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Electron energy levels in superconducting and magnetic nanoparticles

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Abstract

We describe electron-tunneling measurements of the spectrum of discrete energy levels for electrons in metal nanoparticles, for metals with sufficiently strong electron interactions to form superconducting or magnetic states. For aluminum nanoparticles, superconducting pairing interactions produce an energy gap for tunneling, which affects even- and odd-electron spectra differently. As a function of an applied magnetic field, we observe that the correlated electron ground state is disrupted by breaking one Cooper pair at a time. Energy levels in ferromagnetic cobalt particles exhibit effects of strong exchange and magnetic anisotropy forces, with a non-linear, hysteretic dependence on an applied magnetic field.

Keywords: Coulomb blockade; Ferromagnetism; Superconductivity

Spectroscopic measurements of the quantum-mechanical energy levels in atoms and atomic nuclei have for decades yielded information about the nature of interactions between electrons and between nucleons. In more recent years, advances in nanofabrication techniques have made possible analogous measurements of the quantum-mechanical "electrons-in-a-box" energy levels inside semiconductor quantum dots (see Ref. [1]) and metal nanoparticles [2–5]. Just as in atoms and nuclei, it is observed in these condensed-matter systems that the constituent particles are not *non*-interacting. In fact, the various forces and interactions acting on the electrons affect the energy-level spectrum in different ways, so that the level spectra can be used as a tool for understanding the nature of the interactions. In this paper, we will review the effects of superconducting electron interactions in aluminum nanoparticles, and strong magnetic exchange interactions in cobalt particles.

For the mean level spacing in a metal sample to be larger than thermal energies, $k_B T$, at low temperatures, and therefore resolvable experimentally, a simple estimate shows that the sample must be smaller than about 10 nm on a side. This is beyond the resolution limit of conventional electron-beam lithography, so that to perform our measurements we have used a somewhat unusual device geometry (Fig. 1(a)) [2,4]. One can think of the design as being similar to a scanning-tunneling microscope set in concrete, so that it does not scan, vibrate, or drift. The "concrete" in our case is a membrane of insulating silicon nitride, through which a 10-nm-diameter bowl-shaped hole is formed using electron-beam lithography and a reactive ion etch. One aluminum electrode, shaped much like an STM tip, is deposited onto the bowl side of the membrane so as to form an interface near the lower opening. This is connected to either an aluminum or cobalt nanoparticle through an aluminum oxide tunnel junction, and then another aluminum oxide tunnel junction connects the nanoparticle to a second aluminum electrode. Our measurements consist of current–voltage (I–V) curves for electrons tunneling from one electrode to the other, via a nanoparticle. Details of the fabrication steps can be found in Refs. [2,4]. For the Al data we present, the devices also contained a third gate electrode, with which the electric potential of the particle could be tuned. We

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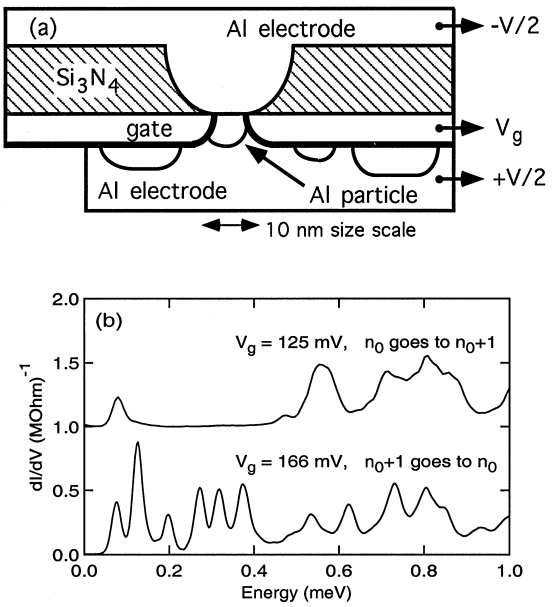

Fig. 1. (a) Schematic sample cross-section. (b) Spectra showing tunneling via discrete electronic states on a superconducting aluminum nanoparticle for (upper curve) odd-to-even electron tunneling and (lower curve) even-to-odd tunneling. The two curves are artificially offset. The measurements were performed at a refrigerator temperature of 50 mK and in a magnetic field of 0.05 T.

