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 Si_3N_4 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 O_2 to form a tunnel barrier near the lower edge of the Si_3N_4 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 Q_0 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 $C_A = 4.9 \pm 0.5$ aF, $C_B = 8 \pm 1$ aF, $R_A/R_B = 8 \pm 2$, $R_A + R_B = 9 \pm 1$ MΩ, and $Q_0/e = 0.20 \pm 0.03$ [6]. The charging energy, $E_c \equiv e^2/[2(C_A + C_B)] \sim 6$ 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, $\geq 70 \times 70$ nm^2, by a similar oxidation procedure, which have C per unit area ~70–80 fF/μm^2. The area of

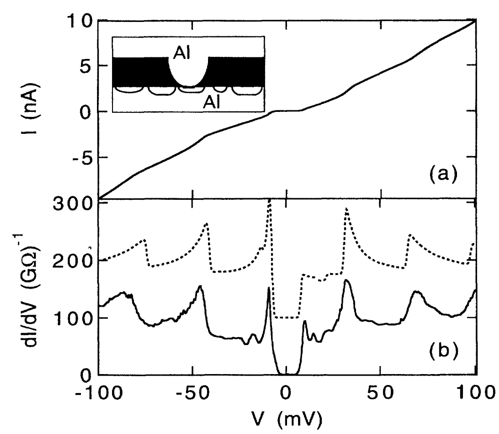

FIG. 1. (a) I vs V and (b) (solid curve) dI/dV vs V for tunneling via a single particle at 4.2 K and $H = 0$. (b) Dashed curve: Theoretical fit discussed in the text, offset 100 GΩ^{-1}. Inset: Schematic diagram of device.

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

Figure 2(a) displays part of the I-V curve at $T = 320$ 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.

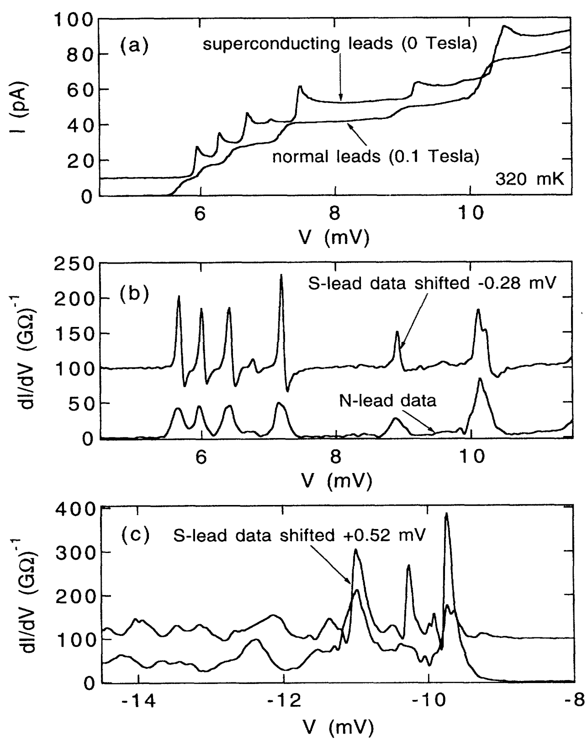

FIG. 2. Signals due to the same device as Fig. 1, at 320 mK. (a) I vs V for superconducting and normal leads. The S-lead curve has been displaced 10 pA in I. (b) and (c) dI/dV vs V for positive and negative bias, with the S-lead data shifted in V, as labeled, so as to align the maxima of dI/dV with the 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).

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 (Γ_E, Γ_S) relative to the rate of electron tunneling (I/e). As long as $\min(\Gamma_E, \Gamma_S) \gg I/e$, 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 Δ (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 surmounted 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 $T_c = \Delta/(1.764 k_B) = 1.18 \pm 0.07$ 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 $C_A/C_B \approx 0.56$. 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 n_0-electron states, which have nonnegligible 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 $\min(\Gamma_S, \Gamma_E) \lesssim (100\ \text{pA})/e \sim 10^9\ \text{s}^{-1}$ for relaxation of the excited n_0-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), as 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 (<6 pA), effects of nonequilibrium occupation of n_0-electron states are minimal. The predicted current then reduces to a simple sequential tunneling form [8,12]

$$I = e\Gamma_1 \Gamma_2/(\Gamma_1 + \Gamma_2), \tag{1}$$

where Γ_1 is the rate of the initial tunneling step (across junction A), and Γ_2 is the rate of the second step. Because Γ_1 is limited by charging while Γ_2 is not,

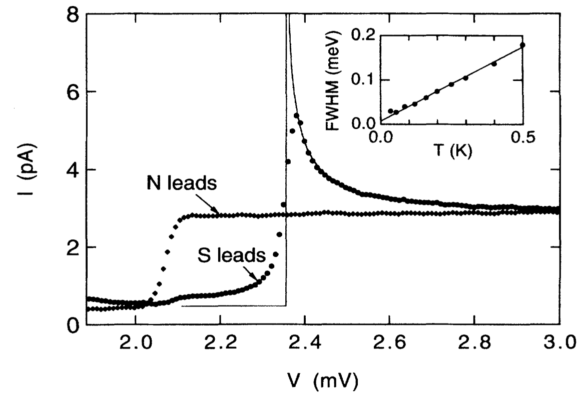

FIG. 3. Points: Tunneling current via one electronic state at 30 mK, for superconducting and normal leads. Line: Fit of the S-lead data to the BCS density of states. $C_A/C_B = 0.656 \pm 0.006$, $\Delta = 0.172 \pm 0.004$ meV, $V_N = 2.070$ mV, and $e\Gamma_{1N}\Gamma_{2N}/(\Gamma_{1N} + \Gamma_{2N}) = 2.16$ pA. Inset: FWHM of dI/dV for the first transition beyond the Coulomb threshold in a different sample, after correcting for capacitance ratio. The fit to the data has slope $3.7 k_B$.

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 Γ_1 with S-state leads (Γ_{1S}) to be proportional to the BCS density of states (DOS):

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

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 Γ_{2N}/Γ_{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 n_0, 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-n_0 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].

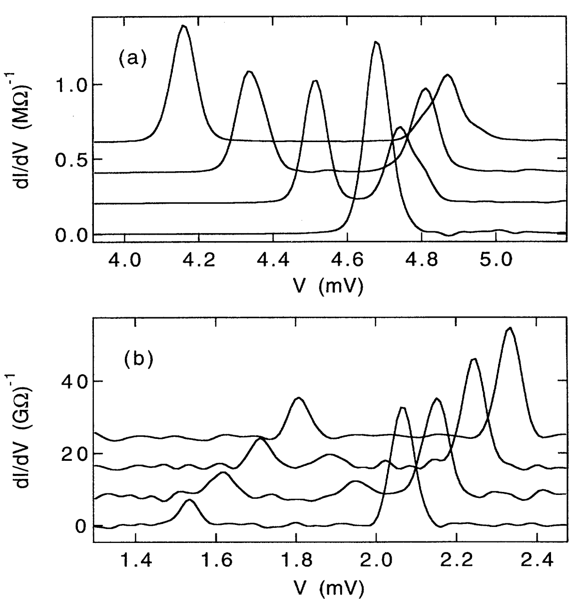

FIG. 4. dI/dV vs V at 50 mK and $H = 0.03$, 1, 2, 3 T from bottom to top, for two different samples. (a) Because the first transition above the Coulomb-blockade threshold exhibits Zeeman splitting, we identify this sample as having an even n_0. (b) A sample in which the first transition does not exhibit splitting and hence is identified as having n_0 odd.

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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[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.

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[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).