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Brillouin-Wigner theory of mixed-valence rare-earth impurities in Bardeen-Cooper-Schrieffer superconductors

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We present a Brillouin-Wigner-type theory for the mixed-valence rare-earth impurities in Bardeen-Cooper-Schrieffer (BCS) superconductors. The impurity is described by a degenerate Anderson model with two configurations $4f^0$ and $4f^1$ in the infinite-correlation limit. Two important quantities characterizing the superconducting state, i.e., the reduced transition temperature T_c/T_{c0} and the reduced specific-heat jump $\Delta C/\Delta C_0$, are calculated as functions of the impurity concentration x and the valence of the $4f^1$ configuration n_f. The T_c/T_{c0} versus x curves obtained display exponential shapes which become steeper quickly with larger n_f. The $\Delta C/\Delta C_0$ versus T_c/T_{c0} curves show upward deviation with respect to the BCS law of corresponding states in contrast to the case of magnetic impurities. The theory is also fitted to the data of dilute superconducting $Th_{1-x}Ce_x$ alloys with a comparison to a previous Hartree-Fock theory.

I. INTRODUCTION

According to Maple's classification,[1] the rare-earth impurities in the superconducting alloys can be divided into three groups: first, those with long-lived local magnetic moments; second, those with short-lived moments; third, those with compensative local magnetic moments (i.e., the Kondo impurities). In addition, a new kind of mixed-valence state of the rare-earth impurities in a normal-metal host which is relevant to the above classification has been identified in recent years,[2] and remarkable progress has been made in understanding this mixed-valence behavior both experimentally and theoretically. Cerium impurity systems such as (La, Th) Ce are of special significance for all of these phenomena.

Generally, systems of metal hosts containing rare-earth impurities are described by the *s-d* exchange Hamiltonian or by a modified version of the Anderson Hamiltonian. Abrikosov and Gorkov[3] calculated the decrease of T_c to second order in the exchange coupling and predicted a critical concentration above which the superconductivity is destroyed. Higher-order perturbations in the exchange coupling give rise to logarithmic Kondo divergences. The resulting temperature dependence of the pair-breaking parameter yields a reentrant normal-superconducting phase boundary[4-6] if the transition temperature of the pure superconductor, T_{c0}, is of the order of the Kondo temperature T_K. If $T_K \gg T_{c0}$, the impurity spin is screened by the conduction electrons and forms a nonmagnetic complex. The Fermi-liquid description is valid and the Cooper pairs are weakened rather than broken in this stron-coupling Kondo limit.[7,8]

Within the Hartree-Fock approximation[9] for the Anderson model, the alloy behaves essentially as a BCS superconductor with an effective concentration-dependent BCS coupling parameter. This approximation is valid in the spin-fluctuation regime i.e., the Coulomb repulsion U is small compared to the width of the impurity levels) and has been extended by making use of the renormalization group.[10] However, the dilute superconducting $Th_{1-x}Ce_x$ alloys ($x \leq 0.1$) are still explained in this approximation although the Coulomb repulsion U is considered to be infinite there. The concentration dependence of T_c of these alloys show a modified exponential shape as found in the Hartree-Fock theory,[9] the renormalization-group extensions,[10] and the strong-coupling Kondo limit of the *s-d* exchange model.[8]

More recently, Schlottmann[11] studied the effects of mixed-valence impurities on superconductivity. The impurities were described by a modified version of the Anderson model with orbital degeneracy in the $U \to \infty$ limit, where two accessible configurations, corresponding to $4f^0$ and $4f^1$ (Ce impurities), were present. The properties of the superconducting alloys were expressed in terms of the *t*-matrix for the scattering off the impurities. The modified exponential concentration dependence of T_c was also discovered which indicated pair weakening rather than pair breaking, being consistent with the picture that the mixed-valence problem is driven by charge fluctuations with spin fluctuations playing a secondary role. However, the direct valence dependence and comparison with experimental data were not available.

In this paper, we present a calculation of the properties of dilute superconducting mixed-valence rare-earth alloys by using $1/N$ expansion technique which has become powerful for the mixed-valence systems[12] after Schlottmann's work. In this technique, a great advantage of the large orbital degeneracy of the $4f^1$ configuration arises within the Brillouin-Wigner theory, where perturbation expansion is nominally in powers of the hybridization width $\Gamma = \rho(E_F)V^2$, and $1/N$ ($N = 2J+1$) is found to be a rapidly convergent expansion parameter. Even the lowest-order Brillouin-Wigner theory, i.e., of the order of $(1/N)^0$, is a good approximation and only lower-order corrections such as $(1/N)^1$ and $(1/N)^2$ are meaningful to account for the properties of the mixed-valence impurity[13,14] and to give calculations in agreement with the exact results of the Bethe ansatz.[15]

Our model is similar to that used by Schlottmann with the local $4f$ orbitals being described by the transfer and projection operators introduced by Hubbard.[16] A brief summary of the mathematical generalization of the mixed Feynmann-Goldstone diagrammatic technique in Nambu's representation and the corresponding Brillouin-Wigner expansions are presented in Sec. II. The lowest-order Brillouin-Wigner perturbation-theory calculation of the reduced superconducting transition temperature T_c/T_{c0} and the reduced specific-heat jump $\Delta C/\Delta C_0$ as functions of E_f, Γ, the valence n_f, and in addition the impurity concentration x is given in Sec. III. As a result, we find a continuous variation of the valence n_f around the superconducting transition temperature T_c. In Sec. IV, numerical results of the T_c/T_{c0} versus x curves at different values of n_f are given. These are of exponential shape as expected for nonmagnetic impurities and become steeper quickly with increasing n_f. The $\Delta C/\Delta C_0$ versus T_c/T_{c0} curves exhibit small upward deviation with respect to the BCS law of corresponding states in contrast to the sharp downward deviation predicted by Abrikosov-Gorkov theory for magnetic impurities as calculated by Skalski *et al.*[17] and by Schlottmann for nonmagnetic rare-earth impurities.[11] Also presented in Sec. IV is the initial suppression of T_c, i.e., $(dT_c/dx)_{x=0}$, as a function of the valence n_f. In particular, we give a numerical fitting to the T_c/T_{c0} versus x curve of the $Th_{1-x}Ce_x$ alloys ($x \le 0.1$) within the present theory. The parameters used are found to be very different from those used in the Hartree-Fock theory. Concluding remarks are included in Sec. V. Some results of the present paper have already been reported in brief form.[18]