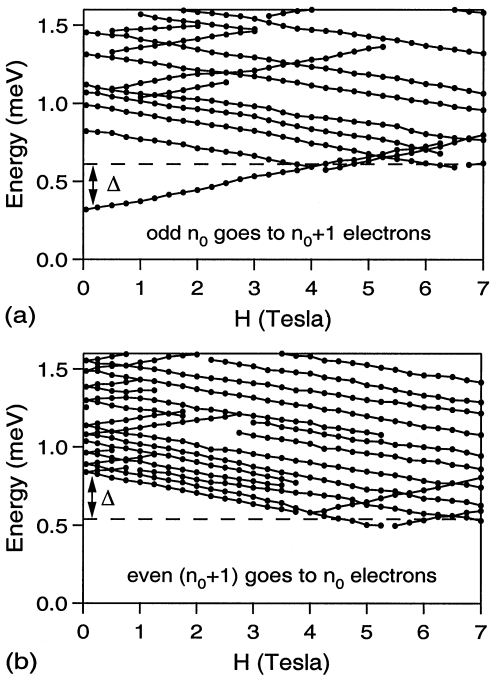

Fig. 2. Magnetic field dependence of the resolved tunneling transition energies for the device of Fig. 1(b) at the gate voltage (a) $V_g = 110$ mV and (b) $V_g = 180$ mV. The dashed lines show the average energy of the tunneling threshold at large H, corresponding to the (V_g-dependent) Coulomb barrier.

have not yet fabricated magnetic-nanoparticle devices with gates.

Two tunneling spectra for an Al particle with an estimated diameter $\approx$8.6 nm are shown in Fig. 1(b). In order for tunneling to occur, the bias voltage V must be sufficiently large that an electron may overcome the Coulomb energy cost for occupying the lowest available energy state of the nanoparticle. As the voltage is increased, higher-energy eigenstates provide alternative channels for a single electron to tunnel. The different peaks in one spectrum therefore correspond to the different eigenstates on the particle, each with the same number of electrons (one more or one less than the initial state before tunneling). The two spectra shown correspond to different numbers of electrons in the ground state of the particle, a number which is adjusted by varying the gate voltage, V_g. The gate voltage is further tuned so that the Coulomb-blockade energy needed to initiate tunneling is small in each case. Details of how the bias voltage can be related to the energy on the nanoparticle, how the particle diameters are estimated, and checks to make sure that all the peaks correspond to eigenstates on the *same* nanoparticle are described in previous publications [2,4].

An important factor for interpreting the tunneling spectra of nanoparticles with superconducting electron interactions is whether the number of electrons in the ground state is even or odd. This can be determined by examining the levels as a function of magnetic field, H (Fig. 2). The key is the presence or absence of Zeeman spin-splitting for the lowest-energy tunneling level. If Zeeman splitting is present, this indicates that the spectrum corresponds to even-to-odd electron tunneling, because both of the spin states of the lowest available orbital state are free for tunneling. However, if Zeeman splitting is absent, and the lowest-energy tunneling level simply moves to higher energy with increasing field, this means that the spectrum is for odd-to-even electron tunneling. The last odd electron fills one of the spin states in the highest-energy occupied orbital level, so that tunneling may proceed via only one of the spin states, and is blocked for the other. By this logic, n_0 is odd in Figs. 1 and 2.

