RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 30, NUMBER 3 1 AUGUST 1984

Free-energy formula for a strong-coupling superconductor with Shiba-Rusinov impurities

Hikaru Yamamoto and A. D. S. Nagi
Guelph-Waterloo Program for Graduate Work in Physics, Department of Physics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1
(Received 27 February 1984; revised manuscript received 14 May 1984)

We derive a formula for calculating the free-energy difference between the superconducting and the normal states of a strong-coupling superconductor with localized states within the gap (induced by magnetic impurities). The present formula is a generalization of the one given by Bardeen and Stephen (for the electron-phonon systems) to include the effect of Shiba-Rusinov impurities.

Bardeen and Stephen[1] (BS) gave a formula for calculating the difference Ω_{S-N} between the free-energy in the superconducting state and the corresponding quantity in the normal state of a strong-coupling superconductor. It is based on the Eliashberg[2,3] formalism of the theory of superconductivity.[4] Mitrovic and Carbotte[5] have shown that the BS formula remains valid when magnetic impurities described by the Abrikosov-Gor'kov[6] (AG) theory are added to the superconductor. Schossmann and Schachinger[7] find that the above formula is still valid when the superconductor contains Shiba[8]-Rusinov[9] (SR) impurities. The purpose of this Rapid Communication is to point out that the BS formula is modified nontrivially in the Shiba-Rusinov case.

The SR theory of magnetic impurities in a weak-coupling superconductor is a generalization of a well-known AG theory. In the AG model the interaction between a conduction electron and a magnetic impurity is assumed weak and the lowest-order Born approximation is used to treat the scattering. In the SR model the scattering is calculated exactly for a single impurity problem by treating the impurity spin classically. This theory shows the existence of localized states within the Bardeen-Cooper-Schrieffer (BCS) energy gap and also modifies the various properties. Several properties of the superconducting alloy in the SR model have been calculated by Nagi and collaborators[10,11] and Ginsberg and collaborators.[12]

We use a 4×4 matrix temperature Green's function

$$\hat{G}_{\vec{k}\vec{k}'}(\tau) = -\langle T_\tau A_{\vec{k}}(\tau); A^\dagger_{\vec{k}'}(0)\rangle \quad , \tag{1}$$

where

$$A^\dagger_{\vec{k}} = (a^\dagger_{\vec{k}\uparrow}, a^\dagger_{\vec{k}\downarrow}, a_{-\vec{k}\uparrow}, a_{-\vec{k}\downarrow}) \quad , \tag{2}$$

$A_{\vec{k}}$ is its conjugate, T_τ the ordering operator for the imaginary time τ, and $a^\dagger_{\vec{k}\mu}$ the creation operator for a conduction electron with energy $\epsilon_{\vec{k}}$ and spin μ.

The self-energy of the impurity-averaged Green's function consists of

$$\hat{\Sigma}(P) = \hat{\Sigma}^{e-p}(P) + \hat{\Sigma}^{e-e}(P) + \hat{\Sigma}^{e-i}(P) \quad , \tag{3}$$

with

$$\hat{\Sigma}^{e-p}(P) = -T\sum_{P'} |g_{P-P'}|^2 D(P-P')\rho_3\hat{G}(P')\rho_3 \quad , \tag{4}$$

$$\hat{\Sigma}^{e-e}(P) = -T\sum_{P'} V^{sc}_{P-P'}\rho_3[\hat{G}(P') - \hat{G}^d(P')]\rho_3 \quad , \tag{5}$$

$$\hat{\Sigma}^{e-i}(P) = n_i\sum_{l=0}^{\infty}(2l+1)\hat{\Sigma}^{e-i}_l(P) \quad , \tag{6}$$

$$\hat{\Sigma}^{e-i}_l(P) = \left\langle \hat{U}_l\left[1 - \sum_{\vec{k}}\hat{G}(\vec{P})\hat{U}_l\right]^{-1}\right\rangle \quad , \tag{7}$$

where $\hat{\Sigma}^{e-p}(P)$ is the contribution from the electron-phonon interaction $(g_{P-P'})$; $D(P-P')$ is the phonon Green's function; $\hat{\Sigma}^{e-e}(P)$ comes from the repulsive screened Coulomb electron-electron interaction $(V^{sc}_{P-P'})$ and has been written following Ref. 5 [$\hat{G}^d(P)$ is the diagonal part of $\hat{G}(P)$]; $\hat{\Sigma}^{e-i}(P)$ is the contribution from the electron-impurity interaction and is based on Refs. 8 and 9. Furthermore, n_i is the impurity concentration, $\langle\cdots\rangle$ denotes the averaging over the positions and spin directions of a low concentration of randomly distributed magnetic impurities and the volume has been taken unity. We have used the abbreviated notation $P = (\vec{k}, i\omega_n)$, where ω_n is Matsubara frequency [i.e., $\omega_n = \pi T(2n+1)$, with T as temperature and n as an integer]. In writing Eqs. (6) and (7), the scattering potential $\hat{U}_{\vec{k}\vec{k}'}$ has been expanded in a series of the Legendre polynomials:

$$\hat{U}_{\vec{k}\vec{k}'} = \sum_{l=0}^{\infty}(2l+1)\hat{U}_l P_l(\vec{e}\cdot\vec{e}') \quad , \tag{8}$$

where $\vec{e} = \vec{k}/|\vec{k}|$ and

$$\hat{U}_l = V_l\rho_3 + J_l\vec{S}\cdot\vec{\alpha} \quad , \tag{9}$$

$$\vec{\alpha} = \frac{1+\rho_3}{2}\vec{\sigma} + \frac{1-\rho_3}{2}\sigma_2\vec{\sigma}\sigma_2 \quad . \tag{10}$$

Here, σ_i and ρ_i $(i = 1,2,3)$ are Pauli spin matrices operating on ordinary spin states and the electron-hole spin states.

By using the stationary properties of the thermodynamic potential with respect to the self-energy, we construct the free-energy functional (hereafter simply called the free energy). This functional was first discussed for normal Fermi systems by Luttinger and Ward,[13] whose work was extended to the electron-phonon system by Eliashberg.[3] The free-energy functional can be written as (volume = 1)

$$\Omega(\hat{\Sigma}) = -\frac{T}{2}\sum_P \mathrm{Tr}\{\ln[-\hat{G}^{-1}(P)] + \hat{\Sigma}(P)\hat{G}(P)\} + \frac{T}{2}\sum_Q \{\ln[-D^{-1}(Q)] + \pi(Q)D(Q)\} + \theta(\hat{G}) \quad , \tag{11}$$

where $\pi(Q)$ is the self-energy of the phonon Green's function. The function $\theta(\hat{G})$ is determined to give the self-energy written in Eqs. (3)–(7) and we obtain

$$\theta(\hat{G}) = -\frac{T^2}{4}\sum_{PP'}|g_{P-P'}|^2 D(P-P')\,\mathrm{Tr}[\hat{G}(P)\rho_3\hat{G}(P')\rho_3]$$

$$-\frac{T^2}{4}\sum_{PP'}V^{sc}_{P-P'}\,\mathrm{Tr}\{[\hat{G}(P)-\hat{G}^d(P)]\rho_3[\hat{G}(P')-\hat{G}^d(P')]\rho_3\} - \frac{n_i T}{2}\sum_n\sum_{l=0}^{\infty}(2l+1)\left\langle \mathrm{Tr}\ln\left[1-\sum_{\mathbf{k}}\hat{G}(P)U_l\right]\right\rangle . \quad (12)$$

After the impurity averaging, the self-energy $\hat{\Sigma}(P)$ and the Green's function $\hat{G}(P)$ are spin independent. Then one can use the functions $G(P)$, $F(P)$, $\Sigma_1(P)$, and $\Sigma_2(P)$ which are related with $\hat{G}(P)$ and $\hat{\Sigma}(P)$ and have been used in Refs. 1 and 3 ($G=\hat{G}_{11}$, $F=-\hat{G}_{14}$, $\Sigma_1=\hat{\Sigma}_{11}$, and $\Sigma_2=\hat{\Sigma}_{14}$). Consequently, Eqs. (11) and (12) give

$$\Omega = -2T\sum_P\{\tfrac{1}{2}\ln[-\phi(P)]+\Sigma_1(P)G(P)-\Sigma_2(P)F(P)\}+\frac{T}{2}\sum_Q\{\ln[-D^{-1}(Q)]+\pi(Q)D(Q)\}$$

$$-T^2\sum_{PP'}\{|g_{P-P'}|^2G(P)D(P-P')G(P')-F(P)[|g_{P-P'}|^2D(P-P')+V^{sc}_{P-P'}]F(P')\}$$

$$-n_iT\sum_{n\geq 0}\sum_{l=0}^{\infty}(2l+1)\ln[R_l(S)R_l(-S)] , \quad (13)$$

with

$$\phi(P)=[i\omega_n-\epsilon_k-\Sigma_1(P)][i\omega_n+\epsilon_k+\Sigma_1(-P)]-\Sigma_2^2(P) , \quad (14)$$

$$G(P)=[i\omega_n+\epsilon_k+\Sigma_1(-P)]/\phi(P) , \quad (15)$$

$$F(P)=-\Sigma_2(P)/\phi(P) , \quad (16)$$

$$R_l(S)=\left[1-(V_l+J_lS)\sum_{\mathbf{k}}G(P)\right]\left[1-(V_l-J_lS)\sum_{\mathbf{k}}G(-P)\right]+[(V_l)^2-(J_lS)^2]\left[\sum_{\mathbf{k}}F(P)\right]^2 . \quad (17)$$

