

Low-Temperature Properties of Anisotropic Superconductors with Kondo Impurities

L. S. Borkowski and P. J. Hirschfeld

Department of Physics, University of Florida, Gainesville, FL 32611, USA

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We present a self-consistent theory of superconductors in the presence of Kondo impurities, using large- N slave-boson methods to treat the impurity dynamics. The technique is tested on the s -wave case and shown to give good results compared to other methods for $T_K > T_c$. We calculate low temperature thermodynamic and transport properties for various superconducting states, including isotropic s -wave and representative anisotropic model states with line and point nodes on the Fermi surface.

1. INTRODUCTION

The problem of a magnetic impurity in a superconductor has been extensively studied, but is not completely solved because of the difficulty of treating the dynamical correlations of the coupled impurity-conduction electron system together with pair correlations. Generally, the behavior of the system can be characterized by the ratio of the Kondo energy scale in the normal metal to the superconducting transition temperature, T_K/T_c . For $T_K/T_c \ll 1$, conduction electrons scatter from classical spins and physics in this regime can be described by the Abrikosov-Gor'kov theory.¹ In the opposite limit, $T_K/T_c \gg 1$, the impurity spin is screened and conduction electrons undergo only potential scattering. In this regime s -wave superconductors are largely unaffected by the presence of Kondo impurities due to Anderson's theorem.² Superconductors with an anisotropic order parameter, e.g. p -wave, d -wave etc., are strongly affected, however and the potential scattering is pair-breaking. The effect of pair breaking is maximal in s -wave superconductors in the intermediate region, $T_K \sim T_c$, while in the anisotropic case it is largest for $T_K/T_c \rightarrow \infty$.³

Regardless of the type of the pairing mechanism, the conduction band density of states is depleted in the neighborhood of the Fermi surface, resulting in the weakening of the coupling to the impurity. On the other

hand, increasing the impurity concentration or the coupling strength reduces T_c . This competition is influenced strongly by the number of states removed from near the Fermi surface by the formation of the superconducting state. In fact, Withoff and Fradkin⁴ have pointed out that for the normal state analogue of this problem, in which the conduction band is assumed to behave as a semimetal, with density of states varying as $N(\omega) \propto |\omega|^r$, $r > 0$, there is a critical coupling strength J_c below which the Kondo effect no longer occurs. One might expect the consequences of such a transition, were it to take place, e.g., as a function of temperature in an unconventional superconducting state providing the power-law density of conduction electron states, to be dramatic. In a previous study of this problem, however, we have shown that under most circumstances a finite density of Kondo impurities in the thermodynamic limit induces a finite density of states at the Fermi level, ensuring that a Kondo effect always occurs, but with reduced effective Kondo temperature. Nevertheless, unusual pairbreaking effects are still to be expected in unconventional superconductors due to the dynamical reduction of the Kondo scale caused by pair correlations.

While this work was begun in anticipation of applications to heavy fermion superconductors, recent measurements of penetration depth,⁵ photoemission,⁶ and Josephson tunneling on YBCO and BSCCO⁷ have provided evidence that the copper oxide superconductors may be unconventional, possibly d-wave as well. This conclusion remains controversial, however, and experimental tests to distinguish conventional from unconventional pairing are of great current interest. One would like, for example, to develop an understanding of the effect of doping Zn and Ni impurities in the CuO₂ planes. Simple models of Zn and Ni acting as strong and weak potential scatterers in a d-wave superconductor, respectively, are consistent with some experiments at low doping levels,⁸⁻¹⁰ but inconsistent with other measurements.^{11,12} Since in some cases Zn impurities appear to possess a magnetic moment at higher temperatures,¹² it is of interest to explore whether an s-d type exchange coupling of conduction electrons to an impurity embedded in an unconventional superconductor can describe the range of behavior observed.

In this work we focus on basic thermodynamic and transport properties of superconductors doped with Kondo impurities. Our aim is to develop a tractable, self-consistent scheme for the calculation of all basic properties of superconductors using methods known to successfully describe the most difficult aspect of the problem, namely the dynamics of the Kondo impurity. For this reason we have adopted the large- N "slave boson" approach of Barnes,¹³ Coleman,¹⁴ and Read and Newns,¹⁵ as this approach is well-known to provide a good description of the spectral

properties of the Kondo impurity for sufficiently low temperatures. We emphasize that this description is adequate for most of our purposes ($T_c \lesssim T_K$) even in the case of spin degeneracy $N=2$, since the impurity spectral resonance is located at the proper position, i.e. exactly at the Fermi level in this approximation.

