Parity-Affected Superconductivity in Ultrasmall Metallic Grains

Jan von Delft,[1] Andrei D. Zaikin,[1,2] Dmitrii S. Golubev,[2] and Wolfgang Tichy[1]
[1]*Institut für Theoretische Festkörperphysik, Universität Karlsruhe, 76128 Karlsruhe, Germany*
[2]*P.N.Lebedev Physics Institute, Leninskii prospect 53, 117924, Moscow, Russia*
(Received 3 April 1996)

We investigate the breakdown of BCS superconductivity in *ultra*small metallic grains as a function of particle size (characterized by the mean spacing d between discrete electronic eigenstates), and the parity (P = even/odd) of the number of electrons on the island. Assuming equally spaced levels, we solve the parity-dependent BCS gap equation for the pairing parameter $\Delta_P(d,T)$. The $T=0$ critical level spacing $d_{c,P}$, the critical temperature $T_{c,P}(d)$ (at which $\Delta_P=0$), and the condensation energy $\mathcal{E}_P$ are parity dependent, and all are so much smaller in the odd than the even case that this should manifest itself in current experiments. [S0031-9007(96)01329-4]

PACS numbers: 74.20.Fg, 74.80.Bj, 74.80.Fp

The study of the properties of ultrasmall metallic particles has witnessed a dramatic development during the last year: Using an ingenious new fabrication technique, Black, Ralph, and Tinkham (BRT) [1] have constructed a single-electron transistor (SET) whose island, a single nm-scale Al grain, is more than 4 orders of magnitude smaller in volume (estimated radii between $r \sim 2.5$ and 13 nm) than that of conventional SETs. Thus a new energy scale, the average level spacing $d = 1/N(\varepsilon_F)$ between discrete electronic levels, enters the problem: Both the free-electron estimate of $d \simeq 2\pi^2\hbar^2/mk_F\mathcal{V}$ and direct observation (discrete steps in the I-V curve) give values of d ranging from 0.02 to 0.3 meV, the latter being much larger than the smallest accessible temperatures ($\simeq$30 mK) and on the order of the bulk superconducting gap ($\Delta_b = 0.18$ meV for Al).

The eigenenergies of the larger grains ($r > 5$ nm) studied by BRT revealed the presence of a gap $2\Omega \gg d$ between the lowest two states of a grain with an even number of electrons (parity $P = e$), but its absence for an odd grain ($P = o$). BRT convincingly interpreted this as evidence for superconductivity: In an even grain, all excited states involve at least two BCS quasiparticles and hence lie at least 2Ω above the BCS ground state; in contrast, in an odd grain *all* states have at least one quasiparticle, and hence no significant gap between ground and excited states. (Remarkably, the excitation spectra of many shell model nuclei whose outer-shell valence nucleons experience an attractive short-range interaction show exactly the same feature [2], namely, the presence or absence of a significant gap $2\Omega \gg d$ for all even or odd isotopes of a given nucleus, respectively, which was explained [2,3] using BCS techniques.) However, smaller particles ($r < 5$ nm) showed no such evidence for superconductivity.

These experiments invite reconsideration of an old but fundamental question: *What is the lower size limit for the existence of superconductivity in small grains?* Anderson addressed this question already in 1959 [4] and argued that "superconductivity would no longer be possible" if the level spacing d becomes larger than the bulk gap Δ_b, for reasons explained below. This answer—although, in general, correct—is not yet quite complete, since it does not address *parity effects*. Even in "large" superconducting islands (with $d \ll \Delta_b$) experiments [5] have demonstrated the dramatic impact of parity on I-V characteristics; moreover, theory [6,7] predicts an even-odd difference for the *superconducting pairing parameter itself* of $\Delta_e - \Delta_o = d/2$ at $T = 0$. Though the latter difference is immeasurably small in large islands, it should certainly become significant in ultrasmall grains. Moreover, since the crossover temperature at which parity effects become observable [5], namely, $T_{\rm cr} = \Delta_b/\ln N_{\rm eff}$ (where in the $d \ll \Delta_b$ limit $N_{\rm eff} = \sqrt{8\pi T\Delta_b}/d$), becomes of order Δ_b when $d \simeq \Delta_b$, parity effects should survive to temperatures as high as T_c itself. Hence $T_{c,P}(d)$ as function of d should be parity dependent too.