The quantity $R_l(-S)$ is obtained from Eq. (17) by changing $S\rightarrow -S$. Equation (13) can be rewritten as

$$\Omega = -T\sum_P\{\ln[-\phi(P)]+\Sigma_1(P)G(P)-\Sigma_2(P)F(P)\}+\frac{T}{2}\sum_P\{\ln[-D^{-1}(Q)]+\pi(Q)D(Q)\}$$

$$-T\sum_P[\Sigma_1^{e-i}(P)G(P)-\Sigma_2^{e-i}(P)F(P)]-n_iT\sum_{n\geq 0}\sum_{l=0}^{\infty}(2l+1)\ln[R_l(S)R_l(-S)] , \quad (18)$$

where we have used

$$-T\sum_P[\Sigma_1(P)G(P)-\Sigma_2(P)F(P)] = -T\sum_P[\Sigma_1^{e-i}(P)G(P)-\Sigma_2^{e-i}(P)F(P)]$$

$$-T\sum_P\{[\Sigma_1^{e-p}(P)+\Sigma_1^{e-e}(P)]G(P)-[\Sigma_2^{e-p}(P)+\Sigma_2^{e-e}(P)]F(P)\} \quad (19)$$

and have canceled the term inside the curly bracket with the terms proportional to $|g_{P-P'}|^2$ and $V^{sc}_{P-P'}$ in Eq. (13).

Ultimately we are interested in calculating the difference Ω_{S-N} between the free energy in the superconducting state Ω_S and the corresponding quantity in the normal state Ω_N. By assuming that $\pi_S(Q)=\pi_N(Q)$ [and consequently $D_S(Q)=D_N(Q)$], we get

$$\Omega_{S-N}=\Omega_{\rm BS}+\Delta\Omega_{\rm SR} , \quad (20)$$

$$\Omega_{\rm BS}=-T\sum_P\{\ln[\phi_S(P)/\phi_N(P)]+[\Sigma_{1S}(P)-\Sigma_{1N}(P)][G_S(P)+G_N(P)]-\Sigma_{2S}(P)F(P)\} , \quad (21)$$

$$\Delta\Omega_{\rm SR}=-T\sum_P\{[\Sigma_{1N}^{e-i}(P)+\Sigma_{1S}^{e-i}(P)][G_S(P)-G_N(P)]-\Sigma_{2S}^{e-i}(P)F(P)\}$$

$$-n_iT\sum_{n\geq 0}\sum_{l=0}^{\infty}(2l+1)\ln[R_{lS}(S)R_{lS}(-S)/R_{lN}(S)R_{lN}(-S)] . \quad (22)$$

In writing Eqs. (21), (22) we have used

$$\sum_P[\Sigma_{1S}(P)G_S(P)-\Sigma_{1N}(P)G_N(P)]=\sum_P\{[\Sigma_{1S}(P)-\Sigma_{1N}(P)][G_S(P)+G_N(P)]+\Sigma_{1N}^{e-i}(P)G_S(P)-\Sigma_{1S}^{e-i}(P)G_N(P)\} \quad (23)$$

and

$$\sum_P\{[\Sigma_{1S}^{e-p}(P)+\Sigma_{1S}^{e-e}(P)]G_N(P)-[\Sigma_{1N}^{e-p}(P)+\Sigma_{1N}^{e-e}(P)]G_S(P)\}=0 . \quad (24)$$

In Eq. (20), $\Omega_{\rm BS}$ represents the term derived by Bardeen and Stephen and $\Delta\Omega_{\rm SR}$ is the correction brought in by the SR theory.

