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Tunneling Through Metallic Quantum Dots

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We discuss single-electron tunneling measurements at dilution refrigerator temperatures on metallic grains, sufficiently small that the quantum levels of the conduction electrons can be resolved. These measurements directly reveal the energy eigenvalues of the electrons in a grain that typically contains a few thousand conduction electrons. Such measurements were first carried out a few years ago by Ralph, et al. on nanograins of Al. More recently, this work has been extended to measurements on nanoparticles of the heavy metal Au by Davidović and on nanoparticles of alloys of Al and Au by Salinas, et al. This more recent work has pointed up the need to go beyond the simplest independent-electron model, to include the Coulomb interaction between electrons and also nonequilibrium electron populations. These interactions cause the energy levels to merge into a continuum above the Thouless energy and can cause a single quasiparticle level to show up as a cluster of resonances. The strong spin-orbit interaction in Au can cause levels to split in magnetic fields with a g-factor of ~ 0.3, *instead of the free electron* $g = 2$. *In addition, there is evidence for a proliferation of low-lying energy levels suggestive of system spin values greater than* $1/2$ *induced by the exchange interaction. This paper will review the evolving progress that has been made in interpreting these observations.*

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1. INTRODUCTION

In this paper, we review the results of experiments in our laboratory on single-electron tunneling through metallic quantum dots, and the interpretation of these results. The quantum dots are produced by deposition of a thin, granular film onto an insulating substrate. A single selected grain is connected to two electrical leads by high-resistance, low-capacitance tunnel junctions. If the tunneling resistances are well in excess of the quantum resistance $R_Q = h/e^2 \approx 23$ kOhm, the number of electrons on the grain is a good quantum number. This number can be changed one at a time by tunneling of individual electrons through the junctions. If the grain is small enough, the low-lying quantum energy levels of the conduction electrons are separated sufficiently to be resolved. In such a system, it is possible to carry out tunneling spectroscopy measurements which directly reveal the energy eigenvalues of the electrons in a small metallic grain which typically contains a few thousand conduction electrons. Such measurements were first carried out a few years ago by Ralph, et al. on nanograins of Al [1–4]. More recent measurements have extended this work to nanoparticles of the heavy metal Au [5,6] and to alloys of Al and Au [7]. This more recent work has pointed up the need to go beyond the simple independent-electron model, which was used for an initial understanding of the spectra, to include both the Coulomb interaction between electrons and the spin-orbit interaction. In addition, we will see that nonequilibrium electronic populations can change the observed spectra, and that the Thouless energy sets an upper limit on the energy at which discrete levels can be resolved.

2. SAMPLE PREPARATION

In the deposition of thin granular metal films, the grains typically nucleate at a certain center-to-center separation (e.g., $\sim$ 12 nm in the work of Davidović [5]) which is determined by such parameters as surface diffusion rates and surface tension. As more metal is deposited, the grains grow in thickness and diameter, retaining the same separation. In preparing samples for the experiments on tunnel spectra of metallic nanograins, the deposition process is stopped before the individual grains form a percolating network. Instead, they form an irregular array of grains of similar but not identical size, and with a shape that is roughly hemispherical (although perhaps facetted), but tends to a pancake shape as the grains grow in area after a certain thickness is achieved. The experimental challenge is to find a way to make electrical tunnel contact with only a *single* grain from this array.

The pioneering experiments of Ralph, et al [1–4] were carried out using a

novel configuration based on first creating a nanometer scale hole in a SiN membrane (by a process developed at Cornell University by Ralls, et al. [8]), and using this hole to select a single grain for tunnel contact. In the more recent experiments of Davidović and Tinkham [6] successive evaporations at carefully controlled angles, without breaking vacuum, are used to arrange that only a single grain is in tunnel contact with both the lower and upper Al electrode. For more details, see the original publications. [1–6] With either technique, it is possible that 2 or 3 grains are contacted, but because of the exponential dependence of tunnel resistance on barrier thickness, the current through one particular grain usually dominates. The dominance of tunneling through a single grain can be confirmed by carefully observing whether the shifts in the positions of features in the measured $I - V$ curves when the superconducting energy gap in the Al electrodes is destroyed by a magnetic field correspond to a unique ratio of the capacitances from the grain to the two electrodes.

