PERGAMON

Solid State Communications 120 (2001) 487–490

solid state communications

www.elsevier.com/locate/ssc

Temperature and magnetic field dependence of superconductivity in nanoscopic metallic grains

Ö. Bozat, Z. Gedik*

Department of Physics, Bilkent University, Bilkent, 06533 Ankara, Turkey

Received 22 August 2001; accepted 27 September 2001 by A.H. MacDonald

Abstract

We study pairing correlations in ultrasmall superconductor in the nanoscopic limit by means of a toy model where electrons are confined in a single, multiply degenerate energy level. We solve the model exactly to investigate the temperature and magnetic field dependence of number parity effect (dependence of ground state energy on evenness or oddness of the number of electrons). We find a different parity effect parameter to critical temperature ratio ($\simeq$4 rather than 3.5) which turns out to be consistent with exact solution of the BCS gap equation for our model. This suggests the equivalence between the parity effect parameter and the superconducting gap. We also find that magnetic field is suppressed as temperature increases. © 2001 Elsevier Science Ltd. All rights reserved.

PACS: 74.20. − z; 74.20.Fg; 74.25.Ha; 74.80.Fp

Keywords: A. Mesoscopic superconductivity; D. Number parity effect

Single electron tunneling experiments of Ralph, Black and Tinkham (RBT) [1] initiated interest on the possibility of superconductivity in a nanometer size Al grain. Although existence of superconductivity in a very small metallic particle has been discussed long time back [2], it has been possible to investigate such small systems only recently with experiments of RBT. Anderson's criterion, that superconductivity ceases when discrete energy level spacing becomes comparable with superconducting gap, which is correct in general, in general, should be treated carefully at such small scales.

Instead of macroscopic properties like zero resistance and Meissner effect, superconductivity in nanometer size metallic grain manifests itself as an odd–even or number parity effect, i.e. dependence of physical properties on whether grain has odd or even number of electrons in it. Evaluation of discrete energy spectrum using BCS model or exact diagonalization of finite systems has been the main subject of theoretical studies [3–7]. For a review see Ref. [8].

For parabolic energy dispersion, which is the case for a grain with perfect symmetry, discrete energy levels are multiply degenerate [9–11]. Fig. 25.1 of Ref. [9] and Fig. 1 of Ref. [11] show explicitly that for parabolic dispersion, degeneracy of energy levels can be very large. For example, the number of solutions satisfying $n^2 = n_1^2 + n_2^2 + n_3^2$, all being integer, can approach to 40 for $n \leq 100$. Although disorder and irregular shape split the degeneracy, as long as they are weak, we can still talk about near degeneracy. The main point is that typical scale of dimensional energy quantization $\delta_1 = \hbar v_F/L$ is, L being the size of the grain, much larger than level spacing $\delta_2 \simeq E_F/N$, where E_F is Fermi energy and N is the total number of electrons, even for disordered samples. If attractive electron–electron interaction is much less than δ_1, but yet larger than δ_2, we can approximate the system as a single, multiply degenerate energy level provided that disorder is not too strong. A single energy level is certainly drastic approximation. Our aim is to find out possibility of superconductivity, or pairing correlations, in this extreme limit. Physical systems are probably between bulk BCS model and the nanoscopic (or quantum) limit. By examining the behavior of a superconductor at both ends, we expect to point out the properties of real systems. Finally, our earlier works [9,10] show that exact solution of multi-level model agrees very well with

* Corresponding author. Tel.: +90-312-290-1388; fax: +90-312-266-4579.

E-mail address: gedik@fen.bilkent.edu.tr (Z. Gedik).

PII: S0038-1098(01)00421-5

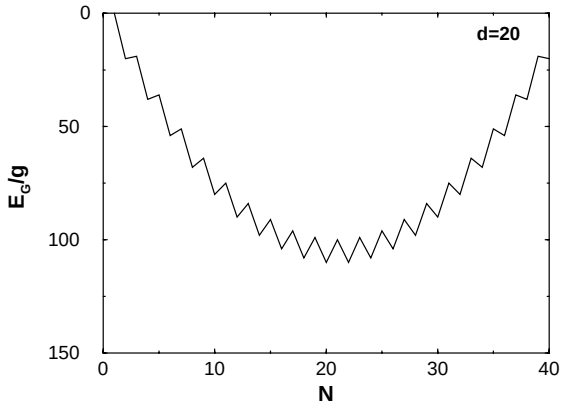

Fig. 1. Ground state energy with respect to the number of particles N in a grain with $d = 20$.

single energy level model in the large level spacing (or nanoscopic) limit. The formula, obtained in the single level approximation, for the ratio of the number parity effect parameters for odd and even cases gives results within one percent neighborhood of the exact solution when level spacing is about ten times larger than the superconducting energy gap.