II. PERTURBATION THEORY IN NAMBU'S REPRESENTATION

We denote the $4f^0$ configuration by $|0\rangle$ and the $4f^1$ configuration by $|m\rangle$, where the $N=2J+1$ states ($m=J,J-1,\ldots-J$) of $4f^1$ are assumed to be degenerate. In terms of Hubbard's projection operators $X_{00}=|0\rangle\langle 0|$, $X_{mm}=|m\rangle\langle m|$ and transfer operators $X_{0m}=|0\rangle\langle m|$, $X_{m0}=|m\rangle\langle 0|$, the Hamiltonian for a single rare-earth impurity in the BCS superconductor can be written as

$$\hat{H}-\mu\hat{N}=\sum_m (E_1-\mu)X_{mm}+E_0X_{00} + \sum_{\mathbf{k}0}(\epsilon_{\mathbf{k}}-\mu)a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}0}+\sum_{\mathbf{k}}(\Delta a^\dagger_{\mathbf{k}\uparrow}a^\dagger_{-\mathbf{k}\downarrow}+\text{H.c.}) + \frac{1}{\sqrt{N_s}}\sum_{\mathbf{k}\sigma m}(V_{\mathbf{k}m\sigma}a^\dagger_{\mathbf{k}\sigma}X_{0m}+\text{H.c.}) . \quad (1)$$

The first two terms describe the atomic properties of the rare-earth ion. The second two terms describe the pure superconducting-band electrons in the BCS fashion with the mean field Δ being averaged over the whole Hamiltonian (1). The last term describes one-electron transitions between the local $4f$ orbitals of the rare-earth impurity and the conduction-band states, ie., the hybridization term. The reason that the other configurations such as $4f^2$ and $4f^3$ can be neglected rely on the fact that the Coulomb repulsion U is much larger than the other energy scales in the system. For cerium and uranium compounds, U is the experimental value of 5 to 10 eV so that configurations other than $4f^0$ and $4f^1$ are too far displaced in energy. In fact, we set U equal to infinity in the following.

We will leave the mathematical generalization of the Keiter-Kimball formalism to the case of superconducting alloys to another publication,[19] but will give a brief description of the major results of the diagrammatic method in Nambu's representation.

The hybridization interaction in Hamiltonian (1) is treated as a perturbation, i.e., $\hat{H}=\hat{H}_0+\hat{H}'$, and in Nambu's representation we have

$$\hat{H}_0-\mu\hat{N}=\sum_m \hat{F}^\dagger_m\hat{E}_m\hat{F}_m+\tfrac{1}{2}\sum_{\mathbf{k}\sigma}\hat{A}^\dagger_{\mathbf{k}\sigma}\hat{\mathcal{E}}_{\mathbf{k}\sigma}\hat{A}_{\mathbf{k}\sigma} \quad (2a)$$

and

$$\hat{H}'=\tfrac{1}{2}\sum_{\mathbf{k}m\sigma}(\hat{A}^\dagger_{\mathbf{k}\sigma}\hat{V}_{\mathbf{k}m\sigma}\hat{F}_m+\text{H.c.}) , \quad (2b)$$

where we use the operators

$$\hat{F}^\dagger_m=(X_{m0},X_{0m}), \quad \hat{A}^\dagger_{\mathbf{k}\sigma}=(a^\dagger_{\mathbf{k}\sigma},a_{-\mathbf{k}-\sigma})$$

for the f and conduction electrons, respectively, and the coefficient matrices

$$\hat{E}_m=\begin{bmatrix} E_1-\mu & 0 \\ 0 & (1/N)E_0 \end{bmatrix}, \quad \hat{\mathcal{E}}_{\mathbf{k}\sigma}=\begin{bmatrix} \epsilon_{\mathbf{k}}-\mu & \Delta \\ \Delta & -\epsilon_{\mathbf{k}}+\mu \end{bmatrix}$$

and

$$\hat{V}_{\mathbf{k}m\sigma}=\begin{bmatrix} V_{\mathbf{k}m\sigma} & 0 \\ 0 & -V_{\mathbf{k}m\sigma} \end{bmatrix}$$

for the f level, the pure BCS superconductor, and the hybridization, respectively.

The process of diagrammatic expansion with respect to H' parallels that of the Keiter-Kimball representation with special attention to the cyclic invariance of the trace of products of both operators and 2×2 matrices. Wick's theorem in the version of the Bloch and De Dominicis theorem can be applied only to the conduction electrons to give "free" superconducting Green's function $\mathcal{G}^0(\tau,\tau')=-\langle T\tau[\hat{A}(\tau)\hat{A}^\dagger(\tau')]\rangle_0$. The thermodynamic expectation of the products of $4f$ transfer operators can be done directly with the help of the properties of these operators. The time-ordered integral in the interaction representation can be transformed into a contour integral. In this way, a mixed Feynmann-Goldstone diagrammatic expansion in Nambu's representation for the grand partition function of the superconducting rare-earth alloys is obtained with all the topological symmetry properties retained.

The grand partition function of the Hamiltonian (1) can be written in terms of the statistical quasiparticles as ($\beta=1/T$)

$$Z=e^{-\beta\Omega}=\text{Tr}(e^{-\beta(\hat{H}-\mu\hat{N})})=Z_s\sum_M e^{-\beta(E_M+\tilde{E}_M)} , \quad (3)$$

where Z_s is the grand partition function for the pure BCS superconductor; M denotes the states $|0\rangle$ and $|m\rangle$ explicitly. The real statistical quasiparticle energies $\tilde{E}_M$ are given by the Brillouin-Wigner equation

$$\tilde{E}_M = \Gamma_M(\tilde{E}_M) , \tag{4}$$

where $\Gamma_M(\tilde{E}_M)$ are the sums of all connected diagrams, i.e., the proper self-energies. The first three diagrams of $\Gamma_M(\tilde{E}_M)$ are shown in Fig. 1. In Fig. 1 the double straight lines on the vertical time axes represent states $(|{}^{0}_{m}\rangle)$ and the double wavy lines represent $(|{}^{m}_{0}\rangle)$, thus each diagram in Nambu's representation includes two diagrams with initial states $|0\rangle$ and $|m\rangle$, respectively. Double curves on the right-hand side of the vertical time axes represent the 2×2 Nambu's Green's function for the pure superconductor. The third diagram in Fig. 1 appears because of the off-diagonal long-range order of superconducting pairing.

The lowest-order Brillouin-Wigner equations read as

$$\tilde{E}_0 = \frac{1}{N_s} \sum_{\mathbf{k}\sigma m} |V_{\mathbf{k}\sigma m}|^2 \left[\frac{u_{\mathbf{k}}^2 f(E_{\mathbf{k}})}{\tilde{E}_0 - E_f + E_{\mathbf{k}}} + \frac{V_{\mathbf{k}}^2 f(-E_{\mathbf{k}})}{\tilde{E}_0 - E_f - E_{\mathbf{k}}} \right] \tag{5a}$$

and

$$\tilde{E}_m = \frac{1}{N_s} \sum_{\mathbf{k}\sigma} |V_{\mathbf{k}\sigma m}|^2 \left[\frac{u_{\mathbf{k}}^2 f(-E_{\mathbf{k}})}{\tilde{E}_m + E_f - E_{\mathbf{k}}} + \frac{v_{\mathbf{k}}^2 f(E_{\mathbf{k}})}{\tilde{E}_m + E_f + E_{\mathbf{k}}} \right] , \tag{5b}$$