2. FORMALISM

We use the large- N slave boson technique for the $SU(N)$ Anderson model describing an N -fold degenerate band of conduction electrons, c_{km} , $m = 1, \dots, N$ with energy ϵ_k hybridizing through matrix element V with a localized impurity state f_m . In general this Hamiltonian contains a term with the Coulomb repulsion U between two electrons present at the impurity simultaneously. In many compounds U is large (5–10 eV in the lanthanides) and for the purpose of studying the low temperature physics we will assume $U = \infty$. The on-site repulsion term is then absent, but a constraint is added to ensure that the system remains in the physical part of the Hilbert space. The conduction band is assumed to have a constant density of states in its normal state, $N(\omega) = 1/2D = N_0$. We also include a BCS-like pairing term of electrons on opposite sides of the Fermi sphere,

$$H = \sum_{k,m} \epsilon_k c_{km}^\dagger c_{km} + E_f \sum_m f_m^\dagger f_m + V \sum_{k,m} [c_{km}^\dagger f_m b^\dagger + h.c.] + \sum_{k,m} [\Delta(k) c_{km}^\dagger c_{-k-m}^\dagger + h.c.] + \lambda \left(\sum_m f_m^\dagger f_m + b^\dagger b - 1 \right) \quad (2.1)$$

where λ is a Lagrange multiplier enforcing the constraint $n_f + n_b = \sum_m f_m^\dagger f_m + b^\dagger b = 1$, preventing double occupancy of the impurity site. In the limit $E_f \rightarrow -\infty$, $N_0 V^2 / E_f = \text{const}$, Eq. (2.1) reduces to the Coqblin-Schrieffer Hamiltonian with pairing studied in Ref. 3. Here we have chosen the more general form (2.1) to study deviations from single occupancy, $n_f \neq 1$, although we do not attempt to explore the fully developed mixed valent regime.

The mean field approximation to this model, with mean-field amplitude $\langle b \rangle$, leads to the two equations

$$\frac{1}{N} = -\text{Im} \int_{-\infty}^{\infty} d\omega f(\omega) \frac{1}{2} \text{Tr}(\tau_0 + \tau_3) G_f(\omega + i0^+) \quad (2.2)$$

and

$$\frac{E_f - \epsilon_f}{V^2} = \text{Im} \int_{-\infty}^{\infty} d\omega f(\omega) \frac{1}{2} \text{Tr}[(\tau_0 + \tau_3)(G^0(k, \omega + i0^+) G_f(\omega + i0^+))] \quad (2.3)$$

which determine $\langle h \rangle$ and ε_f , the latter being the position of the resonant state. Eqs. (2.2) and (2.3) should be solved self-consistently together with the gap equation,

$$\Delta(k) = -T \sum_{\omega_n} \sum_{k'} V_{kk'} \text{Tr} \frac{\tau_1}{2} \mathbf{G}(k', \omega_n) \quad (2.4)$$

The full conduction electron Green's function \mathbf{G} and the impurity Green's function \mathbf{G}_f

$$\mathbf{G} = \begin{pmatrix} G & F \\ F^\dagger & G^* \end{pmatrix} \quad \text{and} \quad \mathbf{G}_f = \begin{pmatrix} G_f & F_f \\ F_f^\dagger & G_f^* \end{pmatrix} \quad (2.5)$$

are calculated from the diagrams shown in Fig. 1, yielding

$$\mathbf{G}(\omega)^{-1} = \mathbf{G}^0(\omega)^{-1} - \Sigma(\omega) = \tilde{\omega} \tau_0 - \varepsilon_k \tau_3 - \tilde{\Delta}(k) \tau_1 \quad (2.6)$$

$$\mathbf{G}_f(\omega)^{-1} = \mathbf{G}_f^0(\omega)^{-1} - \Sigma_f(\omega) = \tilde{\omega} \tau_0 - \varepsilon_f \tau_3 - \tilde{\Delta} \tau_1 \quad (2.7)$$

The Green's functions are now averaged over impurity positions in the usual way. The renormalized frequencies are calculated self-consistently from the Dyson equations,

$$\tilde{\omega} = \omega + \alpha \tilde{\omega} / (-\tilde{\omega}^2 + \varepsilon_f^2 + \tilde{\Delta}^2) \quad (2.8)$$

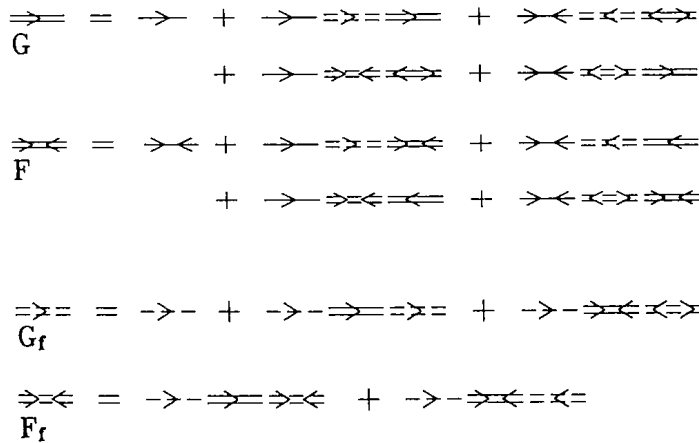


Fig. 1. Dyson equations for the conduction electron and impurity Green's functions.

and

$$\tilde{\omega} = \omega + \Gamma \langle \tilde{\omega} / (\tilde{\Delta}^2(k) - \tilde{\omega}^2)^{1/2} \rangle_k \quad (2.9)$$

Here $\alpha = N\bar{n}\Gamma T_{c0}/2\pi$, $\bar{n} = n/N_0 T_{c0}$ is the scaled impurity concentration, and $\langle \cdots \rangle_k$ is a Fermi surface average. The off-diagonal renormalizations are

$$\tilde{\Delta}(k) = \Delta(k) + \alpha \tilde{\Delta} / (-\tilde{\omega}^2 + \varepsilon_f^2 + \tilde{\Delta}^2) \quad (2.10)$$

and

$$\tilde{\Delta} = \Gamma \langle \tilde{\Delta}(k) / (\tilde{\Delta}^2(k) - \tilde{\omega}^2)^{1/2} \rangle_k \quad (2.11)$$

In superconductors with order parameters where the Fermi surface average in Eq. (2.11) vanishes, off-diagonal corrections vanish and $\tilde{\Delta}(k) = \Delta(k)$. This class includes but is not limited to odd-parity superconducting states.

