Two-electron quantization of the charge on a superconductor

P. Lafarge, P. Joyez, D. Esteve, C. Urbina & M. H. Devoret

Service de Physique de l'Etat Condensé, CEA-Saclay, F-91191 Gif-sur-Yvette, France

THE theoretical understanding of superconductors is based on the notion of electron pairing into Cooper pairs[1]. The first direct evidence for electron pairing was the observation that the flux threading a superconducting ring is always a multiple of the flux quantum, given by the ratio of Planck's constant to the Cooper-pair charge 2*e* (refs 2, 3). Here we report a direct measurement of the total charge on a superconducting electrode which is free to exchange electrons with a metallic reservoir through a tunnel junction. The total charge on a non-superconducting metal electrode has been shown previously[4] to increase in jumps of 1*e*, corresponding to the addition of single electrons. We have also observed steps of 1*e*, with an even–odd asymmetry, for a superconducting electrode when the charging energy exceeds the energy gap between the ground and first excited superconducting state[5]. Our present measurements, with the charging energy below the gap, reveal charging steps strictly quantized in units of 2*e*, corresponding to the simultaneous tunnelling of two electrons. The 2*e* steps break into 1*e* steps when the temperature and magnetic field are increased above threshold values, corresponding to the electrostatic breaking of a single Cooper pair. Our results indicate that Cooper pairs can be manipulated in the same way as single electrons in turnstile and pump devices[4].

Figure 1 shows a schematic diagram of the experiment. A Cu–Al_2O_3–Al tunnel junction of capacitance C_j in series with a

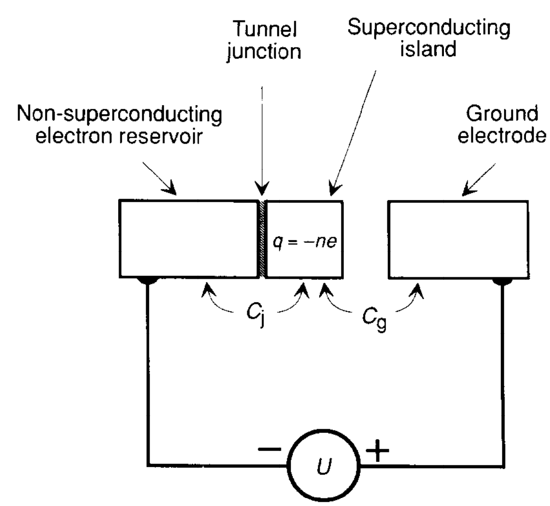

FIG. 1 Schematic diagram of the experiment. The superconducting island is a 30 × 110 × 2,260 nm Al strip containing ~10^9 atoms. Its dimensions are such that the electrostatic energy of one extra electron is much larger than the energy k_BT of thermal fluctuations at temperature T ~ 30 mK. The island can exchange electrons with a Cu (3 wt% Al) thin-film electrode (which acts as an electron reservoir) through a tunnel junction[17]. The total charge q of the island varies under the influence of the externally controlled voltage source U connected between the electron reservoir and a ground electrode. The variation with U of the time average $\bar{q}$ of the island charge is measured by a Coulomb blockade electrometer (not shown) which is weakly capacitively coupled to the island. The nanofabrication and low-noise measurement techniques involved in this type of experiment have been described in refs 5 and 18.

capacitor C_g is biased by a voltage source U. The aluminium electrode which is common to both the junction and the capacitor, the 'island', is surrounded by insulating material. Because the junction tunnel resistance R_t is such that $R_t \gg R_K = h/e^2$, the total charge q of the island is a good quantum number and is given by $q = -ne$ (ref. 6). As U increases, electrons will tend to move into the island to minimize the total energy of the circuit, which is the sum of its electrostatic energy and of the internal energy of the island[7]. The fluctuations of n are determined by the ratio between the energy of thermal fluctuations and the Coulomb energy $E_c = e^2/2(C_j + C_g)$, which is the electrostatic energy cost of putting one extra electron on the island when $U = 0$. By nanofabricating the circuit of Fig. 1, E_c can be made of the order of 2 K. By lowering the circuit temperature to ~30 mK, we can ensure that n has negligible fluctuations and adopts the minimum energy value. This is demonstrated by the following control experiment. We placed the island in the non-superconducting state by applying a magnetic field (0.2 T) and measured the variations of the time-averaged charge $\bar{q}$ with voltage U, using a Coulomb blockade electrometer[8] operated in a feedback mode. The data are shown in Fig. 2*a*. If q was not quantized, the circuit would achieve an equilibrium charge configuration with no potential difference on the junction capacitance C_j and hence, $\bar{q} = C_g U$. Because q is quantized, $\bar{q}$ can only increase in steps, which are located at half-integer values of the reduced voltage $C_g U/e$.

