Spectroscopy of the Superconducting Gap in Individual Nanometer-Scale Aluminum Particles

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We use electron tunneling to measure electronic energy levels in individual nm-scale Al particles. For sufficiently large particles ($\gtrsim 5$ nm in radius), the eigenstate energies reveal the existence of a superconducting excitation gap Ω which is driven continuously to zero by an applied magnetic field. The presence of Ω increases the voltage threshold for tunneling in a particle with an even number of electrons in its ground state, but decreases the tunneling threshold for an odd-electron particle. We discuss the roles of spin and orbital pair breaking in the magnetic-field transition.

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In nanometer-scale metal particles, the discrete electron energy-level spectrum has been predicted to change the superconducting properties of the metal relative to the bulk [1], even to the point of extinguishing superconductivity altogether [2]. Initial attempts to investigate these issues experimentally were made in the 1960s when Giaever and Zeller made tunneling studies of large *ensembles* of nm-scale superconducting particles [3]. We have developed a technique which allows us to measure tunneling via *individual* particles [4], giving us the ability to study the impact of superconductivity in a single nm-scale particle by direct examination of its electron energy levels. In this Letter we present data taken on Al particles of radius $\sim 5-13$ nm. Experimentally, we identify superconductivity in a particle by the presence of an energy gap Ω for tunneling excitations that is significantly larger than the typical energy spacing between electronic eigenstates, and that can be driven to zero by applying a sufficiently large magnetic field.

Each of our samples consists of a single Al particle connected to two external leads via high-resistance tunnel junctions (see schematic in the inset to Fig. 1). We have previously described the procedure by which we fabricate our samples [4]. The devices we discuss here differ from those studied previously only in that the Al particle is slightly larger in size (previous particles ranged from 2.5 to 4.5 nm nominal radius [4,5]). We can roughly estimate the size of the particle by determining the capacitance of the two tunnel junctions composing the device; we do this by measuring the voltage thresholds for steps in the large-scale Coulomb staircase curve, as described in [4]. We have measured the capacitance per unit area of larger tunnel junctions fabricated using the same oxidation parameters (70–80 fF/μm^2), so that if we assume a particle is a hemisphere, we can estimate its radius from the measured larger capacitance value. We use this estimate only as a way to parametrize our samples, since the assumption of a hemispherical shape is not strictly accurate. Atomic force microscopy studies show particles with radius $\sim 5-10$ nm to be somewhat more pancake shaped.

We use electron tunneling at low temperature (≤ 50 mK) to measure the eigenstate spectrum of the

metal particle. As was predicted theoretically [6] and observed in our previous experiment [4], the current-voltage (I-V) curve consists of a sequence of small steps (peaks in dI/dV); each step corresponds to tunneling via an electronic level on the particle. To obtain the eigenstate spectrum of the particle as a function of energy, we must correct for the capacitive division of voltage across the two tunnel junctions in our devices. We can measure the capacitance ratio most accurately by comparing I-V curves for the same device with alternatively superconducting (S) and normal (N) leads [4]. [We suppress superconductivity in the Al leads through application of a weak (0.03 T) magnetic field.] As detailed in our previous publication, for different features in the I-V curves we observe two different voltage shifts between S and N leads, corresponding, respectively, to thresholds for tunneling across the two tunnel barriers of the device. The values of these two shifts allow a determination of the magnitude of the superconducting gap in the Al leads and the capacitance ratio in the device. The fact that we observe only two values of V shift is important, in that it shows that the dI/dV peaks are due to electronic states on a *single* Al particle [4].

Figure 1 shows the dI/dV vs V for sample 1 at selected values of magnetic field (H) applied parallel to
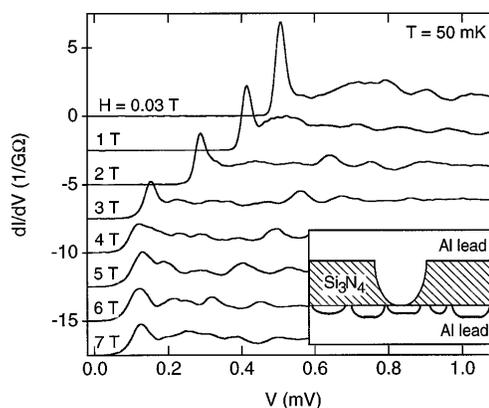
FIG. 1. Differential conductance vs voltage for sample 1, for a range of applied magnetic fields. Curves are offset. Inset: cross-sectional schematic of device.

the plane of the films in our device. In this sample the electronic states are sufficiently dense that signals from neighboring states overlap at $T = 50$ mK, but many individual peaks in dI/dV are resolvable. All of the peaks (for a given sign of V) exhibit the same V shift between signals for S and N leads (S-lead data not shown), and all are located in the first Coulomb staircase step. These two observations indicate that the states are all part of the same (electron addition or subtraction) spectrum, and that they all correspond to the same number of electrons on the particle. Figure 2(a) plots the energy of each state that we resolve in Fig. 1, after correcting for capacitive division of V.

