Re-Entrant Spin Susceptibility of a Superconducting Grain

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We study the spin susceptibility χ of a small, isolated superconducting grain. Because of the interplay between parity effects and pairing correlations, the dependence of χ on temperature T is qualitatively different from the standard BCS result valid in the bulk limit. If the number of electrons on the grain is odd, χ shows a *re-entrant* behavior as a function of temperature. This behavior persists even in the case of ultrasmall grains where the mean level spacing is much larger than the BCS gap. If the number of electrons is even, $\chi(T)$ is exponentially small at low temperatures.

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By now it is well known that the properties of an isolated, mesoscopic superconducting grain are quite different from those of a bulk sample [1]. First of all, since such a grain carries a fixed number, N, of electrons, its behavior depends strongly on whether N is even or odd. Second, fluctuation effects become important as the size of the grain decreases. The interplay between parity and fluctuation effects crucially depends on the ratio δ/Δ_0 of two characteristic energies: the mean level spacing δ and the bulk superconducting gap Δ_0. As long as the grain is not too small, $\delta \ll \Delta_0$, the fluctuation region ΔT around the critical temperature T_c is narrow, $\Delta T/T_c \sim \sqrt{\delta/\Delta_0} \ll 1$, and the mean field description of superconductivity is appropriate. Parity effects [2,3] appear at temperatures lower than a crossover temperature $T_{\mathrm{eff}} \simeq \Delta_0/\ln\sqrt{8\pi\Delta_0^2/\delta^2}$ which, in the experiments [3], is typically of the order of 10%–30% of T_c. The dependence of T_{eff} on Δ_0 signals that the even-odd asymmetry is a collective effect due to pairing correlations. As the size of the grain is decreased, fluctuations start to smear the superconducting transition [4]. The finite level spacing suppresses the BCS gap in a parity-dependent way [5,6]. When δ becomes of the order of Δ_0, $\Delta T \sim T_c$ and the BCS description of superconductivity breaks down even at zero temperature [7]. The regime $\delta \gtrsim \Delta_0$ is dominated by strong pairing fluctuations [8–13].

The present-day interest in ultrasmall superconducting grains was triggered by the experiments of Ralph, Black, and Tinkham [14], who were able to contact a single, nanometer-sized Al grain with current and voltage probes. They obtained tunneling spectra that revealed the presence of a parity-dependent spectroscopic gap, larger than the average level spacing, which could be driven to zero by an applied magnetic field. In this Letter we propose to measure the temperature dependence of a thermodynamic quantity—the spin susceptibility χ—as a means to detect *both* parity effects *and* pairing correlations. As we will show below, pairing correlations give rise to a specific temperature dependence of thermodynamic quantities. This enables a more quantitative investigation of fluctuation effects [15].

Spin paramagnetism of small particles has been considered in the past [16] and very recently parity effects in the susceptibility were measured for an ensemble of small, normal metallic grains [17]. Spin susceptibility is very sensitive to BCS pairing as well. Yosida [18] showed that, due to the opening of the superconducting gap, χ vanishes at zero temperature [19]. We will show that the combined effect of parity and pairing introduces *qualitatively* new features in the temperature dependence of χ. Most interestingly, these effects might be observed even in the regime $\delta \gtrsim \Delta_0$. The results of our work are summarized in Figs. 1–3, where we plot χ as a function of temperature T for odd and even parity. In particular, we want to emphasize that the odd susceptibility shows a *re-entrant* behavior as a function of T *for any value of the ratio* δ/Δ_0. This re-entrance is absent in normal metallic grains; it is a genuine feature of the interplay between pairing correlations and parity effects.