The above description barely hints at the difficulty of actually preparing "good" samples. Such a sample is one with no stray leakage conductances and especially one with a minimum amount of "charge noise" stemming from random motions of electronic charges within the dielectrics surrounding the metallic elements. These considerations account for the dominant use of Al electrodes and Al_2O_3 tunnel barriers in these experiments. These materials are notably free of weakly conductive off-stoichiometry oxides, such as are found with Nb, and of possible additional complications from antiferromagnetism in materials such as Cr and Cr Oxides.

3. THEORETICAL OVERVIEW

The important characteristic energies of a non-interacting electron gas are the Fermi energy $E_F \approx 5eV$ and the spacing between discrete electronic energy levels, namely $\delta \approx E_F/N$, where N is the total number of conduction electrons in the grain. In the grains under study, the diameter is typically 5 - 10 nm, so the number of electrons is typically 10^3 to 10^4, and hence $\delta \approx 0.5 - 5meV$. Because the full width at half maximum of the Fermi function derivative df/dE used to probe the tunnel spectrum is $\sim 3.5k_BT$, it might be expected that these levels would yield resolvable tunneling features so long as the measurements are made at temperatures such that $k_BT << \delta$. However, because of strong Coulomb and spin-orbit interactions, the true situation is not so simple.

The most straightforward effect of the Coulomb interaction is the classical electrostatic energy required to add (or subtract) an electron from an

originally neutral grain. This charging energy is usually approximated by $E_c = e^2/2C_\Sigma$, the expression for the macroscopic charging energy of the capacitance between the grain and the environment. This C_Σ is usually dominated by $C_1 + C_2$, the sum of the capacitances of the two tunnel junctions coupling to the grain. This capacitance is proportional to the area of the tunnel junctions, and so typically scales with the surface area of these ultrasmall grains, while the density of electronic energy levels scales with the volume of the grain. For grains of the size of interest here, the Coulomb energy E_c is typically an order of magnitude larger than the level spacing δ. Consequently, it is possible and necessary to distinguish the spectra of the grain with different numbers of electrons.

The starting point for interpreting the observed spectra is an independent electron model, in which each electron is assumed to occupy an orbital defined by a Hamiltonian in which the Coulomb interaction with the other electrons is taken into account on a mean field basis, and the system energy is simply the sum of the single electron energies of the occupied orbitals. Taking account of the interelectronic Coulomb interaction beyond this simple mean field approximation introduces a whole new level of subtlety and sophistication to the problem. The single-electron eigenstates no longer have rigorous meaning. The true eigenstates of the grain must be many-electron states, because individual electrons can no longer be treated as independent isolated systems. Moreover, because the grain must be coupled to the macroscopic electrodes by tunneling if measurements are to be made, even the whole grain can not be treated as an isolated system with infinitely sharp energy levels. Thus, the sharpest spectral features may reflect many-electron eigenenergies, which, with increasing energy can be much more densely spaced than single-electron eigenenergies, while broader features may reflect the single-particle energies, broadened by interactions with other electrons in the grain.

Agam, et al. [9] approached this problem by generalizing the independent-electron model to the extent of recognizing that the mean-field energy levels will depend to some extent on which other orbitals are occupied. They further pointed out that, while the ground state involves a unique set of occupation numbers and hence unique eigenenergies, non-equilibrium occupancies stemming from incomplete relaxation between tunneling events in an actual experiment can lead to a variety of shifted eigenenergies, forming a cluster of tunneling resonances based on a single independent- electron energy level. Each peak in the cluster is associated with a different nonequilibrium occupation of other single-particle states, i.e., with a different *many-body* state of the grain.

The discussion of the preceding paragraph considers the shifts in the energies of tunneling resonances caused by interactions, but not the effect

of the interactions in broadening the resonances. It is well known that in macroscopic samples interelectronic interactions cause the decay rate or level width of quasiparticle excitations to increase quadratically with energy above E_F. This issue was treated in the context of mesoscopic samples by Sivan, Imry, and Aronov [10] and others [11]. They found that as one considers states further above the Fermi sea ground state, the states become broader in energy, and merge into a continuum above an energy approximated by the Thouless energy $E_T = \hbar/\tau_T$. Here τ_T is roughly the time required for a semiclassical electron to diffuse through the sample. That is, they found that the number of resolved energy levels should be *finite* even at $T = 0$, and only of order E_T/δ, typically ~ 10 in their samples. This theoretical analysis was developed further in a non-perturbative model approach by Altshuler, et al. [12], who predicted that as one considered levels further and further above the system ground state, one should first find completely sharp levels, then clustered levels and levels of finite width, and finally (at $\sim E_T$) a continuous structureless tunneling density of states as found by Sivan, et al. Rather clear evidence for such a progression has been found in the recent experiments of Davidović and Tinkham, [6] reported below.

