Coulomb Suppression of Tunneling Rate from Small Metal Particles

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ac measurements on a "tunnel capacitor," in which small metal particles make tunnel junctions with one of the capacitor plates, reveal information about the electron tunneling process at the junctions. A simple zero-temperature model for the process is presented for the regime in which the Coulomb charging energy suppresses the conductance of the junctions. The prediction of the model that the capacitance and dissipation constant of the structure should scale as (frequency)/(applied ac voltage) is confirmed by the experimental results.

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A detailed understanding of the charge-transfer process involving a small metal particle is important to the achievement of a successful model for the conductivity of small metal particle systems such as three-dimensional cermets and two-dimensional granular films.[1] Near the metal-insulator transition in such systems electron tunneling is an important transport process. Our study concentrates on the transfer process involving a single particle and an electrode, where the two are separated by a thin insulating tunnel barrier. The results of these experiments illustrate the predictions of recent discussions of the influence of Coulomb energy effects on junction conductance,[2,3] effects noted earlier in dc experiments by Zeller and Giaever.[4,5] The experiments illustrate as well the feasiblity of studying single-electron transfer processes from small particle to bulk, or between small particles, using ac techniques involving capacitive coupling to drive the electron transfer.

The system studied is the "tunnel capacitor"[6] of Fig. 1(a) in which an island film of metal particles (average radius $r < 100$ Å) is embedded in a capacitor and is separated from the Al plates on one side by a thick (100 Å) layer of Al_2O_3, and on the other side by a thin (< 15 Å) native oxide tunnel barrier. The particles form a large number of parallel, single-particle tunneling systems. Structures in which the tunnel-barrier oxide was made by oxidizing the particles or by depositing the particles on an oxidized Al electrode were both used. Particles composed of In, Sn, and Au have been studied. All samples show the same physics.

Because of the small capacitance c_I between the particle and the more distant electrode, the characteristic charging voltage e/c_I which must be applied across the full capacitor in order to induce the transfer of a single electron to the particle can be as large as a tenth of a volt. Electrons are added to the particle by tunneling from the closer electrode. Keeping c_I comparable with the capacitance c_R of the particle to the closer electrode and using a substantial filling fraction of particles makes the charge transfer process important in determining the capacitance and dissipation constant of the tunnel capacitor. In discussing the physics of the charge transfer process it will be convenient to speak in terms of voltage at the particle. The charging voltage at the particle $e/(c_R + c_I)$ will be referred to as e/c. Note that the charging energy e^2/c is much larger than the energy level spacing δ within the particles and the discreteness of the level spacing plays no role in this discussion.

The Fermi level of the particle will not, in general, be aligned with the bulk electrode Fermi level; see Fig. 1(b) (i). Since a discrete charging voltage e/c separates particle states that differ by one elec-

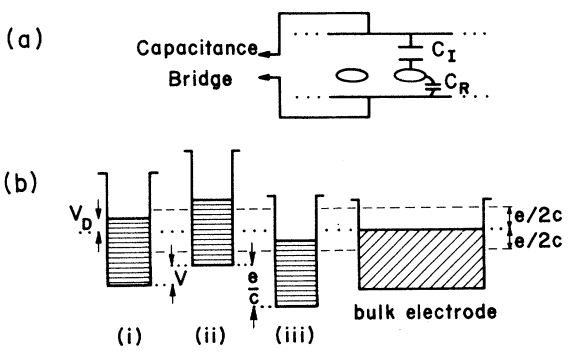

FIG. 1. (a) Schematic of the sample. (b) Energy diagram of the charge transfer process. (i) Zero applied voltage; V_D is the accidental separation between the Fermi levels of the particle and bulk electrode. (ii) Applied step voltage, magnitude V, brings particle Fermi level above the Coulomb threshold. (iii) Charge transferred to bulk electrode, particle Fermi level drops by a charging voltage e/c.

tron transfer, e.g., Fig. 1(b) (ii) versus (iii), tunneling can only bring the Fermi levels to within $e/2c$ of one another. The remaining separation V_D is due to accidents of the particle-electrode capacitance and work functions of the particle and electrode. The redistribution of defects in the oxide can give rise to some ordering in the otherwise random distribution of V_D over an ensemble of particles with a given c. This is seen in the memory effect observed by Lambe and Jaklevic[6]: oscillations in the capacitance as the dc bias is swept. The small magnitude of this capacitance anomaly both in our experiments and those of Ref. 6 indicate a nearly uniform distribution of V_D. A uniform distribution for V_D in the range $-e/2c < V_D < e/2c$ is assumed in the arguments below.

The electron transfer process between particle and electrode is probed by measuring the capacitance C and dissipation constant D of the structure using an audio-frequency capacitance bridge. Keeping the measuring voltage amplitude at the capacitor less than the voltage e/c_l assures that tunneling contributions to C and D are restricted to the transfer of a single electron between the electrode and the particle. For reasons to be discussed shortly, in this experiment we apply to the bridge a square wave at audio frequencies, and balance C and D using lock-in detection of the bridge unbalance at the fundamental frequency of the square wave.