The BCS pairing Hamiltonian for a small grain can be written as [5,8,9]

$$\mathcal{H} = \sum_{n,\sigma=\pm}(\epsilon_n - \sigma\mu_B H)c_{n,\sigma}^\dagger c_{n,\sigma} - \lambda\delta\sum_{m,n}B_m^\dagger B_n\,, \tag{1}$$

where $B_m^\dagger = c_{m,+}^\dagger c_{m,-}^\dagger$. The indices m, n label the single particle energy levels with energy ϵ_m and annihilation operator $c_{m,\sigma}$. The quantum number $\sigma = \pm$ labels time-reversed equally spaced states (with an average spacing $\sim\delta \equiv 1/\nu_0$, where ν_0 is the density of states at the Fermi energy). The external magnetic field H couples to the electrons via the Zeeman term; μ_B is the Bohr magneton. We put the g factor equal to 2, ignoring any spin-orbit effects (see Ref. [20]). At the low magnetic fields of interest here, we can neglect the orbital contribution to magnetic energy, as it is smaller than the Zeeman energy by a factor $\sim(k_F r)(Hr^2/\Phi_0)$ (r is the size of the grain and Φ_0 the flux quantum). Finally λ is the dimensionless BCS coupling constant. Since the Hamiltonian contains only

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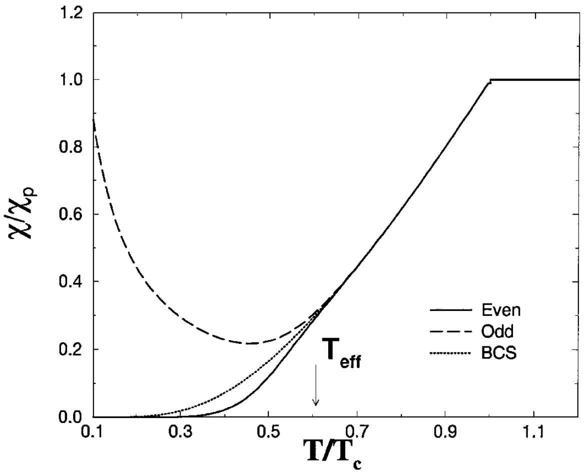

FIG. 1. $\Delta_0 \gg \delta$: Spin susceptibility as a function of temperature T/T_c for an odd (upper curve) and even (lower curve) grain, respectively. The BCS result (middle curve) is reported for comparison. The susceptibility is normalized to its bulk high temperature value $\chi_P = 2\mu_B^2/\delta$. We used $\delta/\Delta_0 = 0.1$.

pairing terms, an electron in a singly occupied level cannot interact with the other electrons.

The spin susceptibility of a grain with an even (e) or an odd (o) number N of electrons is defined as

$$\chi_{e/o}(T) = -\frac{\partial^2 \mathcal{F}_{e/o}(T,H)}{\partial H^2}\bigg|_{H=0}, \tag{2}$$

where $\mathcal{F}_{e/o} = -T \ln Z_{e/o}$ is the free energy of the grain and the partition function $Z(T,N)$ should be evaluated in the canonical ensemble. We will perform the calculation with the help of a parity projection technique [21,22] and by means of exact canonical methods based on Richardson's solution [8]. The grand partition function reads

$$\begin{aligned} Z_{e/o}(T,\mu) &= (1/2)\sum_{N=0}^{\infty} e^{\mu N/T}[1 \pm e^{i\pi N}]Z(T,N) \\ &\equiv (1/2)(Z_+ \pm Z_-). \end{aligned} \tag{3}$$

The partition function Z_+ is the usual grand partition function at temperature T and chemical potential $\mu_+ = \mu$. The grand partition function Z_- describes an auxiliary ensemble at temperature T and chemical potential $\mu_- = \mu + i\pi T$; it is a formal tool, necessary to include parity effects. The chemical potential μ will be placed between the topmost occupied level and the lowest unoccupied level in the even case, while it will be at the singly occupied level in the odd case. Since we are interested in the evaluation of fluctuation effects, it is convenient to express the grand partition functions $Z_\pm$ using the path integral formulation of superconductivity [4,22,23],

$$Z_\pm = Z_\pm^0 \frac{\int \mathcal{D}^2\Delta \exp\{\int_0^\beta d\tau [\mathrm{Tr}\ln(1 - \hat{G}_\pm^0 \hat{\Delta}) - \frac{|\Delta|^2}{\lambda\delta}]\}}{\int \mathcal{D}^2\Delta \exp\{-\int_0^\beta d\tau \frac{|\Delta|^2}{\lambda\delta}\}}. \tag{4}$$