To complete this brief overview, we now mention the consequences of electrons having spin as well as charge. At the simplest level, this makes each single-particle orbital level doubly degenerate with respect to spin. At a somewhat deeper level, spin-orbit coupling mixes the two spin-states for a given orbital level to form a degenerate Kramers doublet state with a g-value which can be considerably reduced from the free-electron value of $g = 2$. Further complexity arises because of the spin-dependent "exchange" energy, which apparently gives rise to unexpectedly many low-lying triplet and even higher multiplicity many-electron states for the system, in addition to the singlet states expected (with an even number of electrons) from a simple sequential level-filling model. These issues will be discussed in section 7 in conjunction with recent experimental results.

4. PARAMETER EVALUATION BY COULOMB STAIRCASE MEASUREMENTS

Before one can quantitatively interpret the spectra of resolved energy levels in a grain, one needs to know the capacitance and resistance of the tunnel junctions by which electrical contact to the grain is made. These parameters can be inferred by fitting the $I - V$ characteristic of the device measured at 4K, where individual energy levels are not resolved, to the predictions of the 'classical "orthodox theory" of Averin and Likharev [13].

In this theory, for given tunnel resistances, transition rates are determined by differences in system energies calculated by classical electrostatics for states with various numbers of excess (or deficiency) charges on the grain, and as a function of the applied bias voltage V (and gate voltage V_g, if a gate electrode is used). With these ingredients, one can set up a "master equation", and solve to find the self-consistent steady-state current through the device as a function of the bias voltage. The junction capacitances C_1 and C_2 and resistances R_1 and R_2 can be determined by fitting the data with $I-V$ curves simulated in this way for various parameter values.

These $I-V$ curves have the form of a "Coulomb staircase". That is, they consist of straight line segments, which change slope (and/or value) at regularly spaced voltage values, at which either the equilibrium number of electrons on the grain changes by one, or at which some new cycle of charging and discharging becomes energetically possible. The values of the two junction capacitances and of the offset charge Q_0 can be inferred directly from the voltages at which these corners occur. The sum of the two tunnel resistances is readily determined from the overall slope of the $I-V$ curve, but the ratio of the two resistances can only be estimated from quantitative simulations. For details on this procedure, see, for example, Hanna and Tinkham [14]. The offset charge Q_0 characterizes the effect of miscellaneous stray charges trapped in the surrounding dielectric. Unfortunately, Q_0 is subject to random shifts, typically with a $1/f$ spectrum, which shows up as "charge noise" superposed on the data. This noise is a major problem in measurements of tunnel spectra. Fortunately, an occasional sample is unusually quiet, allowing high quality data to be obtained, typically after waiting a few days at low temperature for charge relaxation to occur.

When interpreting data from these single-electron tunneling devices, it is important to note that a voltage applied between the two electrodes is split by capacitive voltage divider action, with fractions $C_2/(C_1+C_2)$ and $C_1/(C_1+C_2)$ appearing across C_1 and C_2, respectively. Accordingly, the energy available to transfer an electron from an electrode to the grain when a voltage V is applied to the device will be eV times the one of these ratios which refers to the junction through which the tunneling process occurs. Thus, it is essential to know the ratio of C_1/C_2 in order to be able to correctly convert measured *voltage* intervals into energy level differences. For example, the accuracy with which g-values for spin splittings can be determined is limited by the accuracy with which this ratio is known.

Given a non-zero Q_0 (which is a signed quantity), clearly there is no reason for the $I-V$ curve to be simply antisymmetric about $V=0$, and the asymmetry is further complicated by the differences in capacitance and resistance between the two tunnel junctions. Thus, the $I-V$ curves for

positive and negative voltages may show a certain resemblance to each other, but will not be exact inversion images.