where $E_{\mathbf{k}} = [(E_{\mathbf{k}} - \mu)^2 + \Delta^2]^{1/2}$ is the excitation energy of the pure BCS superconductor and within the energy interval $|\epsilon_{\mathbf{k}} - \mu| \langle \omega_D$, the superconducting coherence factors $u_{\mathbf{k}}^2$ and $v_{\mathbf{k}}^2$ are given by

$$u_{\mathbf{k}}^2 = \tfrac{1}{2} \left[1 + \frac{\epsilon_{\mathbf{k}} - \mu}{E_{\mathbf{k}}} \right], \quad v_{\mathbf{k}}^2 = \tfrac{1}{2} \left[1 - \frac{\epsilon_{\mathbf{k}} - \mu}{E_{\mathbf{k}}} \right] , \tag{6}$$

and $f(E_{\mathbf{k}}) = (1 + e^{-\beta E_{\mathbf{k}}})^{-1}$. $E_f = E_1 - E_0 - \mu$ is the energy of the f level.

It should be emphasized that the lowest-order Brillouin-Wigner theory is only nominally of the order of $|V_{\mathbf{k}\sigma m}|^2$. In fact, once a partial summation of all the "buckle" diagrams as given in Fig. 1(a) has been accomplished in the computation of the grand partition function

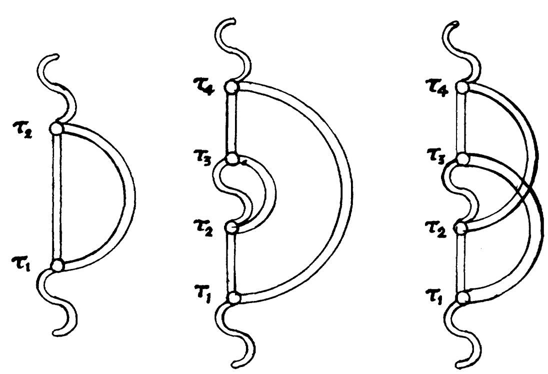

FIG. 1. First three connected diagrams in the Brillouin-Wigner theory.

it is seen that the lowest-order Brillouin-Wigner theory is really of infinite orders in $|V_{\mathbf{k}\sigma m}|^2$. The lowest-order Brillouin-Wigner theory to calculate the thermodynamic properties of mixed-valence rare-earth impurities in a BCS superconductor will be outlined in Sec. III.

III. LOWEST-ORDER BRILLOUIN-WIGNER THEORY OF T_c/T_{c0} AND $\Delta C/\Delta C_0$

A. General forms of T_c/T_{c0}, $\Delta C/\Delta C_0$, and n_f

The free energy of superconducting rare-earth alloys composed of the contributions of the pure BCS superconductor and the statistical quasiparticle corrections can be written as

$$\Omega(\beta,\Delta^2) = -\beta^{-1}\ln Z = \Omega_0(\beta,\Delta^2) - \beta^{-1} \ln\left[\sum_M \exp[-\beta(E_M + \tilde{E}_M)] \right] , \tag{7}$$

where $\Omega_0(\beta,\Delta^2) \equiv -\beta^{-1}\ln Z_s$ is the free energy for the pure BCS superconductor. This applies to the case where only one rare-earth impurity is present. For the case of dilute impurity concentration, we adopt the independent-site approximation for the impurities and write the free energy as the sum of N_i impurities (divided by the number of all lattice sites N_s)

$$g(\beta,\Delta^2) = g_0(\beta,\Delta^2) - x\beta^{-1} \ln\left[\sum_M \exp[-\beta(E_M + \tilde{E}_M)] \right] , \tag{8}$$

where $g_0(\beta,\Delta^2) \equiv \Omega_0(\beta,\Delta^2)/N_s$ and $x = N_i/N_s$.

The order parameter Δ is determined by minimizing $g(\beta,\Delta^2)$ with respect to Δ^2, i.e.,

$$\frac{\partial g(\beta,\Delta^2)}{\partial \Delta^2} = 0 . \tag{9}$$

For the computation of physical properties near the superconducting transition, the right-hand side of Eq. (8) may be expanded in powers of Δ^2 which is a small quantity. This yields [where λ and $\rho(\mu)$ are the BCS coupling constants and the density of states of normal electrons at the Fermi level μ]

$$\frac{\partial}{\partial \Delta^2} g(\beta,\Delta^2) = \frac{1}{\lambda} - \rho(\mu) \int_0^{\omega_D} d\xi \frac{\tanh(\xi/2T)}{\xi} + x \sum_M \tilde{P}_M \left. \frac{\partial \tilde{E}_M}{\partial \Delta^2} \right|_{\Delta^2=0} + \left[\frac{7\rho(\mu)\zeta(3)}{8(\pi T)^2} + x \sum_M \frac{\partial}{\partial \Delta^2} \left. \left[\tilde{P}_M \frac{\partial \tilde{E}_M}{\partial \Delta^2} \right] \right|_{\Delta^2=0} \right] \Delta^2(T) , \tag{10}$$

where the renormalized occupation probabilities of the two configurations are naturally defined as

$$\tilde{P}_M = e^{-\beta(E_M+\tilde{E}_M)} \Big/ \left[\sum_M e^{-\beta(E_M+\tilde{E}_M)} \right] . \tag{11}$$

Noting the following relations in the BCS theory

$$\frac{1}{\lambda\rho(\mu)} = \ln(2e^{r}\omega_D/\pi T_{c0}) ,$$

$$\int_0^{\omega_D} d\xi \frac{\tanh(\xi/2t)}{\xi} = \ln(2e^{r}\omega_D/\pi T) ,$$

and defining

$$A(x,T) = \frac{x}{\rho(\mu)} \sum_M \tilde{P}_M \frac{\partial \tilde{E}_M}{\partial \Delta^2} \bigg|_{\Delta^2=0} , \tag{12}$$

$$B(x,T) = \frac{7\zeta(3)}{8(\pi T)^2} + \frac{x}{\rho(\mu)} \sum_M \frac{\partial}{\partial \Delta^2} \left[\tilde{P}_M \frac{\partial \tilde{E}_M}{\partial \Delta^2} \right] \bigg|_{\Delta^2=0} , \tag{13}$$

and inserting Eqs. (10)–(13) into Eq. (9), we get

$$\ln(T_{c0}/T) = A(x,T) + B(x,T)\Delta^2(T) . \tag{14}$$

Accordingly, setting $\Delta^2(T_c)=0$, the equation for T_c reads as

$$\ln(T_{c0}/T_c) = A(x,T_c) . \tag{15}$$

The initial suppression of T_c is

$$-\frac{dT_c}{dx}\bigg|_{x=0} = T_{c0}\frac{A(x,T_{c0})}{x}\bigg|_{x=0} . \tag{16}$$

The reduced specific-heat jump is obtained by using Eq. (14) again

$$\frac{\Delta C}{\Delta C_0} = \frac{T_c}{T_{c0}} \frac{1+T_c \partial A(x,T_c)/\partial T_c}{1+\tilde{B}(x,T_c)} , \tag{17}$$

where ΔC_0 is the specific-heat jump of pure BCS superconductor at T_{c0},

$$1+\tilde{B}(x,T_c) = B(x,T_c) \Big/ \frac{7\zeta(3)}{8(\pi T_c)^2} .$$

For a derivation of Eq. (17), we refer to Skalski *et al.*[17] or Sakurai.[8] The deviation from the BCS law of corresponding states, i.e.,

$$\frac{\Delta C}{\Delta C_0} = \frac{T_c}{T_{c0}}$$

has been pointed out explicitly.