Here, $\beta = 1/T$ and $Z_\pm^0$ is the partition function for noninteracting electrons. The matrix Green function $\hat{G}_\pm^0$ is given by $\hat{G}_\pm^{(0)}(\epsilon_\nu) = [(i\omega_\nu + \mu_B H)\sigma^{(0)} - (\epsilon_n - \mu_\pm)\sigma^{(z)}]^{-1}$, where ω_ν is a fermionic Matsubara frequency, $\sigma^{(i)}$ ($i = x,y,z$) are the Pauli matrices, and $\sigma^{(0)}$ is the identity. Finally, the matrix $\hat{\Delta}$ is given by $\hat{\Delta} = (\Delta/2)(\sigma^x + i\sigma^y) +$ H.c. A direct calculation of the partition function (4) is impossible in general. Below, we first discuss two limiting cases which are tractable analytically: $\delta/\Delta_0 \ll 1$ and $\delta/\Delta_0 \gg 1$. Then we present the complete temperature dependence of the spin susceptibility evaluating Eq. (4) numerically for arbitrary values of δ/Δ_0, with the help of the static path approximation [4].

Large grains ($\Delta_0 \gg \delta$).—In this limit it is sufficient to evaluate the partition function in a saddle point approximation, since fluctuations will not contribute significantly [24]. As a result we find

$$\chi_{e/o} = \frac{\mu_B^2}{2T}\sum_n \frac{Z_+ \cosh^{-2}\frac{E_{+,n}}{2T} \mp Z_- \sinh^{-2}\frac{E_{-,n}}{2T}}{Z_+ \pm Z_-}, \tag{5}$$

where $E_{\pm,n} = \sqrt{\epsilon_n^2 + \Delta_\pm}$. The saddle point values of $\Delta_\pm$ are found from the equations

$$\frac{1}{\lambda} = \sum_{n,\sigma} \frac{\delta}{4E_{\pm,n}} \mathrm{th}^{\pm 1}\left(\frac{E_{\pm,n} - \sigma\mu_B H}{2T}\right). \tag{6}$$

The partition functions for the two ensembles are

$$Z_\pm = \exp\left\{\sum_{n,\sigma}\left[\ln 2\begin{Bmatrix}\mathrm{ch}\\ \mathrm{sh}\end{Bmatrix}\frac{E_{\pm,n}^\sigma}{2T} - \frac{\xi_n}{2T}\right] - \frac{\Delta_\pm^2}{\lambda\delta T}\right\}, \tag{7}$$

where $E_{\pm,n}^\sigma = E_{\pm,n} - \sigma\mu_B H$ and $\xi_n = \epsilon_n - \mu$.

At low temperatures $T \ll \Delta_0$, the ratio Z_-/Z_+ can be calculated easily; one finds $Z_-/Z_+ \simeq 1 - \sqrt{8\pi T\Delta_0/\delta^2}\exp(-\beta\Delta_0)$. Parity effects are important if this ratio is ~ 1, i.e., at temperatures $T < T_{\mathrm{eff}}$. At temperatures $T_{\mathrm{eff}} \ll T \ll \Delta_0$, parity effects can be ignored and the spin susceptibility is found to decrease exponentially, as in the BCS case,

$$\chi_{e/o} \sim \frac{2\mu_B^2}{\delta}\sqrt{\frac{2\pi\Delta_0}{T}}\, e^{-\beta\Delta_0}. \tag{8}$$

For $T \ll T_{\mathrm{eff}}$, Eq. (5) can be approximated as

$$\chi_e \simeq \frac{8\pi\mu_B^2\Delta_0}{\delta^2}\, e^{-2\beta\Delta_0}; \qquad \chi_o \simeq \frac{\mu_B^2}{T}.$$

We see that χ_e remains exponentially small, as in the BCS case (8), but with an exponent $-2\beta\Delta_0$ rather than $-\beta\Delta_0$. This reflects the fact that excitations are actually created in pairs. In odd grains, the unpaired spin gives rise to an extra paramagnetic (Curie-like) contribution to the spin susceptibility. As a result χ_o will show a *reentrant effect* at low temperatures (see Fig. 1). Although the re-entrant behavior is essentially a single electron effect, we stress that it can be detected experimentally using granular systems with many well-separated grains (to avoid collective effects due to tunneling). Such systems contain even grains as well, but their susceptibility is exponentially small at the temperatures of interest; thus their contribution to the response of the system will be negligible.

