Paramagnetic Breakdown of Superconductivity in Ultrasmall Metallic Grains

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We study the magnetic-field-induced breakdown of superconductivity in nm-scale metal grains having a mean electron level spacing $d \simeq \tilde{\Delta}$ (bulk gap). Using a generalized variational BCS approach that yields good qualitative agreement with measured spectra, we argue that Pauli paramagnetism dominates orbital diamagnetism, as in the case of thin films in a parallel magnetic field. However, the first-order transition observed for the latter can be made continuous by finite size effects. The mean-field procedure of describing the system by a single pairing parameter Δ breaks down for $d \simeq \tilde{\Delta}$. [S0031-9007(97)03675-2]

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When a system of (correlated) electrons is sufficiently small, the electronic spectrum becomes discrete. This allows one to study the nature of electron correlations in unprecedented detail by analyzing the details of the spectrum. It has recently become possible to measure such discrete spectra directly by studying electron transport through nm-scale metallic grains (radius $r \approx 5$ nm), for which the mean spacing $d = 1/\mathcal{N}(\varepsilon_F)$ is $\simeq 0.1-1$ meV [1,2]. For Al grains the effects on the spectrum of spin-orbit interactions [1], nonequilibrium excitations [3], and superconductivity [1,4,5] have been investigated.

Studying the latter is particularly interesting in grains with $d \simeq \tilde{\Delta}$ (bulk gap), near the lower size limit [6] of observable superconductivity. The number of free-electron states that pair correlate (those within $\tilde{\Delta}$ of ε_F) is then of order one. Thus, even in grains in which a gap can still be observed [1], pairing correlations are expected to become so weak that they might be destroyed by the presence of a single unpaired electron [4]. A direct way to probe this is to turn on a magnetic field, whose Zeeman energy favors paramagnetic states with nonzero total spin.

In this Letter, we develop a theory for the paramagnetic breakdown of superconductivity in nm-scale grains. We exploit analogies to thin films in a parallel magnetic field [7], but explicitly take account of the discreteness of the spectrum. To calculate the eigenenergies E_n of the grain's lowest-lying eigenstates $|n\rangle$, we adopt a generalized variational BCS approach that goes beyond standard mean-field theory by using a different pairing parameter Δ_n for each $|n\rangle$. Using the E_n to reconstruct the tunneling spectra, we find qualitative agreement with measured spectra [1], and show that the H-induced first-order transition to the paramagnetic normal state observed for thin films can be softened in ultrasmall grains.

Experimental results.—Our goal is to understand in detail the H dependence of the measured discrete tunneling spectrum (see Fig. 3 of [2]) of an ultrasmall Al grain, coupled via tunnel barriers to one gate and two lead electrodes to form a nm-scale transistor. Each line in the spectrum corresponds to the H-dependent energy $E^N_{n_f} - E^{N\pm1}_{n_i} + (E^N_C - E^{N\pm1}_C)$ needed for some rate-limiting electron tunneling process $|n_i\rangle_{N\pm1} \rightarrow |n_f\rangle_N$ off or onto the grain, where $|n\rangle_N$ is an eigenstate (with eigenenergy $E^N_n + E^N_C$) of the N-electron island with charging energy E^N_C. Since the change in charging energy δE_C depends on the adjustable gate voltage V_g, so does the odd-even ground state energy difference $(E^{N+1}_G - E^N_G)$ (so that the BCS gap for the ground state of an odd grain cannot be measured absolutely). Therefore only the energy differences $E^N_{n_f} - E^N_{n_{f'}}$ between same-N final states of transitions with the same initial $|n_i\rangle_{N\pm1}$, i.e., the spacing *between* lines of a given spectrum, are physically significant. They give the grain's fixed-N eigenspectrum. By appropriately adjusting V_g, both even and odd spectra [$N = 2m + p$, with $p = (0, 1)$ for (e, o) parity] were measured, and nonequilibrium effects [2,3] minimized.

The presence (absence) of a clear spectroscopic gap $2\Omega > d$ between the lowest two lines of the odd-to-even (even-to-odd) measured spectra [Figs. 3(a) and 3(b) of [2]] reveals the presence of pairing correlations [1,4]: in even grains, all excited states involve at least two BCS quasiparticles and hence lie significantly above the ground state, whereas odd grains *always* have at least one quasiparticle and excitations need not overcome an extra gap.

