LT 21 Proceedings of the 21st International Conference on Low Temperature Physics
Prague, August 8-14, 1996
Part S4 - LT Properties of Solids 1: Mesoscopic systems

Superconductivity and Parity Effect in Ultrasmall Metallic Particles

Andrei D. Zaikin[a,b], Dmitrii S. Golubev[b], Jan von Delft[a], Wolfgang Tichy[a]

[a] Institut für Theoretische Festkörperphysik, Universität Karlsruhe, 76128 Karlsruhe, Germany
[b] P.N.Lebedev Physics Institute, Leninskii prospect 53, 117924, Moscow, Russia

Recent experiments [1] allowed to approach an answer on a fundamental question: what are the size limitations for the existence of superconductivity? In this paper we develop a theoretical investigation of the low temperature behavior of ultrasmall metallic particles with BCS interaction and discrete spectrum of electron levels (characterized by the energy level spacing d). We find that the value of a superconducting gap depends on the level spacing and the electron number parity, being so much smaller in the odd than the even case that these differences should be measurable in current experiments.

Very recently a dramatic development in fabrication of utrasmall metallic particles has been achieved in experiments by Black, Ralph and Tinkham (BRT) [1], who have constructed a single-electron transistor (SET) with a single nm-scale Al grain, being more than four orders of magnitude smaller in volume (estimated radii between $r \sim 5.1$ 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.

The eigenenergies of the larger grains studied by BRT revealed the existence of an excitation gap $\Omega > d$ which is driven continuously to zero by an applied magnetic field, and striking gap-dependent parity effects, i.e. differences between islands with an even or odd $[P = e/o]$ number of electrons. BRT very convincingly interpreted these phenomena as evidence for superconductivity.

These experiments allowed to aproach the answers on fundamental questions: What are the size limitations for the existence of superconductivity? And how do they depend on parity? This paper is devoted to a mean field study of the above problems. In particular, we calculate the superconducting gap $\Delta(d,0)$ and $T_c(d)$ by solving the BCS gap equation at $T=0$ and $\Delta_P = 0$, respectively.

As fluctuations in particle number of small grains are strongly suppressed by the charging energy, it is reasonable to 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 $P = (c,o)$ (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. The states $|j+\rangle$ and $|j-\rangle$ are degenerate, time-reversed partners. For a given $n = 2m+p$, we take $j=0$ to describe the first energy level whose occupation in the $T=0$ Fermi sea is not 2 but p, so that $j = -m, \ldots \infty$. Finally, the dimensionless coupling constant $\lambda^{-1} = \ln \frac{2\omega_c}{\Delta}$ is regarded as a phenomenological parameter.

We shall stick to the approach [2, 3] and calculate an auxiliary parity-projected grand-canonical partition function,

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

from which the desired fixed-n partition function Z_n can be exactly projected by integration:

$$Z_n = \int_{-\pi}^{\pi} \frac{du}{2\pi} e^{-iun} Z_P^G(iu/\beta) \,. \quad (3)$$

As usually it is hard to perform the integration exactly, we approximate the integral by its saddle point value, $Z_n \simeq e^{-\beta\mu_n n} Z_P^G(\mu_n)$, where μ_n is fixed by

$$n = -\partial_\mu \Omega_P^G(\mu)\big|_{\mu=\mu_n} \quad [= \langle \hat{N} \rangle_P] \,. \quad (4)$$

We evaluate Z_P^G using a mean-field approach, using $\gamma_{nj\sigma} = u_{nj} c_{nj\sigma} - \sigma v_{nj} c_{nj-\sigma}^\dagger$. 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 $E_{ni\sigma} = [\varepsilon_{nj}^2 + \Delta_P^2]^{1/2}$, $\varepsilon_{ni} \equiv \varepsilon_i^0 - \mu_n$, and $v_{ni}^2 = \frac{1}{2}(1 - \varepsilon_{ni}/E_{ni})$. Eq. (2) can be rewritten [2] using quasiparticle-parity projection, $Z_P^G(\mu_n) = \frac{1}{2}(Z_+^G \pm Z_-^G)$, where

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

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

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

where $f_{ni\sigma} = \langle \gamma_{ni\sigma}^\dagger \gamma_{ni\sigma} \rangle_P$ (see [2, 3]). The above description thus involves the usual BCS quasiparticles, but *their number parity is restricted to be p*.