To proceed further, we use the following form of the single-particle Green's function

$$\hat{G}(P)=\{i\tilde{\omega}_n-[\epsilon_k+\chi(i\omega_n)]\rho_3-\tilde{\Delta}_n\rho_2\sigma_2\}^{-1} \quad (25)$$

Putting this in Eqs. (3)–(7), the various contributions to the self-energy can be obtained by following standard procedures.[5,8,9] Then using Eqs. (21) and (22) we obtain

$$\Omega_{\rm BS}=-2\pi TN(0)\sum_{n\geq 0}\left[[(\tilde{\omega}_n^2+\tilde{\Delta}_n^2)^{1/2}-\tilde{\omega}_n]\left(1-\frac{\tilde{\omega}_n^0}{(\tilde{\omega}_n^2+\tilde{\Delta}_n^2)^{1/2}}\right)\right] , \quad (26)$$

$$\Delta\Omega_{\rm SR}=-2\pi TN(0)\sum_{n\geq 0}\sum_{l=0}^{\infty}(2l+1)\Gamma_{1l}\frac{1-\eta_l^2}{U_n^2+\eta_l^2}\left(\frac{U_n}{(U_n^2+1)^{1/2}}-1\right)-n_iT\sum_{n\geq 0}\sum_{l=0}^{\infty}(2l+1)\left[\frac{1-\eta_l^2}{\eta_l^2+U_n^2}+\ln\left(\frac{\eta_l^2+U_n^2}{1+U_n^2}\right)\right] , \quad (27)$$

$$\Gamma_{1l}=\frac{n_i}{\pi N(0)}\frac{v_l^2(1+v_l^2)+j_l^2(1-2v_l^2)+j_l^4}{(1+v_l^2-j_l^2)^2+4j_l^2} , \quad (28)$$

$$\eta_l^2=\frac{(1+v_l^2-j_l^2)^2}{(1+v_l^2-j_l^2)^2+4j_l^2} , \quad (29)$$

$$U_n=\tilde{\omega}_n/\tilde{\Delta}_n . \quad (30)$$

Here, $\tilde{\omega}_n^0$ is the normal-state value of $\tilde{\omega}_n$, $v_l=\pi N(0)V_l$, $j_l=\pi N(0)J_l$, and $N(0)$ is the one-spin single-particle density of states at the Fermi level for the conduction electrons in the normal state of the pure host metal. We may remark that in the AG approximation η_l becomes 1 and $\Delta\Omega_{\rm SR}$ becomes zero. Thus in the AG approximation $\Omega_{S-N}=\Omega_{\rm BS}$.

Knowing the self-energy $\hat{\Sigma}(P)$, the explicit forms of $\tilde{\omega}_n$ and $\tilde{\Delta}_n$ can be written as

$$\tilde{\omega}_n=\omega_n+\delta\tilde{\omega}_n+\sum_{l=0}^{\infty}(2l+1)\Gamma_{1l}\frac{U_n(1+U_n^2)^{1/2}}{\eta_l^2+U_n^2} , \quad (31)$$

$$\tilde{\Delta}_n=\pi T\sum_{m=-\infty}^{\infty}[\lambda(n-m)-\mu^*]\frac{1}{(U_m^2+1)^{1/2}}+\sum_{l=0}^{\infty}(2l+1)\Gamma_{2l}\frac{(1+U_n^2)^{1/2}}{\eta_l^2+U_n^2} , \quad (32)$$

$$\delta\tilde{\omega}_n=\pi T\sum_{m=-\infty}^{\infty}\lambda(n-m)\frac{U_m}{(1+U_m^2)^{1/2}} , \quad (33)$$

$$\Gamma_{2l}=\frac{n_i}{\pi N(0)}\frac{v_l^2(1+v_l^2)-j_l^2(1+2v_l^2)+j_l^4}{(1+v_l^2-j_l^2)^2+4j_l^2} , \quad (34)$$

where $\lambda(n-m)$ is the electron-phonon interaction parameter and μ^* is the Coulomb pseudopotential. Equations (31) and (32) can be combined to get the equation for U_n:

$$\omega_n+\delta\tilde{\omega}_n=U_n\left(\pi T\sum_{m=-\infty}^{\infty}[\lambda(n-m)-\mu^*]\frac{1}{(U_m^2+1)^{1/2}}-\frac{n_i}{2\pi N(0)}\sum_{l=0}^{\infty}(2l+1)(1-\eta_l^2)\frac{(1+U_n^2)^{1/2}}{\eta_l^2+U_n^2}\right) , \quad (35)$$

where we used

$$\Gamma_{1l}-\Gamma_{2l}=\frac{n_i}{2\pi N(0)}(1-\eta_l^2) . \quad (36)$$

Equation (35) shows that U_n does not depend on the potential scattering explicitly.