Our starting point is a single, multiply degenerate energy level. We consider d states and assume that electrons in the same state are paired. Therefore the model Hamiltonian becomes

$$H = -g \sum_{n,n'=1}^{d} a^{\dagger}_{n'\uparrow} a^{\dagger}_{n'\downarrow} a_{n\downarrow} a_{n\uparrow}, \tag{1}$$

where $a^{\dagger}_{n}\sigma\,(a_{n\sigma})$ creates (annihilates) an electron in state n with spin σ. Such a model has already been used long time back by Mottelson to study pairing of nucleons [12]. In our case, n describes a state where time-reversed partner is n itself. Hence, we assume that electrons occupying the same state are paired and they can be scattered into anyone of the unoccupied states together with the same amplitude. It is an immediate consequence of the form of the interaction that singly occupied states give vanishing matrix elements. Single electrons simply block a state from any scattering event. Therefore, their mere effect is to eliminate certain states in the Hamiltonian. On the other hand, doubly occupied and empty states can be denoted in pseudo-spin representation [13] which allows us to diagonalize the Hamiltonian easily.

Pseudo-spins $\mathbf{s}$ are introduced by the definition $s_{n+} = a^{\dagger}_{n\uparrow} a^{\dagger}_{n\downarrow}$ and $s_{nz} = (1/2)(a^{\dagger}_{n\uparrow} a_{n\uparrow} + a^{\dagger}_{n\downarrow} a_{n\downarrow} - 1)$ which allows us to write the Hamiltonian as $H = -gS_{+}S_{-}$ where $\mathbf{S} = \sum_n \mathbf{s}_n$ is the total spin and $S_{\pm}$ are the corresponding raising and lowering operators. Finally, when it is written as $H = -g(\mathbf{S}^2 - S_z^2 + S_z)$, we obtain energy eigenvalues as

$$E(s) = -\frac{g}{4}(N - s)(2d - s - N + 2) \tag{2}$$

where

$$s = \begin{cases} 0, 2, 4, \ldots, 2d - N, \ldots, N & \text{for } N \text{ even} \\ 1, 3, 5, \ldots, 2d - N, \ldots, N & \text{for } N \text{ odd.} \end{cases} \tag{3}$$

Here, seniority number $s = d - 2S$ has been introduced to simplify the expressions. We note that for a given number of electrons N, z-component S_z of the pseudo-spin is fixed and hence eigenvalues are labeled by only one quantum number S. Degeneracy of each S, i.e. several different ways of obtaining the same total spin value, makes the problem nontrivial. Therefore, we have to find the total number of states $\Omega(s)$ having the same seniority number s to evaluate thermodynamical quantities. Let us start with the ground state, which corresponds to the largest possible total spin S or equivalently the smallest possible seniority s. For even N, $s = 0$ state is unique whereas for odd N, due to un-paired electron, there is $2d$-fold degeneracy. Here, we assume that the grain interacts with a heat bath where spin flip is possible, which gives the factor 2.

Next, we consider the excited states, which can be created not only by pair breaking (single particle excitations) but also by changing total spin value with fixed number of pairs (collective excitations). Single particle and collective excitations turn out to have the same energy spectrum. Hence, the total degeneracy $\Omega(s)$ can be obtained by the summation of degeneracies of each configuration. Contribution of un-paired electrons to degeneracy is nothing but the number of combinations of d states taken s at a time. Including spin degree of freedom results in a factor 2^s. Different ways of obtaining the same total spin S with N spin-1/2 particles, which is given by

$$\binom{N}{N/2 - S} - \binom{N}{N/2 - S - 1}, \tag{4}$$

brings an additional contribution. Total degeneracy is found by proper use of the two formulae. Summation over all possible configurations having the same seniority gives us the total degeneracy

$$\Omega(S) = \sum_{i=0}^{I} \left[\binom{d - s + 2i}{i} - \binom{d - s + 2i}{i - 1} \right] \times \binom{d}{s - 2i} 2^{s-2i} \tag{5}$$

where I is equal to (s/2), (s − 1)/2 for even N and odd N, respectively [14].