5. DISCRETE LEVEL SPECTRA IN NORMAL METALLIC GRAINS

The first successful observations of resolved discrete energy levels in metallic nanoparticles were carried out by Ralph, et al. [1] using aluminum particles and aluminum electrodes, with aluminum oxide tunnel barriers. Although bulk aluminum is superconducting, these first samples were in the normal state because the superconducting size effect prevents superconductivity in such small particles. Instead of the smooth onset of current above the Coulomb blockade seen at 4K, the onset of current at $\sim$ 100 mK occurs in a series of discrete steps. Each step occurs when the applied voltage becomes sufficient to make it possible for an electron to tunnel from the continuum of energy states in one electrode (at the Fermi energy) into an empty additional, higher energy discrete quantum state in the island. Thereafter an electron must tunnel out of the island into the other electrode to complete the cycle, before another electron can enter the grain. These discrete features are shown more clearly by plotting the derivative dI/dV, which displays a peak for each successive tunneling resonance.

Insofar as the energy state in the grain is much sharper than k_BT, the tunneling resonance should have the shape of df/dE, the derivative of the Fermi function. This is a bell-shaped curve with full width at half maximum of $\sim 3.5k_BT$, where T is the temperature of the electrons in the electrode. Experimentally, one finds semi-quantitative agreement with this prediction, except that the resonance widths bottom out at nominal temperatures of about 50 - 100 mK, indicating that the electron temperatures do not follow the dilution refrigerator mixing chamber temperature down below such temperatures. Also, the minimum resonance widths were found to increase with increase in the resonance energy, suggesting an additional energy-dependent intrinsic level width from lifetime considerations. We shall return to this issue in section 6.

When a magnetic field H is applied to the sample, this produces a Zeeman splitting which lifts the spin degeneracy of the orbital levels. In the early experiments on Al grains, the g-value governing the splitting of the tunneling resonances was usually found to be 2 ± 0.05, near the free electron value of 2, as might be expected for a low-Z element for which spin-orbit coupling is weak. In a few samples, however, significantly lower g-values (~ 1.8) were found, and these spectra also showed avoided crossings

of the positions of resonance peaks corresponding to up and down spins [2]. It appears likely that both these unusual features are due to the presence of a few high-Z impurities in these particular grains. This idea has been tested recently by Salinas, et al., [7] who found similar effects in Al grains with a deliberate admixture of $\sim 4\%$ of Au. Much more dramatic departures from $g = 2$ are found in the recent experiments of Davidović and Tinkham [6] on grains of pure gold, a high-Z element. These experiments show g-values of ~ 0.3, indicating that the spin-orbit coupling in Au strongly mixes spin-up and spin-down states in the process of forming a Kramers doublet of time-reversed states which also diagonalizes the Hamiltonian.

One can normally distinguish grains with even and odd numbers of electrons by the nature of the splitting of the tunneling resonances in a magnetic field. If the grain initially contains an even number of electrons, filling paired spin-up/down states, then an additional electron tunneling into the grain can enter any empty higher level with either spin direction, giving resonances that split in a magnetic field. On the other hand, if the number of electrons before tunneling is odd, then the lowest empty state will be the high energy spin orientation of the singly- occupied level. Since this state is uniquely determined, there is no splitting in a magnetic field, only an increase in energy linear in H, proportional to its g-value. This interpretation is based on the assumption that the relevant energy levels can be thought of as those of non-interacting electrons, just filling shells in order of ascending energy. Although this is a useful starting point, it can not readily explain some observations, such as that the single-sided level shift predicted for the lowest resonance can also occur for the second resonance as well. A wider range of possibilities will be considered in the next two sections.

6. EFFECTS OF ELECTRON INTERACTIONS: CLUSTERS AND FINITE LEVEL WIDTHS

We now review in somewhat more detail the experimental observations and theoretical developments which take us beyond the simple picture in which the energy state of the many-electron system is approximated by the occupation of a specified set of quasiparticle eigenstates, with simply additive energies as in basic Fermi liquid theory.

As mentioned above, an important step beyond this approach was made by Agam, et al., [9] They pointed out the need to take account of cross terms in the Fermi liquid energy expansion. That is, the energy associated with a particular quasiparticle (or Fermi liquid excitation) will depend to some extent upon what other excitations are present as well. Thus, instead of a single en-

ergy value associated with tunneling into a quasiparticle state, there will be a cluster of possible values, depending on what other quasiparticle states are excited. This possibility would not arise if one considered only equilibrium states at $T \approx 0$, since only the lowest energy configuration of excitations would be present. But Agam et al. pointed out that if successive tunneling events took place more quickly than relaxation from previous events took place, there would be a certain probability of nonequilibrium occupation numbers, and hence of several possible energies for a given quasiparticle excitation. An important implication of this model in its simplest form is that the lowest tunneling resonance should remain single, because a second tunnel event into a given level could not take place until the level had been vacated by a relaxation process, and the lowest excited level could not be relaxed except to the unique ground state of the island. This model was very successful in accounting for observations made by Ralph, et al. [2]. Indeed, in many samples the lowest resonance appeared to be single, while higher resonances took the form of clusters of subresonances. Moreover, the cluster concept was able to explain in a natural way why the density of observed resonant *peaks* (particularly at somewhat higher energies) was considerably larger than the density expected from the classic density of *single-particle states* in a grain of given size, an observation that had been quite worrisome and puzzling when first made. Essentially, we were seeing eigenenergies of the system, not of single particles.