In this Letter we address these issues by studying parity effects in the pairing parameter $\Delta_P(d,T)$ for general d. In particular, we calculate $\Delta_P(d,0)$ and $T_{c,P}(d)$ by solving the BCS gap equation (derived using parity-projected mean-field theory (MFT) [6,7]) at $T = 0$ and $\Delta_P = 0$, respectively, for the case of equally spaced single-particle levels. We find $T_{c,o}(d)/T_{c,e}(d) < 1$ and a remarkably small ratio of critical level spacings $d_{c,o}/d_{c,e} = 1/4$ at $T = 0$. Our results are completely compatible with BRT's observations. Moreover, the predicted parity effects should manifest themselves in their latest experiments which have variable gate voltage, allowing them to change the number parity of a given grain at will.

The model.—In BRT's experiments, the charging energy $E_C = e^2/2C_{\rm total}$ of an ultrasmall grain is by far the largest energy scale in the problem (with $E_C \simeq 4$ meV $\gg \Delta_b$), so that fluctuations in particle number are strongly suppressed. Therefore in this Letter we consider a completely isolated grain, which should be described using a canonical ensemble with a prescribed number of electrons $n = 2m + p$, where $p = (0,1)$ for $P = (e,o)$ (the labels p, P, *and also* n will be used interchangeably as parity labels below). We adopt a model Hamiltonian having the standard reduced BCS form

$$\hat{H} = \sum_{j\sigma} \varepsilon_j^0 c_{j\sigma}^\dagger c_{j\sigma} - \lambda d \sum_{ij}{}' c_{i+}^\dagger c_{i-}^\dagger c_{j-} c_{j+} . \quad (1)$$

Here $c_{j\sigma}^\dagger$ creates an electron in the particle-in-a-box-like, independent-electron state $|j\sigma\rangle$, where the states $|j+\rangle$ and $|j-\rangle$ are degenerate, time-reversed partners whose energies $\{\varepsilon_j^0\}$ are considered as a given set of phenomenological parameters. The integer j is a discrete quantum number. For a given $n = 2m + p$, we take $j = 0$ to describe the first energy level whose occupation in the $T = 0$ Fermi sea $|F\rangle$ is not 2 but p, so that $j = -m, \ldots, \infty$. Finally, the dimensionless coupling constant $\lambda^{-1} = \ln(2\omega_c/\tilde{\Delta})$ is regarded as a phenomenological parameter determined by the value $\tilde{\Delta} \equiv \Delta(0,0)$ of the effective gap (measured at $d \ll \tilde{\Delta}$) and some cut-off frequency ω_c.

Pair-mixing.—At this point it seems appropriate to briefly address the question of what is meant by the "existence of superconductivity" in ultrasmall grains. It deserves special attention, firstly because the usual MFT definition $\lambda\, d \sum_j \langle c_{j-} c_{j+} \rangle$ for the BCS pairing parameter Δ gives zero in a canonical ensemble, and secondly because most of the standard criteria, e.g., a gap followed by a continuous excitation spectrum, zero resistivity, and the Meissner effect, are not applicable here.

Now the microscopic reason for all of these (large-sample) phenomena is, of course, the *existence of a pair-correlated ground state.* The essence of its correlations is what we shall call *pair-mixing* across ε_F, namely, the partial population of some time-reversed pairs of states ($|j+\rangle, |j-\rangle$) above ε_F ($j > 0$) (with amplitude $v_j \equiv \langle c_{j+}^\dagger c_{j-}^\dagger c_{j-} c_{j+} \rangle^{1/2} > 0$) by partially depopulating some pairs of states below ε_F ($j < 0$) (with amplitude $u_j \equiv \langle c_{j-} c_{j+} c_{j+}^\dagger c_{j-}^\dagger \rangle^{1/2} > 0$). This creates phase space for pair scattering (which is Pauli blocked in the normal ground state) and hence allows the BCS interaction to lower the ground state energy.