Ultrasmall grains ($\Delta_0 \ll \delta$).—A reduction of the grain size leads to a suppression of the gap Δ. For ultrasmall grains with $\Delta_0 \ll \delta$, the mean field approximation gives $\Delta = 0$: the grain behaves as a normal metal. The noninteracting, parity-dependent spin susceptibility can be found from Eq. (5); see the topmost curves in Figs. 2 and 3. Note, in particular, the monotonous dependence of χ_o on T. The temperature scale at which parity effects appear is set by the average level spacing. If $T \gg \delta$, parity effects are exponentially small and $\chi_{e/o}(T) \simeq \chi_P[1 \mp (2T/\delta)\exp(-\pi^2 T/\delta)]$. In the opposite limit $T \ll \delta$, χ_e is exponentially small, $\chi_e(T) \simeq (8\mu_B^2/T)e^{-\beta\delta}$, as we need to excite an electron out of the topmost, doubly occupied single particle level to magnetize the grain. For an odd grain, $\chi_o(T) \simeq \mu_B^2/T$ at $T \ll \delta$: the topmost level is occupied by a single electron that gives a Curie-like contribution.

The saddle point approach entirely ignores the fact that the fluctuation region ΔT around T_c grows as the size of the grains is reduced. Because of the presence of fluctuations, the behavior of small grains will be different in a distinct way from normal metallic grains. In the limit $T \gg \delta$, both fluctuation and parity effects are small; it therefore suffices to consider the fluctuation correction $\delta\chi_{\mathrm{fluc}}$ to χ_P, evaluating Z_+, Eq. (4), in Gaussian approximation. As a result, we find $\delta\chi_{\mathrm{fluc}}/\chi_P \simeq -\delta/2T\ln(T/\Delta_0)$; hence $\chi_{e/o}(T) \simeq \chi_P[1 \mp (2T/\delta)\exp(-\pi^2 T/\delta) - \delta/2T\ln(T/\Delta_0)]$. Superconducting correlations *suppress* the susceptibility; due to its algebraic dependence on T this suppression is stronger than the parity correction at temperatures $T \gtrsim \delta\ln\ln\delta/\Delta_0$. In the opposite limit, $T \ll \delta$, fluctuations are strong and the Gaussian approximation fails. However, the susceptibility can still be obtained analytically by considering a few levels close to the Fermi energy with a renormalized pairing interaction $\tilde{\lambda} = 1/\ln(\delta/\Delta_0)$ [9,11]. Consider first a grain with an even number of electrons. It costs an energy $\sim\delta + \delta/\ln(\delta/\Delta_0)$ to excite an electron from the topmost, doubly occupied level to the lowest unoccupied level. Correspondingly, the leading temperature dependence of the spin susceptibility is

$$\chi_e(T) \simeq 8\,\frac{\mu_B^2}{T}\,e^{-\beta\delta[1+\ln^{-1}(\delta/\Delta_0)]} + \mathcal{O}(e^{-2\beta\delta}). \qquad (9)$$

The even susceptibility is exponentially small, as in the case of a normal metallic grain, but with an exponent $-\beta\delta(1 + \tilde{\lambda})$, rather than $-\beta\delta$. Similarly, we find the spin susceptibility for a grain with an odd number of electrons

$$\chi_o(T) \simeq \frac{\mu_B^2}{T}[1 + 8e^{-\beta\delta[2+\ln^{-1}(\delta/\Delta_0)]}]. \qquad (10)$$

The paramagnetic contribution from the single spin dominates at all temperatures below δ. Compared to the case of a normal metallic grain, the odd susceptibility is nonmonotonous: upon lowering temperature, χ_o first decreases due to superconducting fluctuations; at temperatures $T \sim \delta$ a re-entrant behavior sets in which persists down to the lowest temperatures.

Re-entrant susceptibility.—The various limiting cases discussed so far provide evidence for the appearance of an anomaly in the spin susceptibility χ_o. For large grains ($\Delta \gg \delta$) the mean field approximation, Eq. (5), leads to the re-entrant behavior shown in Fig. 1. We will show that this is a unique signature of pairing correlations which is present even in ultrasmall grains. To this end we study the complete temperature dependence of $\chi_{e/o}$ for arbitrary values of the ratio δ/Δ_0.

