# Measurement of the Even-Odd Free-Energy Difference of an Isolated Superconductor

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(Received 16 November 1992)

We have measured the difference between the free energies of an isolated superconducting electrode with odd and even number of electrons using a Coulomb blockade electrometer. The decrease of this energy difference with increasing temperature is in good agreement with theoretical predictions assuming a BCS density of quasiparticle states, except at the lowest temperatures where the results indicate the presence of an extra energy level inside the gap.

PACS numbers: 74.50.+r, 73.40.Rw, 74.25.Bt

The key concept of the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity [1] is the pairing of electrons. A surprising feature of the theory appears when one considers a macroscopic piece of superconducting metal with a fixed number of electrons $N$. If $N$ is even, all the electrons can condense in the ground state. If $N$ is odd, however, one electron should remain as a quasiparticle excitation. In principle, if one would measure the energy required to add one electron to the superconductor, there should be a difference between the cases of even and odd $N$. This fundamental even-odd asymmetry, which might vanish due to sample imperfections [2], does not manifest itself in conventional experiments on superconductors because these experiments are only sensitive to a finite fraction of quasiparticles. In this Letter, we report a new experiment based on single-electron tunneling [3] with which we measured the even-odd free energy difference introduced by Tuominen *et al.* [4].

Consider a superconducting-normal (SN) tunnel junction in series with a voltage source $U$ and a capacitor $C_s$ (see Fig. 1), a basic Coulomb blockade circuit whose normal-normal junction version has been nicknamed the electron "box" [5,6]. The superconducting electrode which is common to both the junction and the capacitor is surrounded everywhere by insulating material. When the junction tunnel resistance $R_t$ is such that $R_t \gg R_K = h/e^2$, the number $n$ of excess electrons on this "island" is a good quantum number [3,7]. The $n$-dependent part of the ground-state energy of the circuit, including the work done by the source $U$, is given by $E_n = E_c(n - C_sU/e)^2 + \mathcal{E}_n$, where $E_c = e^2/2C_\Sigma$ is the electrostatic energy of one excess electron on the island, $C_\Sigma$ the total capacitance of the island, and $\mathcal{E}_n$ is the nonelectrostatic part of the energy of the island. For a normal island $\mathcal{E}_n = 0$ [Fig. 2(a)], whereas for a superconducting island, one has $\mathcal{E}_n = D_0 p_n$ where $D_0$ is the energy difference between the odd-$n$ and even-$n$ island ground states, and $p_n = n \bmod 2$ [Fig. 2(c)]. The BCS theory yields $D_0 = \Delta$ where $\Delta$ is the superconducting gap of the island. In equilibrium at zero temperature, $n$ will be determined by the lowest $E_n$ and is therefore given by a staircase function of $U$ [Figs. 2(b) and 2(d)]. In the normal case, the steps are of equal size, whereas in the superconducting case even-$n$ steps are longer than odd-$n$ steps. For $D_0 > E_c$, the odd-$n$ steps disappear, while for $D_0 \le E_c$, the ratio $\rho$ between the length of the odd- and even-$n$ steps is related to $D_0$ through $D_0/E_c = (1-\rho)/(1+\rho)$. Thus, from a measurement of the equilibrium value of $n$ as a function of $U$, which can be done by weakly coupling the island to a Coulomb blockade electrometer [5,6,8], as shown in Fig. 1, one can in principle infer the value of $D_0$.

In practice, the measurements are performed at finite temperature and the current in the electrometer is directly related to $\bar{n}$, the temporal average of $n$ which we suppose equal to $\langle n \rangle$, the thermal ensemble average of $n$. The above analysis must be refined to take into account the thermal population of all the possible states of the circuit. These states are characterized not only by the number $n$ of excess electrons in the island, but also by the filling factors of the various quasiparticle states of the island. One finds that the average value of $n$ is given by