The differences between the two spectra in Fig. 1(b) can then be understood in terms of the different effects of superconducting pairing in nanoparticles with odd versus even numbers of electrons. Consider first the upper spectrum in Fig. 1(b), which contains a large energy gap between the first transition and all the others. The lowest-energy transition, for odd-to-even tunneling in a superconducting particle, corresponds to a situation in

which all the electrons in the tunneling state are paired. However, in the next higher-lying energy level, there must be at least two unpaired electrons, so that the energy of this state will be significantly higher than the ground state, by an amount required to break a Cooper pair. The large gap in the upper spectrum of Fig. 1(b) should therefore be approximately 2Δ, where Δ is the superconducting gap on the particle. (This is only approximate, because there will also be a positive contribution from the orbital energy of the excited state, and an additional negative contribution of gap suppression caused by the presence of unpaired quasiparticles in the Al grain.) For the even-to-odd tunneling spectrum, all the tunneling states must contain at least one unpaired quasi-particle, and as a result there is no gap among the levels in the spectrum due to superconducting pairing. However, the pairing-induced gap on the particle is still apparent in the magnetic-field dependence of the levels (Fig. 2(b)). Because of the unpaired quasiparticle's excess energy, the threshold required for tunneling at low magnetic field is higher by Δ than at high magnetic fields where superconducting pairing has been suppressed. Our operational definition for measuring Δ is the difference between the tunneling threshold energy at small H and the average threshold at large H. The values that we measure in aluminum particles are $\Delta \approx 0.3$ meV. This is greater than the value in bulk aluminum, 0.165 meV, but this is to be expected because granular aluminum samples generally show larger gaps and higher superconducting critical temperatures than bulk aluminum.

The level spectra as a function of magnetic field (Fig. 2) give detailed information about the mechanism by which H affects the pair-correlated electron ground state, and the processes by which the pair correlations are eventually destroyed in a large field. The field dependence of individual levels in Fig. 2 is linear, with slopes corresponding to the electron spin g-factor $= 2$. This indicates that by far the primary effect of the field in this sample is to produce spin pair breaking, on account of the spin Zeeman energy. For larger aluminum particles, we have also observed some curvature in the dependence of the energy levels on H, as well as asymmetries in the Zeeman splitting, indicating that orbital effects can eventually become significant [3]. In magnetic fields beyond 4 T, the lowest-energy tunneling threshold begins to undergo a zig-zag motion. This can be understood as a consequence of simple level crossings between spin-up and spin-down electron states, which move with opposite slopes as a function of H. At each level crossing, the ground state changes, increasing its spin by 1 unit of $\hbar$, as one spin level is depopulated and another populated. In this process, Cooper pairs are destroyed one at a time.

This simple picture of level crossings was at first a surprise to us. The existing theory of superconducting transitions due to spin pair breaking in thin metal films predicts a discontinuous transition, with an abrupt jump in the threshold energy for tunneling, at the value of the magnetic field where the energy benefit of Pauli paramagnetism in the normal state becomes greater than the energy benefit of the superconducting condensation energy in the superconducting state [6,7]. The predicted critical field is $H = \Delta/(\mu_B\sqrt{2})$, independent of the level spacing. This effect has been observed in thin superconducting films in a parallel magnetic field [8]. An explanation for the different behavior in superconducting nanoparticles has emerged from a careful consideration of the interplay between superconducting, Zeeman, and orbital energies in a system with a discrete set of levels [9]. For a sufficiently small nanoparticle, the cost in orbital energy associated with promoting electrons to higher spin states requires that this promotion occurs only in single units of $\hbar$. For larger particles, because of the effects of superconducting gap suppression, an electronic state with total spin $S = 2\hbar$ or larger can drop below the energy of the $S = 0$ ground state first, at magnetic fields lower than the $S = 1\hbar$ crossover, and in this case the lowest-energy tunneling transition is predicted to have a discontinuous jump. This has not yet been observed experimentally, but by this means the results for large nanoparticles are expected to converge to the bulk thin-film limit.