Although BCS showed that a brilliantly simple way of calculating the u_j and v_j is to use grand-canonical methods, pair-mixing, of course, can and does also occur in a fixed-n system. Indeed, this pair-mixing can readily be characterized by a "generalized" pairing parameter that is equal to the conventional $\lambda d \sum_j \langle c_{j-} c_{j+} \rangle$ in BCS's grand-canonical mean-field treatment, but (in contrast to the latter expression) is meaningful in a fixed-n system too, namely, $\lambda\, d \sum_j u_j v_j$. An experimental signature of this pair-mixing is the energy cost needed to add or remove single electrons that perturb these correlations (i.e., that "break pairs"). Since BRT quite unambiguously measured such energy costs in their larger grains, it seems reasonable to regard these as "superconducting," in the sense of having a *pair-correlated ground state that measurably exhibits pair-mixing.*

The notion of pair-mixing also provides a simple way to understand why superconductivity ceases to exist in sufficiently small samples. If the level spacing becomes sufficiently large ($d \simeq \tilde{\Delta}$), pair-mixing costs a prohibitive amount of kinetic energy and hence ceases to occur. The task at hand is to describe this breakdown (semi)quantitatively, while keeping track of parity effects.

Canonical and parity projection.—Since in practice it is so much easier to calculate u_j, v_j grand-canonically than canonically, the latter is seldom attempted. An alternative [6,7] is to employ an auxiliary parity-projected grand-canonical partition function,

$$Z_P^G(\mu) \equiv \mathrm{Tr}^G \tfrac{1}{2}[1 \pm (-1)^{\hat{N}}] e^{-\beta(\hat{H} - \mu\hat{N})}, \quad (2)$$

(Tr^G denotes a grand-canonical trace), from which the desired fixed-n partition function Z_n can, in principle, be exactly projected: $Z_n = \int_{-\pi}^{\pi} \frac{du}{2\pi} e^{-iun} Z_P^G(iu/\beta)$. Since in practice, though, it is hard to perform the integral exactly, we approximate it by its saddle-point value, $Z_n \simeq e^{-\beta\mu_n n} Z_P^G(\mu_n)$, where μ_n is fixed by

$$n = \beta^{-1} \partial_\mu \ln Z_P^G(\mu)|_{\mu=\mu_n} \quad [= \langle \hat{N} \rangle_P]. \quad (3)$$

(Here $\langle\,\rangle_P$ is taken in the parity-projected grand-canonical ensemble of Z_P^G.) This equation, the bracketed part of which is the parity-projected version of a standard grand-canonical identity, illustrates the elementary fact that the saddle-point approximation produces nothing but the grand-canonical description we had set out to improve upon. Nevertheless, the above approach firstly illustrates that the parity projection of Eq. (2), which is essential for extracting e/o differences, can be done exactly even when the fixed-n projection cannot; and secondly clarifies that in a canonical ensemble μ_n is simply the saddle-point value of an integration parameter, which, however, has to be determined with special care in ultrasmall grains, for which d is large.

Mean-field approximation.—We evaluate Z_P^G using "naive mean-field theory" (our method is equivalent to that used in [7]): Make the replacement

$$c_{j-} c_{j+} \to \{c_{j-} c_{j+} - \langle c_{j-} c_{j+} \rangle_P\} + \langle c_{j-} c_{j+} \rangle_P \quad (4)$$

in $\hat{H} - \mu_n \hat{N}$, neglect terms quadratic in the fluctuations represented by $\{\}$ and diagonalize, using $\gamma_{nj\sigma} = u_{nj} c_{j\sigma} - \sigma v_{nj} c_{j-\sigma}^\dagger$. One obtains the usual results $\hat{H} - \mu_n \hat{N} \simeq C_n + \sum_{j\sigma} E_{nj\sigma} \gamma_{nj\sigma}^\dagger \gamma_{nj\sigma}$, where $E_{nj\sigma} = [\varepsilon_{nj}^2 + \Delta_P^2]^{1/2}$, $\varepsilon_{nj} \equiv \varepsilon_j^0 - \mu_n$, $v_{nj}^2 = \frac{1}{2}(1 - \varepsilon_{nj}/E_{nj})$, and $C_n = \Delta_P^2/\lambda d + \sum_j (2\varepsilon_{nj} v_j^2 - 2\Delta_P u_j v_j)$. Moreover, since the parity of electron number and quasiparticle number are always the same, Eq. (2) can be rewritten [6] using quasiparticle-parity projection, $Z_P^G(\mu_n) = \frac{1}{2}(Z_+^G \pm Z_-^G)$,

$$Z_\pm^G(\mu_n) = e^{-\beta C_n} \prod_{j\sigma} (1 \pm e^{-\beta E_{nj\sigma}}) . \quad (5)$$

