Observation of the Incremental Charging of Ag Particles by Single Electrons

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We have studied electron tunneling in ultralow-capacitance silver particles sandwiched between artificial tunnel barriers. We have observed steps in the current-voltage characteristics of these systems with voltage widths of e/C (C being the capacitance of the particles), and associated current rises of e/RC. This represents the first observation of the so-called Coulomb staircase, expected for the charging of particles with extremely small capacitance by a discrete number of electrons.

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Very recently, excitement has been generated by the realization that with currently developed materials-preparation techniques, it should be possible to observe the charging of metal particles by a small and countable number of electrons. Indeed, by employing recently developed techniques for the preparation of artificial electron tunnel barriers, we have performed tunneling studies of Ag particles sandwiched between these barriers in structures of the form metal/barrier/particles/barrier/metal, wherein such effects have been observed. We discuss in this Letter tunneling measurements which reveal clear, periodic modulations of the dc and ac conductance as a function of voltage corresponding to the occupation of ultralow-capacitance silver particles by discrete numbers of electrons.

Begun originally by Giaever and Zeller[1] to see whether superconductivity would persist in dimensionally restricted samples, the study of tunneling in small metal particles has been of continual interest because of the myriad outstanding questions regarding the nature of conductors on an ultrasmall scale. Recently, tunneling in small-particle and granular systems has been employed as a natural means of studying Coulomb and localization effects, which tend to be amplified in such systems. The subject has been approached from the standpoint of temperature and finite-frequency effects theoretically by Ho[2] and experimentally by Cavicchi and Silsbee[3] by means of tunnel-capacitor structures of the type originally described by Lambe and Jaklevic.[4] Transport measurements have also been made by Raven[5] in small-particle systems, and tunneling investigations have been performed by White, Dynes, and Garno[6] in granular materials, the latter in conjunction with the study of localization and interaction effects.

The goal of the present work is the direct observation of the charging of particles by small, countable numbers of electrons. To accomplish this, we performed tunneling measurements of ultralow-capacitance ($< 10^{-17}$ F) Ag particles wherein the charging voltage corresponding to a single electron, e/C, is in an easily measurable range ($> 10^{-2}$ V).

The systems studied consist of structures containing a layer of isolated Ag particles sandwiched between well-defined artificial tunnel barriers. These systems were prepared by the layer-by-layer deposition of thin films as follows: base electrode/barrier/particles/barrier/counterelectrode. The barriers consist of sputter-deposited Al_2O_3 films in the 25- to 40-Å thickness range. As previously discussed,[7] these films consistently exhibit the large barrier heights (> 1 eV) and low leakage currents ($\approx 0.1\%$) representative of high-quality electron tunnel barriers. The base electrode and counterelectrode are normally 500- to 2000-Å Cu or Ag films. The particle layers consist of thin (75 Å as measured by an evaporation-rate monitor) thermally evaporated Ag films, which exhibit island formation. The active area of the junctions was 0.025×0.025 cm^2, and the resistance of a given junction was normally in the range of 1–100 MΩ.

The layer of particles into which tunneling occurs consists of isolated, well-defined Ag particles. A scanning electron micrograph of a sample consisting of a nominal 75-Å Ag film deposited on an Al_2O_3 layer, in the same way as tunnel junctions are prepared, is shown in Fig. 1. The picture clearly shows the presence of Ag particles. Careful measurements of particle size from this and additional micrographs give a mean diameter of 75 Å and a standard deviation, σ, of $\simeq 20\%$ of the mean particle area. Although large clusters are in evidence, they are few in number and occur in the expected statistical proportions. Electron-diffraction studies show the particles to be crystalline (the inset shows a representative diffraction picture). A more detailed discussion of the sample preparation and materials properties of these systems will be included in a future regular article.

In the context of the semiclassical picture,[8-10] one expects for tunneling into ultrasmall-capacitance particles an initial voltage gap of $e/2C$, leading to an overall offset in the current-versus-voltage curve. Secondly, and more strikingly, it has been recently shown[11] that for the voltage-controlled case, a series of steps in the current-versus-voltage characteristics should also appear; in this case, with a voltage spacing of e/C. Simply said, the first "Coulomb gap" is due to the charging energy of a capacitor by a single electron, whereas the subsequent series