Aluminum particles smaller than the one featured in Figs. 1 and 2 can approach the range in which the single-particle level spacing is comparable to the superconducting gap — a range in which pairing correlations have been predicted to be suppressed [10]. In recent years, the exact nature of the electronic state in this regime has been of considerable interest, with predictions of parity-dependent order parameters and also exact numerical diagonalization studies [11–16]. Comparison between some of these theories and experiments can be tricky, in that the experimentally observable quantities are spectroscopic gaps, not order parameters, and it can be difficult to distinguish gaps due to superconducting interactions from gaps due simply to the discrete level spacing. Also, the tunneling measurements always measure energy differences between states with even and odd numbers of electrons, so that it is not straightforward to disentangle even and odd superconducting gaps separately. The present-day state of experimental affairs is shown in Fig. 3, where we plot the measured superconducting gap, determined as described above, versus estimated nanoparticle radius. We also plot the measured mean level spacing, and predictions of the parity-dependent order parameter from von Delft et al. (Refs. [11–13]). As long as the level spacing is much less than the superconducting gap, we measure no significant size dependence. When the mean level spacing becomes comparable to the superconducting gap, we cannot separate these two types of gaps. Unfortunately, this is precisely the range in which interesting parity-dependent effects are expected to emerge. Matveev and Larkin [14] have

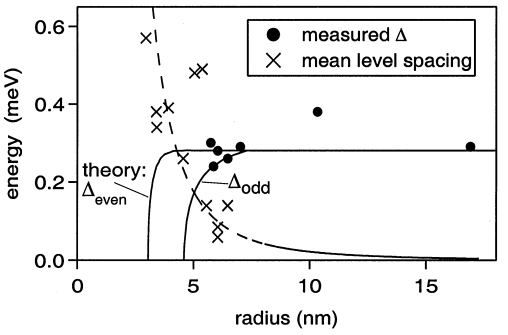

Fig. 3. Dependence of the measured superconducting tunneling gap as a function of particle size, compared to the measured mean level spacing and the predicted dependence of the parity-dependent order parameter.

suggested that a more useful way to study parity-dependent gaps is to analyze the energies of electronic ground states (rather than excited states) by scanning the gate voltage. These studies are not yet possible in our current devices, due to problems with charge noise.

We now turn from the properties of superconducting nanoparticles to those of ferromagnetic particles. Whereas superconducting particles always have a total electronic spin of 0 or $\hbar/2$, on account of strong pairing interactions, the exchange interactions in ferromagnetic particles can lead to large magnetic moments, on the order of $1000\hbar$ for our particles. This has a number of important consequences. First, the time-reversal symmetry present in Al between spin-up and spin-down states is broken, so that there is no degeneracy between these states at low applied magnetic fields in Co. The electronic states in Co may also depend on the direction in which the total magnetic moment vector points. This introduces issues related to magnetic anisotropy, as well as hysteresis effects. Finally, the existence of a net magnetization allows for the existence of *collective* spin-wave excitations coupled to the independent-electron-like electron–hole excitations observed in Al. We believe that this is at the root of observations, described below, that the tunneling spectra in Co nanoparticles show an increased low-energy density of states compared to Al.

Fig. 4(a) shows the energy of the first 3 tunneling resonances as a function of H for a Co nanoparticle smaller than 4 nm in diameter (the largest of the particles in the distribution made by our procedure, as measured by STEM). Unlike in Al, where the energy levels have a simple linear dependence on H due to Zeeman splitting, in Co the dependence is strikingly non-monotonic, hysteretic with respect to the direction of the field sweep, and quantitatively much more sensitive to the field magnitude. Concentrating on the lowest energy level, as a function of increasing field, the dependence on H is continuous over most of the field range, but then exhibits