The energy scale Γ is the renormalized resonance width, $\Gamma = \langle h \rangle^2 \pi N_0 V^2$. The low-temperature Kondo scale in the large- N slave boson theory is given by $T_K \equiv \sqrt{\Gamma^2 + \varepsilon_f^2}$. Although the width of the actual spectral feature corresponding to the Abrikosov-Suhl resonance is modified below T_c , in what follows we will normalize all quantities with respect to this T_K , evaluated from Eqs. (2.2) and (2.3) with $\Delta = 0$ at $T = 0$. In the regime of principal interest, $T_K > T_c$, corrections to this definition will be small in any case.

3. RESULTS FOR AN S-WAVE SUPERCONDUCTOR

The early history of the problem of a Kondo impurity in an s-wave superconductor has been reviewed by Müller-Hartmann.¹⁶ Abrikosov and Gor'kov first discussed the pair-breaking effects of magnetic impurities weakly coupled via exchange interactions to conduction electrons.¹ Shiba¹⁷ extended this approach to treat strong scattering by classical spins, using the t -matrix approximation, and showed the existence of bound states in the gap. At finite concentration of impurities the bound states were found to form an impurity band whose width and center scaled with impurity concentration and exchange strength. These early works neglected the dynamical screening of the localized spin by the conduction electron gas. These effects were incorporated by Müller-Hartmann and Zittartz,¹⁸ adopting an equation of motion decoupling scheme previously used by Nagaoka¹⁹ to calculate the dynamical spin correlations in the normal state. This approach correctly reproduced results in the Abrikosov-Gor'kov limit, $T_K/T_c \rightarrow 0$, and made the remarkable prediction of a reentrant superconducting phase if $T_K \ll T_c$, subsequently observed in experiments on $\text{La}_{1-x}\text{Ce}_x\text{Al}_2$.^{20,21} The failure of the decoupling scheme used to capture the

correct crossover to Fermi liquid behavior in the normal state as $T \rightarrow 0$ invalidated the Müller-Hartmann-Zittartz approach in the low temperature regime $T_K > T_c$, however.

The physics of the Fermi liquid regime, $T_K/T_c \rightarrow \infty$, was studied by Matsuura, Ichinose and Nagaoka²³ and by Sakurai²⁵ by extending the Yamada-Yosida theory²⁴ to the superconducting state. They obtained an exponential T_c -suppression with increasing impurity concentration \bar{n} , $T_c \simeq T_{c0} \exp(-p\bar{n}/\lambda)$, where λ is the BCS dimensionless coupling constant, and p is a constant of order unity. This is commonly referred to as "pair-weakening" as opposed to pair-breaking, since the effective superconducting coupling constant is reduced due to correlations on the impurity site. The exponential form breaks down for concentrations sufficiently close to a critical \bar{n}_c , for which $T_c = 0$. In this regime the reentrant behavior found by Müller-Hartmann and Zittartz does not occur. A further characteristic signature of the Fermi liquid regime is the reduced specific heat jump, $C^* \equiv (\Delta C/\Delta C_0)/(T_c/T_{c0})|_{T_c=T_{c0}}$ which is always less than one,^{25,26} in contrast to the high temperature regime.

Not surprisingly, qualitatively similar results were obtained by other early workers for Kondo and Anderson impurities using a variety of other approaches.¹⁶ More recent treatments include the use of a self-consistent large- N ,^{27,3} Monte Carlo²⁸ and NRG methods.²⁹ Schlottman³⁰ has treated the mixed-valence regime using Brillouin-Wigner perturbation theory. Out of these efforts has evolved a qualitatively consistent picture of the effect of Kondo impurities on the superconducting transition,³¹ but little understanding of the low-temperature properties of Kondo-doped superconductors because of the difficulty of the calculations involved. In this section we show that the current theory reproduces the known effects of Kondo impurities on the critical temperature, specific heat jump and bound state spectrum of an s-wave superconductor.

3.1. Critical Temperature

The simplest and most direct effect of impurity scattering on a superconductor is the suppression of the critical temperature. Scattering from impurities with internal quantum-mechanical degrees of freedom leads to deviations from the classic Abrikosov-Gor'kov prediction for the dependence of T_c on impurity concentration.¹ These effects depend sensitively on the low-energy behavior of the self-energy $\Sigma(\omega)$, which enters the linearized gap equation, obtained from Eq. (2.4) near T_c ,

$$\ln(T_c/T_{c0}) = 2\pi T_c \sum_{n \geq 0} \frac{1}{\omega_n(1 + \alpha/B(\omega_n))} - \sum_{n \geq 0} \frac{1}{n + 1/2} \quad (3.1)$$

where $B(\omega_n) = (\omega_n + \Gamma)^2 + \epsilon_f^2$.