Pauli paramagnetism.—The measured levels' approximately linear behavior with H can be attributed to the electrons' Zeeman energies $\pm h \equiv \pm\frac{1}{2}\mu_B g H$; indeed, the differences between measured slopes of up- and down-moving lines correspond to g factors between 1.95 and 2. (Deviations from $g = 2$ probably result from spin-orbit scattering, known to be small but nonzero in thin Al films [7], but neglected below.) Thus, the H dependence of the spectroscopic gap $\Omega(H)$ is almost entirely of Zeeman origin. Note that $\Omega(H)$ must be distinguished from the BCS pairing parameter $\Delta(H)$. In contrast to bulk samples, in ultrasmall grains the suppression of $\Delta(H)$ through orbital diamagnetism is very weak, just as in thin

films in parallel fields [7]: The flux through the grain (whose radius 5 nm $\ll$ the penetration length of 50 nm) is of order 5% of a flux quantum ϕ_0 at $H = 7$ T, i.e., too small to significantly affect the orbital motion of electrons between reflections off the grain boundaries. Slight deviations from H linearity observed in some larger grains [1] probably reflect the onset of orbital diamagnetism (giving corrections to eigenenergies of order $\lesssim \hbar v_F r^3 (H/\phi_0)^2$ [8]). But for the spectra of interest here, they are much smaller than Zeeman effects and hence will be neglected.

Now, Clogston and Chandrasekhar (CC) [9] argued that in the absence of orbital diamagnetism, superconductivity will be destroyed by Pauli paramagnetism: Let $|s\rangle$ denote the ground state of the spin-s sector ($s = J + p/2$ with J an integer) of the $(2m + p)$-electron Hilbert space [10], with exact eigenenergy $E_s(h, d) = E_s(0, d) - 2sh$ ("spin" simply means $\sum s_z$ with $s_z = \pm\frac{1}{2}$). CC pointed out that a ground state transition will occur from $|p/2\rangle$ to some *normal* state $|\bar{s}\rangle$ when $E_{p/2}(\bar{h}, d) = E_{\bar{s}}(\bar{h}, d)$ at some sufficiently large field $\bar{h}$. For $d \ll \tilde{\Delta}$ (as in thin films), $E_{p/2}(0, d) = -\tilde{\Delta}^2/2d$ and $E_{\bar{s}}(0, d) = (\bar{s}^2 - p/4)d$, with $\bar{s} \simeq \bar{h}/d$ [to ensure $\partial_{\bar{s}} E_{\bar{s}}(h, d) = 0$]. Thus, CC predicted a first-order transition at a critical field $\bar{h}_{\rm CC} = \tilde{\Delta}/\sqrt{2}$, the new spin $\bar{s} = \tilde{\Delta}/\sqrt{2}\,d$ being macroscopically large. In tunneling measurements [7] into thin (5 nm) Al films ($\tilde{\Delta} = 0.38$ meV and $H_{\rm CC} = 4.7$ T) this first-order transition was observed as a *jump* in the tunneling threshold from $\Delta - h_{\rm CC}$ to 0 at $\bar{h}_{\rm CC}$. In contrast, the measured energy levels for ultrasmall grains evolve *continuously* with h, showing kinks but no jumps. We suggest that this reflects a "softening" of the transition that occurs when $d \simeq \tilde{\Delta}$, for which $\bar{s}$ should become of order one. We shall show this explicitly by performing model calculations of the energies $E_{\bar{s}}(h, d)$ of BCS-like pair-correlated variational states $|s\rangle$.

The model.—We adopt the reduced BCS Hamiltonian used in Ref. [4] with an additional Zeeman term:

$$H = \sum_{j\sigma} (\varepsilon_j + \sigma h) c^\dagger_{j\sigma} c_{j\sigma} - \lambda d \sum_{j,j'} c^\dagger_{j+} c^\dagger_{j-} c_{j'-} c_{j'+} . \tag{1}$$

$c^\dagger_{j\pm}$ create free time-reversed states $|j, \pm\rangle$, whose energies $\varepsilon_j = jd + \varepsilon_0 - \mu$, measured relative to the chemical potential μ, are taken uniformly spaced for simplicity (though this is not essential [11]). $j = 0$ labels the first level whose occupation in the $T = 0$ Fermi sea is not 2 but p, and $|F\rangle = \prod_{j=-m}^{-1} c^\dagger_{j+} c^\dagger_{j-} |\text{Vac}\rangle$ is the even Fermi sea.