If we define n_0 as the number of electrons in the $V = 0$ ground state of the particle, we can interpret our data as follows. For an electron to tunnel via the metal particle, the applied voltage must supply the tunneling electron with energy equal to the difference between the n_0-electron ground state and one of the ($n_0 \pm 1$)-electron states. This energy difference includes the electrostatic energy needed to charge the particle [7]. An external field H changes the energy difference between the n_0 ground state and the $n_0 \pm 1$ state. One contribution comes from the effect of H on the electron spins. For instance, we can tell that the particle of Figs. 1 and 2(a) corresponds to an *even* value of n_0, because its lowest-voltage tunneling state displays Zeeman spin splitting, with the energy difference between split peaks growing proportional to H [4]. Other states exhibit Zeeman spin splitting as well. At the same time, there is a much stronger effect evident in Fig. 2(a), which causes a decrease in *all* of the resolved transition energies with increasing H. Based on the similarity of this behavior to predictions of pair-breaking theories in superconducting particles (discussed below), we attribute this strong dependence to the effect of H on the orbital energies of the electrons. The fact that H appears to have a similar effect on all the states may be a consequence of energy-level repulsion between
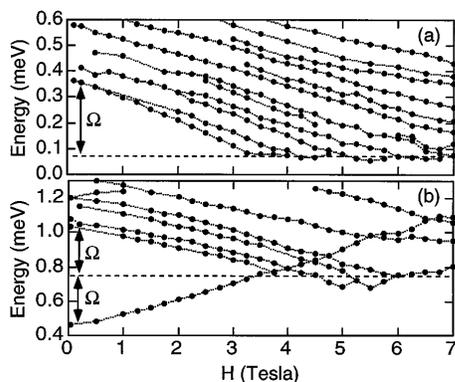
FIG. 2. Magnetic field dependence of resolvable transition energies at 50 mK for (a) sample 1, an even-n_0 particle and (b) sample 4, an odd-n_0 particle. Dotted lines are guides to the eye. Spacings in voltage have been converted to energy using the capacitance ratio $eC_1/(C_1 + C_2) = 0.73$ meV/ mV for (a) and 0.66 meV/mV for (b).

states. We note that the energy threshold for tunneling is greatest at $H = 0$, and drops until $H \approx 3.25$ T. Beyond this field, the initial threshold moves up and down slightly, due to the level crossings which change the lowest-energy tunneling transition. However, the threshold energy is always considerably less than the $H = 0$ value by an amount much larger than the average energy-level spacing. We interpret the increased threshold for tunneling at low H to be due to the presence of a superconducting energy gap Ω on the particle, which must be overcome in order for a quasiparticle to tunnel on or off the even-n_0 particle. As the energies of the excited states are driven lower by the applied H, the excitation gap is reduced until, at $H \approx 3.25$ T, the particle becomes gapless [7]. To allow for the likelihood of gapless superconductivity on the particle at large H, we label the field where $\Omega \to 0$ as H_Ω, as distinct from the critical field where the order parameter Δ goes to zero. We estimate the low-H value of Ω on the particle as the difference between the tunneling threshold at $H = 0.03$ T and the average threshold at high H. For the sample of Figs. 1 and 2(a), $\Omega = 0.29 \pm 0.02$ meV.

The effects of superconducting correlations are even more striking for a particle which contains an *odd* number of electrons in its ground state. Figure 2(b) shows the transition energies vs H for sample 4 which we identify as having n_0 odd, because the lowest-voltage tunneling state does not exhibit Zeeman spin splitting [4]. For small values of H, the lowest-energy transition in the spectrum is separated from all others by a large gap. As H is increased, the energy of the lowest level increases, and the size of the separation between the first two levels shrinks until, at $H \approx 3.75$ T, the two lowest levels cross. Our interpretation of these data is that, for an odd-n_0 superconducting particle, the transition energies correspond to the differences in energy between an odd-n_0 state containing one unpaired quasiparticle and even ($n_0 \pm 1$)-electron states. At $H = 0$, the lowest-energy $n_0 \pm 1$ state is one in which all electrons are paired. Higher-lying $n_0 \pm 1$ states must contain at least two unpaired quasiparticles, and so they are separated from the lowest-energy state by a large energy gap $\approx 2\Omega$ on the metal particle. As H is increased, the energies of the high-lying unpaired states decrease in a way similar to the excited states in the even-n_0 particle [Fig. 2(a)] until Ω is driven to zero, and the energy separation between the fully paired and excited states is eliminated. As with the even-n_0 particles, we estimate Ω as the difference in energy between the threshold for tunneling at $H = 0.03$ T and the average position of the threshold at high H. In Fig. 2(b) we find $\Omega = 0.31 \pm 0.04$ meV.