The usual MF self-consistency condition $\Delta_P = \lambda\, d \sum_j' \times \langle c_{j-} c_{j+} \rangle_P$ takes the form

$$\frac{1}{\lambda} = d \sum_{|j| < \omega_c/d} \frac{1}{2E_{nj}} \left(1 - \sum_\sigma f_{nj\sigma} \right), \quad (6)$$

where $f_{nj\sigma} = \langle \gamma_{nj\sigma}^\dagger \gamma_{nj\sigma} \rangle_P = -\beta^{-1} \partial_{E_{nj\sigma}} \ln Z_P^G(\mu_n)$. This description thus involves the usual BCS quasiparticles, but *their number parity is restricted to be P*; accordingly $f_{nj\sigma}$ differs from the usual Fermi function $f_{j\sigma}^0$ [6,7].

Determination of μ_n.—Following [8], let us henceforth consider the case of equal level spacing, $\varepsilon_j^0 = j\,d + \varepsilon_0^0$ (which seems reasonable for large n, due to level repulsion). Then Eq. (3), which fixes μ_n [6] and has the form $\langle \hat{N} \rangle_P = \sum_{j\sigma} [v_{nj}^2 + (u_{nj}^2 - v_{nj}^2) f_{nj\sigma}]$, holds provided that $\mu_n = \varepsilon_0^0 - \frac{1}{2} d\, \delta_{P,e}$, which confirms the seemingly obvious: In the language of $|F\rangle$, μ_n lies exactly halfway between the last filled and first empty levels if $P = e$, and exactly on the singly occupied level if $P = o$.

We are now ready to study the gap equation (6).

Gap equation at $T = 0$.—The quasiparticle occupation function reduces to $f_{nj\sigma} = \frac{1}{2} \delta_{j0} \delta_{P,o}$ at $T = 0$, as intuitively expected, because then the even or odd systems have exactly zero or one quasiparticle, the latter in the lowest quasiparticle state, namely, $j = 0$. This e/o difference has a strong impact on the $T = 0$ gap equation: In the odd case, the $j = 0$ level, for which E_{nj}^{-1} is largest, is *absent*, reflecting the fact that the odd quasiparticle in the $j = 0$ state obstructs pair scattering involving this state. To compensate this missing term, Δ_o must therefore become significantly smaller than Δ_e as soon as d is large enough that a single term becomes significant relative to the complete sum.

To quantify this statement, it is convenient to rewrite Eq. (6) at $T = 0$ as follows: Writing $E_{nj}^{-1} = \int d\omega/\pi\, (E_{nj}^2 + \omega^2)^{-1}$, transferring the cut-off ω_c from $\sum_j$ to $\int d\omega$, and performing the j sum (by contour integration) gives

$$\ln \frac{2\omega_c}{\tilde{\Delta}} = \int_0^{\omega_c} \frac{d\omega}{E_{P\omega}} \left[(\tanh \pi E_{P\omega}/d)^{1-2p} - \frac{d\, \delta_{P,o}}{\pi E_{P\omega}} \right], \tag{7}$$

where $E_{P\omega} = (\omega^2 + \Delta_P^2)^{1/2}$. Since, amusingly, for $P = e$ Eq. (7) is identical in form (with $d \to 2\pi T$) to the well-known gap equation for the T dependence of the bulk gap [curve A in Fig. 1(a)], we have $\Delta_e(d, 0) = \Delta_P(0, d/2\pi)$. In contrast, for $\Delta_o(d, 0)$ one easily finds from Eq. (7) that $\Delta_o(d, 0) = \tilde{\Delta} - d/2$ for $d/\tilde{\Delta} \ll 1$, in agreement with [6,7].