The approach of Agam, et al., was essentially a perturbative one, taking account of higher-order Fermi liquid corrections to excitation *energies*, based on interelectronic interactions. Somewhat earlier, Sivan, et al., [10,11] had applied a perturbative approach, based on earlier work by Altshuler and Aronov [15] to estimate the level *width* which results from the lifetime limitation due to the interelectronic interactions. Their conclusion was that the level widths should increase with excitation energy E, as expected from general considerations, and become as large as the level spacing when $E \sim E_T$, the Thouless energy. [This energy is of order $\hbar/\tau_T$, where τ_T for a sample of size L with diffusive transport is quite a well defined time $\sim L^2/D$, where D is the diffusion constant. For particles with ballistic transport and diffuse surface scattering, τ_T is less well defined but thought to be similar to the diffusive case, except that the sample dimension would set the effective mean free path.] This result implies that above E_T, the quasiparticle excitations, although still well-defined, are broad enough to overlap, forming a continuum. Careful analysis of experimental measurements by Sivan, et al., [10,11] on semiconductor quantum dots supported this conclusion. For example, an autocorrelation analysis of the tunneling data suggested that only ~ 10 discrete levels were found for a semiconductor system containing thousands

of electrons.

Another important step in developing the theory of quasiparticle lifetimes was a *non*perturbative model treatment by Altshuler, et al. [12]. Their approach was to map the problem of lifetimes limited by electron-electron interactions into a problem of localization in the Fock space of wavefunctions, analogous to the problem of Anderson localization of wavefunctions in coordinate space. From this perspective, localized and delocalized regimes correspond to quasiparticle resonances of zero and finite width, respectively. According to their analysis, the quasiparticle spectrum of a quantum dot should fall into a series of four regimes with increasing excitation energy. The borders of these regimes are most conveniently described in terms of the dimensionless conductance $g = E_T/\delta$, a parameter whose value is typically only of order $5 - 10$ in these small grains. In terms of this parameter, the quasiparticle states are predicted to be sharp and single up to an energy $\sim (g/lng)^{1/2}\delta$, then sharp but clustered up to $\sim (g)^{1/2}\delta$, then broad but resolvable up to $\sim g\delta$, and finally forming an unresolved continuum above the Thouless energy $E_T = g\delta$. This summary does not do justice to the subtlety of the theory. Moreover, these simplified results should be used with caution, since the parameters E_T and g can only be estimated, either from the data or *a priori* for a (presumably) ballistic grain. Nonetheless, these results provide a framework for interpreting data from tunnel spectroscopy.

The early data of Ralph, et al., were in qualitative agreement with the basic prediction that with increasing energy, the tunneling resonances should show a tendency to clustering and blending into an unresolved continuum. However, since these data were taken before this detailed theory was available, careful measurements were not made over a sufficient range of energies to provide a real test.

This situation has been remedied to a considerable degree by the recent data of Davidović [6] shown in Fig. 1 for three different samples. For samples 1 and 2, the complete progression from resolved narrow resonances to an effectively uniform tunneling density of states is displayed, while for sample 3, one sees the progression from sharp isolated peaks to clusters, but the data do not extend to high enough voltage to reach the continuum. For the first two samples our estimates of the Thouless energy (37 and $75meV$) agree within a factor of 2 with the voltage of the transition to a uniform continuum density of states, while for sample 3 the estimated value ($40meV$) is above the range of available data, and hence consistent with it, since the data do not extend far enough to reveal the start of the continuum. Taken all together, these data display rather directly the progression of regimes that are predicted by the theory, but further work will be required to test the more quantitative aspects of the theory by studies of a greater variety of

