Mixed-valence impurities in a superconducting matrix: $1/N_f$ expansion

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The ground-state properties of a superconductor containing intermediate-valence impurities are analyzed. The impurities are described by a degenerate Anderson model in the infinite correlation limit. We consider two accessible configurations, one nonmagnetic and one magnetic with a degeneracy factor N_f. The $1/N_f$ expansion is formulated. With the assumption that no correlations exist between impurities, the gap parameters and critical fields at zero temperature are calculated. A brief discussion of the excitation spectrum and the existence of bound states near the gap edge is included.

I. INTRODUCTION

The effect of Ce impurities on the superconductive properties of metallic matrices has been extensively studied.[1] Depending on the matrix or external pressure, the Ce impurities can behave as Kondo or mixed-valence impurities. It is currently believed that with external pressure the impurities suffer a continuous demagnetization and the crossover between the Kondo-like behavior and the intermediate-valence (IV) region has been studied in LaCe and (La_xTh_{1-x}) Ce alloys.[2,3]

In the Kondo limit (Ce^{3+} impurities), the physics of the system is dominated by the spin fluctuations of Ce ions. A characteristic feature of these systems is the shape of the curves T_c versus impurity concentration. Three different regions can be distinguished according to whether the Kondo temperature of the impurities is smaller, of the order or larger than the critical temperature T_{c0} of the pure matrix. For $T_K \ll T_{c0}$, the local-moment region, the curves T_c versus concentration bend downwards according to the Abrikosov-Gorkov theory.[4] If $T_K \sim T_{c0}$ the so-called reentrance phenomenon occurs as predicted by Müller-Hartmann and Zittartz[5] and studied in Refs. 6 and 7. For $T_K \gg T_{c0}$, the strong-coupling Kondo limit, well above the critical temperature, the spin of the impurity is screened by the conduction electrons and its effect on the superconductive properties of the matrix is weaker than in the former cases. In this case,[8,9] the curvature of the curve T_c versus concentration is positive in similitude with that obtained from nonmagnetic impurities.

This problem of IV impurities in superconductors has been studied theoretically in different approximations. The Hartree-Fock approximation of the nondegenerate Anderson model has been used to describe the effect of impurities on the superconductivity.[10,11] This approximation is valid for small Coulomb repulsion and thus is more appropriate for transition-metal impurities than for rare-earth ions.

The critical temperature and specific-heat jump has been calculated by Wiecko and Lopez[6] using a decoupling procedure in the Green's functions for an Anderson impurity in the limit of infinite correlation. The atomic limit has been used to give a qualitative description in both the IV region and the Kondo limit.[12]

Finally, a more realistic description of the impurities is given in Ref. 13. The effect of impurities is studied by calculating the self-energy of the Green's functions in second order in the hybridization parameter V. For the models of IV impurities in a normal metal, exact results have been obtained by using the Bethe-ansatz technique[14] and numerical renormalization-group methods.[15] Because of the difficulties of extending the above two methods to describe IV impurities on a superconducting matrix, new techniques are to be developed.

The $1/N_f$ expansion[16] has been used to study the degenerate Anderson model and the results obtained for the ground-state energy and the average of the $4f$ shell are in excellent agreement with the Bethe-ansatz results.[17] In this paper we generalize the method to study the problem of impurities in superconducting matrices.

As pointed out in Refs. 17 and 18 this method provides an exact result for the ground-state wave function in the limit $N_f \rightarrow \infty$ and $N_f V^2 = \text{const}$ and for the ground-state energy in the limit of infinite-conduction bandwidth. Thus, the Kondo and IV regimes can be studied.

In this limit, the Kondo region corresponds to the problem of a classical spin coupled antiferromagnetically with conduction electrons. In a more realistic model, where N_f is taken as the real degeneracy factor of the $4f$ shell, the results are approximate and the method can be used only to study the IV region. In what follows, we present the method and the results for the ground-state properties.