As in the normal state, the valence of the rare-earth impurity in a BCS superconductor is defined as the occupation probability of the $4f^1$ configuration, i.e.,

$$n_f(T) = \sum_m \langle X_{mm} \rangle \tag{18}$$

and according to Eq. (3), we obtain

$$n_f(T) = \frac{\partial \Omega}{\partial E_f} = \tilde{P}_0 \frac{\partial \tilde{E}_0}{\partial E_f} + \sum_m \tilde{P}_m \left(1 + \frac{\partial \tilde{E}_m}{\partial E_f}\right) . \tag{19}$$

Because $\partial\tilde{E}_0/\partial E_f$ and $\partial\tilde{E}_m/\partial E_f$ vary continuously from T_c+0^+ to T_c-0^+ as the superconducting order parameter $\Delta(T)$ is built up gradually, n_f does not have a discontinuity at T_c, i.e.,

$$n_f(T_c-0^+) - n_f(T_c+0^+) = 0 . \tag{20}$$

We mention in passing that the chemical valence of a rare-earth compound is defined as the number of ionized electrons of the rare-earth atom, e.g., the chemical valence of a cerium impurity in the mixed-valence regime is $3+[1-n_f(T)]$.

B. Derivatives of the energy shifts $\tilde{E}_0$ and $\tilde{E}_m$

The theory outlined above for the thermodynamic properties of BCS superconductors containing dilute rare-earth impurities is generally valid to all orders of the Brillouin-Wigner expansion if $\tilde{E}_0$ and $\tilde{E}_m$ and their derivatives can be calculated. As already mentioned in Sec. I, the lowest-order $[(1/N)^0]$ theory has proved to be rather accurate for normal mixed-valence rare-earth alloys. Accordingly, we try to account for the mixed-valence states in the case of a superconducting alloys with this lowest-order theory as a starting point.

Firstly, we simplify Eqs. (5) given for the energy shifts $\tilde{E}_0$ and $\tilde{E}_m$ in lowest-order perturbation theory forms in order to calculate the derivatives such as $\partial\tilde{E}_M/\partial\Delta^2$, $\partial^2\tilde{E}_M/\partial(\Delta^2)^2$, and $\partial\tilde{E}_M/\partial E_f$, etc.

The summation over the states $|m\rangle (m=J, J-1, \ldots, -J)$ of the $4f^1$ configuration can be replaced by the prefactor N because the states $|m\rangle$ are assumed to degenerate and $\tilde{E}_m=\tilde{E}_1$. The summation over momenta can be transformed into an integration over $\xi_{\mathbf{k}}=\epsilon_{\mathbf{k}}-\mu$. This can be done easily if a conventional flat band is assumed for the conduction electrons with bandwidth $2D$ and density of states $\rho(\mu)=1/2D$ distributed symmetrically around μ. Inserting the corresponding value for $u_{\mathbf{k}}^2$ and $v_{\mathbf{k}}^2$ in the respective energy regime, Eqs. (5a) and (5b) become

$$\tilde{E}_0 = N\rho(\mu)V^2 \int_0^{\omega_D} \partial\xi \left[\frac{f(E)}{y+E} + \frac{f(-E)}{y_0-E} \right] + N\rho(\mu)V^2 \int_{\omega_D}^{D} d\xi \left[\frac{f(\xi)}{y_0+\xi} + \frac{f(-\xi)}{y_0-\xi} \right] \tag{21a}$$

and

$$\tilde{E}_1 = \rho(\mu)V^2 \int_0^{\omega_D} d\xi \left[\frac{f(-E)}{y_1-E} + \frac{f(E)}{y_1+E} \right] + \rho(\mu)V^2 \int_{\omega_D}^{D} d\xi \left[\frac{f(-\xi)}{y_1-\xi} + \frac{f(\xi)}{y_1+\xi} \right] \tag{21b}$$

where $y_0=\tilde{E}_0-E_f$, $y_1=\tilde{E}_1+E_f$, $E=(\xi^2+\Delta^2)^{1/2}$.

It is easy to show that Eq. (21a) is reduced to the equation previously obtained by Proetto and Balseiro[20] using the Bogoliubov's transformation in the limit $T=0$ K. The right-hand side of Eq. (21b) can be obtained by deleting the degeneracy factor N and replacing y_0 by y_1 on the right-hand side of Eq. (21a).

In principle, Eqs. (21) can be inserted into Eq. (10) to give results for the normal ($T<T_c$) as well as for the superconducting state ($T>T_c$). We will leave, however, this laborious work for a future study and presently deal only with the situation close the the superconducting transition point T_c.

Taking derivatives with respect to Δ^2 on both sides of Eq. (21a), the derivative $\partial\tilde{E}_0/\partial\Delta^2$ is obtained as

$$\frac{\partial\tilde{E}_0}{\partial\Delta^2}=\tfrac{1}{2}N\rho(\mu)V^2\frac{\mathrm{Re}\psi(\frac{1}{2}+z_0)-\psi(\frac{1}{2})}{y_0[y_0+N\rho(\mu)V^2u_0\,\mathrm{Im}\psi'(\frac{1}{2}+z_0)]}\,, \tag{22}$$

where $\psi(\frac{1}{2}+z_0)$ is the digamma function. $\partial\tilde{E}_1/\partial\Delta^2$ can be obtained easily by making the simple substitution mentioned above. Thus $A(x,T_c)$ defined by Eq. (12) reads as

$$\frac{A(x,T_c)}{x}=\frac{NV^2}{2}\left[\tilde{P}_0\frac{\mathrm{Re}\psi(\frac{1}{2}+z_0)-\psi(\frac{1}{2})}{y_0[y_0+N\rho(\mu)V^2u_0\,\mathrm{Im}\psi'(\frac{1}{2}+z_0)]}+\tilde{P}_1\frac{\mathrm{Re}\psi(\frac{1}{2}+z_1)-\psi(\frac{1}{2})}{y_1[y_1+\rho(\mu)V^2u_1\,\mathrm{Im}\psi'(\frac{1}{2}+z_1)]}\right], \tag{23}$$

where $u_j=\beta\,|\,y_j\,|\,/2\pi$, $z_j=iu_j$, $j=0,1$.

