Even-Odd Asymmetry of a Superconductor Revealed by the Coulomb Blockade of Andreev Reflection

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(Received 20 October 1992)

We have measured at low temperatures the current through a submicrometer superconducting island connected to two normal metal leads by ultrasmall tunnel junctions. As the bias voltage is lowered well below twice the superconducting energy gap, the current changes from being e periodic with gate charge to $2e$ periodic. This behavior is clear evidence that there is a difference in the total energy between the ground states of an even and odd number of electrons on the island. The $2e$-periodic current peaks are the first observation of the Coulomb blockade of Andreev reflection.

PACS numbers: 73.40.Gk, 73.40.Rw, 74.50.+r

Systems with a small number of particles like nuclei behave differently if the number of particles is even or odd [1]. Does this symmetry breaking occur for a large metallic particle or "island" where the number of conduction electrons is macroscopic, say, 10^9? In a superconductor, according to the BCS theory, the electronic state consists of pairs of electrons. At very low temperatures, a simple view is that all the electrons should condense into the ground state if their number is even. However, if the number is odd, one electron should remain in an excited quasiparticle state with energy Δ, the superconducting gap. This simple picture might not be applicable to a real experimental system because, for example, there might be quasiparticle states located within k_BT of the Fermi level. Even one of these states, normally undetectable in usual tunneling experiments, could then capture and release single electrons and restore the even-odd symmetry.

The isolated superconducting island can be conveniently probed by connecting it to metal leads via two tunnel junctions. If the tunnel junction resistances are much greater than the resistance quantum, then the charge on the island is quantized, and this Coulomb blockade electrometer can be used to probe the energy of the island [2]. In experiments with a device having both superconducting island and leads, the SSS electrometer [3], a current $2e$ periodic with a gate charge applied to the island has been measured for bias voltages in a certain range [4,5]. These $2e$-periodic data, which could be observed only on some samples, display a complicated structure which is difficult to interpret since the basic model should at least include, in addition to the charging energy of the system, both quasiparticle and Josephson tunneling. Nevertheless, Tuominen *et al.* [5] have observed that the amplitude of the $2e$-periodic component vanished at a temperature of about 300 mK, which they explain as the temperature at which a single quasiparticle of energy Δ can be thermally excited and thus restore the even-odd symmetry.

In this Letter, we present the first measurements on a superconducting island with normal metal leads, the NSN electrometer. This system can be more readily understood because the two SN junctions do not allow Josephson tunneling [6]. The only allowed conduction process at low bias voltages is the Andreev reflection [7] of an electron into a hole on the N side, a process which can also be described as the simultaneous tunneling of two electrons from the N side to form a Cooper pair on the S side. Since we know the tunneling process that produces the $2e$-periodic current, the voltage and temperature dependences can be well interpreted.

In Fig. 1 we show a schematic of the electrometer made by a series connection of two tunnel junctions with resistances R_{T1} and R_{T2} and capacitances C_1 and C_2. An external gate voltage V_g polarizes the island with gate charge $Q=C_gV_g+Q_0$, where C_g is the gate capacitance and Q_0 is a random background charge. The characteristic charging energy is $E_c=e^2/2C_\Sigma$, where $C_\Sigma=C_1+C_2+C_g$ is the total island capacitance. At zero-bias voltage

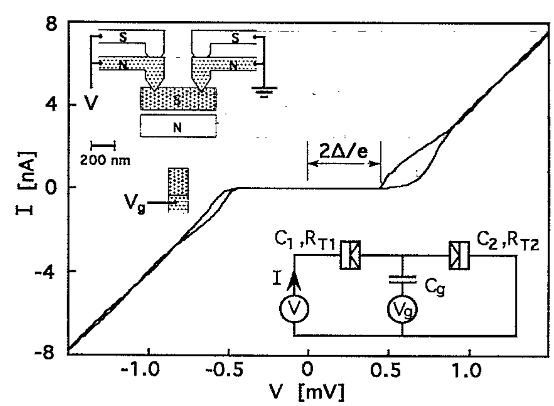

FIG. 1. Current-voltage characteristic of NSN Coulomb blockade electrometer. Two traces are for gate voltage V_g adjusted for minimum and maximum gap at positive voltage. Arrow indicates the value of $2\Delta/e=470$ μV, where the nominal value of Δ is obtained from our aluminum SSS electrometers. Lower inset shows electrical schematic for the electrometer, where the boxed symbols represent ultrasmall tunnel junctions. Upper inset depicts the device layout. Normal and superconducting metals are indicated by N and S, respectively. The shaded regions indicate metals used for the NSN electrometer. The gate is actually 3 μm from the island.