II. MODEL AND CALCULATIONS

The degenerate Anderson model for a single rare-earth impurity is described by the following Hamiltonian:

$$H = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_M E_f \,|\, M \rangle\langle M \,| + \sum_{kM\sigma} (V_{kM\sigma} c_{k\sigma}^\dagger \,|\, 0 \rangle\langle M \,| + V_{kM\sigma}^* \,|\, M \rangle\langle 0 \,|\, c_{k\sigma}) \,, \tag{1}$$

where $c_{k\sigma}^\dagger$ creates an electron with crystal momentum k, spin σ and energy ϵ_k measured from the Fermi level, $|\, M \rangle$ represents the impurity state with $n+1$ $4f$ electrons and quantum number (J,M), and $|0\rangle$ the state with n $4f$ electrons and $J=0$. E_f is the energy difference between the two ionic configurations.

In order to describe a superconducting metal, we add an attractive electron-electron interaction to Hamiltonian (1), which is treated in the BCS approximation. The complete Hamiltonian can be written in terms of the quasiparticle operators in the following way:

$$H=U_0+\sum_k E_k(\alpha_k^\dagger\alpha_k+\beta_k^\dagger\beta_k)+\sum_M E_f|M\rangle\langle M|+\sum_{kM}[V_{M\uparrow}|M\rangle\langle 0|(u_k\alpha_k+v_k\beta_k^\dagger)+V_{M\uparrow}^*(u_k\alpha_k^\dagger+v_k\beta_k)|0\rangle\langle M|$$
$$+V_{M\downarrow}|M\rangle\langle 0|(-v_k\alpha_k^\dagger+u_k\beta_k)$$
$$+V_{M\downarrow}^*(-v_k\alpha_k+u_k\beta_k^\dagger)|0\rangle\langle M|]\ . \tag{2}$$

Here, U_0 is the energy of the BCS ground state:

$$U_0=\sum_k(\epsilon_k-E_k)+\Delta^2/\lambda\ , \tag{3}$$

where

$$E_k=(\epsilon_k^2+\Delta_k^2)^{1/2}$$

and

$$\Delta_k=\begin{cases}\Delta \text{ if } |\epsilon_k|\le\omega_D\\ 0 \text{ otherwise .}\end{cases}$$

Δ is the superconducting order parameter and, as we show below, is also the gap in the quasiparticle spectrum even in the presence of IV impurities, ω_D is a characteristic frequency of phonons and λ an effective electron-electron coupling.

The operator $\alpha_k^\dagger$ and $\beta_k^\dagger$ are Bogoliubov creation operators, and the coherence factors u_k and v_k are

$$u_k^2=\frac{1}{2}\left[1+\frac{\epsilon_k}{E_k}\right] \text{ and } v_k^2=\frac{1}{2}\left[1-\frac{\epsilon_k}{E_k}\right]\ . \tag{4}$$

In (2) we have taken $V_{kM\sigma}=V_{M\sigma}$ independent of k.

Following the diagramatic expansion developed for impurities on normal metals;[16,18] we assume for the ground state the many-particle wave function given by:

$$|\psi\rangle=a|\phi\rangle+\sum_{kM}(b_{kM}\alpha_k^\dagger|\phi,M\rangle+d_{kM}\beta_k^\dagger|\phi,M\rangle)\ , \tag{5}$$

where $|\phi\rangle$ represents the BCS ground state with the impurity in the $|0\rangle$ configuration and $\alpha_k^\dagger|\phi,M\rangle$ describes a state with one quasiparticle and the impurity in the $|M\rangle$ configuration.

In this approximation, the energy of the state $|\psi\rangle$ is given by

$$E_g=U_0+E_s\ , \tag{6}$$

where E_s is given by

$$E_s=N_fV^2\sum_k\frac{v_k^2}{E_s-E_f-E_k}\ , \tag{7}$$

with

$$N_fV^2=\sum_{M\sigma}V_{M\sigma}^2\ .$$

In the limit $N_f\to\infty$ and $N_fV^2=$const, the wave-function (5) is the exact ground state of Hamiltonian (2). If N_f is taken as the real degeneracy factor of the $4f$ shell, the approximation is valid only for the intermediate-valence region, that is, if $E_f>0$. In Ref. 16, a discussion of the range of validity of the approximation for a normal metal is given. In the present case, the same analysis can be made. The systematic expansion in $1/N_f$ developed for normal metals can be extended for the present case.

In what follows, we restrict ourselves to the study of IV *impurities*. In Eq. (6), E_s is the impurity contribution to the total energy. Assuming that correlation between impurities can be neglected, the total energy per atom of a system with N_i impurities and N atoms is given by

$$E_g=\frac{1}{N}U_0+cE_s\ , \tag{8}$$

where the impurity concentration $c=N_i/N$ is taken as a small parameter. The justification of this approximation is also given in Ref. 16, where it is shown that correlations are of the order $1/N_f$.