The full solutions of Eq. (7) for $\Delta_P(d_P, 0)$, obtained numerically and shown as curves B and C in Fig. 1(a), reveal that $\Delta_o(d, 0)$ *vanishes much sooner than* $\Delta_e(d, 0)$. The critical values $d_{c,P}$ at which $\Delta_P(d_{c,P}, 0) = 0$ can be found analytically by setting $\Delta_P = T = 0$ in Eq. (6):

$$\frac{d_{c,e}}{\tilde{\Delta}} = 2e^\gamma \simeq 3.56 \quad \text{and} \quad \frac{d_{c,o}}{\tilde{\Delta}} = \frac{1}{2} e^\gamma \simeq 0.890\,. \tag{8}$$

Critical temperature.—Although ultrasmall grains cannot undergo a sharp thermodynamic phase transition (this would require $n \to \infty$), the quantity $T_{c,P}(d)$, defined simply as the solution to the $\Delta_P \to 0$ limit of Eq. (6), is another measure of how rapidly pair-mixing correlations break down as function of level spacing. Our numerical results for $T_{c,P}(d)$ [9], shown as curves D and E of Fig. 1(a) for $P = e/o$, have the expected limits at $d = 0$ and $d_{c,p}$, but behave unexpectedly in between.

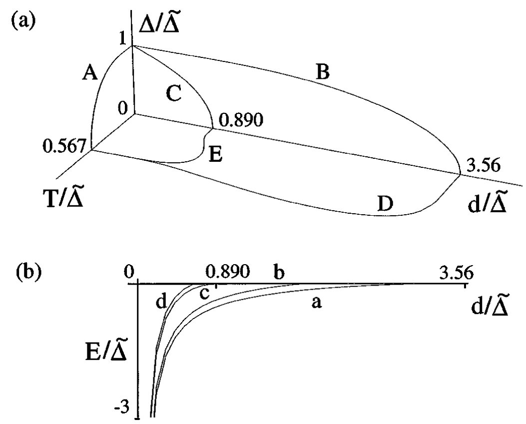

FIG. 1. (a) Curve A gives the bulk gap $\Delta(0, T)$; curves B–E give $\Delta(d, T)_P/\tilde{\Delta}$ as a function of $d/\tilde{\Delta}$ and $T/\tilde{\Delta}$ for $P = e$ (B,D) and $P = o$ (C, E). (b) Curves a–d give, respectively, $(\mathcal{E}_e^{\rm MF}, \mathcal{E}_e^{\rm var}, \mathcal{E}_o^{\rm MF}, \mathcal{E}_o^{\rm var})/\tilde{\Delta}$ as functions of $d/\tilde{\Delta}$. Here $\tilde{\Delta} = \Delta(0, 0)$.

Even.—In the even case, $T_{c,e}(d)$ is nonmonotonic, initially increasing slightly before dropping to zero very rapidly as $d \to d_{c,e}$. The intuitive reason for the initial increase is that the difference between the actual and usual quasiparticle occupation functions is $f_{nj\sigma} - f_{j\sigma}^0 < 0$ for an even grain (becoming significant when $d \simeq \tilde{\Delta}$), reflecting the fact that exciting quasiparticles two at a time is more difficult than one at a time. Therefore the quasiparticle-induced breakdown of superconductivity with increasing T will set in at slightly higher T if $d \simeq \tilde{\Delta}$.

Odd.—In the odd case, the critical level spacing $d_{c,o}(T)$ is nonmonotonic as a function of increasing T, first increasing to a maximum before beginning to decrease toward $d_{c,o}(T_c) = 0$. The intuitive reason for this is that for $0 < \Delta_o \ll T, d$ the odd $j = 0$ function $f_{n0\sigma}(T)$ becomes somewhat smaller than its $T = 0$ value of $\frac{1}{2}$, because with increasing T some of the probability for finding a quasiparticle in state j "leaks" from $j = 0$ to higher states with $j \neq 0$, for which $E_{nj}^{-1} < E_{n0}^{-1}$ in Eq. (6). Thus the dramatic blocking-of-pair-scattering effect of the odd quasiparticle becomes slightly less dramatic as T is increased, so that $d_{c,o}$ increases slightly.

