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Studies of electron energy levels in single metal particles

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Abstract

We describe the fabrication of point-contact tunnel junctions containing a single Al particle of diameter < 10 nm, and discuss how we have used such devices to measure the energy spectrum of discrete electronic states in the particle. For a full understanding of the eigenstate spectra, we suggest that consideration of many-electron excitations is necessary. We also describe the magnetic-field dependence of the energy levels, emphasizing the role of spin–orbit scattering.

We have recently developed a procedure with which we can, for the first time, measure the discrete spectrum of electronic energy levels in a small piece of metal [1]. The potential power of this new capability can be understood in analogy to nuclear and atomic physics. In these fields, examination of eigenstate spectra has led to a detailed understanding of the forces which act upon nucleons or atomic electrons. In much the same way, we are beginning to use our studies of energy levels in metal particles to gain new insights into the forces governing the behavior of electrons inside metals.

We measure the eigenstates in a metal particle by connecting it to two separate metal leads via high-resistance tunnel junctions. At low temperature, the current–voltage (I–V) curve consists of a sequence of steps, each corresponding to tunneling via an electronic energy level in the particle. A schematic diagram of our device is shown in the inset to Fig. 1. Following a procedure developed by Ralls et al. [2], we start device fabrication by using electron beam lithography and reactive ion etching to form a bowl-shaped hole in an insulating Si_3N_4 membrane. The opening at the lower edge of the membrane is 3–10 nm in diameter. We evaporate Al onto the bowl-shaped side of the membrane, and subsequently oxidize the Al surface for 3 min in 50 mtorr of O_2. This forms a tunnel barrier in the vicinity of the small hole in the membrane. We then flip the membrane and deposit a small amount of Al (1.5–3 nm by mass). Because of surface tension effects, this produces a layer of electrically isolated particles, 10 nm or less in diameter [3]. Following a second oxidation, we finally deposit a thick layer of Al on top of the particles, to act as a second electrical lead. In approximately 25% of devices, one Al particle covers the hole in the nitride membrane, so that electrons passing between the two leads must tunnel via the particle. These good devices are easily identified by a clear Coulomb staircase [4] structure in their I–V curves at 4.2 K.

The low-temperature I–V curves of the devices contain structure with 2 characteristic voltage scales. On large scales, the Coulomb staircases have broad steps with widths typically between 10 and 125 mV. (For an example of a large-scale I–V curve, see Ref. [1].) This structure reflects the classical charging energy required to add additional electrons to one particle. Fits to the staircase pattern allow a determination of the capacitances and resistances of the two tunnel junctions composing the device [1]. We can use these capacitances to determine the area of the tunnel junctions, using a capacitance per unit area (75 fF/μm^2) measured in larger-area oxide junctions. On a much smaller voltage scale, the broad steps in the Coulomb staircase are themselves composed of

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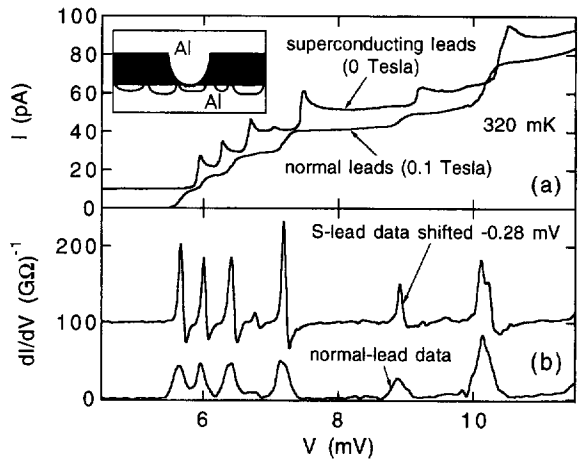

Fig. 1. (a) Current steps due to tunneling via discrete eigenstates on an Al particle. (b) dI/dV versus V for the same sample. Data for superconducting leads are offset in I or dI/dV for visibility. For this particle, we determine from the Coulomb staircase that $C_1 = 4.7$ aF, $C_2 = 8.3$ aF, so particle volume $\approx 150\,\mathrm{nm}^3$. Inset: schematic diagram of device.

well-resolved small steps (Fig. 1). This fine structure has the qualitative form predicted theoretically for tunneling via eigenstates in a small particle [5]. Throughout this article we will discuss only the fine structure that occurs in the voltage range of the first Coulomb-staircase step, so that all the energy levels we will describe will correspond to the same number of electrons on the particle, and complications from additional charge states will not enter.