The gap parameter Δ is obtained by minimizing E_g. It is convenient to write E_s in terms of E_n, the impurity energy in the normal phase. We take

$$E_s=E_n+\delta E\ , \tag{9}$$

where E_n is given by the solution of the following equation:

$$E_n=N_fV^2\sum_{k<k_f}\frac{1}{E_n-E_f+\epsilon_k}\ . \tag{10}$$

In the intermediate-valence region, (E_n-E_f) is a large quantity and we calculate the correction δE using an expansion in terms of $\Delta/(E_n-E_f)$ which gives

$$\delta E=\widetilde{\Gamma}\int_0^{\omega_D}d\epsilon\frac{(\epsilon^2+\Delta^2)^{1/2}-\epsilon}{(E_n-E_f-\epsilon)^2}d\epsilon\ , \tag{11}$$

with

$$\widetilde{\Gamma}=\Gamma/\{1+\Gamma[(E_n-E_f-D)^{-1}-(E_n-E_f)^{-1}]\}\ . \tag{12}$$

Here, $\Gamma=\rho N_fV^2$ and we have taken a constant density of band states ρ of width $2D$.

Finally, the total energy referred to the energy of the normal state is given for $\omega_D\gg\Delta$ by

$$E_g = + \frac{\Delta^2}{\lambda} - \rho \left[\Delta^2 \ln(2\omega_D/\Delta) + \frac{\Delta^2}{2} \right] + c\delta E \; . \qquad (13)$$

The superconducting order parameter Δ at zero temperature is then taken as the one that minimizes E_g. In the next section we show the results.

III. RESULTS AND DISCUSSION

The numerical results obtained are shown in Fig. 1. We have taken $\Gamma = 100$ K, E_f varying from -200 to 500 K and $D = 10.000$ K. If $N_f = 6$ as it would be for Ce ions, in this range of parameters the approximation is very good.

We calculate the critical field as the energy difference between the normal and superconducting states. For the sake of comparison we have calculated the mean number of $4f$ electrons in the normal phase. For the parameters used we obtain $\langle n_f \rangle \lesssim 0.4$. In Fig. 1(a) $\langle n_f \rangle$ is plotted as a function of E_f; in Fig. 1(b) the results for $\Delta/\Delta(0)$ are shown for different concentration, $\Delta(0)$ is the superconducting gap for the pure matrix. Similarly, $H_{\text{crit}}/H_{\text{crit}}(0)$ is shown in Fig. 1(c).

By making an expansion in terms of Δ in Eq. (6) we obtain analytical results for the superconductor order parameters

$$\Delta = 2\omega_D \exp \left[- \frac{1/\rho\lambda - cA(B + \frac{1}{2})}{1 - cA} \right] , \qquad (14)$$

where

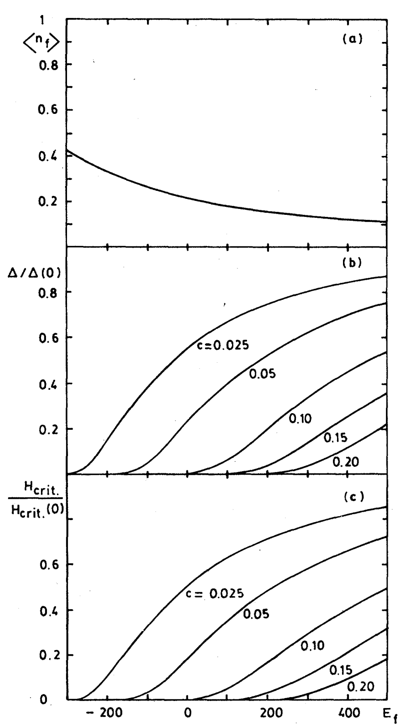

FIG. 1. (a) Occupation of localized state, (b) energy gap, and (c) critical field as functions of E_f. Impurity concentrations are indicated in (b) and (c).

$$A = \frac{\widetilde{\Gamma}}{2(E_n - E_f)^2 \rho} \qquad (15)$$

and

$$B = \frac{E_n - E_f + 3\omega_D}{2(E_n - E_f + \omega_D)} + \ln \left[\frac{E_n - E_f + \omega_D}{E_n - E_f} \right] . \qquad (16)$$

For the whole range of parameters studied numerically, Eq. (14) gives an excellent approximation.

