Incremental Charging of Single Small Particles

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We report the first observation of the incremental charging of single isolated small particles, which act as a common electrode in a series configuration of two small-capacitance tunnel junctions. The steplike structures in the I-V characteristic, due to the quantization of the charge on the small particle, can be well described by a Monte Carlo simulation. We discuss the observation of an apparent bistability and of discrete voltage shifts of the step structure, possibly induced by the ionization of single impurity states in the oxide layer.

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Recent theoretical predictions have revived interest in the macroscopic quantum effects that can be observed in small-capacitance tunnel junctions, where the fundamental macroscopic charging energy $e^2/2C$ of the capacitor C is much larger than the thermal energy k_BT. For small voltages across the capacitor the tunneling probability is strongly reduced as a result of the so-called Coulomb blockade. In that case it is predicted[1-3] that the tunneling process in a current-biased junction is no longer of a purely stochastic nature, but becomes more or less coherent (single-electron tunneling), at a frequency $\nu = I/e$. As a result the voltage across the junction will oscillate with the same frequency, and could in principle be used to define a "quantum" standard for the current.

Another interesting phenomenon can be observed in systems composed of two tunnel junctions in series, with a small common electrode.[1,4] The net charge on the central electrode will be quantized in units of the electron charge. The I-V characteristic of such a configuration will display current steps at equal voltage intervals (the so-called Coulomb staircase or incremental charging effect). It can be shown that the size of these intervals is inversely proportional to the larger of the two junction capacitances: $\Delta V = e/C_2$, $C_2 > C_1$. At a temperature of 1 K the effects should be observable in capacitances below 10^{-15} F.

The basic effects associated with low-capacitance tunnel junctions have already been studied several years ago.[5,6] Only recently were new experimental techniques exploited to study the effects of single-electron tunneling in a single small junction.[7,8]

The Coulomb staircase has recently been observed by Barner and Ruggiero[9] in a structure consisting of a granular layer of Ag particles embedded in the oxide layer between two continuous Ag or Cu films. This configuration can be seen as a parallel array of a very large number of junctions. Because of variations in particle size the effect could only be observed in an averaged way. The observation of the Coulomb staircase in a configuration where most of the tunnel current flows through only a few grains has been reported by Kuz'min and Likharev.[10]

In this Letter we report the first observation of the Coulomb staircase due to the incremental charging of single metallic grains, using a scanning tunneling microscope. We compare the results with quantitative calculations based on Monte Carlo simulations, and obtain good agreement. In addition we describe the observation of an apparent bistable behavior of current steps at even ($V = \pm ne/C_2$) or odd [$V = \pm(2n+1)e/2C_2$] positions, where n is a positive integer. A second possibly related phenomenon is the observation of discrete phase shifts of the staircase structure, probably due to the ionization of single impurity states in the oxide layer.

The samples used in our experiments consist of a 35–40-Å granular Al film on top of a thick (500 Å) oxidized continuous Al film. The experimental setup consists of a very compact low-temperature scanning tunneling microscope, immersed in a liquid-helium bath, which is pumped to a temperature of 1.2 K. The I-V and dI/dV-V characteristics were measured with the scanning tunneling microscope feedback system switched off, with a dc voltage source.

When the tip is positioned above a metal grain a tunnel junction is formed between the tip and the grain, in series with a second junction between grain and base electrode. As discussed in Ref. 8, capacitances of the order of 5×10^{-18} F can easily be established in this type of point contacts. The capacitance and tunnel resistance of a point contact can be varied by the adjustment of the distance between tip and grain.

Figure 1 shows the I-V and corresponding dI/dV-V characteristics of a point contact on a granular-Al/oxide/Al double layer. The peaks in dI/dV correspond to clearly observable stepwise increments of the current in the I-V curve. The peaks show up in a periodic pattern with a period of $\langle\Delta V\rangle = 15.0 \pm 1.6$ mV. Assuming that $\Delta V = e/C_2$, we derive a capacitance $C_2 = 1.1\times10^{-17}$ F. For voltages smaller than $\Delta V/2$ the current is strongly suppressed. This range is much wider than the voltage which can be associated with the energy gap of superconducting aluminum, even in the case of an increased critical temperature due to the small size of