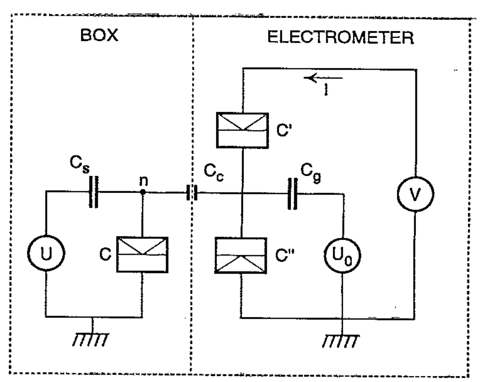


FIG. 1. Circuit diagram of the experiment. The rectangular symbols represent SN tunnel junctions. The V-shaped marks denote superconducting electrodes. The symbol $n$ denotes the number of electrons in the island of the box (marked by a full dot). The variations of its average $\bar{n}$ with the voltage $U$ are detected by monitoring the current $I$ through the SNS electrometer which is coupled to the box through the capacitor $C_c$. The bias voltage $V$ and the gate voltage $U_0$ set the working point of the electrometer.

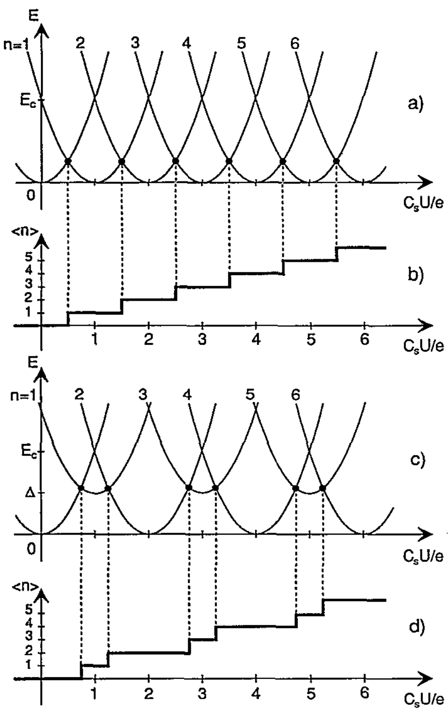


FIG. 2. Ground-state energy of the box in the (a) normal and (c) superconducting states as a function of the polarization $C_sU/e$, for several values of the excess number $n$ of electrons in the island. $E_c$ is the electrostatic energy of one excess electron on the island for $U=0$. In an ideal superconductor, the minimum energy for odd $n$ is $\Delta$ above the minimum energy for even $n$. The dots correspond to level crossings where single electron tunneling is possible. Equilibrium value $\langle n\rangle$ vs $C_sU/e$ is shown in the (b) normal and (d) superconducting states, at $T=0$.

$$\langle n\rangle=\frac{C_sU}{e}+\frac{C_\Sigma}{C_s\beta e}\frac{\partial}{\partial U}\left\{\sum_n Z_n e^{-\beta E_c(n-C_sU/e)^2}\right\}, \tag{1}$$

where $\beta=1/k_BT$ and where $Z_n$ is the partition function of the island with $n$ excess electrons. We now follow Ref. [4]: We assume Fermi statistics for the quasiparticle excitations of this isolated system and we set the parity of the number of quasiparticles equal to the parity of $n$. We get $Z_n=[Z_+ + (-1)^n Z_-]/2$, with $Z_\pm=\prod_q[1\pm\exp(-\beta\epsilon_q)]$, where $q$ denotes a generic quasiparticle state with energy $\epsilon_q$.

At temperatures such that $k_BT\ll E_c$, the $\langle n\rangle$ vs $U$ staircase is just slightly rounded. The length of the steps is now defined from the values of $U$ where $\langle n\rangle$ is a half integer and $D_0$ in the expression of the odd-even step length ratio is now replaced by $D(T)=\mathcal{F}_1-\mathcal{F}_0$, the difference between the free energies $\mathcal{F}_n=-k_BT\ln Z_n$ of the island with an odd and an even number of electrons [9]. Introducing the transform $\tilde\rho(T)=\int_0^\infty\rho(\epsilon)\ln[\coth(\beta\epsilon/2)]d\epsilon/2$ of $\rho(\epsilon)$, the density of quasiparticle states, one can express $D(T)=-k_BT\ln[\tanh\tilde\rho(T)]$. We now suppose that $\exp(-\epsilon_{\min}/k_BT)\ll 1$, where $\epsilon_{\min}$ is the lowest energy for which $\rho(\epsilon)$ is nonzero. In this limit, $\tilde\rho(T)$ can be evaluated analytically for mathematically simple $\rho$. If we assume a continuous BCS density of states, $\tilde\rho(T)=N_{\text{eff}}(T)e^{-\beta\Delta}$ where