The critical concentration at which superconductivity is destroyed, is given by $c_{\text{crit}} = 1/A$ and it can be large, however, in concentrated systems, impurity-impurity correlation can be important and we expect deviations of Eq. (14). Similarly, the critical field is given by

$$\frac{H_{\text{crit}}}{H_{\text{crit}}(0)} = \frac{\Delta}{\Delta(0)} (1 - cA)^{1/2} \; . \qquad (17)$$

The square root in Eq. (17) comes from the energy correction of the impurities and in general is a small quantity. In Fig. 2, $\Delta/\Delta(0)$ versus c is shown. These curves resemble the curves T_{crit} versus c obtained by other authors.

As we mentioned, a systematic expansion in terms of $1/N_f$ has been developed for the energy of the impurity in the normal metal. Extending this method to the present problem, a systematic expansion of Δ in powers of $1/N_f$ is obtained.

We also studied the excitation spectrum as it would be obtained in a tunneling experiment, i.e., adding a quasiparticle to the superconductor. We constructed many-particle wave functions starting with $\alpha_k^\dagger \mid \phi \rangle$. In the presence of impurities, k is not a good quantum number and the quasiparticle is scattered from the state $\mid k \rangle$ to states $\mid k' \rangle$. Thus, we assume the following wave function:

$$\mid \psi_\nu \rangle = \sum_k a_k^\nu \alpha_k^\dagger \mid \phi \rangle + \sum_{kk'M} (c_{kk'M}^\nu \alpha_{k'}^\dagger \alpha_k^\dagger \mid \phi, M \rangle + d_{kk'M}^\nu \beta_{k'}^\dagger \alpha_k^\dagger \mid \phi, M \rangle) + \sum_{kM} e_{kM}^\nu \mid \phi, M \rangle \; . \qquad (18)$$

The difficulty here is that the coefficients a_k^ν are given by an integral equation. Solving this equation in an approximate way, a secular equation for the energies E_ν of the states $\mid \psi_\nu \rangle$ is obtained. It can be shown that these energies form a continuum with a sharp edge at $U_0 + E_s + \Delta$

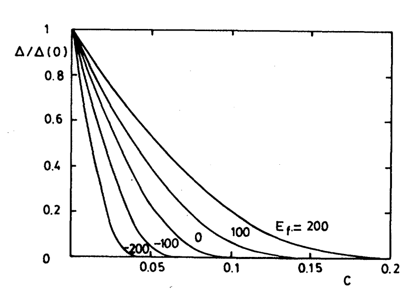

FIG. 2. Superconducting gap vs concentration for different values of E_f.

and a bound state occurs near this edge. In concentrated systems, impurity correlations can split these states and a band would appear. The details of this calculation will be published in a separate paper.

IV. SUMMARY AND CONCLUSIONS

We have calculated the ground-state properties of superconductors with IV impurities. We considered the case of impurities fluctuating between two ionic configurations, say $4f^n$ and $4f^{n+1}$, the $4f^n$ configuration being nonmagnetic and the $4f^{n+1}$ state having a total angular momentum J. Superconductivity is treated in the BCS approximation and the effect of the IV impurities on the ground state of the BCS Hamiltonian is calculated exactly in the limit $J\rightarrow\infty$.

For the range of parameters which give IV behavior and for finite $J(J=5/2)$, the results obtained are a very good approximation. Analytical expressions are found for the gap Δ, the critical field H_{crit}, and the critical concentration c_{crit}. The gap decreases linearly with concentration for very dilute samples and exponentially for concentration near c_{crit}. The same behavior is obtained for H_{crit}. Similar results have been obtained by Schlottmann.[13]

The excitation spectrum is a continuum with a sharp edge at an energy Δ above the energy of the ground state. An impurity bound state is obtained near this edge.

The systematic expansion of Δ in powers of $1/N_f$ is straightforward. The generalization of the theory to calculate the critical temperature and the thermodynamics of superconductors with IV impurities can be formulated by expanding the partition function of the system as was done by Keiter and Kimball for a normal metal.[19]

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