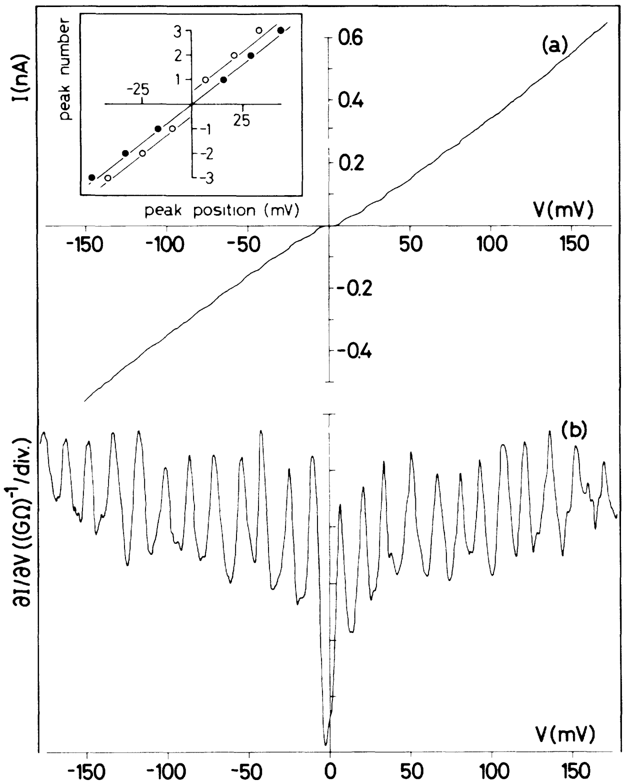

FIG. 1. (a) I-V and (b) dI/dV-V characteristics of a point contact on a sample consisting of a granular Al film (35 Å) deposited on an oxidized continuous Al film (500 Å). Inset: The positions of the successive low-voltage peaks in (b) (open circles) and of a similar trace taken on the same contact immediately afterwards (filled circles).

the grains. The open circles in the inset of Fig. 1 indicate the positions of the low-voltage peaks in Fig. 1(b) [$V=\pm(2n+1)\Delta V/2$]. The filled circles represent the peak positions of a second dI/dV-V characteristic, measured immediately after Fig. 1(b). In this case the peaks are at even positions ($V=\pm n\Delta V$). The fact that the step structure switches between even and odd positions has been observed in all contacts.

Also in many cases at higher voltages discrete current jumps appear in the I-V characteristic, accompanied by discrete shifts in the peak structure. This shift can be of arbitrary value, but after the shift the distance between adjacent peaks remains the same as before. In many cases the current switches back and forth between two stable I-V characteristics.

At present it is not clear whether the apparent bistability is fundamental—for example, due to resonance effects. Such a discrete shift cannot be explained in terms of a polarization of the oxide layer, as proposed by Kuz'min and Likharev.[10] We suggest that in our case electrons can get trapped in single localized impurity states in the oxide layer. The trapped charge then changes the potential on the particle, and thus shifts the positions of the peaks or equivalently the positions of the steps. It is possible that in this case the step which is closest to zero disappears because of the Coulomb blockade, and the apparent distance between the two steps around zero bias has doubled to $2e/C_2$.

The Coulomb staircase and the other effects mentioned above could be observed on several contacts and on all, similar, samples. Measured capacitances vary between 5.5×10^{-18} and 1.1×10^{-17} F, while the tunnel resistances vary between 5×10^{6} and 9×10^{8} Ω. The capacitance of a metal grain with respect to the continuous film can be estimated by use of $C=\epsilon_0\epsilon_r A/d$, with A the area of the grain and d the thickness of the oxide layer. Taking $\epsilon_r=8$, $A=(100\text{ Å})^2$, and $d=10$ Å, we calculate a capacitance of 5.5×10^{-18} F, in good agreement with the measured values.

The effects described above can occasionally also be observed in tunneling experiments on materials that contain naturally oxidized conducting particles. In Fig. 2(a) we have reproduced an example of an I-V characteristic of a junction between a tungsten tip and a single crystal