Confirmation that the fine structure is due to tunneling via discrete electronic eigenstates in a single particle comes from analyzing the difference between I–V curves taken with leads that are superconducting versus leads that are driven normal with a small magnetic field (Fig. 1). The same sequence of current steps is seen in both cases, but the steps for superconducting leads are shifted to slightly higher voltage and they possess a cusp-like shape. We have shown previously [1] that these two changes are easily understood as due to the modification of tunneling into a discrete state caused by the superconducting gap (Δ) in the leads and the cusp in the quasiparticle density of states in the leads. The fact that the rate of current flow directly reflects the BCS density of states in the leads demonstrates that the current steps are due to tunneling via discrete electronic states, and not, for instance, due to sudden shifts in the electrostatic potential of the particle caused by charge trapping. The threshold voltages of the current steps for superconducting leads are shifted relative to the normal-lead data by either $\Delta(C_1 + C_2)/eC_2$ or $\Delta(C_1 + C_2)/eC_1$, according to whether the threshold for tunneling via a particular eigenstate is across the first or second tunnel junction. In each of our samples only two values of voltage shift are in fact observed, confirming that all the current steps are due to states on the *same* particle. (Only one shift value is displayed in Fig. 1, the other, 0.52 mV, occurs for negative bias.) From the two shifts, we can solve for Δ in the leads and the capacitance ratio: $\Delta = 0.18 \pm 0.01$ meV and $C_1/C_2 = 0.56 \pm 0.03$ for the sample of Fig. 1. The value for Δ is in good agreement with the gap for bulk Al, 0.175 meV, and the capacitance ratio is consistent with the value determined from the Coulomb staircase [1].

In determining the nature of the discrete states that we measure, it is important to ask whether they can be understood simply in terms of single-electron particle-in-a-box states, or whether a more complicated picture is necessary. We therefore compare the measured mean level spacing to the expression for the average independent-electron particle-in-a-box spacing, $\delta E \sim 2\pi^2\hbar^2/[mk_F\mathcal{V}]$. Here $\mathcal{V}$ is the volume of the particle, m is the electron mass, and k_F is the Fermi wave vector. We can make a rough determination of the volume of our particles because we can measure the capacitances, and hence the areas, of the tunnel junctions in our devices [1]. To estimate the volume, we model a particle as a hemisphere, with the curved surface equal in area to the larger tunnel junction. Based on atomic-force microscope studies of typical particle shapes, we expect the volume estimates to be accurate to within approximately 50%. The comparison between the measured mean level spacing (corrected to account for capacitive division of the applied voltage across the two tunnel junctions) and the single-electron estimate is shown in Fig. 2. The measured spacing is significantly smaller than the particle-in-a-box value in our smallest particles, although the agreement is reasonable for larger particles (such as in Fig. 1). In the smaller particles, we note that the observed states occur in clusters, and there is increasing state density at higher voltages (Fig. 3). The clumping of states is contrary to our initial expectation, based on random matrix theories, that we should observe energy-level *repulsion*. The energy spacing between clusters is in better accord with the particle-in-a-box estimate than is the mean level spacing.

Based on these observations, we suggest that it is incorrect to assume that the discrete states that we measure correspond simply to single-electron particle-in-a-box eigenstates. One should consider the accessible eigenstates of the full, interacting many-electron system. In the presence of interactions, the energy of an electron tunneling onto a particle may be partitioned among excitations of more than one electron. At high bias there can be many possible ways to partition the energy of the incoming electron, so that the density of accessible many-electron eigenstates should be expected to grow

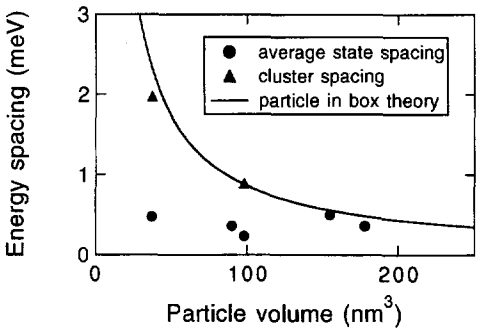

Fig. 2. Comparison of the measured mean eigenstate spacing and mean cluster spacing for several particles to the particle-in-a-box prediction for single-electron excitations.