V, the system energy is given by $E_n = E_c(n - Q/e)^2$, where n is the excess number of electrons on the island.

We consider first the case of the electrometer with a normal metal island. In Fig. 2(a) we plot E_n vs Q and for various n. At sufficiently low temperatures ($k_B T \ll E_c$) the zero-bias conductance [Fig. 2(b)] vanishes unless $Q/e = n + \frac{1}{2}$, that is, where $E_n = E_{n+1}$. At this gate charge, one electron can enter the central electrode through the left junction and another can leave through the right without changing the energy of the system. Because the electrostatic energy is minimized by single-electron tunneling, the quantization of electric charge makes all current-voltage characteristics periodic in the gate charge Q with period e.

With a superconducting island the situation is altered significantly by the energy gap for excitations. We expect the energy of the system at zero-bias voltage to be given by $E_n = E_c(n - Q/e)^2 + p_n \Delta$, where p_n takes the value 1 if n is odd or 0 if n is even. In Fig. 2(c) we now show E_n vs Q for various n and assume that $\Delta > E_c$. Now single-electron tunneling can possibly occur for values of Q/e different from $n + \frac{1}{2}$. However, for conduction to occur the *same* quasiparticle state has to be filled and emptied as charge moves through the electrometer, and thus one should expect a very low conductance [$< (100\ \mathrm{G\Omega})^{-1}$] from this channel [8]. Since there is no Cooper pair tunneling, we must consider a higher order process such as Andreev reflection which allows the simultaneous tunneling of two electrons through one junction. Conduction can then occur when the even-numbered levels cross, which takes place at $Q/e = 2n + 1$ [Fig. 2(d)] and is therefore $2e$ periodic.

The sample was fabricated using electron-beam lithography and double-angle evaporation. First we deposited a 35 nm thick aluminum film to form the island with dimensions 0.23 μm$\times$0.86 μm. This layer was then oxidized in 13 Pa of oxygen for 5 min. The sample was then tilted for the second evaporation which consisted of a 5 nm thick buffer layer of aluminum followed immediately by a 55 nm thick layer of gold; the buffer layer was used to promote adhesion. Because of its contact to the thicker gold film, the thin aluminum buffer layer should remain in the normal state by the proximity effect [9]. We show in Fig. 1 that, in fact, the large-scale current-voltage characteristic shows a sharp current rise at $2\Delta/e$ when the gate charge is adjusted for minimum gap. In contrast, SSS electrometers [5,10] have a current rise at $4\Delta/e$. Although the current rise occurs within 10% of our nominal value for $2\Delta/e$, we cannot rule out that a small vestige of superconductivity or superconducting fluctuations might remain in the gold layer. Although the double-angle evaporation leaves extraneous copies of the structures (the unshaded regions in Fig. 1), these structures should not affect the behavior of the NSN electrometer. The sample was mounted in a shielded copper box and was cooled to a base temperature of 35 mK in a dilution refrigerator with no applied magnetic field. Electrical measurements were made through carefully filtered coaxial cables [11].

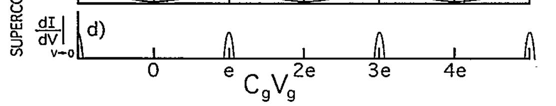

FIG. 2. System energy E_n vs gate voltage V_g for several values of the excess number of electrons n, in the normal (a) and superconducting (c) states. In an ideal superconductor, the minimum energy for odd n is Δ above the minimum energy for even n. Conductance in the vicinity of zero-bias voltage vs V_g is shown in the normal (b) and the superconducting (d) state.

The behavior of the electrometer for $V > 2\Delta/e$ is explained by the usual Coulomb blockade theory for the normal metal electrometer modified to account for the quasiparticle density of states in the island. Hence, the threshold for tunneling occurs when the energy change across one junction is greater than Δ. Thus, the minimum gap occurs for $V = 2\Delta/e$, with an additional Coulomb gap that modulates with charge as predicted for the normal metal electrometer. Our data (not shown) agreed with this model, and we were thus able to measure [12] the circuit parameters $R_{T1} \approx R_{T2} \approx 65$ kΩ, $C_1 \approx 0.35$ fF, $C_2 \approx 0.28$ fF, $C_g \approx 7.2$ aF, and $\Delta/e \approx 235$ μV. These parameters give $E_c/e \approx 126$ μV $< \Delta/e$.