Let us consider the case of equal level spacing, $\varepsilon_j^0 = j\, d + \varepsilon_0^0$. Using $n = \langle \hat{N} \rangle_P = \sum_{j\sigma} \left(v_{ni}^2 + (u_{ni}^2 - v_{ni}^2) f_{ni\sigma}\right)$ Eq. (4) gives [2] $\mu_n = \varepsilon_0^0 - \frac{1}{2} d\, \delta_{P,e}$.

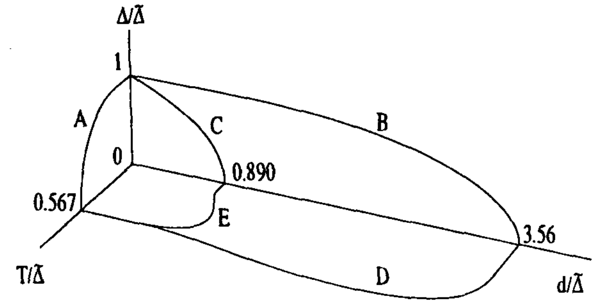
We first study the gap equation (6) at $T = 0$. The quasiparticle occupation function reduces to $f_{ni\sigma} = \frac{1}{2}\delta_{i0}\delta_{P,o}$ at $T = 0$, as intuitively expected, because then the even or odd systems have exactly zero or one quasiparticle, the latter in the lowest quasiparticle 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.

The full solutions of Eq. (6) for $\Delta_P(d, T)$, obtained numerically, are shown in Figure. 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):

$$\frac{d_{c,e}}{\tilde{\Delta}} = 2e^\gamma \simeq 3.56 \quad \text{and} \quad \frac{d_{c,o}}{\tilde{\Delta}} = \frac{1}{2}e^\gamma \simeq 0.890 , \qquad (7)$$

where $\tilde{\Delta}$ is the macroscopic order parameter. For $d/\tilde{\Delta} \ll 1$ and $T = 0$ the even gap has the form $\Delta_e(d, 0) = \tilde{\Delta}(1 - \sqrt{\tilde{\Delta} d}\, e^{-2\pi\tilde{\Delta}/d})$; in contrast, one easily finds from Eq. (6) that the odd gap drops linearly, $\Delta_o(d, 0) = \tilde{\Delta} - d/2$, in agreement with [2, 3].

An important general feature of our results is that level discreteness *always reduces* $\Delta_P(d, 0)$ below $\tilde{\Delta}$. The most important conclusion of this paper is summarized by Figure and Eq. (7): there is a



large regime in which $\Delta_o = 0$ while Δ_e is still $\simeq \tilde{\Delta}$, in other words, *superconducting correlations vanish significantly sooner for odd than even grains as their size is reduced*. Moreover, the largeness of the ratio $d_{c,e}/d_{c,o} = 4$ opens the exciting possibility to study grains with $d_{c,o} < d < d_{c,e}$, which have $\Delta_o = 0$ while Δ_e is still $\simeq \tilde{\Delta}$. BRT should be able to test this prediction directly, since they can change and control the electron parity of a given grain.

Although in such small systems fluctuations are quite large and can in principle change some details of our mean-field-based predictions, there are several reasons to believe that at least in the (experimentally accessible) regime of $T/d \simeq 0$, our main results are indeed robust. Without going into details here we only quote one of these reasons: it is well known even for systems much smaller than ultrasmall grains (that have $n \sim 10^4$), namely shell model nuclei (with $n \sim 100$), the $T = 0$ BCS-description of pairing interactions has been remarkably successful (see e.g. [4]), despite the presence of large fluctuations.

In conclusion, we have investigated the influence of parity on the superconducting mean-field order parameter in ultrasmall grains. We have found that as a function of decreasing grain size, superconductivity breaks down in an odd grain significantly earlier than in an even grain, which should be observable in present experiments.

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