The slope of the T_c -suppression evaluated at $\bar{n} = 0$ is

$$\left(\frac{1}{T_{c0}} \frac{dT_c}{d\bar{n}} \right)_{\bar{n}=0} = -\frac{N}{2\pi} \sum_{n \geq 0} \frac{\Gamma T_{c0}}{(n + 1/2) B(\omega_n)} \quad (3.2)$$

In an insert to Fig. 2, we have plotted a numerical evaluation of Eq. (3.2) for an s-wave superconductor. Note the curve is drawn with a broken line for small T_K/T_{c0} to reflect the fact that the slave boson mean field theory breaks down there. The maximum of the T_c -suppression is found to occur at $T_K \simeq 3T_c$, similar to the NCA result.²⁷ The early high-temperature theory of Müller-Hartmann and Zittartz¹⁸ locates this maximum at $T_K/T_c \simeq 12$, whereas in the more recent Monte Carlo calculation²⁸ for the symmetric Anderson model with finite U the maximum slope of the T_c -suppression is at $T_K \simeq T_c$. Unfortunately a direct quantitative comparison with the latter work is not possible, as the simulation is not performed in the fully developed Kondo regime.

The present theory predicts an exponential decrease of T_c at small concentrations, in agreement with other theories of the Fermi liquid regime.^{25,26}

$$T_c \simeq T_{c0} \exp \left[-\frac{\alpha}{T_K^2} \Psi(T_K/2\pi T_{c0}) \right] \simeq T_c \left(1 - \frac{\alpha}{T_K^2} \ln(T_K/T_{c0}) \right) \quad (3.3)$$

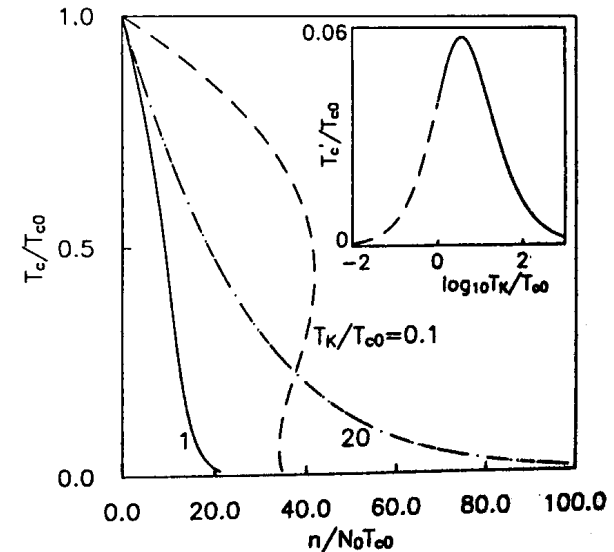


Fig. 2. The critical temperature for an s-wave superconductor as a function of impurity concentration. The inset shows the slope of this dependence evaluated at $T_c = T_{c0}$. Here, $T'_c = -dT_c/d\bar{n}$.

where Ψ is the digamma function. In Refs. 33 and 25 the initial suppression of T_c is proportional to $\ln^2(T_K/T_{c0})$. A full evaluation of Eq. (3.2) for arbitrary concentrations and various values of the ratio T_K/T_c is shown in Fig. 2. It is interesting to note that the theory reproduces the reentrant behavior characteristic of the high temperature regime¹⁶ although we do not expect it to be accurate in this case (dashed line).

As is evident in the Figure the current theory predicts no critical concentration n_c for which $T_c = 0$. This is a subtle point discussed by Sakurai,²⁵ who suggests that a failure to include the dynamics of magnetic scattering by states close to the Fermi surface can lead to such an effect. Such processes are included in the finite- U perturbation theory through Coulomb vertex corrections to the impurity averaged pair correlation function. In our $U = \infty$ theory, such vertex corrections arise first in leading order $1/N$ corrections due to the exchange of slave bosons, whose dynamics are neglected in this work. We expect that effects arising from the absence of these fluctuations in the theory will be quantitatively small for $T_c \lesssim T_K$, except for impurity concentrations so large such that $T_c \ll T_{c0}$.

3.2. Bound States

For conventional isotropic superconductors, $\Delta(k) = \Delta$, Eqs. (2.9) and (2.11) are simply

$$\tilde{\omega} = \omega + \Gamma \frac{\tilde{\omega}}{(\tilde{\Delta}^2 - \tilde{\omega}^2)^{1/2}} \quad (3.4)$$

and

$$\tilde{\Delta} = \Gamma \frac{\tilde{\Delta}}{(\tilde{\Delta}^2 - \tilde{\omega}^2)^{1/2}} \quad (3.5)$$

It is obvious from Eq. (3.5) that a finite gap in the conduction electron spectrum induces a gap in the impurity spectrum. When the Abrikosov-Suhl resonance, which develops at temperatures below T_K , falls in the superconducting gap, bound states appear in the conduction electron spectrum. These peaks are placed symmetrically relative to the center of the gap and their spectral weight depends on T_K/T_c and on impurity concentration. The density of states for $N=2$ and $N=4$ is shown in Fig. 3. In the high-temperature regime the bound states emerge from the edges of the gap and move towards the center of the gap as T_K/T_c increases.³² In the low-temperature limit, the bound states disappear into the gap edges again.³³ Recently, Shiba *et al.*²⁹ studied the position of bound states in the gap in an s-wave superconductor using the numerical renormalization group