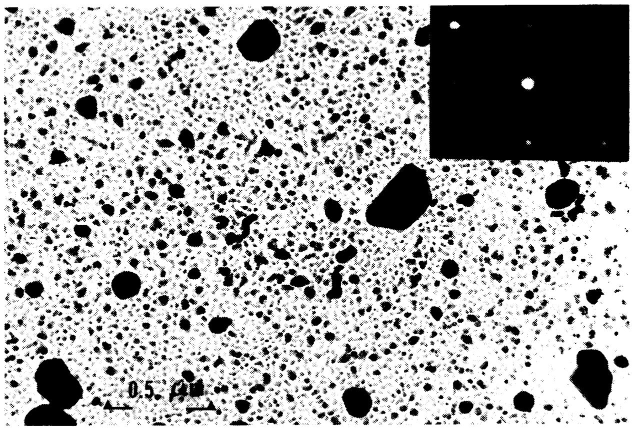

FIG. 1. Transmission-electron micrograph of Ag particles deposited on an amorphous Al_2O_3 surface, prepared in the same manner as for completed tunnel structures. The average size of the smaller particles, which are numerically dominant in the picture, is comparable to the nominal film thickness of 75 Å (magnification here is 66×10^3). The inset shows a typical electron-diffraction pattern for the particles, indicating a crystalline structure.

of gaps is due to the quantization of electronic charge which constrains the sustainable voltage difference between the particles and an electrode to ne/C, where $n=0, 1, 2, \ldots$. Taken together, these effects should result in a series of steps with a 1, 3, 5, . . . sequence in units of $e/2C$ starting from zero bias. These steps should be observable for temperatures $kT < e^2/2C$.

The origin of the behavior can be seen by consideration of a single particle situated between two electrodes. The capacitance of and potential difference between the particle and electrodes 1 and 2 are taken as C_1, V_1, and C_2, V_2, respectively. The voltage across the electrodes, the external voltage, is $V = V_{ext} = V_1 + V_2$, where $V_1 = V_{ext}C_2/(C_1+C_2)$ and $V_2 = V_{ext}C_1/(C_1+C_2)$. Thus V_1 and V_2 are proportional to V_{ext}. If we take $C_2 > C_1, V_{ext} > 0$, and define electrode 1 to be at zero potential, then $V_1 > V_2$. Thus, in order for the metal particle to take on an additional electron, V_{ext} must be increased to the point where, after accepting an electron, the particle potential V_1 remains positive. Otherwise the electron will tend to tunnel back to where it came from. If V_{ext} is held fixed and an additional electron is placed on the particle, then the potential V_1 will change to an amount $\Delta V_1 = -e/(C_1+C_2)$, as can be seen by an elementary calculation. Hence, V_{ext} must be increased sufficiently to compensate for this such that

$$|\Delta V_1| = \Delta V_{ext} C_2/(C_1+C_2) = e/(C_1+C_2).$$

Thus, in order for the particle to accept an additional electron, we must increase the external voltage by an amount

$$\Delta V_{ext} = e/C, \tag{1}$$

where here $C = C_2$.

Therefore, the number of electrons on the particle, n, will be determined by the external voltage and the (larger) capacitance. Since, as discussed in the semiclassical model,[8-10] an energy $e^2/2C$ is required to place the first electron in the particle, the first state, $n=0$, occurs over the voltage range $-e/2C < V_{ext} < e/2C$. Therefore, for $n=1$, $-e/2C < V_{ext} < 3e/2C$; for $n=2$, $3e/2C < V_{ext} < 5e/2C$, etc. This same series will arise for negative bias ($V_{ext} < 0$) as well.

Note that although we can fix the average number of electrons residing on a particle, finite resistances R_1 and R_2 imply that electrons will enter and leave at a fixed rate. If $R = R_2 > R_1$ then this rate will be $\tau = 1/RC$. Thus as n changes its value in response to V_{ext}, the current I will increase in a series of jumps of magnitude

$$\Delta I = e/RC \tag{2}$$

and will be constant over those voltage ranges where n is constant. The only exception is the first current step where $\Delta I = e/2RC$, again because of the initial charging energy. Note that if there are N particles, each with an average resistance R_2, then the magnitude of the current jumps becomes $\Delta I = N(e/R_2C) = e/RC$, where R is now the total (external) resistance of the entire system.

Taken together, these effects produce a series of steps as shown in the inset of Fig. 1, the so-called "Coulomb staircase." The steps have a voltage width of e/C and a current rise of (except for the first step) e/RC. Since the magnitude of the first current rise is $e/2RC$, a characteristic offset in the current-voltage curve is produced which appears as a shift in voltage of $e/2C$ about zero bias, as indicated by the dotted line.