Before evaluating the thermodynamical quantities, let us first calculate the ground state energy as a function of number of electrons N, for a given degeneracy d. Fig. 1 shows $d = 20$ case. For $N = 20$, the level is half-filled and we reach the minimum. This is an expected result since both the number of pairs and the number of the empty states into which they scatter are maximized to have the optimum energy. Zig-zag structure of the curve is due to the parity

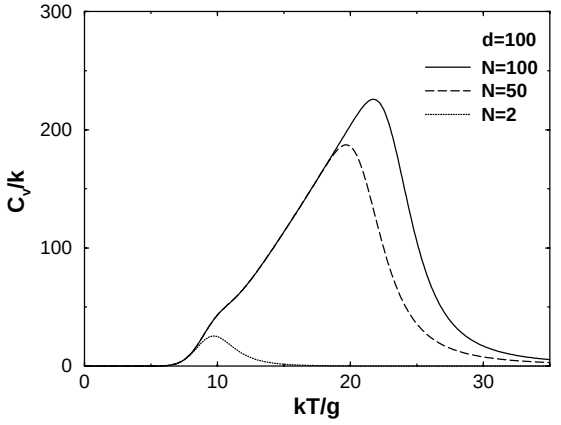

Fig. 2. Specific heat of a grain with $d = 100$ and $N = 100$, 50, 2. Smooth transition occurs from pair-correlated region to normal region around the maximum of C_v.

effect. When N is odd, there is an unpaired electron, which is neither scattered out nor allows any pair to be scattered into the state it occupies. This *blocking effect* effectively decreases the number of states by one.

Noting the fact that Zeeman energy shifts of discrete levels are much more important than orbital diamagnetism [15], we can immediately write down energy eigenvalues in the presence of a uniform magnetic field as

$$E_H = E_{H=0} - \mu_B H(n_\uparrow - n_\downarrow), \tag{6}$$

where $n_\uparrow$ and $n_\downarrow$ denote the number of spin-up and spin-down electrons, respectively. Although, we find E_H easily, degeneracy expression is not simpler but instead changes with magnetic field. However, for small number of states, it is not difficult to count the energy levels to find degeneracy of each energy eigenvalue.

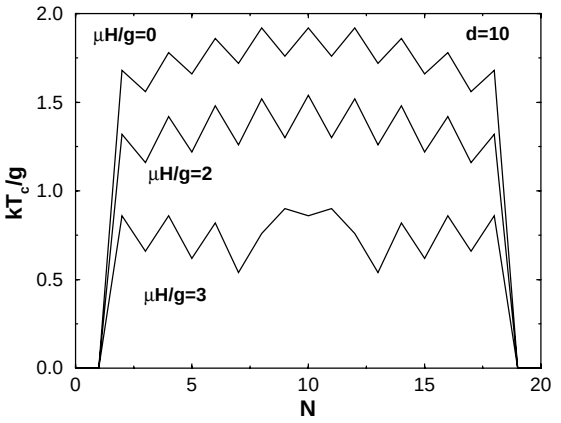

Fig. 3. Critical temperature with respect to number of particles for a grain with $d = 10$ for different magnetic fields $\mu H/g = 0$, 2, 3. Number parity dependent T_c decreases with increasing magnetic field.

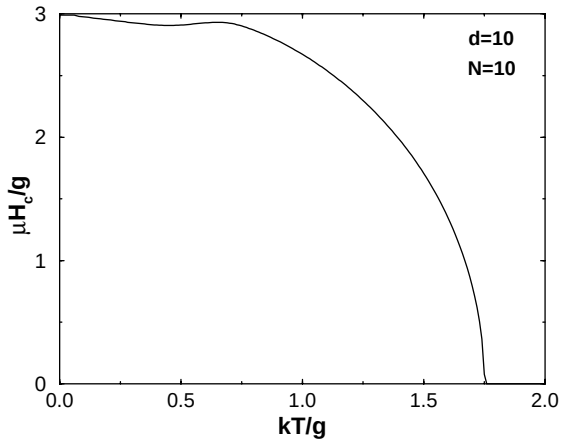

Fig. 4. Critical magnetic field with respect to temperature where $d = 10$ and $N = 10$. H_c is suppressed with temperature.

Having the degeneracy of each state, we can evaluate specific heat $C_v = \partial\langle E\rangle/\partial T$ as a function of temperature, where

$$\langle E\rangle = \frac{\sum_s E(s)\,\Omega(s)\,\mathrm{e}^{-E(s)/kT}}{\sum_s \Omega(s)\,\mathrm{e}^{-E(s)/kT}}. \tag{7}$$

Observation of specific heat variation is one of the most direct ways to find critical temperature T_c and magnetic field H_c.

Fig. 2 shows variation of $C_v(T)$ with temperature for different number of electrons. The increasing specific heat, which is a indication of a second-order phase transition in macroscopic systems, now manifests itself as a relatively fast variation in $C_v(T)$ curve. Absence of a sharp change results in ambiguity in the determination of T_c. We identify the temperature at which the maximum of $C_v(T)$ curve is reached as T_c. We note that the linear background, i.e. contribution to $C_v(T)$ which is of the form const T, is absent. This is because linear term is a result of Fermi–Dirac distribution and continuous spectrum near Fermi energy. Since in our case, we have a single level, $C_v(T)$ curve has a flat background.