All samples show a strong dependence of C and D upon the amplitude of the sample voltage V_s and frequency f at 4.2 K and a similar, but much reduced, voltage dependence at 77 K. Figure 2 shows a data set at 4 K for a sample with a 35-Å average thickness indium layer, in which the indium particles were oxidized to make the tunnel barrier. The plot of D contains a correction for the 1-Ω series resistance of the electrode, which is only a shift of 4% of the observed D at 50 kHz, and, going linearly with f, is negligible at the lower measuring frequencies.

The curves are suggestive of a Debye loss mechanism which would be described by $D(f) \sim 2\pi f\tau_c/[1+(2\pi f\tau_c)^2]$ and with $\tau_c \equiv rc = c/g$ where r and g are respectively the resistance and conductance of the tunneling contact between the particle and the near electrode. The experimental loss peaks are broader than the Debye expression would imply, hardly surprising when one notes that the tunneling conductance g depends exponentially on the height and thickness of the tunneling barrier. The most important feature of the data is the slowing of the electron transfer rate, or decreased conductance g, as the measuring voltage is reduced.

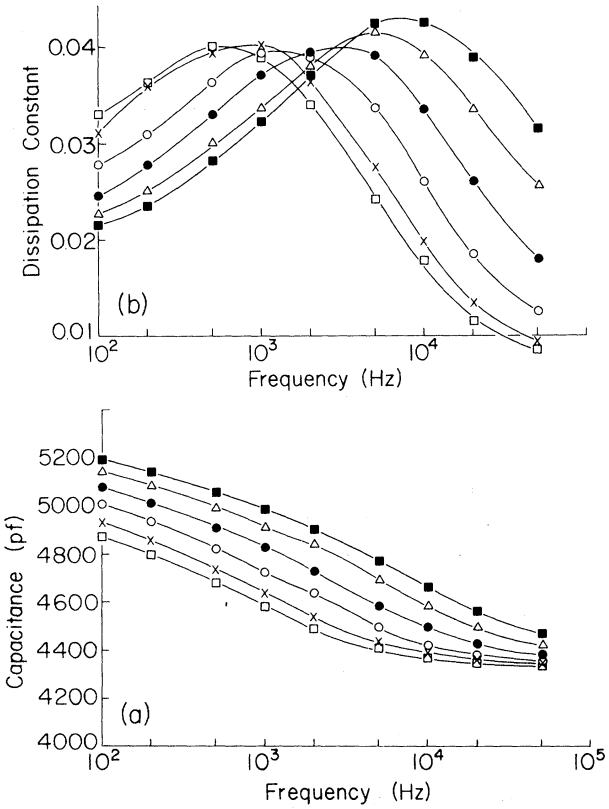

FIG. 2. Measurement of D and C as a function of frequency for several applied voltages: open squares, 0.0027 V; crosses, 0.0054 V; open circles, 0.011 V; solid circles, 0.022 V, open triangles, 0.043 V, solid squares, 0.086 V.

To explain the physics of these samples, we use a zero-temperature model in the low-voltage limit in which at most one electron transfer per cycle occurs. The response of the system to square-wave excitation is much easier to calculate than its sinusoidal response and we consider here only the square-wave problem. The charge transfer process is illustrated in Fig. 1(b). Initially the Fermi level of the particle is displaced by V_D from the Fermi level in the bulk electrode. A negative step voltage of amplitude V is applied. Only if $V+V_D > e/2c$ will the total energy of configuration (iii) be lower than that of configuration (ii). Further, only electrons in the range $(V+V_D)-e/2c$ below the particle Fermi level can tunnel and conserve energy for the full system in the final state. Remembering that the number of electrons per unit voltage difference in the particle is e/δ, one obtains for the tun-

neling probability per unit time

$$\frac{1}{\tau}=\left[\frac{V+V_D-e/2c}{\delta/e}\right]\frac{1}{\tau_0}e^{-\alpha h}. \quad (1)$$

Here $(1/\tau_0)\exp(-\alpha h)$ is the usual WKB tunneling rate with h the tunneling barrier thickness, α the barrier attenuation coefficient, and $1/\tau_0$ a rate constant.