A further check on the NSN behavior of the sample was obtained by measuring the inelastic cotunneling [13] current for voltages greater than $2\Delta/e$ and for $Q \approx 0$ where the Coulomb gap was maximum. This process occurs only for $V > 2\Delta/e$ because two quasiparticles are created in the superconducting island per cotunneling event. We calculate at maximum gap and $T \to 0$ a cotunneling current $I_{ct} = (2R_K/3\pi^2 R_{T1} R_{T2})(C_\Sigma/e)^2[(3\pi/2) \times \delta V^2 \Delta/e + \delta V^3]$, where $\delta V = V - 2\Delta/e$ and $R_K = h/e^2$. Our data (not shown) agree with the predicted behavior and magnitude for V slightly above $2\Delta/e$ within 25%.

In Fig. 3 we show experimental I vs V_g data at 478 μV ($V \approx 2\Delta/e$) and 63 μV ($V \approx \Delta/4e$) and at 35 mK. The large-voltage data give the e periodicity of the conductance, as explained previously and for Fig. 2(b). The data at low voltage have twice the period of the high-voltage data, and the peaks are positioned at minima of the high-voltage data. This behavior is exactly what is predicted from Fig. 2(d) in both the period and position of the peaks. The particular $2e$-periodic current that we measure requires a symmetry breaking that is strong

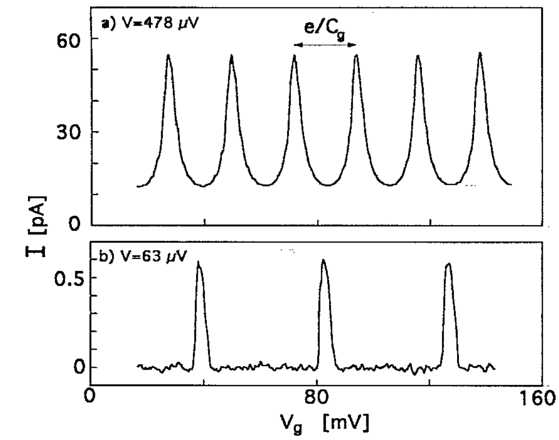

FIG. 3. Current through the electrometer vs V_g for bias voltage (a) $V \approx 2\Delta/e$ and (b) $V \approx \Delta/4e$. Arrow in (a) shows gate voltage corresponding to e periodicity.

enough so that the even states are always lower in energy than the odd states. This requires $\Delta > E_c$.

In Fig. 4 we show a succession of I-V_g curves taken similarly to that of Fig. 3(b). Each V_g trace took 200 s, and successive traces were displaced downward slightly. Apart from small random offsets [14] and a slow drift which we attribute to the relaxation of the background charge, we have observed shifts in the curves corresponding to an abrupt change of charge e which occurred intermittently on a time scale of several hours. A possible model to explain these data involves the infrequent tunneling of conduction electrons from the island to localized states within the insulator at the surface of the island. The empty conduction state left by this event is immediately filled by an electron tunneling through a junction, and the filled localized state polarizes the island with charge e, thus giving a shift of e in C_gV_g. This process can conceal the even-odd symmetry breaking if the data are taken on time scales much longer than the typical time of tunneling into the defect states. This time scale could be sensitively dependent on the material properties of the superconducting island.

Figure 5 examines in more detail the $2e$-periodic feature by showing the current-voltage characteristics at bias charges corresponding to 0, e, and $1.06e$. The different characteristic between the 0 and e data again shows the $2e$ periodicity. A linear I-V characteristic around $V=0$ for $Q=e$ is in agreement with our discussion of Fig. 2(d). The data at $Q=1.06e$ show that a small gap opens up near $V=0$ for Q slightly different than $Q=e$. This behavior is quite different from the supercurrents observed in SSS electrometers [4]. It points not to a coherent transport of electrons through the island (supercurrent), but to an incoherent process where voltage thresholds for each of the two junctions must be exceeded for sequential tunneling to occur. We envision a process where two electrons enter the island through the left junction and form a Cooper pair, followed by the destruction of a Cooper pair as two electrons exit through the right junction. This sequential $2e$-transfer process is identical to Andreev reflection [7] in each SN junction. It does not require voltages greater than Δ/e since no quasiparticles are excited, it is $2e$ periodic in Q because of the two-electron transfer, and its rate is linearly proportional to the applied voltage. At $Q=e$, we calculate the zero-bias conductance to be $R_K f^2(E_c/\Delta)/8M_{\text{eff}}(R_{T1}^2+R_{T2}^2)$, where $f(x)=2\cos^{-1}(-x)/\pi(1-x^2)^{1/2}$ and M_{eff} is a material parameter corresponding to the number of effective conduction channels through the junctions. Our observed resistance of 100 MΩ corresponds to an