$$N_{\text{eff}}(T)=N_0(2\pi k_BT/\Delta)^{1/2}+O[(T/\Delta)^{3/2}]$$

is the effective number of quasiparticle states available for excitation [10] and where $N_0=\rho_AN_A\Delta$, $\rho_A$ being the normal density of states at the Fermi energy per atom and $N_A$ the number of atoms in the island. Because $\ln N_{\text{eff}}$ depends weakly on the sample parameters and on temperature, $D(T)$ is approximately given at temperatures such that $N_0\exp(-\Delta/k_BT)\ll 1$ by $\Delta(1-T/T_0)$, with $T_0=\Delta/(k_B\ln N_0)$ in the range 200–300 mK for realistic Al islands. More generally, if there is inside the gap discrete quasiparticle states with energies $\epsilon_{q_i}$ and degeneracies $g_{q_i}$, they each contribute to $\tilde\rho(T)$ by $g_{q_i}\exp(-\beta\epsilon_{q_i})$. Their effect is to reduce $D(T)$, which is given in the limit $T=0$ by $D(T)=\epsilon_{q_0}-k_BT\ln g_{q_0}$, where $q_0$ is the lowest discrete quasiparticle state. Finally, we must point out that the $2e$-periodic behavior of the SN box is similar to the $2e$ periodicity which has been observed for the current through the SSS [4,11] and NSN [12] Coulomb blockade electrometers as a function of the charge induced on the gate. However, note that when $D(T)<E_c$, the box experiment, in contrast with the transport experiments on Coulomb blockade electrometers, gives access to the ratio $D(T)/E_c$ and not simply to the temperature at which it vanishes.

The sample was fabricated using $e$-beam lithography and double-angle $e$-beam evaporation through a suspended mask [13]. First we deposited a 30 nm thick aluminum film to form the superconducting island of the box, with lateral dimensions 2.2 $\mu$m×0.1 $\mu$m, as well as the leads of the electrometer. This first layer was then oxidized in 300 Pa of oxygen for 15 min at room temperature. A 50 nm thick layer of Cu alloyed with 3% by weight of Al was then deposited to form the normal lead connected to the box and the island of the electrometer. The two nominally identical junctions of the electrometer had an area of $\sim 8\times10^{-3}$ $\mu$m$^2$, and were much larger than the box junction. The suspended mask was designed so that there was no overlap of the Al island of the box with its Cu-Al copy, which is inherent to the double evaporation technique. The current-voltage curve (inset of Fig. 3) of a single junction fabricated with the same technique showed a sharp current rise at $\Delta/e=180\pm10$ $\mu$V, with the square-root voltage dependence characteristic of NS junctions. Figure 3 shows a current-voltage characteristic of the electrometer: When the gate charge is adjusted so as to suppress Coulomb blockade for positive voltage, the sharp current rise at $2\Delta/e=360\pm10$ $\mu$V indicates that the electrometer consists indeed of two NS junctions in series. Detailed analysis of these $I(V)$ curves yielded the capacitance parameters of the electrometer. They served as calibrations for numerical electrostatic

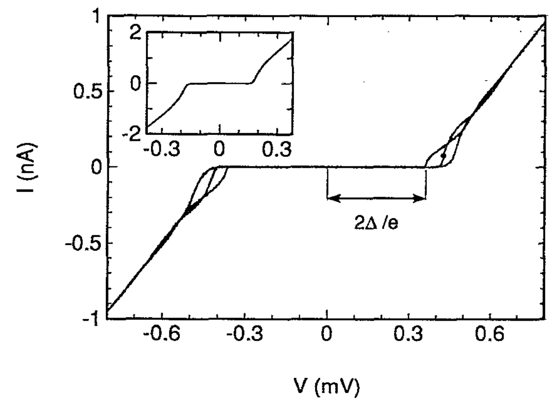


FIG. 3. $I(V)$ curves for the SNS electrometer at $T=25$ mK, and zero magnetic field, for three values of the gate voltage $U_0$ corresponding to maximum, intermediate, and minimum gap. The minimum gap corresponds to the bare superconducting gap $2\Delta$ of two NS junctions in series. The dot indicates the optimal bias point for maximum sensitivity. Inset: $I(V)$ curve for a single SN junction under the same conditions.