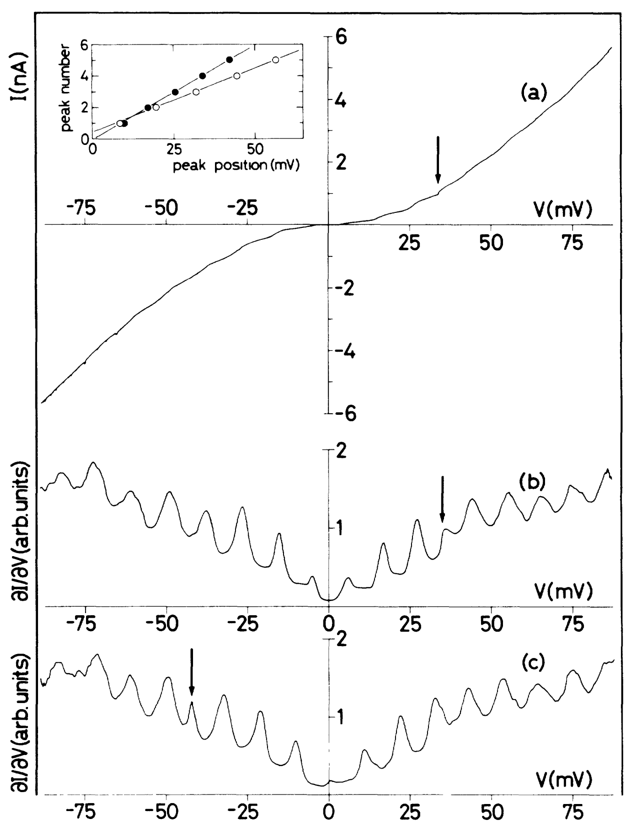

FIG. 2. (a) I-V characteristics and (b) corresponding dI/dV-V characteristics of a point contact on a single-crystal $YBa_2Cu_3O_7$ sample. (c) A dI/dV-V trace taken at the same point contact immediately after the measurement represented by (a) and (b). Inset: The peak positions for two other tip-sample distances.

of the new high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$, which was probably covered with some small conducting particles coming from the melt in which the crystal was grown. We again observe a regular, equidistant series of steps in the *I-V* characteristics, and corresponding peaks in dI/dV-V, as shown in Fig. 2(b), which was recorded simultaneously with Fig. 2(a). In Fig. 2(c) we have plotted a second dI/dV-V curve, which was measured immediately after Figs. 2(a) and 2(b). This again illustrates the bistable behavior mentioned above.

By our increasing the distance between tip and sample (decreasing one of the two capacitances), the voltage spacing between the peaks could be increased by roughly 50%. In the inset of Fig. 2 we have plotted the peak positions in dI/dV at two different tip-sample separations. The fact that the periodicity of the step structure can be tuned by variation of the capacitance is a clear proof of the Coulomb charging effect, and rules out other possible explanations based on multiple energy gaps in the superconductor, or quantum size effects in the small particles. Most of the curves recorded on this point contact also displayed the occasional shifts in the position of the peaks in dI/dV at higher voltages, accompanied by a small sharp change in the current, as indicated by arrows in Fig. 2.

The periodic peak structure in dI/dV can easily be mistaken for the energy gap in this high-T_c superconductor. One should therefore be cautious to interpret tunneling results which show multiple peak structures as indications for (multiple) energy gaps. The above analysis, in particular the dependence of the voltage spacing between the peaks on the distance between tip and surface, can be used to distinguish unambiguously between the two different phenomena.

Let us finally turn to a more quantitative theoretical analysis of the experimental results. For this purpose we will use a semiclassical approach, based on Monte Carlo simulations. We start with a voltage difference V_0 across the series configuration of two junctions with tunnel resistances R_1,R_2 and capacitances C_1,C_2. The potential of the central electrode can be approximated by $V_1=V_0C_2/(C_1+C_2)$. Now consider the case that an electron tunnels across the junction R_1,C_1. In the case of an isolated current-biased junction this would lead to a relative shift of the Fermi energy ϵ_F by $e/2C_1$ at both sides of the junction as the net charge on the capacitor changes by e. The "missing" charge is then supplied from the leads, driven by the gradient in ϵ_F. It is usually not correct to assume that a strict voltage bias can be realized in practice. Because of the finite bandwidth, or *RC* time, of the electrical circuit the junction is effectively current biased for all phenomena that occur at very short time scales and the external supply mainly serves to fix the time-averaged voltage $\langle V_0\rangle$. This is, for example, illustrated by the fact that in the same nominally voltage-biased setup we observed a clear manifestation of a Coulomb blockade,[8] which can only occur if the junction is essentially current biased.

In the case of two junctions with a small common electrode the excess charge on the particle is rapidly redistributed until the Fermi energy is equal at both sides of the small particle. The intermediate equilibrium state is then a situation where the Fermi levels both of the outer point of the tip and of the local area of the base electrode are temporarily decreased by $e/2(C_1+C_2)$, while the Fermi energy of the particle increases by the same amount. The tunneling probability for the above process is proportional to the number of available states on the particle, or in other words proportional to $V_0-V_1-e/2(C_1+C_2)$. The rapid redistribution of the charge on the small particle leads to an effective decrease of the Coulomb blockade to $e/2(C_1+C_2)$ instead of $e/2C_1$ for a single junction.