Variational approach.—Since in the experiments $T = 50$ mK $\ll d, \tilde{\Delta}$, we set $T = 0$. For the spin-s ground state $|s\rangle$, we make a generalized BCS-like variational ansatz [12], which pair correlates all time-reversed states, except for $2s$ unpaired spin-up electrons placed as close as possible to the Fermi surface, to minimize the kinetic energy cost of having more spin ups than downs:

$$|s\rangle = \prod_{j=-J}^{J+p-1} c^\dagger_{j+} \prod_j{}' (u^{(s)}_j + v^{(s)}_j c^\dagger_{j+} c^\dagger_{j-}) |\text{Vac}\rangle . \tag{2}$$

The prime over products (and over sums below) indicates exclusion of the singly occupied states $j = -J$ to $J + p - 1$ (for which $u^{(s)}$, $v^{(s)}$ are not defined). Since $\langle s \,|\, s'\rangle = \delta_{ss'}$, the variational parameters $v^{(s)}_j$ and $u^{(s)}_j$ must be found *independently* for each s (hence the superscript s), by minimizing the variational "eigenenergies"

$$\begin{aligned} \mathcal{E}_s(h, d) &\equiv \langle s|H|s\rangle \\ &= -2hs + \sum_{j=-J}^{J+p-1} \varepsilon_j + 2 \sum_j{}' \varepsilon_j (v^{(s)}_j)^2 \\ &\quad - \lambda d \left(\sum_j{}' u^{(s)}_j v^{(s)}_j \right)^2 + \lambda d \sum_j{}' (v^{(s)}_j)^4 , \end{aligned} \tag{3}$$

which we use to approximate the exact eigenenergies $E_s(n, d)$. The v^4 term, not extensive and hence neglected in the bulk case, is non-negligible, but not dominant either. Solving $\partial \mathcal{E}_s / \partial v^{(s)}_j = 0$ and $u^2 + v^2 = 1$ simultaneously yields $(v^{(s)}_j)^2 = (1 - \bar{\varepsilon}_j / [\bar{\varepsilon}_j^2 + \Delta_s^2]^{1/2})/2$, with Δ_s determined by the generalized gap equation $\Delta_s = \lambda d \sum_j{}' u^{(s)}_j v^{(s)}_j$, and $\bar{\varepsilon}_j = \varepsilon_j - \lambda d (v^{(s)}_j)^2$. (To simplify our calculations, we used $\bar{\varepsilon}_j = \varepsilon_j$; this changes $\mathcal{E}_s$, which is stationary under small changes in $v^{(s)}_j$, only to order λ^2. Then $\langle \hat{N} \rangle = 2m + p$ fixes the chemical potential to $\mu = \varepsilon_0 - \delta_{p,0} d/2$.)

The pairing parameter Δ_s.—In the variational approach, Δ_s is merely an auxiliary quantity in terms of which the $v^{(s)}_j$ and hence $\mathcal{E}_s$ are parametrized, and certainly not directly measurable. It does serve as a measure of the pairing correlations present in $|s\rangle$, though, if $\Delta_s = 0$, $|s\rangle$ reduces to the paramagnetic spin-s ground state $|s\rangle_0 = \prod_{j=0}^{J+p-1} c^\dagger_{j+} \prod_{j=-J}^{-1} c_{j-} |F\rangle$, and the "correlation energy" $\langle s|H|s\rangle - {}_0\langle s|H|s\rangle_0$ vanishes [see Fig. 1(b)]. The gap equation for $\Delta_s(d)$ is h independent (since the h dependence of $\mathcal{E}_s$ is so trivial), and differs from the standard bulk $T = 0$ case (for which $s = p/2$, $d \ll \tilde{\Delta}$)

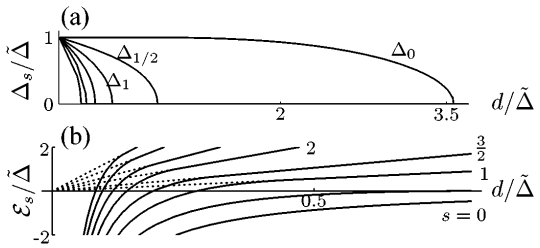

FIG. 1. (a) Pairing parameters $\Delta_s(d)$ for some spin-s states $|s\rangle$, as a function of level spacing d ($\Delta_{0,1/2} = \Delta_{e,o}$ of [4]). (b) The variational energies $\langle s|H|s\rangle - \langle F|H|F\rangle$, plotted as functions of d at magnetic field $h = 0$ (solid lines, $\approx -\tilde{\Delta}^2/2d$ as $d \to 0$) smoothly approach the energies ${}_0\langle s|H|s\rangle_0 - \langle F|H|F\rangle = (s^2 - p/4)d$ (dotted lines) of the uncorrelated states $|s\rangle_0$, since $\Delta_s(d) \to 0$ with increasing d.