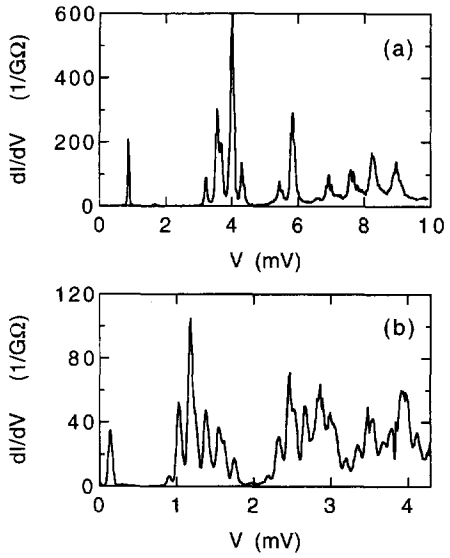

Fig. 3. Differential conductance at 30 mK for two very small particles, showing the spectrum of eigenstate energies. For (a), $C_1 = 1.5$ aF, $C_2 = 3.2$ aF, particle volume $\approx 40\,\mathrm{nm}^3$, for (b), $C_1 = 2.5$ aF, $C_2 = 6.3$ aF, particle volume $\approx 100\,\mathrm{nm}^3$.

with increasing bias, quickly becoming greater than the single-electron estimate. Our proposed explanation for the clumping of observed states in Fig. 3 is that the amount of current which can tunnel via a given many-electron eigenstate is determined by the rate at which a single electron may tunnel onto the particle to produce that state. The many-electron states which will contribute most significantly to the current (and are therefore measurable) will be those which mix strongly with the single-electron excitations. Consequently, many-electron states carrying significant current may occur in clusters

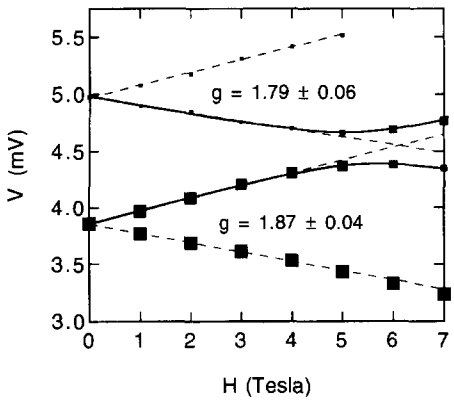

Fig. 4. Bias position of peaks in dI/dV, plotted versus magnetic field, showing the evolution of eigenstate energies with H. To convert from voltage to eigenstate spacing, multiply by $eC_1/(C_1 + C_2) = 0.54\,\mathrm{meV/mV}$. Area of symbols represents the magnitude of current carried by each state. Dotted lines: extrapolation of linear Zeeman splitting at low fields. Solid lines: solution of 2×2 matrix Hamiltonian with spin–orbit matrix element of $77\,\mu\mathrm{eV}$.

with energies close to single-particle excitation levels. This picture in which one must take into account the mixing of many-body states with single-particle excitations is central to neutron-capture experiments in nuclear physics [6].

We now turn to the magnetic-field dependence of the energy levels. Previously, we described how an analysis of the field dependence allows a determination of whether the number of electrons on a particle is even or odd [1]. Here we will concentrate on energy levels in one particular sample, which demonstrate the effects of spin–orbit scattering (Fig. 4). At low field, all of the levels in this sample undergo linear Zeeman splitting, with a g factor significantly different from 2 ($g = 1.87 \pm 0.04$ and 1.79 ± 0.06 for the states shown). The fact that g is less than 2 is the first sign that spin–orbit scattering is significant, because spin–orbit scattering mixes pure spin-up and spin-down states and hence reduces the g-value below the free-electron value [7]. At fields large enough that primarily spin-up and spin-down levels from adjacent states begin to cross, a second effect of spin–orbit scattering becomes evident; the levels exhibit an avoided crossing. (In the absence of spin–orbit scattering, the levels would cross without perturbing each other, because no matrix element would connect states with different spin.) The minimum energy separation in the avoided crossing provides a direct measure of the spin–orbit scattering matrix element between the two affected states. The sizes of the symbols in Fig. 4 represent the amount of current due to tunneling via each state. Near the avoided

crossing, current weight is transferred from the stronger transition to the weaker one. This transfer can be understood quantitatively in terms of the linear superposition of electronic states occurring in the crossing region.

We currently do not know the origin of the spin–orbit scattering that we observe. The strength of spin–orbit scattering appears to vary unsystematically from particle to particle. We suspect that the underlying cause is scattering from uncontrolled defects in the particle or at its surface.

In summary, we have described our initial observations of discrete electronic energy levels in single nanometer-scale Al particles. We have suggested that the measured states contain contributions from many-electron excitations, and therefore one should not assume that the these states can be fully understood within a simple independent-electron picture. The quality of our spectroscopic measurements is sufficiently high that the influence of effects such as spin–orbit scattering are clearly evident.

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