With these results in mind, we present in Fig. 2 the current-voltage characteristic of a system of Ag particles, prepared identically as those shown in Fig. 1. These data represent the first observation of the Coulomb staircase as predicted above. Both the overall offset in the curve from zero bias and the periodic, steplike structure predicted by theory (and schematically depicted in the figure) are quite discernable. Evident are both horizontal voltage steps of magnitude e/C and corresponding vertical current jumps of magnitude e/RC. Taking a value of $e/C = 27$ mV (as discussed below) and the measured junction resistance of 38.8 MΩ, we find $\Delta I = e/RC = 0.696$ nA. The measured value of ΔI from Fig. 2 is seen to be ≈ 0.720 nA, consistent with the above.

For such direct-current measurements as shown in Fig. 2, however, the large resistance involved makes for a significant noise contribution to the step structure. To see these effects more clearly, we show in Fig. 3 conductance data (dI/dV vs V) again for the voltage-controlled case. Here we see the predicted series of equally spaced

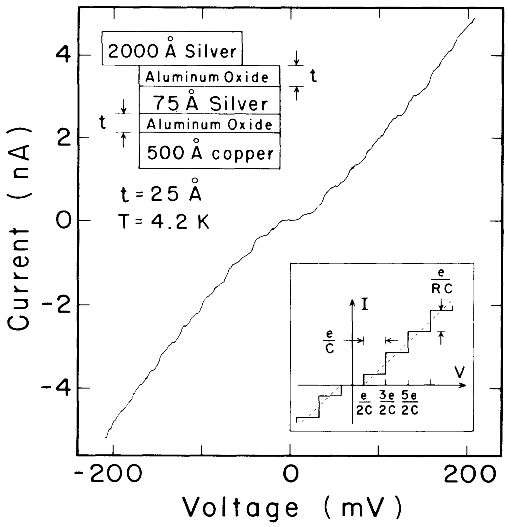

FIG. 2. Current-voltage characteristics taken with a voltage source for a tunnel system where tunneling occurs into an isolated layer of silver particles 75 Å on average in diameter (see Fig. 1). Both the expected offset in the curve at zero bias (for both polarities) by an amount $e/2c$—the "Coulomb gap"—and a series of steps separated by a voltage e/C—the so-called "Coulomb staircase"—are evident in this trace. Also observed are corresponding current steps of magnitude e/RC. The measured value of the steps is 0.72 nA, and the junction resistance is 38.8 MΩ. This is consistent with the measured e/C voltage spacing of 27 mV (see Fig. 3). The inset shows an idealized representation of the current-voltage characteristic expected from theory.

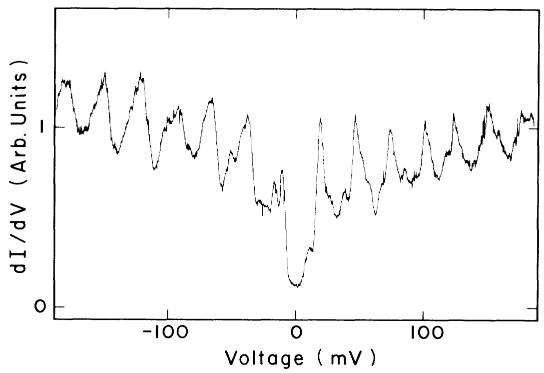

FIG. 3. Conductance trace (dI/dV vs V) accentuating the structure shown in Fig. 2. Here we see, beginning at zero bias, the gap of $e/2C$ in voltage, followed by a series of peaks separated by a voltage of $e/C=27$ mV. The latter are clear manifestation of the so-called Coulomb staircase expected for tunneling into particles with ultrasmall capacitance. The Ag particles accept a single additional electron each time a peak is passed.

peaks in conductance associated with the leading edges of individual current steps in the 1, 3, 5, . . . sequence from zero bias. The peaks should thus be spaced by a voltage difference of e/C. Assuming spherical particles of radius $r=(75\text{ Å})/2$, and Al_2O_3 barriers with a thickness $t=25$ Å and dielectric constant $\varepsilon=8$,[12] we estimate e/C [where $C\approx \varepsilon r(1+r/2t)$] to be 28 mV, compared with the observed peak spacing of 27 mV.[13] Although the level of agreement here may be to some degree fortuitous because of some uncertainty in the actual effective capacitance of the particles, it nontheless serves to bear out the basic consistency of our interpretation.

We have observed the same spacing (to within ± 2 mV) in a number of samples prepared under nominally identical conditions and found that the structure for a given sample is fully reproducible. Finally, we note that the e/C peaks disappear at 77 K at which temperature $kT\approx e^2/4C$, which is also consistent with theory.