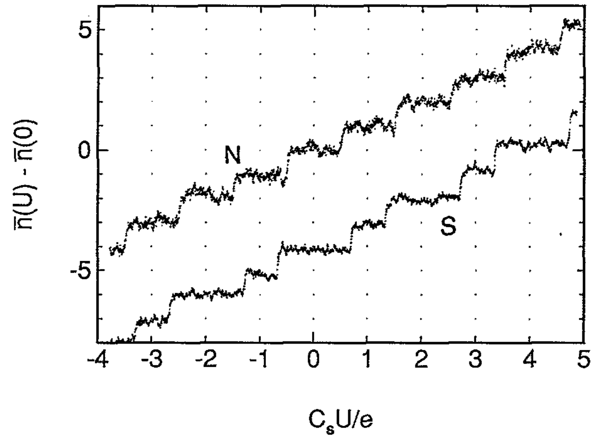


FIG. 4. Variations of the average value $\bar{n}$ of the number of extra electrons in the box as a function of the polarization $C_sU/e$, at $T=25$ mK. Trace $N$: normal island. Trace $S$: superconducting island. For clarity, trace $S$ has been offset vertically by 4 units.

calculations of the box parameters which gave $C_\Sigma=0.2\pm0.05$ fF, $C_s=25\pm5$ aF, and $C_c=11\pm2$ aF. The experiments were done with the sample mounted in a shielded copper box thermally anchored to the mixing chamber of a dilution refrigerator. All voltage and current lines were carefully filtered [14]. When necessary, the sample was put in its normal state by a 1 T magnetic field produced by a superconducting coil.

To perform the measurements of $\bar{n}$ vs $U$ the bias and gate voltages $V$ and $U_0$ of the electrometer were first adjusted to maximize $\partial I/\partial U_0$ (dot in Fig. 3). The electrometer current $I$ was then recorded as a function of $U$. The resulting sawtooth signal is a measurement, apart from a gain factor, of the second term of Eq. (1). We obtained $\bar{n}$ by adding to this sawtooth signal a linear term whose coefficient was adjusted to null out the slope of the teeth. In Fig. 4 we show the measured equilibrium value $\bar{n}$ as a function of the polarization $C_sU/e$ for the sample in both the normal and the superconducting state, at 20 mK. The even-odd symmetry of the steps in the normal state is clearly broken in the superconducting state. Note that the middle of the steps in the superconducting state coincides with the middle of the steps in the normal state, as predicted by theory [see Figs. 2(b) and 2(d)] in the case $D(T)<E_c$. Our previous experiments on a box with an SS junction never showed any even-odd asymmetry [5]. We believe that this was due to the presence of a few long-lived, out-of-equilibrium quasiparticles which in the present experiment are "purged" by the normal metal lead.

Because of the unavoidable electrostatic cross talk between the $U$ voltage and the electrometer island, which was only partially corrected for in our setup, the gain of the electrometer depends on the $U$ voltage. This leads to the noticeable step height variations as $U$ departs from zero. Nevertheless, these vertical scale distortions do not affect the conclusions we draw from our data, which are based only on the length of the steps along the horizontal axis. The scaling factor used for this axis corresponds to $C_s=21\pm0.5$ aF, in good agreement with our numerical estimates. When the temperature was increased the steps became gradually rounded (data not shown). From a fit of the temperature dependence of the data in the normal state using Eq. (1) we obtained a direct measurement of $C_\Sigma=0.20\pm0.05$ fF, also in good agreement with our numerical estimates.