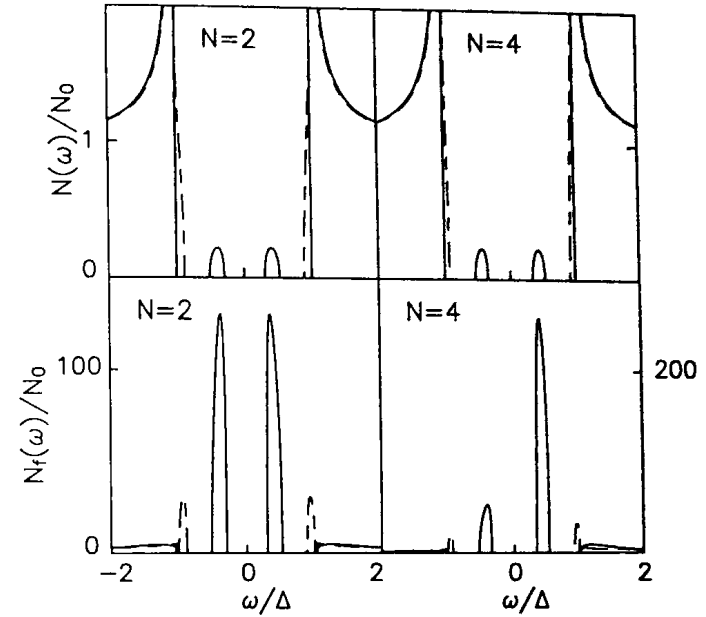


Fig. 3. Conduction electron and impurity spectral functions in the Kondo limit in an s-wave superconductor for $N=2$ and $N=4$. The solid and dashed lines correspond to $T_K = T_c$ and $T_K = 10T_c$, respectively. The concentration of impurities in all cases is $\tilde{n} = 0.4$.

(NRG). Their results cover both the high- and low-temperature limits reliably. The Monte Carlo study by Jarrell *et al.*³⁴ confirms the overall dependence of ω_B on T_K/T_c .

Bound states correspond to the poles of the t-matrix for conduction electrons, $T(\omega) = V^2 G_F(\omega)$ and are given by

$$|\omega| = \left(T_K^2 + \frac{\Gamma^2 \omega^2}{\Delta^2 - \omega^2} \right)^{1/2} - \frac{\Gamma |\omega|}{(\Delta^2 - \omega^2)^{1/2}} \quad (3.6)$$

We compare the solution of Eq. (3.6) with the NRG result in Fig. 4. There is a good agreement for $T_K > T_c$. For $T_K \gg T_c$ the position of bound states ω_B/Δ is a quadratic function of T_K/T_c , $|\omega_B/\Delta| \simeq 1 - 2\Delta^2/T_K^2$. The discrepancy between the NRG result and our calculation for $T_K < T_c$ is not surprising since the slave-boson theory fails in the high temperature regime. The slave-boson mean-field amplitude vanishes around $T \sim T_K$ and the theory is unable to describe the crossover to temperatures above T_K . In

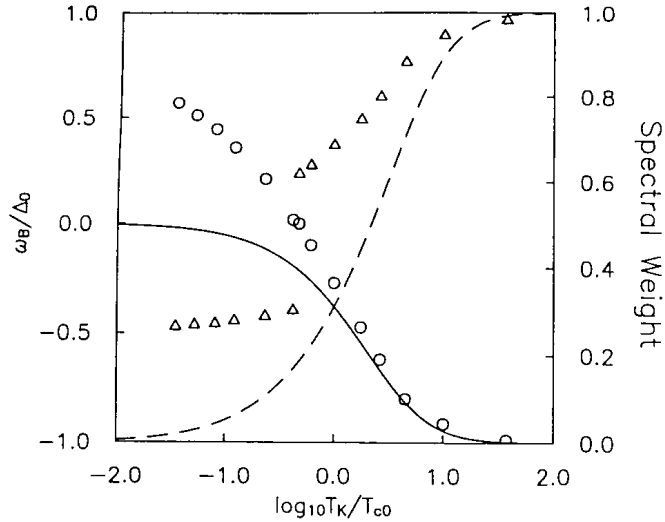


Fig. 4. The position and spectral weight of the bound states in the gap for an s-wave superconductor with Kondo impurities. The solid (dashed) line is the location (spectral weight) of bound states. Only one of the bound states is indicated here, the other one is located at positive energies, symmetrically with respect to the gap center. Circles (triangles) refer to the position (spectral weight) obtained from an NRG calculation.²⁹

Fig. 4 we also show the spectral weight of the bound states in the gap which again agree with the NRG calculation for $T_K \gg T_c$.²⁹