In Fig. 3, we plot critical temperature for different magnetic fields as a function of number of electrons. Higher value of T_c for even number of electrons is an indication of number parity effect, which can be defined as

$$\Delta_P = \left| E^{2N+1} - \frac{E^{2N} + E^{2N+2}}{2} \right| \tag{8}$$

where E^{2N} is the ground state energy for $2N$ electrons. Δ_P has no N label because for our model, it can be shown that $\Delta_P = gd/2$, independent of N. However, at finite temperature, Δ_P should be redefined. One possibility is to replace ground state energies by thermal averages where we obtain $\Delta_P(T)$ as a decreasing function of temperature [14]. We note

that for $H = 0$, $kT_c/g \simeq 2$ while $\Delta P/g = 5$ which gives $2\Delta_P/kT_c = 5$. With increasing d, we observe that the ratio decreases. For $d = 100$, which is not plotted due to invisibility small odd–even dependence, $2\Delta_P/kT_c = 4.6$. Here the interesting point is that BCS gap equation

$$\Delta_{\mathbf{k}} = -\sum_{\mathbf{l}} V_{\mathbf{kl}} \frac{\Delta_l}{2E_{\mathbf{l}}} \tanh \frac{E_{\mathbf{l}}}{2kT} \tag{9}$$

can be solved analytically, with $V_{\mathbf{k1}} = -g$, $E_{\mathbf{k}} = E$ and $\Delta_{\mathbf{k}} = \Delta$, to give $kT_c/g = d/4 = \Delta_0/2g$, and we find $2\Delta_0/kT_c = 4$ (rather than 3.5).

Finally, in Fig. 4, we plot critical magnetic as a function of temperature. We attribute the feature at low temperatures to slight ambiguity in the definition of critical temperature. In interpreting $H_c(T)$ curve, we should keep in mind that the critical magnetic field is determined by Zeeman splitting. For a different geometry, for example for a ring shaped conductor, orbital coupling can also play an important role.

In conclusion, we can understand basic physics of thermal and magnetic properties of a nanoscopic superconductor using our very simple model, which can be solved exactly. In the extreme nanoscopic limit where a single degenerate or nearly degenerate energy level is left, we predict a different gap to critical temperature ratio. Our results, with increasing number of levels, approach to exact solution of the BCS gap equation, which gives $2\Delta_0/kT_c = 4$ (rather than 3.5). This suggests the equivalence between the parity effect parameter Δ_P and the superconducting gap Δ. Finally, we observe that the critical magnetic field is suppressed with increasing temperature.

Acknowledgements

We gratefully acknowledge useful discussions with Prof. I.O. Kulik.

References

[1] D.C. Ralph, C.T. Black, M. Tinkham, Phys. Rev. Lett. 78 (1997) 4087.
[2] P.W. Anderson, J. Phys. Chem. Solids 11 (1959) 26.
[3] K.A. Matveev, A.I. Larkin, Phys. Rev. Lett. 78 (1997) 3749.
[4] J. von Delft, A.D. Zaikin, D.S. Golubev, W. Tichy, Phys. Rev. Lett. 77 (1996) 3189.
[5] R.A. Smith, V. Ambegaokar, Phys. Rev. Lett. 77 (1996) 4962.
[6] A. Mastellone, G. Falci, R. Fazio, Phys. Rev. Lett. 80 (1998) 4542.
[7] S.D. Berger, B.I. Halperin, Phys. Rev. B 58 (1998) 5213.
[8] J. von Delft, Ann. Phys. 10 (2001) 1.
[9] H. Boyaci, Z. Gedik, I.O. Kulik, Proceedings of NATO Advanced Study Institute: Quantum Mesoscopic Phenomena and Mesoscopic Devices in Microelectronics, 13–25 June 1999, Ankara/Antalya, Turkey, p. 371.
[10] H. Boyaci, Z. Gedik, I.O. Kulik, J. Supercond. 13 (2000) 1031.
[11] I.O. Kulik, H. Boyaci, Z. Gedik, Physica C 352 (2001) 46.
[12] B.R. Mottelson, The many-body problem, Ecole d'Eté de Physique Théorique LesHouches, Willey, New York, 1959.
[13] P.W. Anderson, Phys. Rev. 112 (1958) 1900.
[14] Ö. Bozat, MS Thesis. Bilkent University, Ankara, Turkey, 2001.
[15] D.G. Salinas, S. Guéron, D.C. Ralph, C.T. Black, M. Tinkham, Phys. Rev. B 78 (1999) 6137.