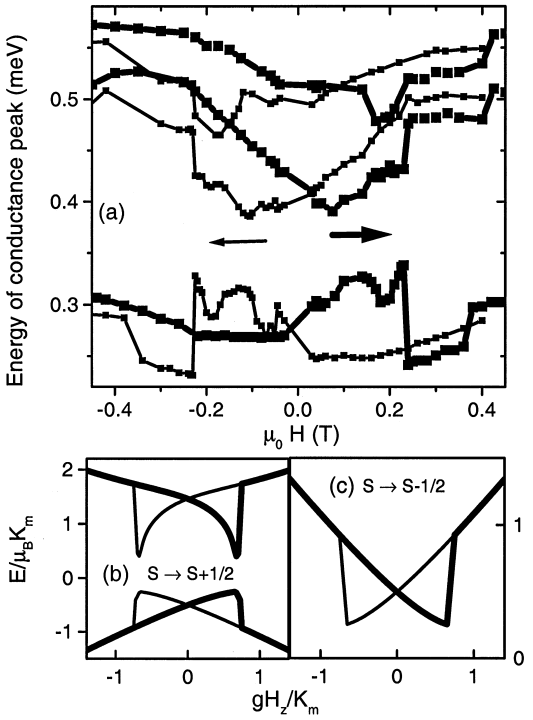

Fig. 4. (a) Hysteresis curves showing the dependence of tunneling energies on H for a cobalt nanoparticle, at $T = 50$ mK. (b,c) Lowest-energy transitions calculated using a simple quantum Hamiltonian within the ground state spin multiplet, for a ground-state $S = 50\hbar$, easy-axis magnetic anisotropy of strength K_m, and H oriented 45° from the easy axis, for the case where S increases during tunneling (b) and decreases (c). The qualitative features are independent of the value of S.

a downward jump at $H = 0.23$ T. The other energy levels also exhibit jumps at the same field, and the field at which these jumps occur changes sign when the direction of the field sweep is reversed. We ascribe this behavior to shifts in the energy levels inside the nanoparticle that occur when the magnetic moment vector of the particle is rotated by the applied magnetic field. As H is swept from a large negative value to zero, the moment vector is expected to rotate continuously from the field direction to the easy-axis direction. However, as the field is reversed, eventually the moment vector undergoes reversal, which we associate with the jumps in the energy levels. We have made a simple model of this process for small spin systems (up to $S = 50\hbar$) by direct diagonalization of the spin Hamiltonian within one ground-state spin multiplet, under the influence of simple uniaxial magnetic anisotropy. The results (Fig. 4(b,c)) capture the qualitative behavior of the hysteresis and the energy-level jumps. However, more detailed analysis of the magnetic state, the form of the anisotropy, and the consequences of interactions between nearby Co particles is called for.

An additional puzzling feature of the tunneling data from Co particles is the density of resonances observed in the spectra. For the range of particle sizes in our samples, 1–4 nm in diameter as measured by STEM, the average energy level spacing predicted for simple non-interacting electrons should be between 40 and 0.75 meV, given the calculated density of states for Co of 0.88 $eV^{-1}\,atom^{-1}$ [17]. We observe mean level spacings less than 0.2 meV in all of our samples. We suspect that the cause of the increased density of states is that the tunneling excitations are not purely of independent-electron character, but are coupled to collective spin excitations. It is not yet clear whether the extra resonances that are observed may be due to inelastic excitation of spin waves during tunneling, or the occupation of non-equilibrium spin states [18]. Other issues to be investigated include the relative coupling of tunneling electrons to s versus d states in Co, and measurements of spin-polarized tunneling via individual quantum-mechanical energy levels.

In summary, we have described the effects of electron interactions on the discrete "electrons-in-a-box" energy levels in both superconducting aluminum and ferromagnetic cobalt nanoparticles. Pairing interactions in Al produce energy gaps for tunneling. We have investigated the nature of the superconducting transition in a magnetic field by following the evolution of the individual electronic states. The energy levels in Co are influenced by the presence of the large magnetic moment in the particle, with strong shifts in the levels as the magnetic moment is reoriented by an applied magnetic field. Co particles possess an increased density of tunneling transition compared to Al, which may be due to the influence of collective spin-wave excitations.

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