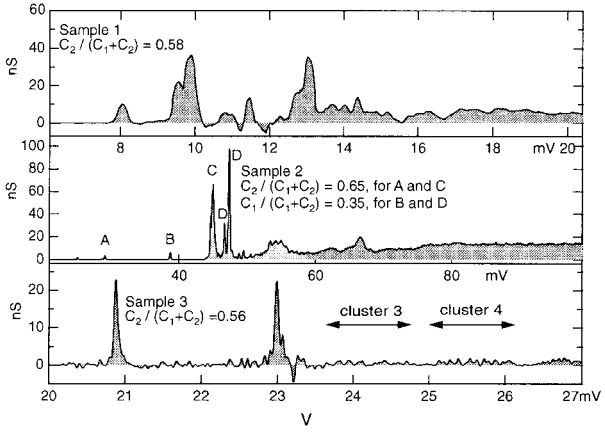

Fig. 1. Excitation spectra in three different Au samples, at $T = 30$ mK (and $H = 1T$ to suppress superconductivity in the Al leads). In order to convert from voltages to particle eigenenergies, voltages must be multiplied by the appropriate capacitance-ratio factor, indicated for each graph. (After ref. 6.)

samples.

The theory ignores the Coulomb blockade charging energy, treating it as just a (large) additive constant for all the excited states for any given charge state of the grain. But all tunneling experiments involve a tunneling cycle, where one adds an electron followed by an electron leaving to the other electrode, so that the full energy $eV(>> \delta)$ is supplied by the bias source in each cycle. Our data suggest that it is this total energy eV, rather than only the energy in excess of the Coulomb blockade energy which should be compared with the estimated Thouless energy in comparison with theory. This result is qualitatively consistent with the earlier work of Ralph, et al.[3] in which it was found that a given tunneling resonance became sharper when a gate electrode was used to reduce the Coulomb blockade, and hence the resonance voltage, by adjusting the offset charge Q_O.

7. SHELL STRUCTURE, EXCHANGE INTERACTIONS, AND PROLIFERATION OF LOW-LYING EXCITATIONS

In building up the periodic table of ordinary atoms, one fills the successive shells and subshells in order of ascending energy: 1s, 2s, 2p, 3s, etc. until the desired number of electrons are accommodated. If this occurs at a

point when all shells either are completely filled or completely empty, this leads to a non-degenerate ground state. However, for all other cases, there will be a partially filled shell, which implies a choice of the specific orbital or spin states that are occupied, all at the same zero-order total energy. In the next order, this degeneracy is lifted by interelectronic interactions, so that, a particular many-electron state will be lowest. This is the province of the famous Hund Rules, the first of which stipulates that the state of maximum total spin S that can be formed without elevating any electrons to higher subshells will have the lowest energy. Physically, this is a consequence of the correlation of motion of electrons with parallel spins to avoid each other in space that is enforced by the antisymmetry of the wavefunction under exchange of electrons. This correlated motion acts to reduce their mutual Coulomb repulsion energy. These effects are often referred to as "exchange" energies, and they are of the same order as other interelectronic Coulomb energies. In a metallic quantum dot, we assume that the symmetry is low enough that each orbital has a distinct energy, so that there are no exact spatial degeneracies to split. Still, if the interelectronic interactions are comparable with, or larger than, the level separation, these exchange energies may still play a role in controlling the order of filling of energy levels. For example, they might make a triplet ($S = 1$) state of two electrons lie lower than a singlet ($S = 0$) state, even if it requires one electron to occupy a slightly higher energy orbital to allow the two spins to be parallel.

This qualitative idea has been carried to a more quantitative level by Brouwer, Oreg, and Halperin [17]. Taking account of the statistical distribution of level spacings in a random matrix toy model, they found that the probability that the ground state have $S = 1$ exceeds the probability that $S = 0$, even when the ratio of interaction energy to mean level spacing is as small as 0.4. An even greater deviation from the simple picture was found experimentally by Gueron, et al. [19] in studying nanoparticles of ferromagnetic Co; a substantial fraction of the electrons were found to be polarized, as in macroscopic samples. This conventional ferromagnetism is a very different regime from the case considered in [17] in which the net spin is found to be of order unity even in larger grains, and not to scale with grain size.