through both the discreteness and the s-dependent restriction on the sum, which respectively cause the d and s dependence of $\Delta_s(d)$. Its numerical solution [see Fig. 1(a)] shows that $\Delta_s(d)$ decreases to zero as d is increased, because the kinetic energy cost of pairing correlations, which shift electron occupation probability from below to above ε_F, grows with increasing d [4]. Moreover, $\Delta_s(d)$ *decreases rapidly with increasing* s at fixed d (reaching zero roughly at $d = \tilde{\Delta}/2s$, as can be shown analytically). This s dependence of Δ_s, a generalization of the even-odd effect (namely, $\Delta_{1/2} < \Delta_0$) found in [4], is so strong because for $d \simeq \tilde{\Delta}$ there are only a few ε_j's within $\tilde{\Delta}$ of ε_F (where pairing correlations are strongest), so that increasing s and hence the number of unpaired electrons in this regime *dramatically reduces the strength of pairing correlations.* Evidently, for $d \simeq \tilde{\Delta}$ the standard mean-field description of superconductivity in terms of only a *single* pairing parameter Δ is no longer sufficient.

Conceivably the $\mathcal{E}_s$, which are upper bounds on the exact spin-s ground state energies E_s, can be lowered by using better variational wave functions that sample a larger portion of the spin-s Hilbert space, i.e., by "including fluctuations" about the variational state $|s\rangle$. But in the present context this would hardly be worthwhile, since the E_s also depend quite sensitively on the unknown input energies $\{\varepsilon_j\}$ [11], and here we merely seek a qualitative understanding of the measured tunneling spectra.

Critical fields.—Having obtained $\Delta_s(d)$, we find the energies $\mathcal{E}_s(h, d)$ numerically from Eq. (3). For two same-parity spins $s' = s + J$, $\mathcal{E}_{s'}$ drops below $\mathcal{E}_s$ at the field:

$$h_{s,s'}(d) = [\mathcal{E}_{s'}(0, d) - \mathcal{E}_s(0, d)]/(2s' - 2s). \quad (4)$$

Figure 2 shows several $h_{s,s'}$ as functions of d. For given p, let their lower envelope be denoted by $\overline{h}_{p/2,\bar{s}}(d) = \min[h_{p/2,s'}(d)]$. This gives the "critical field" at which, if h is increased from 0 at fixed d and p, the *first* change of ground state occurs from $|p/2\rangle$ to a new ground state $|\bar{s}(d)\rangle$, whose spin depends on d. Numerically we find $\overline{h}_{p/2,\bar{s}}(d \to 0) = \tilde{\Delta}/\sqrt{2}$, which is CC's bulk result. We also find that *for any* d, $|\bar{s}(d)\rangle$ always has $\Delta_{\bar{s}}(d) = 0$. Thus, the first ground state transition is always directly into a normal paramagnetic state with no pairing correlations.

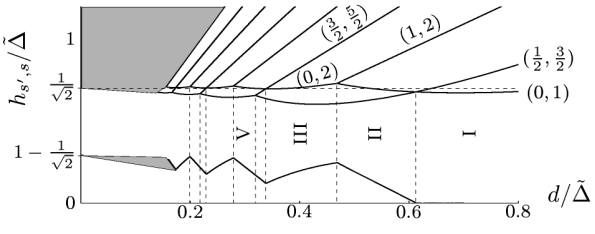

FIG. 2. d dependence of the critical fields $h_{s,s'}$, at which h induces, at *fixed* electron number N, a ground state transition from $|s\rangle$ to $|s'\rangle$, labeled by (s, s') (in contrast we label the N-*changing* tunneling transitions in Fig. 3 by $|n\rangle \to |n'\rangle$). The lower curve gives the jump at $\overline{h}_{0,\bar{s}}(d)$ predicted for the lowest line of the $e \to o$ tunneling spectra of Fig. 3.