The properties of four samples in which we can unambiguously identify a superconducting gap are summarized in Table I. Uncertainty in our determination of Ω stems from the ambiguity inherent in distinguishing differences between eigenstate energies caused by superconductivity from those due to discreteness of the level spectrum. The measured values of Ω do not display a strong dependence on particle size. We emphasize that Ω is clearly dis-

tinguishable *only* because it is much larger in magnitude than the mean spacing between adjacent eigenstates. We have also performed measurements on nine smaller particles [4,5], with nominal radii ranging from 2.5 to 4.5 nm. Because the electronic level spacing grows as the particle size is reduced, we cannot track the evolution of Ω in these smaller particles. We emphasize that the effects of superconducting interactions are not necessarily zero in these samples; however, we doubt that it is possible *in principle* to separate the possible presence of Ω from simple independent-electron level discreteness in particles this small, except perhaps by employing statistical tests on ensembles of different eigenstate spectra.

It is well known that thin films composed of small Al grains exhibit enhanced values of Ω and T_c (e.g., [8]). Several different theoretical models have predicted a dependence of Ω on particle size [1,2,9–11]. We find values of Ω ranging between 1.6 and 2.2 times the bulk gap of Al (0.175 meV). (In every sample we measure a gap ≈ 0.18 meV in the Al *leads*.) While it may be tempting to attribute the increase in Ω to discreteness of the electronic spectrum in the particle [9], we cannot rule out other mechanisms [1,10,11].

The form of the H dependence of Ω in superconducting particles much smaller than both the coherence length and the penetration depth has been the subject of a great deal of theoretical analysis [12–15], and is similar in many respects to the problem of a thin superconducting film in a parallel magnetic field [16]. All of these studies assume a continuous, rather than discrete, electron spectrum, so their applicability to nm-scale particles may be questionable. Nevertheless, we will use them qualitatively to consider the mechanisms behind the superconducting transition that we observe. The form of the evolution of the lowest-energy eigenstates (e.g., Fig. 3) with H is similar to predictions for the dependence of the spectroscopic superconducting gap Ω_g under the influence of a pair-breaking field [12,17]. For a first analysis, we fit the H dependence of the lowest eigenstate energies as the sum of Ω_g and the measured Zeeman energy of the spin system. While clearly oversimplified, this analysis allows an examination of the effectiveness of H as a pair breaker in our particles. The solid lines in Fig. 3 correspond to fits [17] for samples 1 [Fig. 3(a)] and 2 [Fig. 3(b)], with pair-breaking

parameters (defined below) given by $2\alpha/H^2 = 0.011$ and 0.013 meV/T^2, respectively.

The strength of pair breaking is in reasonable accord with predictions for the effect of H on the electronic orbital energies. For a spherical particle with diffuse surface scattering, the calculated orbital pair-breaking parameter (2α) is [1,12]

$$2\alpha = (\pi/45)h\upsilon_F r^3 H_2/\Phi_0^2, \qquad (1)$$

where υ_F is the Fermi velocity, r is the particle radius, and Φ_0 is the flux quantum. The pair-breaking parameters for our particles correspond to effective radii ranging from 3.5 to 4.6 nm. These values lie between the radius estimates determined from our capacitance measurements (see Table I) and the thickness of Al we deposit to make our granular particles (2.5 nm). Since H is applied parallel to the plane of the films in our devices, the effective pair-breaking radii r_{pb} are consistent with the fact that the particles are not approximately spherical, but are more pancake shaped [18]. The reasonable agreement of the measured field dependence with both the form and the expected strength of orbital pair breaking gives us some confidence that this mechanism is primarily responsible for the destruction of Ω in our particles.