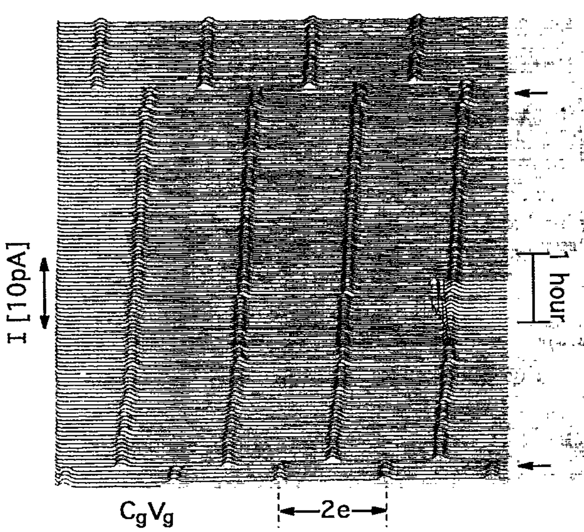

FIG. 4. Time evolution of I-V_g characteristics. Repeated traces are shifted downward with time. Arrows at right indicate the positions of e shifts. Current peaks are 0.5 pA.

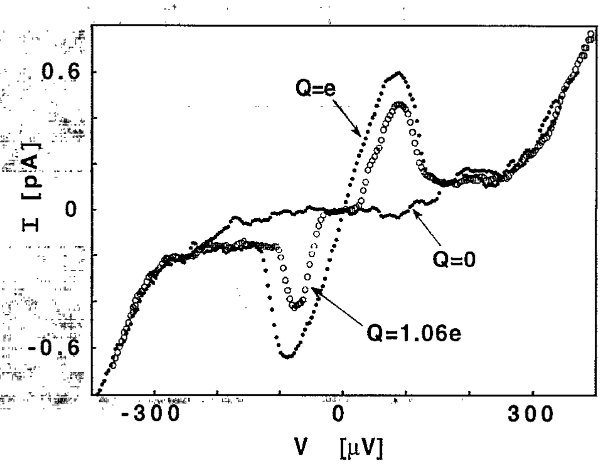

FIG. 5. Fine scale current-voltage characteristics for $Q=C_gV_g \bmod 2e=0$, e, and $1.06e$. A small Coulomb gap is seen for the $Q=1.06e$ data.

$M_{\rm eff}$ of 100, which we think is a reasonable order of magnitude considering the granularity of the electrode films [15]. At bias voltages approaching $2(\Delta - E_c)/e = 218$ μV tunneling transitions to odd states become allowed. This accounts for the vanishing of the $2e$-periodic current at roughly this voltage.

As we increased the temperature, the zero-bias conductance associated with the $Q=e$ curve of Fig. 5 remained roughly constant. However, the height of the peak decreased linearly with increasing temperature and disappeared completely at $T_0 = 130$ mK. This temperature dependence can be understood by replacing in the calculation of the population of the odd state the even-odd energy difference Δ with a free energy $F(T) = \Delta - k_B T \times \ln N_{\rm eff}$, where $N_{\rm eff}$ is the effective number of quasiparticle states [5]. At zero-bias voltage and $Q=e$ the odd state becomes significantly populated when $F(T_0) = E_c$, and from this we predict $T_0 = 140$ mK which is in good agreement with our data. Our results differ from those of Tuominen *et al.* who observed the vanishing of their $2e$-periodic component at $T_1 \approx 300$ mK, which they interpret as the solution of $F(T_1) \approx 0$. There is probably no contradiction as our $2e$-periodic tunneling mechanism can operate if the island is only in the even state, whereas their unknown mechanism can perhaps operate whatever the parity of the island electron number. Symmetry breaking should persist to 300 mK in our sample, but our current-producing mechanism vanishes at a lower temperature because the energy difference is lower than Δ at the gate charge $Q=e$ where we measure the current.

In conclusion, we present the first experimental data on an NSN electrometer. This system allows for the first time an understanding of the electron tunneling *mechanism* that produces a $2e$-periodic current with gate charge. The dependence of the data with both bias voltage and temperature agrees quantitatively with the predictions based on this mechanism. Our results reveal simply and directly the even-odd number symmetry breaking of a superconducting island. Furthermore, our observation of random e shifts in the gate charge demonstrates that this symmetry breaking may be observable only on a short enough time scale. Finally, this experiment shows that the Coulomb blockade may be used to discriminate Andreev reflection processes against a background of single-electron tunneling since at $Q=e$ only two-electron tunneling is allowed.

We acknowledge helpful discussions with D. Esteve and L. Glazman. This work was supported in part by the Office of Naval Research under Contract No. N00014-92-F-0003.

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[15] A uniform tunnel barrier gives a maximum value of $M_{\rm eff}$ to be the area divided by the square of the Fermi wavelength, a value of about 10^4 for our sample. A nonuniform barrier gives a lower value of $M_{\rm eff}$.