As anticipated above, the change in spin, $\bar{s} - p/2$, macroscopically large at small $d/\tilde{\Delta}$, *decreases with increasing* d. In this sense the first-order transition observed in thin films is "softened" for ultrasmall grains. $\bar{s} - p/2$ reaches unity when the correlation energy becomes smaller than the Zeeman energy gained by flipping a single spin: for $p = 0$ (or 1) we find $\bar{s} = 1$ (or $3/2$) when $d/\tilde{\Delta} > 0.47$ (or 0.32). This regime displays "minimal superconductivity": correlations are strong enough to cause a measurable gap, yet so weak that breaking a *single* pair destroys them.

Tunneling spectra.—In analogy to $|s\rangle$, one can also define excited states $|s, n\rangle$ in the spin-s sector of Hilbert space by placing the unpaired spins farther away from the Fermi level, and variationally calculate their energies $\mathcal{E}_{s,n}(h, d)$ (writing $\mathcal{E}_s = \mathcal{E}_{s,0}$). It is easy now to reconstruct the expected tunneling spectra as a function of h at fixed d, by finding the energy cost for all $|s_i, n_i\rangle_{N\pm1} \to |s_f, n_f\rangle_N$ single-electron tunneling transitions. Since these satisfy the selection rule $s_f - s_i = \pm 1/2$, only slopes of ± 1 can occur. Neglecting nonequilibrium effects [2,3], we always take the ground state of a given spin-s sector as the initial state and denote it by $|s_i(h, d), 0\rangle$. The appropriate $s_i(h, d)$ must be determined from Fig. 2.

Whenever h passes through one of the critical fields $h_{s_i,s_i'}$, the current ground state of the $N \pm 1$ electron Hilbert space changes to $|s_i'\rangle$. This produces a discontinuity in the lowest line of the tunneling spectrum if $s_f - s_i'$ now violates the selection rule, or else a kink if only its sign changes relative to $s_f - s_i$. According to Fig. 2, depending on d one can distinguish different regimes I, II, III, ..., in each of which the various s_i to s_i' ground state changes occur in a different order, leading to different magnitudes and positions of jumps in the tunneling spectra. In regime I, where the order of occurrence of ground state changes with increasing h is $(0, 1)$, $(\frac{1}{2}, \frac{3}{2})$, $(1, 2)$, $(\frac{3}{2}, \frac{5}{2})$, ..., there are no discontinuities in the evolution of the lowest line [see Figs. 3(a) and 3(b)]. For example, for the $e \to o$ spectrum, the lowest $|0\rangle \to |1/2\rangle$ line changes *continuously* to $|1\rangle \to |1/2\rangle$ at $h_{0,1}$, since $s_f - s_i' = -1/2$. However, in all other regimes, $\bar{s} > 1$ for the first ground state transition at $h_{0,\bar{s}}$, implying a *jump* in all $e \to o$ lines. The jump's magnitude for the lowest $e \to o$ line, shown as a function of d by the lower line in Fig. 2, starts at $d = 0$ from the CC value $\tilde{\Delta}(1 - 1/\sqrt{2})$ measured for thin Al films [7], and decreases to 0 (nonmonotonically, due to the discrete spectrum), again illustrating the softening of the transition.

The absence of observable jumps in the measured lowest lines can be explained by assuming the grain to lie in the "minimal superconductivity" regime I [13]. Indeed, the overall evolution of the lowest lines of Fig. 3 of [2] qualitatively agrees quite well with those predicted for regime I [Figs. 3(a) and 3(b)], in which the correlation energy is nonzero only for $s = 0, 1/2$. The prediction of $h_{0,1} \simeq 0.95 h_{CC}$ is compatible with the experimentally observed value of $H_{0,1} = 4$ T, which is about 85% of $H_{CC} = 4.7$ T for thin films [7]. The jumps in *higher*