A combinatoric state-counting argument may provide useful insight here. By analogy with the structure of the BCS ground state of a superconductor, we consider the low-lying excited states above the Fermi sea ground state which might be used to form a many-body state in which the exchange interaction energy is sufficient to overcome the small increase in kinetic energy. For example, consider a grain with an even number of electrons, and let the kinetic energy of the Fermi sea ground state be taken as zero. Then consider the four excited states that can be formed by electron and hole

excitations in the first level above and the first below E_F, taking account of both possible spin orientations. To conserve electron number, 2 of these 4 states must be occupied. There are $4!/2!2! = 6$ such combinations, with an average energy equal to the level spacing δ. Of these 6 many-body states, 3 form a triplet, and the other 3 form three singlets. That is, there is a 50% *a priori* probability that a low-lying level will be part of a triplet state. If one doubled the energy range of states considered, to include the first two orbitals above and below E_F, there would be $8!/4!4! = 70$ many-body states with an average extra kinetic energy of 4δ. Five of the 70 would form one state with $S = 2$, while 45 of them would form 15 states with $S = 1$, and the remaining 20 would be singlets. In this example, the density of many-particle states per unit energy would be $\sim 70/4 \sim 17$ times the density of single-particle states, and the density of many-body states is known to grow exponentially with energy. Thus, when spin is taken into consideration, the number of low-lying states proliferates very rapidly, whatever the spin of the actual *ground* state.

There is considerable experimental evidence from a proliferation of low-lying resonances that such higher spin states are observed. Fig. 2 shows the low-energy excitation spectra of three ultrasmall Au grains. [18] In each spectrum, there are considerably more resolvable resonances than can be accounted for in the simple picture of sequential filling of independent-electron levels. For example, in the 4.7 nm grain shown in Fig. 2(a), the lowest resonance is clearly not single, as predicted by the Agam model, but at least double; in a field of $5T$, a total of 5 peaks can be resolved. In the 2 nm sample shown in Fig. 2(c), the lowest resonance shows ~ 10 subresonances in zero field, and about 20 in a field of $7T$. It is hard to account for these observations without introducing the notion of higher spin states.

In metallic quantum dots with low symmetry, orbital angular momentum is not a good quantum number, and no simple result such as the Lande' g-factor for level splittings in a magnetic field is possible. Nonetheless spin-orbit coupling *does* reduce the effective g-value below the free-electron value of 2 by mixing together states with spin up and spin down [20]. If the total angular momentum is half integral, these composite states exist as time-reversed pairs of states, forming a so-called Kramers doublet. In a magnetic field, the energies of these pairs of states split apart just like the spin up and down energies of a free electron, except that the splitting is described by a non-obvious g-value. This g-value can be much less than 2 if the spin-orbit coupling mixing the spin states is strong, as it is for a high-Z element like Au. For example, Davidović [6,18] finds g-values in the range $0.3 - 0.4$ in pure Au grains, while Salinas, et al. [7] find g-values of $\approx 1.7 - 1.8$ in Al grains containing a few percent of Au. These values are to be compared with the

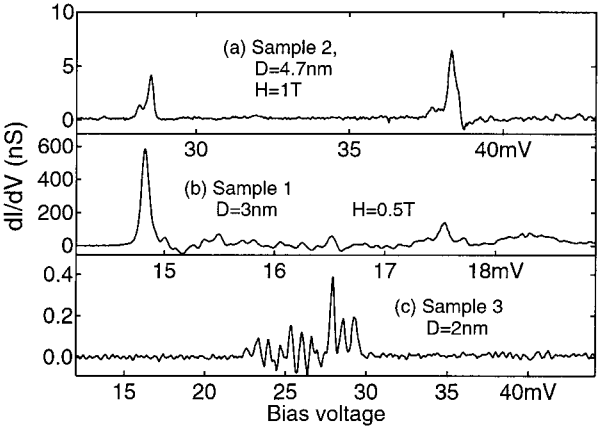

Fig. 2. Fine structure in electronic tunneling spectra in three different Au nanoparticles at dilution refrigerator temperatures (After ref.18.)

g-values of 1.98 ± 0.03 found for pure Al grains [3] and the g-value 2.1 reported from spin-resonance measurements on pure bulk Au [21].

Summing up this final section, recent experiments [6,7,18] together with the earlier data of Black [16] show that a model of filling successive single-electron orbitals, with alternating spin up and spin down, is too simplistic to account for all the data. Interelectronic coupling energies often make the available energy level structure depend on the number of electrons present to an extent that can not be described in the simple scheme based on non-interacting electrons. In addition, spin-orbit coupling mixes up and down spins to reduce the g-value. Clearly more experimental and theoretical work is needed to build a complete understanding of these phenomena.

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