We then placed the island in the superconducting state by suppressing the magnetic field. The results are shown in Fig. 2*c*. There is again a stepwise variation of $\bar{q}$ versus U, but the height and length of the steps have doubled, indicating that only electron pairs are transferred from the reservoir into the island. When we applied an intermediate magnetic field, so as to reduce substantially the superconducting gap without suppressing superconductivity, we observed an intermediate staircase pattern that consisted of a succession of long and short e-steps (Fig. 2*b*). This was similar to the pattern observed in a previous experiment involving a different sample[5]. The ratio between the length of the short (S) and long (L) steps was observed to decrease as we lowered the field. Below a threshold field $H = 0.02$ T, the short steps disappeared completely and perfect $2e$-quantization was recovered.

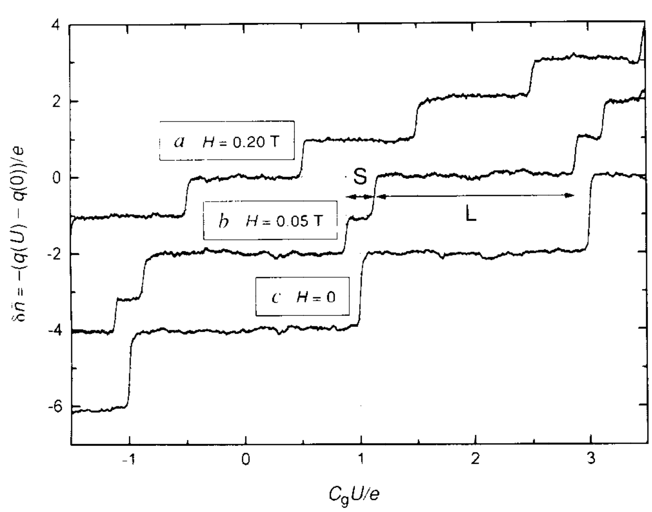

FIG. 2 Variations of the average value $\bar{q}$, in units of e, with the polarization C_gU/e, at $T = 28$ mK, for three values of the magnetic field H applied to the sample. *a*, Non-superconducting island. *b* and *c*, Superconducting island. For clarity, *b* and *c* have been offset vertically by 2 and 4 units, respectively. The letters L and S refer to the long and short steps, respectively.

These results can be understood by considering the total free energy of the circuit: $E = E_c(n - C_gU/e)^2 + (n \bmod 2)\tilde{\Delta} +$ terms independent of n. The first term is simply the electrostatic energy of the circuit, that is the electrostatic energy of C_j and C_g and the work of the voltage source U (ref. 7). The second term is the island internal energy which depends on n only through its parity[9], the parameter $\tilde{\Delta}$ denoting the odd–even free energy difference[10]. Such an odd–even difference is expected for a superconductor, because given an odd number of electrons, one of them cannot be paired and must remain as a quasiparticle excitation the energy cost of which is the superconducting energy gap. From this model we can predict the ensemble average $\langle n \rangle$ which we suppose equal to the temporal average $\bar{n}$ measured in