Substituting Eq. (31) and the corresponding expression of $\tilde{\omega}_n^0$ in Eqs. (20), (26), and (27), we obtain

$$\Omega_{S-N}=-2\pi TN(0)\sum_{n\geq 0}\left[\omega_n\left(\frac{(1+U_n^2)^{1/2}}{U_n}+\frac{U_n}{(1+U_n^2)^{1/2}}-2\right)+\delta\tilde{\omega}_n\left(\frac{(1+U_n^2)^{1/2}}{U_n}-1\right)+\delta\tilde{\omega}_n^0\left(\frac{U_n}{(1+U_n^2)^{1/2}}-1\right)\right]$$
$$-n_iT\sum_{n\geq 0}\sum_{l=0}^{\infty}(2l+1)\left[\frac{1-\eta_l^2}{\eta_l^2+U_n^2}+\ln\left(\frac{\eta_l^2+U_n^2}{1+U_n^2}\right)\right] . \quad (37)$$

It may be pointed out that Eq. (27) contained a term proportional to Γ_{1l} which depends explicitly on the potential scattering. This term has canceled out with a contribution coming from Eq. (26). It means that $\Omega_{\rm BS}$ and $\Delta\Omega_{\rm SR}$ separately violate the Anderson theorem,[14] but the final result, Eq. (37) conserves the theorem.

For a weak-coupling superconductor with SR impurities, the quantity Ω_{S-N} is usually calculated by using[10]

$$\Omega_{S-N}=\int_0^g\delta\left(\frac{1}{g}\right)\Delta^2 , \quad (38)$$

where g and Δ, respectively, are the BCS interaction constant and the order parameter. It can be shown that the above equation gives an expression for Ω_{S-N} which agrees exactly with the weak-coupling limit of Eq. (37) (i.e., with $\delta\tilde{\omega}_n$ and $\delta\tilde{\omega}_n^0$ equal to zero). For a strong-coupling host superconductor, Eq. (37) in conjunction with Eqs. (33) and (35) must be used.

It is appropriate here to discuss the origin of the difference between our result and that of Schossmann and Schachinger.[7] The last term of our Eq. (12) agrees with the corresponding term in Eq. (16) of Ref. 7 when the logarithmic function is expanded in series. In going to Eq. (17), the authors of Ref. 7 assume that the difference of the Green's function for the superconducting and the normal phases $\Delta\hat{G}\,(=\hat{G}_S-\hat{G}_N)$ is small and neglect all terms of third and higher order in $\Delta\hat{G}$. No such approximation has been made in our calculation.

Summarizing, we have derived a formula [Eq. (37)] for calculating the free-energy difference Ω_{S-N} for a superconductor containing Shiba-Rusinov impurities. This formula represents an essential modification of the Bardeen-Stephen formula. In the weak-coupling approximation our expression agrees exactly with the one derived by using the alternative approach given by Eq. (38). The real strength of Eq. (37) lies in treating the strong-coupling superconductors where Eq. (38) is not applicable.

Financial support provided by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

[1]J. Bardeen and M. Stephen, Phys. Rev. **136**, A1485 (1964).

[2]G. M. Eliashberg, Zh. Eksp. Teor. Fiz. **38**, 966 (1960) [Sov. Phys. JETP **11**, 696 (1960)].

[3]G. M. Eliashberg, Zh. Eksp. Teor. Fiz. **43**, 1005 (1962) [Sov. Phys. JETP **16**, 780 (1963)].

[4]A recent review of the Eliashberg formalism of the theory of superconductivity is given by P. B. Allen and B. Mitrovic, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1982), Vol. 37, pp. 1–92.

[5]B. Mitrovic and J. P. Carbotte, Can. J. Phys. **61**, 872 (1983).

[6]A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [Sov. Phys. JETP **12**, 1243 (1961)].

[7]M. Schossmann and E. Schachinger, Phys. Status Solidi (b) **120**, 723 (1983).

[8]H. Shiba, Prog. Theor. Phys. **40**, 435 (1968).

[9]A. I. Rusinov, Zh. Eksp. Teor. Fiz. **56**, 2047 (1968) [Sov. Phys. JETP **29**, 1101 (1969)].

[10]A. N. Chaba and A. D. S. Nagi, Can. J. Phys. **50**, 1736 (1972).

[11]Y. Okabe and A. D. S. Nagi, Phys. Rev. B **28**, 1320 (1983); **28**, 1323 (1983), and earlier references therein.

[12]D. M. Ginsberg, Phys. Rev. B **20**, 960 (1979); A. B. Kunz and D. M. Ginsberg, *ibid.* **22**, 3165 (1980); T. R. Lemberger, D. M. Ginsberg, and G. Rickayzen, *ibid.* **18**, 6057 (1978); **22**, 4527 (1980).

[13]J. M. Luttinger and J. C. Ward, Phys. Rev. **118**, 1417 (1960).

[14]P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).