Only particles for which V_D is within V of $\pm e/2c$ can contribute to the tunneling current. During the negative step, the number of these particles $N_D(t)$ with the same V_D, c, δ, α, and h that have not transferred their electron will decay according to $N_D(t)=N(0)\exp(-t/\tau)$. $N_D(0)$, a complicated function of V_D, V, and square-wave period T, is determined by matching boundary conditions with the previous positive step. If we define a dimensionless variable $y=(V_D-e/2c)/V$, $N_D(0)$ can be expressed simply as a function $N_D(0;y,VT)$ of y and the combination VT. We integrate $N_D(t)$ over the allowed range of V_D assuming a uniform distribution of V_D between $\pm e/2c$ to give $N(t)$. In terms of the variable y the integral can be expressed as

$$N(t)=\int_{-1}^{1}N_D(0;y,VT)\exp\left[-\frac{Vt}{\delta/e}\frac{(1+y)}{\tau_0}e^{-\alpha h}\right]dy. \quad (2)$$

The argument may be continued to obtain formal expressions for C and D in terms of integrals over appropriate distributions of the parameters c, δ, α, and h describing the properties of the individual particles. We omit those tedius details because Eq. (2) already gives the most important result: the time t, square-wave period T, and voltage V appear only in the products Vt and VT. Thus with no further argument, one can predict that data taken with different measuring voltage amplitudes should differ only by a scale factor in time, or equivalently that the capacitance and dissipation constant should depend only on the ratio f/V.

Figure 3 gives the data of Fig. 2 in a scaled plot, for the applied voltage V_s from 0.005 to 0.04 V. The scaling prediction of the model is well obeyed for both D and C for this voltage range. The scaling breaks down with applied voltages of 0.086 and 0.0027 V. At 0.0027 V, the contribution to the number of electrons available for tunneling by thermal excitation at 4.2 K has become important. At 0.086 V, the requirement $V<e/2c$ is being violated, and many particles are transferring two electrons per cycle. This is confirmed by a rough measurement of $e/2c$ using the dc memory effect observed in the sample.

We have investigated details of the tunneling transfer of electrons from a bulk metal to small metal particles in the regime in which the Coulomb charging energy of the particles suppresses the junction conductance. The results confirm the physical ideas discussed in the theoretical references,[2,3] but for explicit comparisons the theories must be appropriately modifed to include the effects of the distribution of residual chemical potential differences V_D of the particles with respect to the bulk. Our ac experiment probes the dynamics of the charge-transfer process, allowing the suppression to be seen as a slowing down of the average electron transfer rate as the applied voltage becomes small compared to the charging energy. The experimental results are entirely consistent with a predicted scaling law, predicated on a uniform distribution of

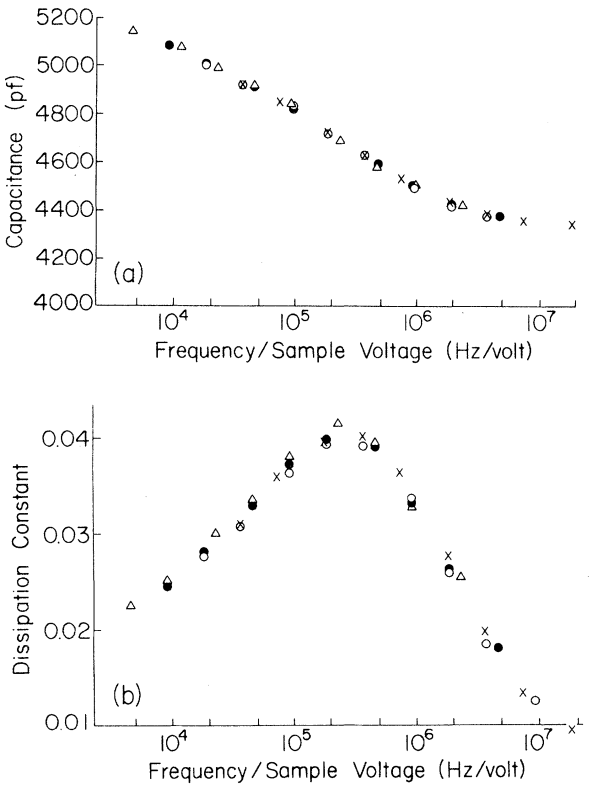

FIG. 3. Data from Fig. 2 in the voltage range 0.0054–0.043 V plotted as a function of the scaling parameter f/V_s.

V_D, which implies a response rate linearly proportional to the voltage for that voltage in the range $kT/e < V < e/2c$. The success of the scaling arguments emphasize the need to consider the effects of chemical potential variations in modeling the conductivities of such systems as granular composites.

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[1]Shang-Lin Weng, S. Moehlecke, Myron Strongin, and A. Zangwill, Phys. Rev. Lett. **50**, 1795 (1983).

[2]T. L. Ho, Phys. Rev. Lett. **51**, 2060 (1983).

[3]E. Ben-Jacob, E. Mottola, and G. Schön, Phys. Rev. Lett. **51**, 2064 (1983).

[4]I. Giaever and H. R. Zeller, Phys. Rev. Lett. **20**, 1504 (1968).

[5]H. R. Zeller and I. Giaever, Phys. Rev. **181**, 789 (1969).

[6]J. Lambe and R. C. Jaklevic, Phys. Rev. Lett. **22**, 1371 (1969).