We have measured the odd-even step length ratio $\rho$ as a function of temperature, thereby obtaining $D(T)/E_c$. The experimental results are shown in Fig. 5 together with the theoretical predictions in the case of a continuous BCS density of states (dashed line). Since $N_A$ is known from the sample dimensions, the only adjustable parameters are $C_\Sigma^{\rm fit}=0.19$ fF and $\Delta^{\rm fit}/e=195$ $\mu$V. The parameter $C_\Sigma^{\rm fit}$ is in the error range of $C_\Sigma$ while the uncertainty range for $\Delta^{\rm fit}$ is adjacent to the error range of $\Delta$ deduced from the electrometer $I(V)$. Apart from this minor discrepancy which may be due to the fact that the island, contrary to the S leads of the electrometer, is not covered by a normal layer, there is good agreement between theory and experiment for temperatures higher than 50 mK. At lower temperatures, the data deviate significantly from theory, in a manner which could be explained by a failure of the box to follow the temperature of the thermometer. However, we find this explanation unlikely. In a previous run on a NN box with parameters adapted to calibration purposes, the staircase sharpness precisely followed the temperature down to 35 mK. A more likely explanation is that the density of states of the island may not be a strictly smooth BCS one. To illustrate this point, we show in Fig. 5 a complete fit of the data (full line) using a minimal model: In addition to the

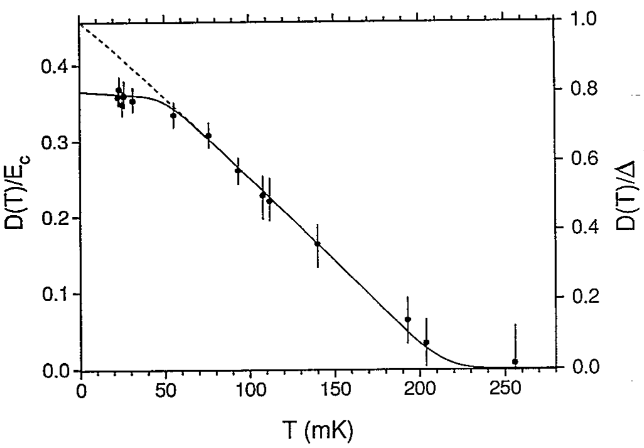


FIG. 5. Difference $D$ between the free energies of the island with an odd and an even number of electrons as a function of temperature. Experimental values (dots) are directly measured in units of $E_c$. Dashed line is a theoretical expression of $D(T)/\Delta$ (scale on the right-hand side), assuming a continuous BCS density of states, $\rho_A=0.572\ \mathrm{eV}^{-1}$, $N_A=38\times 10^7$, and $\Delta^{\mathrm{fit}}/e=195\ \mu\mathrm{V}$ (see text). Full line is a modified expression corresponding to a single, twofold degenerate state added at $0.8\Delta$. The vertical scale factors of theory and experiment coincide for $C_\Sigma^{\mathrm{fit}}=0.19$ fF.

continuous BCS density of states, it includes a single, twofold degenerate, quasiparticle state at $0.8\Delta$. Even though the number of available states at the gap $\Delta$ is of the order of $N_0\sim 10^4$, the behavior of the box at the lowest temperatures is completely dominated by this single state. This box experiment is thus a very sensitive quantitative probe of the deviations of the density of states from the ideal BCS form, in contrast with transport measurements [4,11,12]. It is remarkable that the sample imperfections like surface states and impurities do not lead to a more severe suppression of the even-odd asymmetry. Additional experiments (data not shown) showed that $D(T=25\ \mathrm{mK})$ decreases under the application of a magnetic field applied perpendicularly to the plane of the substrate and vanished at 0.1 T, a reasonable critical field value given the dimension of the island [15].

In conclusion, we have measured the free energy cost of putting a single extra electron in a superconducting island. We have found that this energy depends on the parity of the total number of electrons in the island and is in good agreement with theoretical predictions based on Tuominen *et al.* [4] assuming a continuous BCS density of quasiparticle states. At the lowest temperatures, though, the experiment is sensitive to individual discrete states and the results are better accounted for if one incorporates in the theory a single energy level inside the gap.

We acknowledge fruitful discussions with A. Cleland, T. Eiles, J. Martinis, G. Sarma, G. Schön, and J. Schrieffer, as well as the technical help of P. F. Orfila.

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