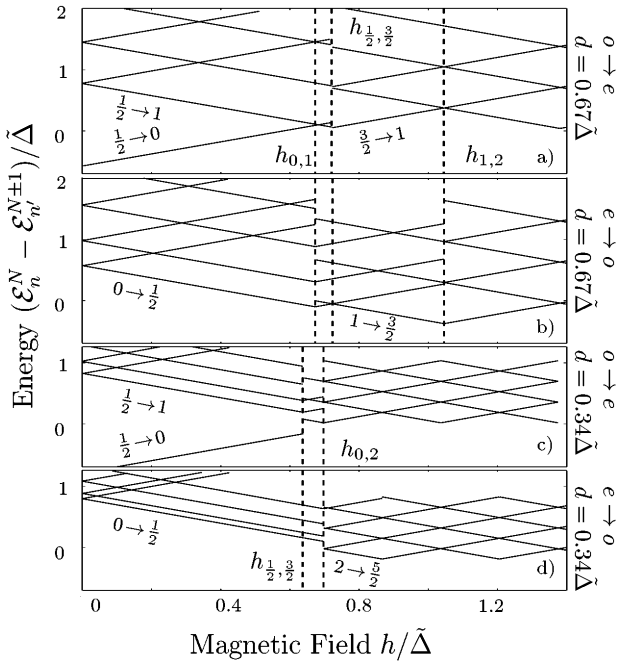

FIG. 3. Tunneling spectra predicted for an ultrasmall superconducting grain for $d/\tilde{\Delta} = 0.67$ and 0.34. Some lines are labeled by the tunneling-induced change $s \to s'$ in the grain's spin. For clarity, not all higher lines are shown. Dashed lines indicate some of the critical fields $h_{s,s'}$.

lines (e.g., in Fig. 3(b) at $h_{1,2}$) are due to correlations left in excited states $|s, n\rangle$ ($\Delta_{s,n} > \Delta_{s,0}$ since the unpaired electrons are farther away from ε_F). Experimentally, these jumps have not been observed. This may be because up-moving resonances lose amplitude and are difficult to follow with increasing h [2], or because the widths of the excited resonances ($\approx 0.13\tilde{\Delta}$) limit energy resolution [3]. More than qualitative agreement between theory and experiment cannot be expected, for we assumed constant level spacing, neglected nonequilibrium effects, and the tunneling matrix elements are unknown.

Our theory predicts that for somewhat larger grains (in regimes II or higher) the tunneling spectra should show jumps even in the lowest line. It remains to be investigated, though, whether orbital diamagnetic effects, which rapidly increase with increasing grain size ($\sim r^3$), would not smooth out such jumps.

Non-time-reversed pairing.—By using the *reduced* BCS Hamiltonian in Eq. (1), we neglected interaction terms $-d\sum_{iji'j'} \lambda(i, j, i', j') c_{i+}^\dagger c_{j-}^\dagger c_{i'-} c_{j'+}$ between non-time-reversed pairs $c_{i+}^\dagger c_{j-}^\dagger$, following Anderson's argument [6] that for a short-ranged interaction, the matrix elements involving time-reversed states $c_{j+}^\dagger c_{j-}^\dagger$ are much larger than all others, since their orbital wave functions interfere constructively [14]. Interestingly, the experimental results provide strikingly direct support for the correctness of purely time-reversed pairing at $h = 0$: if the $\lambda(j + \delta j, j, j' + \delta j, j')$ were all roughly equal to λ for a finite range of δj (instead of being negligible for $\delta j \neq 0$, as assumed in $H_{\rm red}$), then for $2s < \delta j$ one could construct spin-s states with manifestly lower energy than $|s\rangle$, by pair-correlating *non*-time-reversed states, with the $2s$ uncorrelated electrons at the band's *bottom,* where having them uncorrelated costs hardly any correlation energy:

$$|s\rangle' = \prod_{j=-m}^{-m+2s-1} c_{j+}^\dagger \prod_{j=-m}^{\infty} (u_j^{(s)} + v_j^{(s)} c_{(j+2s)+}^\dagger c_{j-}^\dagger)\,|\mathrm{Vac}\rangle\,.$$

However, since it then costs no correlation energy to increase s (as can be checked explicitly), there would be no large threshold for h to induce ground state changes, and the change $|p/2\rangle$ to $|p/2 + 1\rangle$ would occur at roughly $h \simeq d$ (as in a normal paramagnet), contradicting the experimental finding that the first kinks occur only after a sizable threshold $\overline{h}_{p/2,\bar{s}} \simeq \tilde{\Delta}/\sqrt{2}$.

In conclusion, the dominant mechanism for destroying pairing correlations in ultrasmall grains is Pauli paramagnetism. Calculating the variational eigenenergies of the lowest-lying eigenstates by a generalized variational BCS method, we have shown that decreasing grain size softens the first-order transition observed for thin films by reducing the number of spins flipped from being macroscopically large to being of order one for $d \simeq \tilde{\Delta}$. Our approach qualitatively reproduces the measured tunneling thresholds, explaining why they do not show jumps.

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