One issue yet to be addressed is the effect of the distribution of particle size on the observed structure. As discussed in connection with Fig. 1, the system of Ag particles has a standard deviation of particle area of $\simeq$20%. The question is why does such clear structure as seen in Fig. 3 persist in the presence of this variation. We note first that if we assume that the effective tunneling resistance of a particle, R, is inversely proportional to its area, then the product RC, and hence ΔI, will not be a strong function of particle size. However, $\Delta V=e/C$ will be directly affected by any variations in C. We note in this regard that computer simulations of the problem of tunneling into a system of particles such as ours with a nonzero deviation in size has been conducted by Mullen *et al.*,[11] who conclude that a multiple steps in e/C should persist in the tunneling current-voltage characteristics even for values of σ as large as 25%. Therefore the issue becomes the appropriate magnitude of σ given the degree of coherence we observe. As discussed by Lambe and Jaklevic,[4] coherent tunneling structure which is a function of particle capacitance will be attenuated as a function of bias voltage, V, in the presence of a distribution of capacitance, β, by the Gaussian prefactor $\exp\{-[(\pi\beta/e)V]^2\}$. On the basis of the rate of decrease of the peak height for the data in Fig. 3, we find a value of $\beta=3.6\times10^{-19}$ F. Thus taking $C=e/\Delta V=5.9\times10^{-18}$ F (where ΔV is the measured-peak spacing) gives a value for β/C of 6.1%. Therefore, the magnitude of the variation of particle size, 20%, although greater than the effective variation in capacitance deduced from tunneling measurements, $\simeq$6%, is nonetheless smaller than the upper limit of $\simeq$25% inferred by the simulation studies. However, the origin of the discrepancy between the first two values is not fully understood at present. Since the values for σ are derived in different ways—from tunneling data on one hand, which are a measure of capacitance deviation, and from measurements of actual particle size on the other—there may well be an additional factor related to the detailed structure or geometry of the particles which somewhat favors tunneling into the majority-size particles. In any case, what *is* clear from the number of conductance peaks observed is that the system, in fact, exhibits a well-defined effective value of capacitance. This value of capacitance is the same as that independently calculated for particles with a 75-Å diameter, which is the mean particle size observed.

Thus the structure observed in Fig. 3 is a manifestation of a collective change in the charge residing on the Ag particles. The particles are occupied by, on average, the same number of electrons, and each time a peak is passed it means that each particle has accepted a single additional electron, giving rise to a current jump. This must occur in unison in order for discernable peaks to appear in the tunneling conductance as shown. This demonstrates that the charge occupation of the particles is a coherent phenomenon.

Although previous tunneling experiments were performed on Sn, In, and other particles[1,4] of comparable size, conductance peaks were not observed. The reason for this appears to be the reliance upon the natural oxidation of the particles to create a tunnel barrier between the particles and the top electrode. While this puts barrier material (native metal oxide) on the particles themselves, it does not fill the space between them. Therefore, there are relatively low-resistance tunneling paths parallel to the particles, tending to shunt out tunneling current through them. In our case artificial, sputter-deposited Al_2O_3 barriers are employed which uniformly cover both the particles and the space between them, creating a continuous barrier layer. This is apparently necessary in obtaining the periodic conductance oscillations we have observed.

In conclusion, we have experimentally verified for the first time the Coulomb staircase associated with the occupation of ultrasmall-capacitance particles by an integral number of electrons. We have observed the $e/2C$ gap in conduction at zero bias, and a periodic series of steps with a current height of e/RC and voltage width of e/c. We also see a suppression of the staircase structure with increasing temperature. All of these observations are in complete accord with theoretical predictions for tunneling into small particles.

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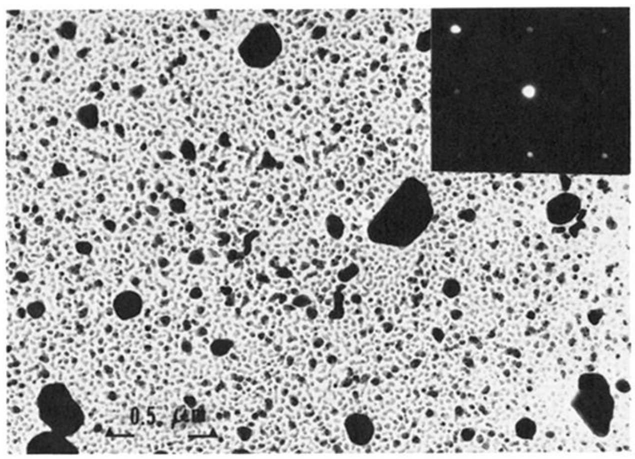

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