$\tilde{E}_0$ and $\tilde{E}_1$ in Eq. (23) take the same values as for the normal host given previously by Ramakrishnan and Sur[14] for $T=T_c(\beta_c=1/T_c)$:

$$\tilde{E}_0=N\rho(\mu)V^2\left[-\ln\left[\frac{\beta_c D}{2\pi}\right]+\mathrm{Re}\psi\left[\frac{1}{2}+i\beta_c\frac{|\,\tilde{E}_0-E_f\,|}{2\pi}\right]\right] \tag{24a}$$

and

$$\tilde{E}_1=\rho(\mu)V^2\left[-\ln\left[\frac{\beta_c D}{2\pi}\right]+\mathrm{Re}\psi\left[\frac{1}{2}+i\beta_c\frac{|\,\tilde{E}_1+E_f\,|}{2\pi}\right]\right]. \tag{24b}$$

Inserting Eqs. (23)–(24) into Eq. (15), the superconducting transition temperature T_c can be calculated numerically.

For the reduced specific heat jump $\Delta C/\Delta C_0$, we have to calculate some more derivatives. Using

$$\sum_M\frac{\partial}{\partial\Delta^2}\left(\tilde{P}_M\frac{\partial\tilde{E}_M}{\partial\Delta^2}\right)\bigg|_{\Delta^2=0}=-\beta_c\sum_M\tilde{P}_M\left[\frac{\partial\tilde{E}_M}{\partial\Delta^2}\bigg|_{\Delta^2=0}\right]^2+\beta_c\left[\sum_M\tilde{P}_M\frac{\partial\tilde{E}_M}{\partial\Delta^2}\bigg|_{\Delta^2=0}\right]^2+\sum_M\tilde{P}_M\frac{\partial^2\tilde{E}_M}{\partial(\Delta^2)^2}$$

and

$$\frac{\partial}{\partial T_c}A(x,T_c)=-x\beta_c^2\left\{\left[\left[\tilde{E}_0+\beta_c\frac{\partial\tilde{E}_0}{\partial\beta_c}\right]\left[\frac{A(x,T_c)}{x}-\frac{1}{\rho(\mu)}\frac{\partial\tilde{E}_0}{\partial\Delta^2}\bigg|_{\Delta^2=0}+\frac{1}{\rho(\mu)}\frac{\partial}{\partial\rho_c}\left[\frac{\partial\tilde{E}_0}{\partial\Delta^2}\bigg|_{\Delta^2=0}\right]\right]\right]\tilde{P}_0\right.$$
$$\left.+N\left[\left[\tilde{E}_1+E_f+\beta_c\frac{\partial\tilde{E}_1}{\partial\beta_c}\right]\left[\frac{A(x,T_c)}{x}-\frac{1}{\rho(\mu)}\frac{\partial\tilde{E}_1}{\partial\Delta^2}\bigg|_{\Delta^2=0}\right]+\frac{1}{\rho(\mu)}\frac{\partial}{\partial\beta_c}\left[\frac{\partial\tilde{E}_1}{\partial\Delta^2}\bigg|_{\Delta^2=0}\right]\right]\tilde{P}_1\right\},$$

where the derivatives $\partial\tilde{E}_0/\partial(\Delta^2)^2\,|_{\Delta^2=0}$ and $\partial\tilde{E}_0/\partial\rho_c$ can be calculated in a way similar to $\partial\tilde{E}_0/\partial\Delta^2\,|_{\Delta^2=0}$. The detailed expressions are listed in the Appendix.

C. Analytic expressions of T_c/T_{c0} and $\Delta C/\Delta C_0$

For $|\,u\,|=|\,y\,|\,/2\pi T_c\gg 1$, the digamma function $\psi(\frac{1}{2}+z)$ can be replaced by a simple but accurate interpolation formula[14]

$$\mathrm{Re}\psi(\tfrac{1}{2}+z)\cong\tfrac{1}{2}\ln(1+4u^2)-(1+6u^2)^{-1} \tag{25}$$

and similarly for the polygamma functions

$$\mathrm{Im}\psi'(\tfrac{1}{2}+z)\cong-4[(1+4u^2)^{-1}+3(1+6u^2)^{-2}] \tag{26}$$

and

$$\mathrm{Re}\psi''(\tfrac{1}{2}+z)\cong 4[(4u^2-1)(1+4u^2)^{-2}+3(18u^2-1)(1+6u^2)^{-3}]\,. \tag{27}$$

In Sec. IV, these three expressions are used for numerical calculations for the corresponding quantities. Now, since numerically we have ($T_{c0}=1.36$ K for pure thorium)

$$|\,u\,|=|\,y\,|\,/2\pi T_{c0}\cong 10^3\,, \tag{28}$$

the low-temperature limit is almost completely reached at the superconducting transition temperature T_c with

$$\mathrm{Re}\psi(\tfrac{1}{2}+z)-\psi(\tfrac{1}{2})\cong\ln(T_{c0}/T_c)+\ln(4e^{\gamma}\,|\,y\,|\,/\pi T_{c0}) \tag{29}$$

and

$$u\,\mathrm{Im}\psi'(\tfrac{1}{2}+z)\cong-1,\quad u^2\,\mathrm{Re}\psi''(\tfrac{1}{2}+z)\cong 1\,. \tag{30}$$

If $\tilde{E}_0<\tilde{E}_1+E_f$ (i.e., in the mixed-valence regime, see Sec. IV), we have

$$\tilde{P}_0\equiv(1+Ne^{\beta(\tilde{E}_0-\tilde{E}_1-E_f)})^{-1}\cong 1 \tag{31a}$$

and

$$\tilde{P}_1\equiv(e^{-\beta(\tilde{E}_0-\tilde{E}_1-E_f)}+N)^{-1}\cong 0\,. \tag{31b}$$

Accordingly, the $A(x,T_c)$ function in Eq. (15) for T_c simplifies to

$$A(x,T_c)=x\frac{NV^2}{2}\frac{\ln(T_{c0}/T_c)+\ln(4e^{\gamma}|y|/\pi T_{c0})}{y_0[y_0-N\rho(\mu)V^2]} \tag{32}$$

so that a modified exponential law of T_c/T_{c0} versus x is also derived as

$$T_c/T_{c0}=\exp[-Ax/(1-Bx)] , \tag{33}$$

which is of the same form as derived in other theories,[8,9] the coefficients A and B are given by

$$B\equiv\frac{NV^2}{2}\frac{1}{y_0[y_0-N\rho(\mu)V^2]} \tag{34}$$

and

$$A\equiv B\ln(4e^{\gamma}|y_0|/\pi T_{c0}) . \tag{35}$$

Similarly, the expression for the valence of the $4f^1$ configuration n_f simplifies[14]

$$n_f=-N\rho(\mu)V^2\frac{1}{y_0-N\rho(\mu)V^2} . \tag{36}$$

Finally, the parameters in the modified exponential concentration dependence of T_c/T_{c0} may be expressed as functions of the valence n_f of the impurity, the half bandwidth D of the conduction electrons, the degeneracy factor N of the $4f^1$ configuration and the transition temperature of the pure BCS superconductor in the form

$$B=\frac{Dn_f^2}{N(1-n_f)} \tag{37}$$

and

$$A=B\ln\left[\frac{4e^{\gamma}N(1-n_f)}{\pi n_f T_{c0}}\right] , \tag{38}$$

where D, T_{c0}, and y_0 are scaled by the effective hybridization width $\Gamma=\rho(\mu)V^2$.