To calculate the specific heat jump we use Eqs. (2.5), (2.7) and (3.1), (3.2), and expand the gap equation near T_c in terms of Δ/T ,

$$\ln \frac{T_{c0}}{T} = - \sum_{n \geq 0} \frac{1}{(n+1/2)(1 + \alpha/B(\omega_n))} + \sum_{n \geq 0} \frac{1}{n+1/2} + \frac{1}{2} h_1 \left(\frac{\Delta}{2\pi T} \right)^2 \quad (3.7)$$

where

$$h_1 = \sum_{n \geq 0} \frac{(1 + 2\alpha\Gamma(\omega_n)/B^2(\omega_n)) E(\omega_n)}{(n+1/2)^3 E^3(\omega_n)} \quad (3.8)$$

and $E(\omega_n) = 1 + \alpha/B(\omega_n)$. After expanding the free energy to fourth order in Δ we obtain

$$C_s(T_c) - C_n(T_c) = \frac{8\pi^2 N_0 T_c}{b_1} \left(1 - \sum_{n \geq 0} \frac{4\pi\alpha T_c (\omega_n + \Gamma)}{(B(\omega_n) + \alpha)^2} \right)^2 \quad (3.9)$$

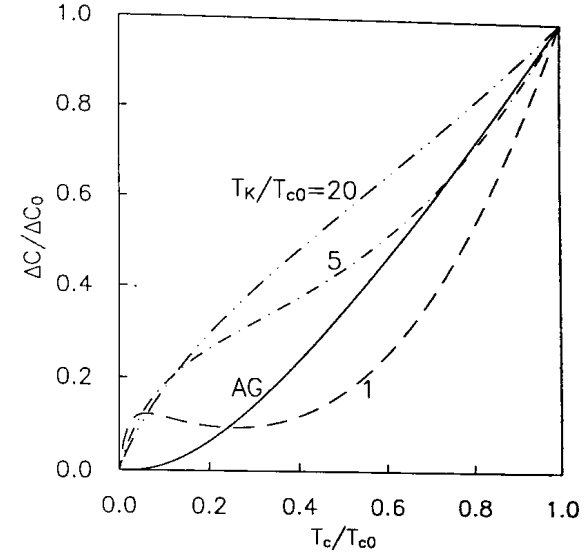


Fig. 5. Specific heat jump as a function of T_c/T_{c0} . We included the result of the Abrikosov-Gor'kov theory³⁵ for comparison.

As can be seen in Fig. 5, the dependence of $\Delta C/\Delta C_0$ on T_c/T_{c0} , for $T_K \approx T_{c0}$, is qualitatively different from the Fermi liquid regime. In that limit, $C^* \approx 1 - 1/\ln(T_K/2T_{c0})$, see Fig. 6. Ichinose²⁶ and Sakurai³⁵ have obtained a somewhat different result, $C^* \approx 1 - 1/\ln^2(T_K/T_{c0})$.

4. IMPURITIES IN UNCONVENTIONAL SUPERCONDUCTORS

The problem of an Anderson impurity in an unconventional superconductor is of considerable interest for several reasons. First, it serves as a testing ground for the ideas of Withoff and Fradkin, who argued that in the analogous Kondo problem with power law conduction electron density of states, $N(\omega) = C|\omega|^r$, there existed a critical coupling below which impurities are effectively decoupled from the conduction band.^{4,36} We showed in Ref.3 that in an unconventional superconductor a critical coupling indeed exists for the 1-impurity problem, but that for a finite density of impurities there is always a finite density of conduction electron states

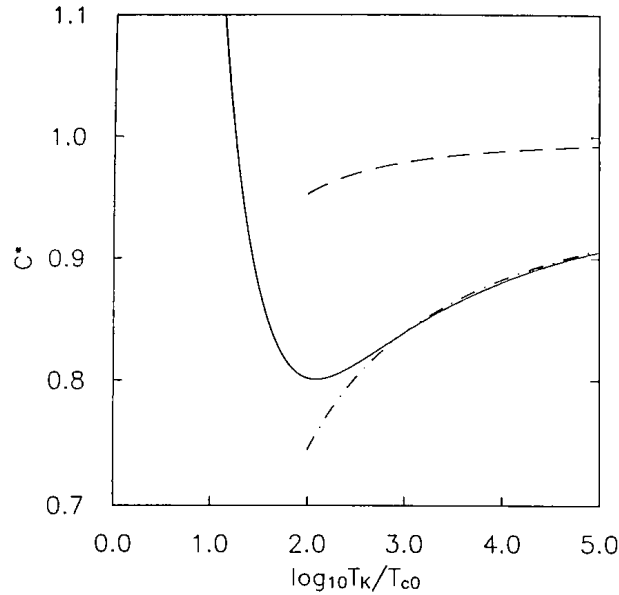


Fig. 6. The derivative of the specific heat jump evaluated at zero impurity concentration as a function of T_K/T_c for an s-wave superconductor. The dash-dotted line shows the asymptotic behavior, $1 - 1/\ln(T_K/2T_{c0})$. The dashed line is the asymptotic form at $T_K/T_c \rightarrow \infty$ found in Refs. 26 and 35. $C^* \approx 1 - 1/\ln^2(T_K/T_{c0})$.

at the Fermi level, provided $N=2$ or if $r \leq 1$. This is consistent with phenomenological studies of potential scattering in unconventional superconductors.^{37,38} This does not exclude the possibility of observing some vestige of this transition as the Kondo temperature becomes quite small, however.

Secondly, Kondo impurities in unconventional superconductors have been proposed as analogues of defects in Kondo lattices,³⁹ with the argument that a vacancy in a Kondo lattice may induce a *relative* phase shift close to $\pi/2$. While such a picture clearly cannot account for the degradation of coherent transport by such defects, it is interesting to further explore the analogy, which has been successful in describing the superconducting state of heavy fermion materials.