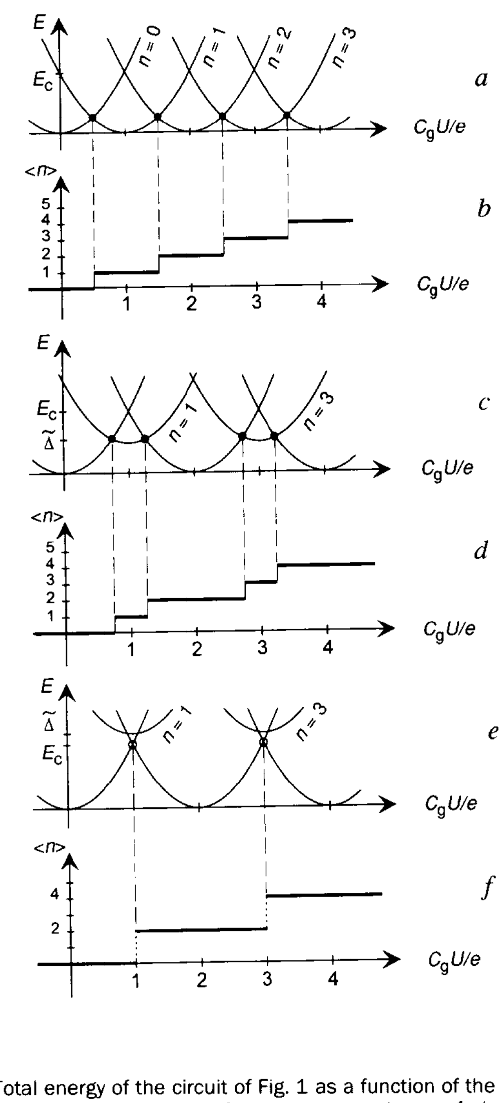

FIG. 3 Total energy of the circuit of Fig. 1 as a function of the polarization C_gU/e, for several values of the excess number n of electrons in the island, in the non-superconducting state (*a*) and superconducting state (*c*, *e*). E_c is the electrostatic energy of one excess electron on the island for $U = 0$. The minimum energy for odd n is $\tilde{\Delta}$ above the minimum energy for even n. Panels c and e differ by the relative magnitude of $\tilde{\Delta}$ and E_c. The black dots correspond to level crossings where a single electron tunnels into and out of the island. The hollow circles correspond to level crossings where the only allowed process is the simultaneous tunnelling of two electrons into the island to form a pair (Andreev process). The equilibrium value $\langle n \rangle$ versus C_gU/e is shown in the non-superconducting (*b*) and superconducting (*d*, *f*) states, at $T = 0$. The Andreev process is shown in *f* by a vertical dashed line to distinguish it from the single electron tunnelling process shown in *b* and *d* by a vertical continuous line.

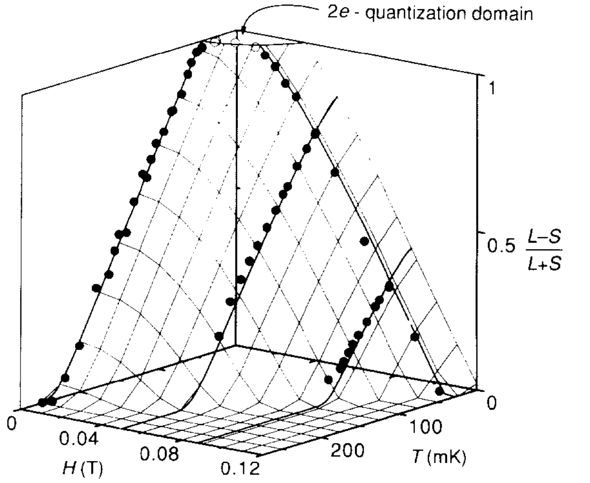

FIG. 4 Odd–even step-length ratio, plotted as $(L-S)/(L+S)$, as a function of the temperature T and magnetic field H. The fully 2e-quantized steps are shown as hollow circles with unit height. The black dots are such that $1>(L-S)/(L+S)=\tilde{\Delta}/E_c$. The surface defined by the grid is the theoretical prediction combining references 5, 10, 15 and 16. Note that the 2e-quantization domain is only a small portion of the odd–even asymmetry domain ($\tilde{\Delta}>0$) which is itself a small part of the superconductivity domain ($\Delta>0$).

the experiment. In Fig. 3*a* we show, as a function of U, the energy of the different n states for the non-superconducting case $\tilde{\Delta}=0$. At temperatures T such that $k_BT \ll E_c$, n will adopt the value of the integer closest to C_gU/e, which corresponds to the lowest energy state, hence the staircase pattern of Fig. 3*b*. In Fig. 3*e* we show the case of a superconducting island such that, at the lowest temperatures, $\tilde{\Delta}>E_c$ in zero magnetic field. In that case, for every value of U, the ground state of the circuit always corresponds to an even n, which explains the doubling in Fig. 3*f* of the step height compared to Fig. 3*b*. The energy asymmetry between states with even and odd n has recently been observed through the 2*e*-periodicity of the gate-charge dependence of the current in Coulomb blockade electrometers with a superconducting island[10-12] and of the asymmetric *e*-staircase of a superconducting box[5]. It is important to note that although 2*e*-quantization implies necessarily 2*e*-periodicity, the converse is not true, as shown by Fig. 3*d*. The results reported here reveal new information: direct transitions between fully paired even states, which do not create a quasiparticle excitation, can be the sole charge-transfer mechanism, provided that $\tilde{\Delta}>E_c \gg k_BT$, conditions which could not be satisfied in previous island-charge measurements. This perfect 2*e*-quantization necessitates that the system finds, as U is increased, its lowest energy state by the coherent tunnelling of two electrons from the reservoir into the island to form a Cooper pair. The rate of this process, also known as Andreev reflection[13] is proportional to $(R_K/R_t)^2$ (ref. 14) and is therefore much weaker than single-electron tunnelling, the rate of which is proportional to R_K/R_t. Nevertheless, because the 2*e*-steps of Fig. 2*c* did not display any measurable out-of-equilibrium behaviour, the timescale of the Andreev process is shorter than our measurement timescale which is of the order of 10^{-2} s.