We have also considered the effect of H on the electron spins, as we clearly observe the contributions of Zeeman spin energies in the energy levels. For very small particles with little spin-orbit scattering, it is predicted that the influence of H on the spins can lead to a first-order transition from S to N, when the paramagnetic energy of electron spins in the particle becomes equal to the superconducting condensation energy [15,19]. Using the bulk value for Ω in Al, one might expect this transition to occur at $H \approx 2.2$ T, which would mean [setting Eq. (1) equal to Ω] that for particles with effective radius < 6.3 nm a discontinuous collapse of Ω should occur at a field lower than that of the continuous transition we observe. We propose that two factors contribute to reducing the importance of this spin effect, so that it is not the dominant mechanism in eliminating Ω. As we have shown, Ω in our particles is significantly larger than that of bulk Al, indicating an increased superconducting condensation energy density relative to bulk Al. Second, in several samples, the size of the Zeeman spin splittings we measure

TABLE I. C_{smaller} and C_{larger}: capacitances determined from large-scale Coulomb staircase curve. E_C: $e^2/2C_{\mathrm{total}}$. Radius: estimated from C_{larger} assuming a hemispherical particle. $\overline{\delta_{\mathrm{calc}}}$: independent-electron particle-in-a-box estimate of mean energy-level spacing based on radius. R_{sum}: sum of tunnel junction resistances. Parity of n_0. Ω: measured superconducting excitation gap. H_Ω: field where $\Omega \to 0$. g factor: determined from magnitude of Zeeman splittings. $2\alpha/H^2$: measured pair-breaking parameter. r_{pb}: effective particle radius determined from pair-breaking parameter as discussed in text.

Sample	C_{smaller} (aF)	C_{larger} (aF)	E_C (meV)	Radius (nm)	$\overline{\delta_{\mathrm{calc}}}$ (meV)	R_{sum}	Parity	Ω (meV)	H_Ω (T)	g factor	$2\alpha/H^2$ (meV/T^2)	r_{pb} (nm)
1	29	80	0.73	13	0.02	350 kΩ	Even	0.29 ± 0.02	3.25	0.27	0.011	4.3
2	14	30	1.8	8	0.08	600 kΩ	Even	0.38 ± 0.04	3.5	1.0	0.013	4.6
3	13	16	2.8	5.7	0.22	670 kΩ	Even	0.29 ± 0.03	3.5	0.4	0.009	4.0
4	6.2	12	4.4	5.1	0.32	1.2 MΩ	Odd	0.31 ± 0.04	3.75	1.9	0.006	3.5
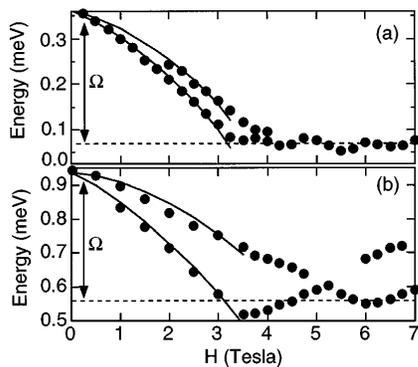
FIG. 3. Comparison of the predictions of orbital pair breaking plus Zeeman spin splitting (lines) to the measured field dependence of the lowest-energy tunneling transitions (dots) for (a) sample 1 and (b) sample 2.

indicates a g value much less than two for the electronic states, demonstrating the presence of significant spin-orbit scattering within some particles. This reduces the paramagnetic energy of the electron spins in an applied H. At present we do not fully understand the origin of the spin-orbit scattering. We note that in similarly fabricated smaller particles with radi <5 nm we have always observed g factors between 1.85 and 2.0 [4].

In each of our even-n_0 samples we observe a large peak in dI/dV just beyond the threshold for current flow at small H, followed by a sequence of smaller peaks at higher voltages (Figs. 1 and 4). As H is increased, the height of the first peak drops gradually, and it becomes comparable in amplitude to the rest of the spectrum when H is sufficiently large that Ω is driven to zero. We interpret this large first peak in dI/dV as the counterpart, for a nm-scale metal particle, of the singularity in the BCS density of states in a bulk superconductor. The integrated areas under the high and low field conductance curves in Fig. 4 are equal to within 1%.

In summary, we report the first study of the electronic eigenstates of single nm-scale superconducting particles. Due to the difficulty inherent in distinguishing a supercon-

ducting gap Ω from simple level discreteness, the presence of Ω can be unambiguously identified only in particles sufficiently large that the mean spacing between eigenstates is significantly smaller than Ω. The presence of Ω affects the spectra of even- and odd-electron particles differently. We observe Ω on the particle to be reduced continuously to zero by an applied magnetic field. The behavior of the S to N transition is well described in terms of the effect of H on the orbital state of the electrons plus a smaller Zeeman contribution from the electron spins.

FIG. 4. Comparison of differential conductance at low magnetic field with the conductance at sufficiently high field that $\Omega = 0$ for (a) sample 1 and (b) sample 3. Note the strong peaks at the threshold voltage for low H.

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