The terms for $\Delta C/\Delta C_0$ simplicity as

$$T_c\frac{\partial A(x,T_c)}{\partial T_c}=-Bx \tag{39}$$

and

$$\tilde{B}(x,T_c)=-3Bx+1.9(\pi T_c)^2\ln(T_{c0}/T_c)\left[\frac{3}{4y_0^2}+\frac{B}{2Dy_0}-\frac{1}{xD}\ln(T_{c0}/T_c)\left[\frac{1}{y_0}+\frac{B}{4D}\right]\right] . \tag{40}$$

IV. NUMERICAL RESULTS

In this section, we present numerical results for T_c/T_{c0} and $\Delta C/\Delta C_0$ calculated from expressions (15) and (17). Firstly, however, we want to gain some insight into the influence of rare-earth impurities in the mixed-valence regime on the BCS superconductor using quantitative arguments in the light of the above Brillouin-Wigner theory.

In the ground state ($T=0$ K), the preference of the occupation of the configurations $4f^0$ or $4f^1$ reversed if one passes from $\tilde{E}_0>\tilde{E}_1+E_f$ to $\tilde{E}_0<\tilde{E}_1+E_f$ by lifting the bare $4f^1$ energy level E_f (actually, the energy difference between the two configurations $E_1-E_0-\mu$) through a critical value $-\epsilon_c$ as found by Ramakrishnan and Sur,[14] $\epsilon_c=18\rho(\mu)V^2$ if $N=6$. At the superconducting transition temperature T_c, which is much smaller than other energy scales in the system, the physical picture of valence fluctuations is similar as in the ground state of a normal host. If $E_f<-\epsilon_c$, we have $\tilde{P}_0\ll\tilde{P}_1$ since $\tilde{E}_0>\tilde{E}_1+E_f$ i.e., the impurity is in the magnetic multiplets; and if $E_f>-\epsilon_c$, the singlet state $4f^0$ is occupied with larger weight, in other words more $4f$ electrons of the rare-earth impurity are ionized and located in the conduction band. This latter case characterizes the mixed-valence regime of the rare-earth impurity.

Accordingly, it is inferred that the suppression of superconductivity by the mixed-valence rare-earth impurities comes mainly from the change fluctuation between the two $4f$ configurations. Fewer electrons are available near the Fermi surface for superconducting pairing since some of them are fluctuating from the Fermi level to the $4f^1$ orbitals and vice versa. If $\tilde{E}_1+E_f<\tilde{E}_0$, more fluctuating charges will stay more time on the local $4f^1$ orbitals. The deeper the $4f^1$ energy level is, the stronger superconductivity is suppressed. If $\tilde{E}_1+E_f>\tilde{E}_0$, i.e., $E_f>-\epsilon_c$, a smaller amount of conduction electrons near the Fermi surface is lost. Thus the mixed-valence rare-earth impurities behave like nonmagnetic impurities following the pair-weakening mechanism.[9]

At the same time, $\tilde{E}_0<\tilde{E}_1+E_f$ is also a criterion for the lowest-order Brillouin-Wigner theory to be a good approximation.[15] Thus the present calculations of the thermodynamic properties near the superconducting transition temperature T_c is reliable in the strong mixed-valence regime. The following numerical results prove to support these interpretations quantitatively.

A. $-[d(T_c/T_{c0})/dx]_{x=0}$ versus n_f curves

The $-[d(T_c/T_{c0})/dx]_{x=0}$ versus n_f curve is given in Fig. 2. This initial depression of superconductivity increases very rapidly. This behavior is similar to the one known for the high T_K part of the $-[d(T_c/T_{c0})/dx]_{x=0}$ versus T_K/T_{c0} curve where a peak appears when T_K is reduced.[1,4] However, the range of validity of the present

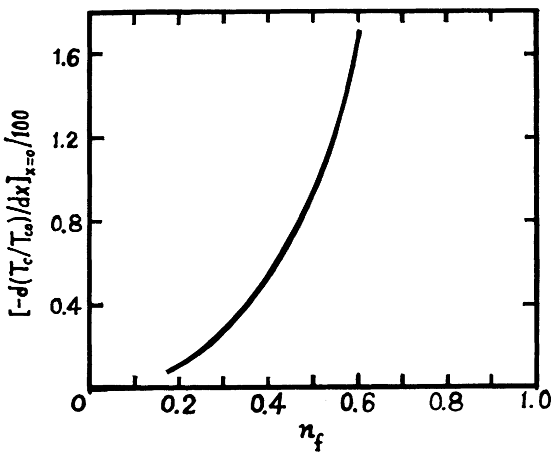

FIG. 2. The initial depression of T_c/T_{c0} vs the valence n_f with $\Gamma=0.02$ eV, $D=150\Gamma$, and $N=6$.

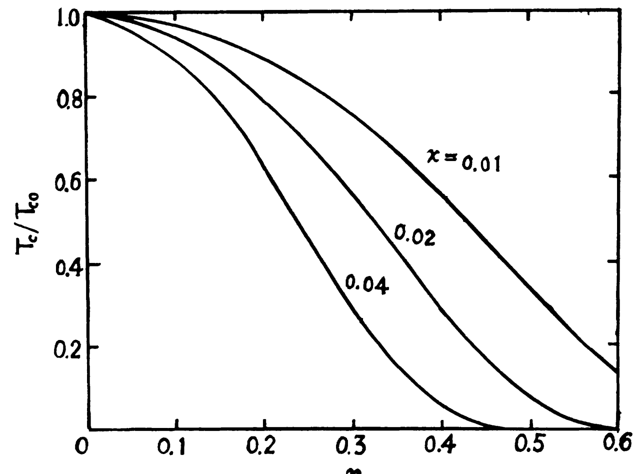

FIG. 4. T_c/T_{c0} vs valence n_f at different impurity concentrations. The parameters have the same as used in Fig. 1.

theory applies only up to $E_f=-16\rho(\mu)V^2\simeq-\epsilon_c$ or for $n_f\simeq 0.6$.

B. T_c/T_{c0} versus x curves and T_c/T_{c0} versus n_f curves

T_c/T_{c0} versus x curves are presented in Fig. 3. The curves all show a exponential form which become steeper when the valence n_f is increased. Curves with smaller valence n_f are of the nonmagnetic impurity type while those with larger n_f are as steep as the magnetic impurity. The dependence of T_c/T_{c0} on the valence n_f is plotted in Fig. 4 and is consistent with the physical picture developed earlier. It is seen that only a very small number of rare-earth impurities ($x<0.01$) can be dissolved in a superconductor when $n_f>0.6$. However, the present theory should not be continued beyond the valence $n_f\simeq 0.6$ for $N=6$.