At intermediate magnetic fields and temperatures (Fig. 3*c*), the odd–even free-energy difference, although non-zero, is such that $\tilde{\Delta}<E_c$. Odd-n states can now exist in a finite U range (Fig. 3*d*). In this regime, we can measure $\tilde{\Delta}/E_c$ from the length ratio S/L of the short and long steps. This can be done quite accurately because the sharpness of the steps makes S/L insensitive to the long-term drift in the electrometer output due to offset charges[7]. The measurement of $(L-S)/L+S)=\tilde{\Delta}/E_c$ with temperature and magnetic field, which was applied perpendicularly to the strip, is shown in Fig. 4. At a fixed magnetic field, we found that we could fit the measured $\tilde{\Delta}(T)/E_c$ using the theory of refs 5 and 9 with the quasiparticle density of states of Skalski *et al.*[15], in which only one field-dependent parameter occurs, namely the pair-breaking energy Γ. The other parameter in this expression for the density of states is the zero-temperature zero-field energy gap Δ. Using the de Gennes and Tinkham prediction $\Gamma/\Delta=(\pi^3/18)H^2d^2\ell\xi_0/\Phi_0^2$ for a strip of dirty superconductor in a perpendicular field H (ref. 16), we derived a theoretical expression for $\tilde{\Delta}(T,H)/E_c$ which depends only on three parameters: the gap Δ, the Coulomb energy E_c and the elastic mean free path ℓ (in the expression for Γ, d (=110 nm) is the width of the strip, ξ_0 (=1600 nm) is the coherence length and Φ_0 is the flux quantum $h/2e$). The best fit, shown in Fig. 4, yields $\Delta/e=210\ \mu V$, $\Delta/E_c=1.23$, values that are consistent with independent measurements, and $\ell=6$ nm. This latter value is one order of magnitude smaller than the mean free path we extracted from a conductivity measurement of a nanofabricated Al wire with same lateral dimensions as the island. This discrepancy may, however, simply reflect the fact that electron diffusion is not isotropic in the island; the main result shown in Fig. 4 is that 2*e*-quantization occurs in only a small portion of the superconductivity domain. □

Received 4 May; accepted 17 August 1993.

1. Bardeen, J., Cooper, L. N. & Schrieffer, J. R. *Phys. Rev.* **108**, 1175–1204 (1957).
2. Deaver, B. S. & Fairbank, W. M. *Phys. Rev. Lett.* **7**, 43–47 (1961).
3. Doll, D. & Näbauer, M. *Phys. Rev. Lett.* **7**, 51–55 (1961).
4. Devoret, M. H., Esteve, D. & Urbina, C. *Nature* **360**, 547–553 (1992).
5. Lafarge, P., Joyez, P., Esteve, D., Urbina, C. & Devoret, M. H. *Phys. Rev. Lett.* **70**, 994–998 (1993).
6. Grabert, H. *Proc. 20th Low-Temperature Phys. Conf.* (Elsevier, Amsterdam, in the press).
7. Averin, D. V. & Likharev, K. K. in *Mesoscopic Phenomena in Solids* (eds Altshuler, B., Lee, P. A. & Webb, R. A.) 173 (Elsevier, Amsterdam, 1991).
8. Fulton, T. A. & Dolan, G. J. *Phys. Rev. Lett.* **59**, 109–113 (1987).
9. Averin, D. V. & Nazarov, Yu, V. *Phys. Rev. Lett.* **69**, 1993–1996 (1992).
10. Tuominen, M. T., Hergenrother, J. M., Tighe, T. S. & Tinkham, M. *Phys. Rev. Lett.* **69**, 1997–2001 (1992).
11. Eiles, T. M., Martinis, J. M. & Devoret, M. H. *Phys. Rev. Lett.* **70**, 1862–1866 (1993).
12. Tuominen, M. T., Hergenrother, J. M., Tighe, T. S. & Tinkham, M. *Phys. Rev.* B (in the press).
13. Andreev, A. F. *Zh. eksp. teor. Fiz.* **46**, 1823 (1964); also as *Soviet. Phys. JETP* **19**, 1228–1231 (1964).
14. Hekking, F. W. J., Glazman, L. I., Matveev, K. A. & Shekter, R. I. *Phys. Rev. Lett.* **70**, 4138–4141 (1993).
15. Skalski, S., Betbeder-Matibet, O. & Weiss, P. R. *Phys. Rev.* **A136**, 1500–1518 (1964).
16. de Gennes, P. G. & Tinkham, M. *Physics* **1**, 107–126 (1964).
17. Clarke, J. in *Non-equilibrium Superconductivity* (eds Langenberg, D. N. & Larkin, A. I.) 1 (Elsevier, Amersterdam, 1983).
18. Lafarge, P. *et al. Z. Phys.* **B85**, 327–332 (1991).

ACKNOWLEDGEMENTS. We thank P. F. Orfila for technical assistance, and T. Eiles and J. Martinis for discussions. This work was partly supported by the Bureau National de la Métrologie.