An important general feature of our results is that level discreteness *always reduces* $\Delta_P(d, 0)$ to be $< \tilde{\Delta}$ (thus contradicting Ref. [10], which was convincingly criticized in Ref. [8]). However, BRT's experiment found an effective gap $\tilde{\Delta}$ that is larger by a factor of 1.5 to 2 than its bulk value Δ_b. Following the argumentation of [8] for thin films, we can attribute this to presumed changes in the phonon spectrum in small samples, which can be modeled by using a constant value of λ larger (by a few percent) than the usual bulk value λ_b.

The rather rapid drop of $\Delta_P(d)$, once it happens, could be the reason why BRT see a well-developed gap $\tilde{\Delta}$ even for $d \simeq \tilde{\Delta}$ but do not see any for their smallest grains. More importantly, Fig. 1(a) and Eq. (8) show that there is a large regime in which $\Delta_o \ll \Delta_e$, implying our *main result: Pair-mixing correlations vanish significantly sooner for odd than even grains as their size is reduced*. Since by tuning the gate voltage BRT can study the *same* grain in both its even and odd states, they should be able to observe the effects of $\Delta_o \ll \Delta_e$ for a grain with appropriate size in the measured excitation spectra, since these are governed by quasiparticle energies which certainly depend on Δ_P. Moreover, because Δ_o drops linearly in d, such effects should set in already at $d < \tilde{\Delta}$, where the quasiparticle excitation gap caused by pairing correlations can still unambiguously be distinguished from ordinary level discreteness. A detailed analysis of the measured spectra, which requires a complete understanding of its magnetic field dependence and goes beyond the scope of this paper, will be presented elsewhere [9].

Condensation energy.—How robust are our MFT-based results? Since corrections to MFT are small [11] only for $d/\tilde{\Delta} \ll 1$, it is, for instance, doubtful that the unexpected nonmonotonic subtleties of $T_{c,P}(d)$, though intuitively plausible, have physical significance, since they fall in the $\Delta_P \simeq 0$ regime where $d/\Delta_P \gg 1$. To show that, at least in the (experimentally accessible) regime of $T/d \simeq 0$, our main result is indeed robust against corrections to MFT, we shall now establish approximate lower and exact upper bounds on the exact, parity-dependent condensation energies $\mathcal{E}_P(d) \equiv {}_P\langle G|H|G\rangle_P - \langle F|H|F\rangle$, which are also a measure of the amount of pair-mixing correlations present. Because MFT neglects quantum fluctuations, which tend to raise the ground state energy by weakening pair-mixing correlations, the $T = 0$ MF expressions $\mathcal{E}_P^{\rm MF}(v_{nj}) = C_n + \delta_{P,o}\Delta_o - \sum_{j<0} 2\varepsilon_j$ (C_n given above) provide approximate *lower* bounds on $\mathcal{E}_P$. (In the regime $d/\tilde{\Delta} < 1$, where only Gaussian fluctuations matter, these bounds are rigorous [12]; when $d/\tilde{\Delta} > 1$ and the $\mathcal{E}_P^{\rm MF}$ approach zero, they becomes less reliable as lower bounds because non-Gaussian fluctuations now matter too, but (because of the latter) pair-mixing correlations will be immeasurably weak in this regime anyway.) On the other hand, *upper* bounds on $\mathcal{E}_P$ can be found variationally using the trial ground states $|G\rangle_e = \prod_j(\bar{u}_{nj} + \bar{v}_{nj}c_{j+}^\dagger c_{j-}^\dagger)|0\rangle$ and $|G\rangle_o = \bar{\gamma}_{0,\sigma}^\dagger|G\rangle_e$, and minimizing the corresponding $\mathcal{E}_P^{\rm var}$, which can be written in the form [9,13] $\mathcal{E}_P^{\rm var} = \mathcal{E}_P^{\rm MF}(\bar{v}_{ni}) + \lambda d[\delta_{P,0}\bar{v}_{n0}^4 + \sum_j(\theta(-j) - \bar{v}_{nj}^4)]$. Figure 1(b), which gives $\mathcal{E}_P/\tilde{\Delta}$ vs $d/\tilde{\Delta}$, shows (as expected) that $\mathcal{E}_P^{\rm MF}(d_{c,P}) = 0$ and $\mathcal{E}_P^{\rm var}(d'_{c,P}) = 0$ with $d'_{c,P} < d_{c,P}$. Moreover, it confirms that our main result is robust against corrections to MFT, since *the lower bound on $\mathcal{E}_o$ lies significantly above the upper bound* on $\mathcal{E}_e$ (with $d_{c,o}$ significantly smaller than $d'_{c,e}$). The conclusion that $d_{c,o} < d_{c,e}$, in fact, even follows from the back-of-the-envelope estimate $\mathcal{E}_P = -\tilde{\Delta}^2/(2d) + \tilde{\Delta}\,\delta_{P,o}$ (obtained by using standard expressions from bulk BCS theory).