Finally, there is currently considerable interest in the possibility that the cuprate superconductors may be characterized by an unconventional order parameter, as suggested by both experimental^{5,8} and theoretical⁴⁰ studies. Studies of $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)\text{O}_7$, where M are Zn or Ni dopants in

the CuO planes, suggest that the behavior of the two ions can be quite different. Maple and collaborators have claimed that Pr may act as a Kondo-like dopant in YBCO. We believe that a Kondo- or Anderson-type model may be sufficiently rich to describe the unusual features of the Zn and Ni doping studies as well, in conjunction with an understanding of the different gap nodes in unconventional superconductors. To this end we study the effects of Kondo impurities on model unconventional states, bearing in mind that the theory may be inadequate to describe the fully developed magnetic regime $T_K \lesssim T_c$.

We chose to do our calculations for the axial, $\Delta(k) = \Delta_0(\hat{k}_x + i\hat{k}_y)$, and polar, $\Delta(k) = \Delta_0\hat{k}_z$, states for simplicity. These two states, nominally p-wave pairing states over a spherical Fermi surface in 3D, are quite generally representative of two classes of order parameters. States with order parameters vanishing at points on the Fermi surface, like the axial state, have low temperature properties associated with a quasiparticle density of states $N(\omega) \sim \omega^2$, whereas the states with lines of nodes, like the polar state, correspond to $N(\omega) \sim \omega$. More complicated order parameters, such as those having a d-wave symmetry, will have similar properties at low temperatures, since the main factor determining the low- T properties is the order parameter topology, i.e. whether there are points or lines of zeros of the order parameter. In the case of points (lines) of nodes, the low-temperature specific heat of pure superconductors is proportional to $T^2(T)$. The deviation of the penetration depth $\Delta\lambda$ from its zero temperature value $\lambda(0)$ along the main axes of symmetry of the order parameter is either $\sim T^2$ or $\sim T^4$ in the axial state, according to the direction of current flow,⁴¹ whereas for the polar state it is either $\sim T$ or $\sim T^3$. The presence of strong impurity scattering complicates the picture and these power laws do not hold in general.

Due to the absence of the Anderson theorem for p-wave-like or d-wave-like superconductors, the influence of impurity scattering on the critical temperature is qualitatively different from that of s-wave-like superconductors.^{42,43} For the unconventional states of interest, there are no off-diagonal corrections to the superconducting Green's function, $\tilde{\Delta} = \Delta$. In this case T_c is determined by

$$\ln(T_c/T_{c0}) = 2\pi T_c \sum_{n \geq 0} \frac{1}{\omega_n(1 + \alpha/B(\omega_n)) + \alpha/B(\omega_n)} - \sum_{n \geq 0} \frac{1}{n + 1/2} \quad (4.1)$$

The initial T_c -suppression is then given by

$$\left(\frac{1}{T_{c0}} \frac{dT_c}{dn} \right)_{n=0} = -\frac{N}{4\pi^2} \sum_{n \geq 0} \frac{\Gamma(\omega_n + \Gamma)}{(n + 1/2)^2 B(\omega_n)} \quad (4.2)$$

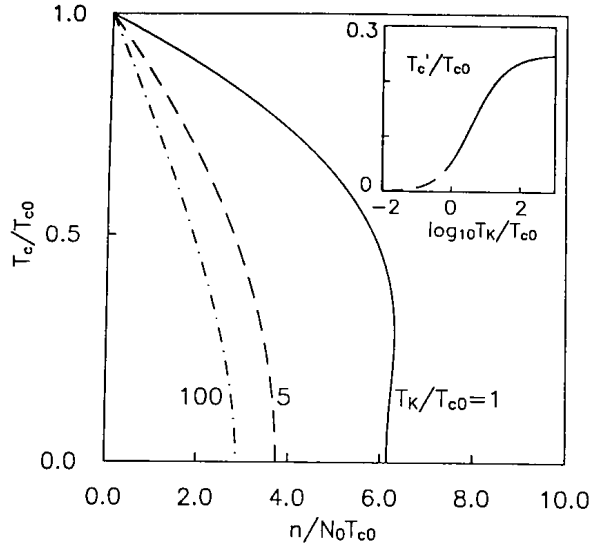


Fig. 7. Critical temperature vs. impurity concentration for unconventional states considered in this work. The initial slope at T_{c0} is shown in the inset.

and approaches $-N\Gamma^2/8T_K^2$, in the limit $T_K/T_{c0} \rightarrow \infty$, see Fig. 7. Note that $\bar{\omega}_n/\Delta \rightarrow \alpha\Gamma/\Delta T_K^2$, as $T_c \rightarrow 0$, and as a consequence the critical concentration n_c is finite.