C. $\Delta C/\Delta C_0$ versus T_c/T_{c0} curve

Another important characteristic of superconducting alloys is the T_c/T_{c0} dependence of the reduced specific-heat jump $\Delta C/\Delta C_0$ plotted in Fig. 5. To our surprise we find that our numerically calculated curve shows an upward deviation with respect to the BCS law of corresponding states given by the straight line in Fig. 5. The curve obtained by the Abrikosov-Gorkov theory[3] as calculated by Skalski *et al.*[17] for magnetic impurity alloys is also shown in Fig. 5. The experimental data of $Th_{1-x}Ce_x$ and $Th_{1-x}U_x$ alloys are also given for comparison. We suggest that more experimental measurements be carried out on the superconducting mixed-valence rare-earth alloys to make sure of this upward deviation.

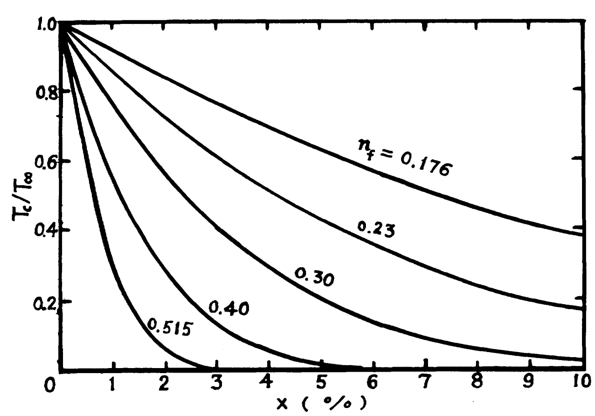

FIG. 3. Reduced transition temperature T_c/T_{c0} vs impurity concentration x with different valence. The parameters have the same values as used in Fig. 1.

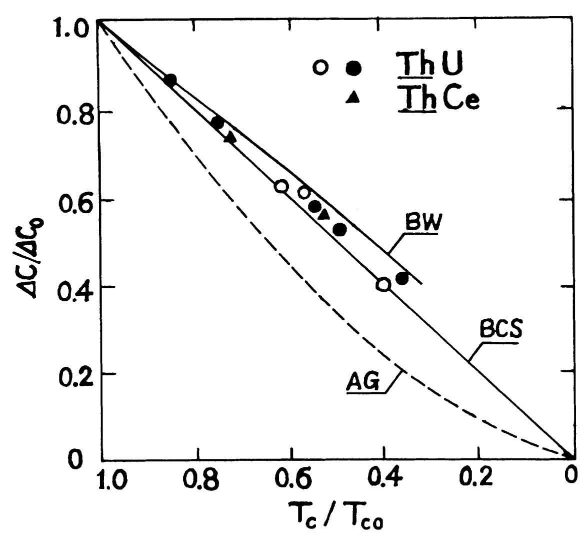

FIG. 5. Reduced specific heat jump $\Delta C/\Delta C_0$ vs T_c/T_{c0}. BCS, AG, and BW represent the results of the BCS, Abrikosov-Gorkov, and the present Brillouin-Wigner theories. The parameters are $n_f=0.45$, $\Gamma=0.01$ eV, and $D=75\Gamma$. The experimental points are taken from Ref. 1.

D. Reinterpretation of T_c/T_{c0} versus curves of $Th_{1-x}Ce_x$ alloys

Since $Th_{1-x}Ce_x$ alloys are believed to be typical mixed-valence systems in the normal state,[21] it is necessary to interpret the data of superconducting $Th_{1-x}Ce_x$ alloys in terms of the mixed-valence state. For that purpose we use the present lowest-order theory as a first step. In Fig. 6, we present the data of T_c/T_{c0} versus x of superconducting $Th_{1-x}Ce_x$ alloys to which Eqs. (33), (37), and (38) are fitted. Parameters used together with those used in the Hartree-Fock theory[22] are listed in Table I for comparison. As mentioned in Sec. I, the Coulomb repulsion U adopted in the Hartree-Fock theory is too small for a rare-earth impurity such as cerium and uranium. Furthermore, the value 0.75 of the valence n_f was obtained from the chemical valence of about 3.25 estimated from measurements done at a temperature of about 800 K.[23] However, due to thermally induced valence transitions, the high-temperature value of the valence may be considerably reduced.[21,24] On the other hand, all the parameters in Table I are very different from those found for cerium impurities in some metal host other than thorium.[25] Accordingly, further experimental studies on the mixed-valence state at lower temperatures (e.g., $T < 10$ K) are urgently needed. Theoretical work based on a higher-order Brillouin-Wigner perturbation theory, and which will apply to larger valence n_f in order to interpret the data of $Th_{1-x}Ce_x$ alloys, is presently in progress.[26]

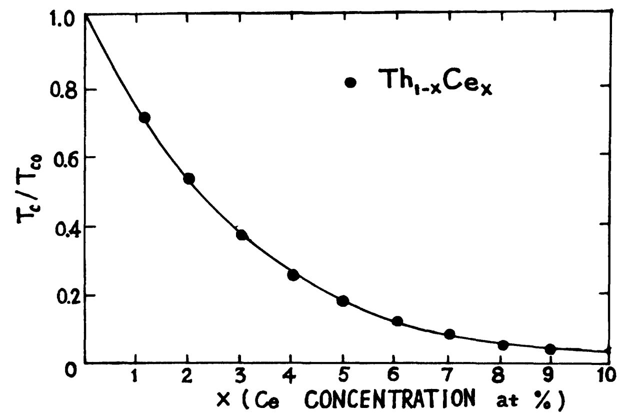

FIG. 6. Reduced transition temperature T_c/T_{c0} of $Th_{1-x}Ce_x$ alloys vs the Ce concentration from Ref. 22. The solid line shows result of present theory.

V. CONCLUDING REMARKS

We have presented a Brillouin-Wigner type theory for the thermodynamic properties of BCS superconductors containing mixed-valence rare-earth impurities relevant to superconducting $Th_{1-x}Ce_x$ alloys. The influence of mixed-valence impurities on superconductivity derives mainly from the charge fluctuations between the $4f$ configurations $4f^0$ and $4f^1$. The T_c/T_{c0} versus x curves show exponential form which become steeper rapidly when the valence n_f is increased. An upward deviation from the BCS law of corresponding states is found in the $\Delta C/\Delta C_0$ versus T_c/T_{c0} curve.