Finally, note that "empirical" support for the adequacy of our methods in the regime $d \simeq \tilde{\Delta}$ comes from nuclear physics, where the $T = 0$ variational grand-canonical BCS description of pairing interactions in shell model nuclei (with $n \sim 100$) has been remarkably successful [3] despite the smallness of n and $d/\tilde{\Delta}$ ratios approaching 1.

In conclusion, we have investigated the influence of parity on the existence of superconducting (pair-mixing) correlations in ultrasmall grains. As a function of decreasing grain size, these correlations break down in an odd grain significantly earlier than in an even grain, which should manifest itself in present experiments.

It is a pleasure to thank BRT for showing us their preliminary results and to acknowledge discussions with V. Ambegaokar, C. Bruder, B. Janko, H. Kroha, A. Rosch, G. Schön, and J. Siewert. This research was supported by "SFB 195" of the Deutsche Forschungsgemeinschaft.

Note added.—After this paper had been submitted, we learned that M. Tinkham had independently reached very similar conclusions.

[1] C. T. Black, D. C. Ralph, and M. Tinkham, Phys. Rev. Lett. **76**, 688 (1996); **74**, 3241 (1995); Physica (Amsterdam) **218B**, 258 (1996).
[2] See, e.g., L. S. Kisslinger and R. A. Sorensen, Mat. Fys. Medd. Dan. Vid. Selsk. **32**, No. 9, 1 (1960), Figs. 1–4.
[3] See, e.g., A. Bohr and B. R. Mottelson, *Nuclear Structure* (W.A. Benjamin, New York, 1975), Vol. II, p. 641, footnote 34.
[4] P. W. Anderson, J. Phys. Chem. Solids **11**, 28 (1959).
[5] M. T. Tuominen, J. M. Hergenrother, T. S. Tighe, and M. Tinkham, Phys. Rev. Lett. **69**, 1997 (1992); P. Lafarge *et al.*, Phys. Rev. Lett. **70**, 994 (1993).
[6] B. Janko, A. Smith, and V. Ambegaokar, Phys. Rev. B **50**, 1152 (1994).
[7] D. S. Golubev and A. D. Zaikin, Phys. Lett. A **195**, 380 (1994).
[8] M. Strongin *et al.*, Phys. Rev. B **1**, 1078 (1970).
[9] Jan von Delft (to be published).
[10] R. H. Parmenter, Phys. Rev. **166**, 392 (1968).
[11] The microscopic reason for the breakdown of MFT for $d/\tilde{\Delta} \gtrsim 1$ is as follows: In principle, one can associate with every quasiparticle state $\gamma_{j_1\sigma_1}^\dagger \ldots \gamma_{j_n\sigma_n}^\dagger|\mathrm{BCS}\rangle$ a *different* set of parameters $\{u_j, v_j, \Delta\}_{j_1\sigma_1,\ldots,j_n\sigma_n}$, to be determined variationally [13]; the MFT assumption, namely, that for all states $|j_1\sigma_1,\ldots,j_n\sigma_n\rangle$, these parameters are all equal to a single set $\{u_j, v_j, \Delta\}$, i.e., that "Δ does not fluctuate from state to state," is true only when $d/\tilde{\Delta} \ll 1$ [9].
[12] B. Mühlschlegel, J. Math. Phys. **3**, 522 (1962).
[13] V. G. Soloviev, Mat. Fys. Skrif. Kong. Dan. Vid. Selsk. **1**, No. 11, 1 (1961), and references therein.