. We observed no evidence of a superconducting or normal transition in the particles as a function of field for $H \lesssim 7$ T, $T \approx 0.5$ K.
[10] In Fig. 2(a) all current steps shown are due to thresholds across junction A, as determined from the $V$ shift between $S$ and $N$ leads.
[11] This is due to the influence of the charging energy and the fact that $R_a > R_b$.
[15] Our arguments do not apply to ferromagnetic particles with ground states having spin $> \hbar / 2$.
[16] $H$ dependence of the orbital energy of the electronic state can cause the measured splitting to be asymmetric, as observed in Fig. 4(a).