This lowest-order Brillouin-Wigner theory is considered suitable under the condition that $\tilde{E}_0 < \tilde{E}_1 + E_f$ or $E_f > -\epsilon_c$ hold, i.e., in the strong mixed-valence regime when $n_f < 0.6$. For the weakly mixed-valence rare-earth alloys ($n_f > 0.7$ or $E_f < -\epsilon_c$), higher-order terms as shown in Figs. 1(a) and 1(b) should also be used in order to account for spin fluctuations, especially spin-flip processes, and to obtain a Brillouin-Wigner theory of the order of $(1/N)^1$. The limiting case where the valence n_f approaches an integer value (one for cerium systems) can only be handled by including the sum of all terms of the order $1/N$.

A certain difficulty within the present theory is that the impurity concentration should be dilute. When the impurity concentration is increased, interaction between impurities become important. A Ruderman-Kittel-Kasuya-Yosida–type interaction also of the order of $(1/N)^1$ is found in the dense mixed-valence impurity system in the normal host.[27] This effect should be considered together with the Feynmann diagrams depicted in Figs. 1(b) 1(c) in order to reach a more suitable description of simultaneous charge and spin fluctuations in superconducting mixed-valence rare-earth alloys and their influence on superconductivity.

Eventually, we point out that with respect to a comparison of experiment and theory, some additional effects have to be considered. For example, one should take into account that the crystal field will destroy the large orbital degeneracy of the $4f^1$ configuration which is in fact the basis of the $1/N$ expansion. However, in some cases, the crystal-field splitting of the N states of the $4f^1$ configuration can be ignored if it is much smaller than the

TABLE I. Parameter values in two theories.

Theory	$\gamma = \rho(\mu)V^2 = \pi\Gamma$ (eV)	E_f (γ)	U (eV)	$\rho(\mu)$ $\left(\frac{\text{states}}{\text{eV atom}}\right)$	n_f
Brillouin-Wigner	0.031	-1.71	∞	0.67	0.43
Hartree-Fock	0.013	5.85	0.12	0.92	0.75

energy difference between the configurations $4f^0$ and $4f^1$. Finally, we want to stress that the theory presented here is only the first step towards an understanding of the physics of the rare-earth impurities in BCS superconductors.

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APPENDIX: HIGHER-ORDER PARTIAL DERIVATIVES OF $\tilde{E}_0$ AND $\tilde{E}_1$

We list here some higher-order partial derivatives of $\tilde{E}_0$ and $\tilde{E}_1$ used in Sec. III for calculating $\Delta C/\Delta C_0$ and n_f. The second-order derivative of $\tilde{E}_0$ with respect to Δ^2 is calculated directly from Eq. (21a) in the form

$$\frac{\partial^2\tilde{E}_0}{\partial(\Delta^2)^2}\bigg|_{\Delta^2=0}=N\rho(\mu)V^2\left[1+N\rho(\mu)V^2\frac{u_0}{y_0}\,\mathrm{Im}\psi'(\tfrac{1}{2}+z_0)\right]^{-1}$$
$$\times\left[-\frac{21\zeta(3)}{4}\frac{u_0^2}{y_0^4}+\frac{3}{4}\frac{1}{y_0^4}[\,\mathrm{Re}\psi(\tfrac{1}{2}+z_0)-\psi(\tfrac{1}{2})]\right.$$
$$-\frac{1}{\rho(\mu)}\frac{\partial\tilde{E}_0}{\partial\Delta^2}\bigg|_{\Delta^2=0}\left[\frac{2}{y_0^3}[\,\mathrm{Re}\psi(\tfrac{1}{2}+z_0)-\psi\tfrac{1}{2})+\frac{u_0}{y_0^3}\,\mathrm{Im}\psi'(\tfrac{1}{2}+z_0)\right]$$
$$\left.-\left[\frac{1}{\rho(\mu)}\frac{\partial\tilde{E}_0}{\partial\Delta^2}\bigg|_{\Delta^2=0}\right]^2\frac{u_0^2}{y_0^2}\,\mathrm{Re}\psi''(\tfrac{1}{2}+z_0)\right].$$

The temperature derivatives are found to be

$$\beta_c\frac{\partial\tilde{E}_0}{\partial\beta_c}=-N\rho(\mu)V^2\left[1+N\rho(\mu)V^2\frac{u_0}{y_0}\,\mathrm{Im}\psi'(\tfrac{1}{2}+z_0)\right]^{-1}[1+u_0\,\mathrm{Im}\psi'(\tfrac{1}{2}+z_0)]$$

and

$$\beta_c\frac{\partial}{\partial\beta_c}\left[\frac{\partial\tilde{E}_0}{\partial\Delta^2}\bigg|_{\Delta^2=0}\right]$$
$$=-\frac{N\rho(\mu)V^2}{2}\left[\frac{u_0\,\mathrm{Im}\psi'(\tfrac{1}{2}+z_0)\left[1+\dfrac{\beta_c}{y_0}\dfrac{\partial\tilde{E}_0}{\partial\beta_c}\right]}{y_0[y_0+N\rho(\mu)V^2u_0\,\mathrm{Im}\psi'(\tfrac{1}{2}+z_0)]}+[\,\mathrm{Re}\psi(\tfrac{1}{2}+z_0)-\psi(\tfrac{1}{2})]\right.$$
$$\left.\times\frac{N\rho V^2y_0(u_0\,\mathrm{Im}\psi'+u_0^2\,\mathrm{Re}\psi'')+\beta_c\dfrac{\partial\tilde{E}_0}{\partial\beta_c}(2y_0+2NPV^2u_0\,\mathrm{Im}\psi'+NPV^2u_0^2\,\mathrm{Re}\psi'')}{y_0^2[y_0+N\rho(\mu)V^2u_0\,\mathrm{Im}\psi'(\tfrac{1}{2}+z_0)]^2}\right].$$

The partial derivatives

$$\frac{\partial\tilde{E}_1}{\partial(\Delta^2)^2}\bigg|_{\Delta^2=0}$$

and

$$\beta_c\frac{\partial}{\partial\beta_c}\left[\frac{\partial\tilde{E}_1}{\partial\Delta^2}\bigg|_{\Delta^2=0}\right]$$

can be obtained from the above expressions by deleting N and replacing y_0 by y_1.

The partial derivatives of $\tilde{E}_0$ and $\tilde{E}_1$ with respect to E_f are calculated from Eqs. (24) in the form

$$\frac{\partial\tilde{E}_0}{\partial E_f}=N\rho(\mu)V^2\frac{u_0\,\mathrm{Im}\psi'(\tfrac{1}{2}+z_0)}{y_0+N\rho(\mu)V^2u_0\,\mathrm{Im}\psi'(\tfrac{1}{2}+z_0)}$$

and

$$\frac{\partial\tilde{E}_1}{\partial E_f}=-\rho(\mu)V^2\frac{u_1\,\mathrm{Im}\psi'(\tfrac{1}{2}+z_1)}{y_1+\rho(\mu)V^2u_1\,\mathrm{Im}\psi'(\tfrac{1}{2}+z_1)}\,.$$

The explicit expressions (39), and (40) for $\Delta C/\Delta C_0$ given in Sec. III are obtained by taking the low-temperature limit (29)–(31) in the corresponding expressions.

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