The various tunneling processes can now be cast into the form of a Monte Carlo simulation where the various tunneling probabilities depend on the instantaneous potential differences. Upon completion of this analysis we learned of the work by Mullen *et al.*[4] Their approach leads essentially to the same results. A major difference is that their model is based on the assumption of a strictly voltage biased configuration.

A typical result of our Monte Carlo simulation is shown in Fig. 3. The shape of the steps depends strongly on the ratios C_1/C_2 and R_1/R_2. If these ratios are close to unity, the step structures are strongly smeared out and only the first step can be discerned. In Fig. 3 we have reproduced a calculation where $C_2=1.6\times10^{-17}$ F, $C_1=3.2\times10^{-18}$ F, and $R_2/R_1=5$. In Fig. 4 we compare the low-voltage part of the experimental *I-V* curves shown already in Fig. 1 and Fig. 2 with two calculations

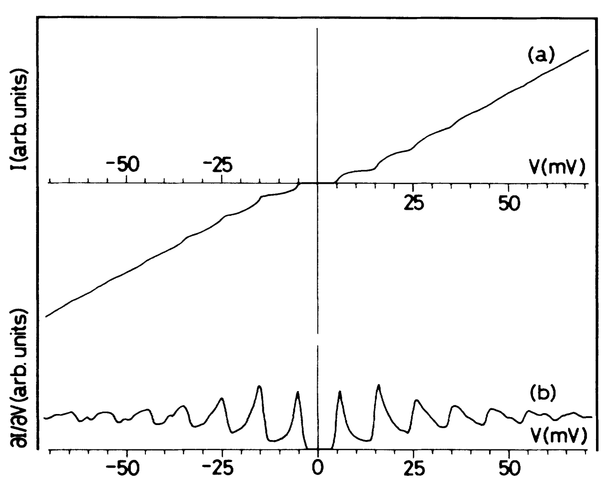

FIG. 3. (a) *I-V* characteristic and (b) dI/dV-V characteristics calculated from Monte Carlo simulations, as described in the text, for $C_1=3.2\times10^{-18}$ F, $C_2=1.6\times10^{-17}$ F, and $R_2/R_1=5$.

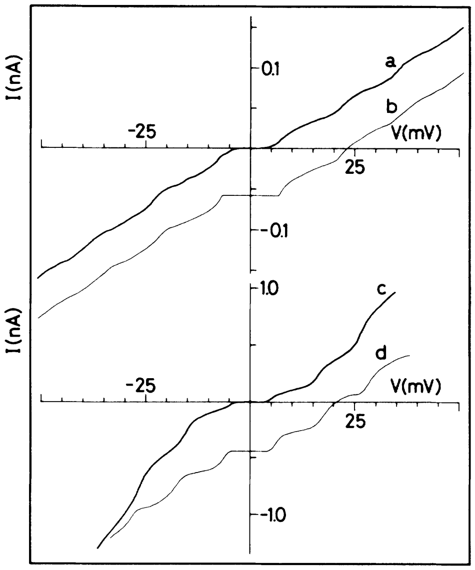

FIG. 4. Comparison of measured and calculated *I-V* characteristics. Curve *a* represents the low-voltage part of Fig. 1(a). Curve *b* is a numerical calculation for $C_1=5\times10^{-18}$ F, $C_2=1\times10^{-17}$ F, and $R_2/R_1=5$. Curve *c* is the low-voltage part of the *I-V* characteristic in Fig. 2(a). Curve *d* is a numerical calculation for $C_1=3.2\times10^{-18}$ F, $C_2=1.6\times10^{-17}$ F, and $R_2/R_1=5$. Both theoretical curves are displaced along the *y* axis for clarity.

for different assumptions of their resistance and capacitance ratios, as indicated in the caption. The agreement for both the dc *I-V* characteristics and the *dI/dV-V* characteristics is quite satisfactory.

In conclusion, we have observed the incremental charging of a single isolated small particle in two very different systems. The results are in good agreement with a quantitative calculation based on a Monte Carlo simulation. In addition, we observe an apparent bistability in the *I-V* characteristics, and discrete voltage shifts in the structure, probably induced by the ionization of single impurity states in the oxide layer.

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