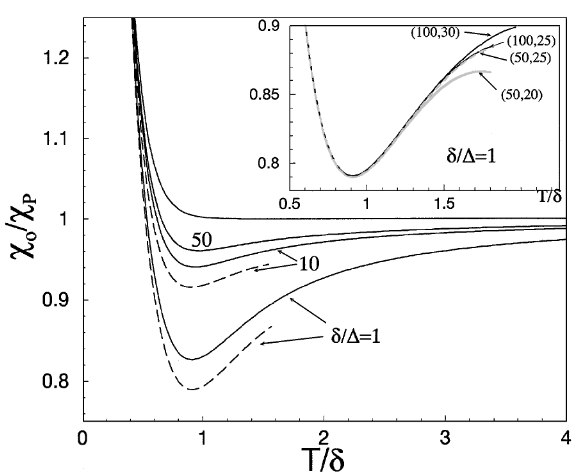

FIG. 2. $\Delta_0 \leq \delta$: Re-entrant spin susceptibility as a function of temperature for an odd grain in the static path approximation (solid lines); the topmost curve without re-entrance is the noninteracting limit. The dashed lines are obtained by an exact canonical calculation (see text), using $N = 100$ electrons and a large enough maximum excitation energy ($\Lambda \sim 40\delta$). In the inset the dependence of the susceptibility as a function of N and Λ. Curves are labeled with (N, Λ).

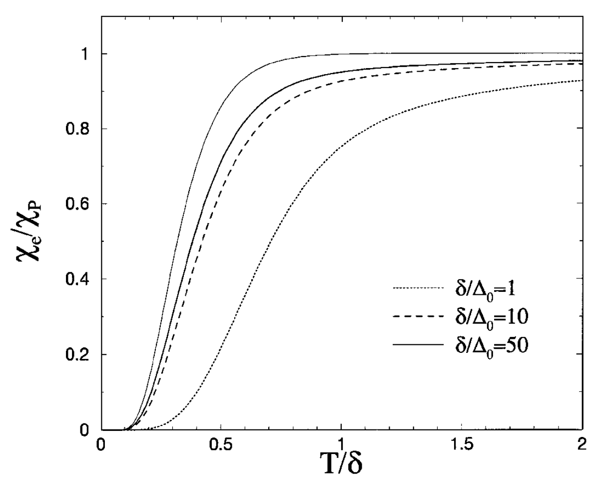

FIG. 3. $\Delta_0 \leq \delta$: Spin susceptibility as a function of temperature for an even grain. As in the previous figure, the thin solid line is the noninteracting limit.

The physics of re-entrant susceptibility can be grasped by evaluating Eq. (4), in the static path approximation [4]. This amounts in retaining only the static fluctuations (beyond the Gaussian approximation) in the path integral. In Figs. 2 and 3 we show the results of this calculation for the odd and the even cases, respectively. The re-entrance in the odd case is visible even in systems with a ratio $\delta/\Delta_0 \sim 50$ (!) and provides the signature of the existence of pairing correlations in an ultrasmall grain. The results are plotted for a system of $N = 200$ electrons at half filling and the BCS coupling is chosen to fix the ratio δ/Δ ($\lambda \sim 0.1 - 0.2$). The merit of the static path approximation combined with the analytic analysis in the limiting cases is that it allows us to obtain a coherent quantitative physical picture in the whole temperature range.

As a final check of our results we computed χ_o using the exact solution of Ref. [8]. The result is presented in Fig. 2 (dashed lines). As expected, the re-entrant effect is slightly larger ($\sim$15%). In order to obtain this result we considered all the different states with excitation energy up to a cutoff $\Lambda \sim 40\delta$ for a system with $N \leq 100$ electrons. In the inset we show the scaling analysis for different N and different energy cutoffs. This analysis becomes more and more difficult upon increasing temperature because of the exponential increase of the number of excited states needed.

In this Letter we proposed to study the spin susceptibility of a metallic grain as a very sensitive probe to detect superconducting correlations. For grains in the nanometer size regime the odd spin susceptibility is a unique signature of pairing. In grains of dimensions of the order of few nanometers as those studied in Ref. [14] the re-entrance should be of the order of 10%–20% of the Pauli value and it could be measured using the technique used in Ref. [17].

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