The specific heat jump at T_c can be found by the method already mentioned in the preceding section,

$$C_s(T_c) - C_n(T_c) = \frac{8\pi^2 N_0 T_c}{h_1} \left[1 - \sum_{n \geq 0} \left(\frac{G(\omega_n)}{((n+1/2)E(\omega_n) + \alpha/B(\omega_n))^2} \right)^2 \right] \quad (4.3)$$

where

$$h_1 = \sum_{n \geq 0} \frac{b + cH(\omega_n)}{[(n+1/2)E(\omega_n) + \alpha/B(\omega_n)]^3} \quad (4.4)$$

with $b = 4/5$ (3/5), and $c = 2/3$ (1/3), for the axial (polar) state, and

$$H(\omega_n) = \alpha\Gamma[2(\omega_n + \Gamma)^2/B(\omega_n) - 1]/B(\omega_n),$$

$$G(\omega_n) = 2\alpha\omega_n(\omega_n + \Gamma)(n+1/2 + \Gamma/2\pi T_c)/B^2(\omega_n) + \alpha\Gamma/2\pi T_c B(\omega_n).$$

The effect of Kondo impurities on the density of states is shown in Fig. 8. As in the s-wave case, the resonant states move towards the edges of the gap as T_K/T_c increases, except in the special case $N=2$, where they are pinned at the gap center.³ In all cases the impurity bands are broadened relative to the s-wave case by the continuum in which they are embedded. In the limit $T_K \rightarrow \infty$, the current theory coincides with the results given by phenomenological t-matrix treatments^{37,38} for $N=2$.

To obtain the specific heat we differentiate the entropy with respect to temperature $C = TdS/dT$. The entropy of conduction electron quasiparticles renormalized by impurities is given by

$$S = -k_B \int_0^\infty d\omega N(\omega) [f \ln f + (1-f) \ln(1-f)] \quad (4.5)$$

where $f = f(\omega)$ is the Fermi function. Note that the density of states $N(\omega)$ is calculated self-consistently, using Eqs. (2.2-2.4).

The presence of resonances at low energies leads to pronounced features in the low- T specific heat, as shown in Fig. 9. For $T_K \gg T_c$, $N=2$,

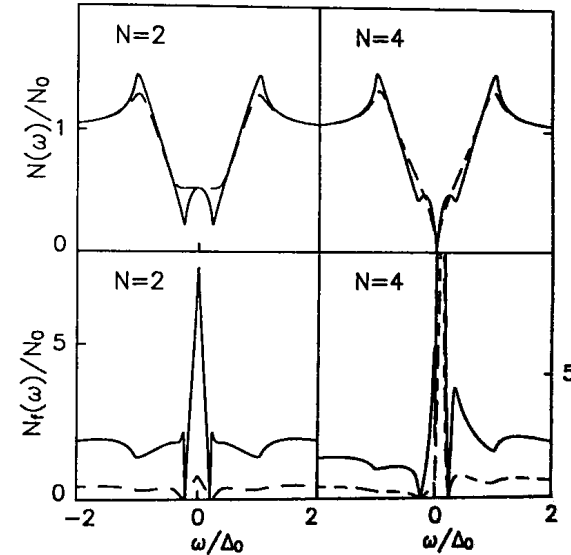


Fig. 8. Conduction electron and impurity spectral functions in the Kondo limit in a polar state for $N=2$ and $N=4$. The solid and dashed lines correspond to $T_K = T_c$ and $T_K = 10T_c$, respectively. The concentration of impurities is $\bar{n} = 0.4$.

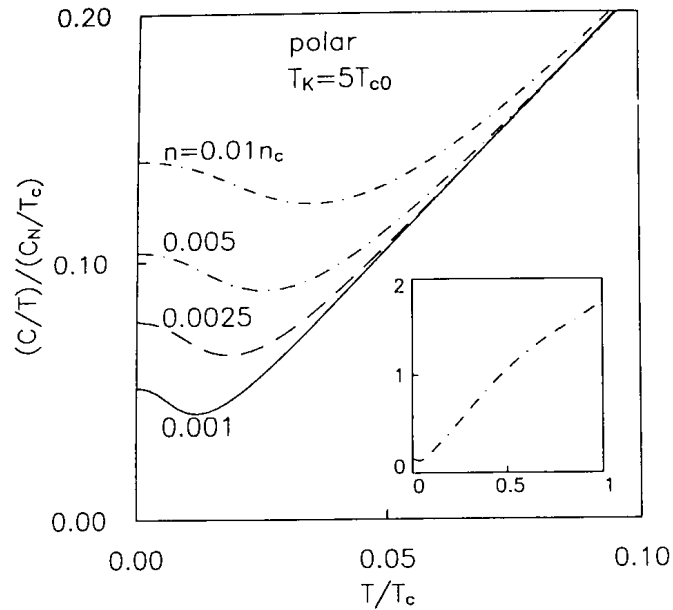


Fig. 9. The low- T part of C/T in the polar state for $N=2$ in the Kondo limit. The inset shows C/T for $n=0.01n_c$ over the full temperature range.

these features are identical to those predicted by the phenomenological theory of Refs. 37 and 38. For smaller T_K/T_c , the resonance sharpens, as is evident from, e.g., Fig. 8. In this case resonances in the low-temperature specific heat may be quite dramatic. Figure 10 shows the temperature dependence of C/T for $N=2$ in the axial state for the case when the resonance is very narrow, $\Gamma \ll T_c$ and just above the Fermi surface, $\varepsilon_f \ll T_c$. Such pronounced features are possible only when the bare impurity level is close to the Fermi surface, and the hybridization is weak. They will be sharper for superconducting states with larger exponent r in the unperturbed density of states $N(\omega) \simeq C|\omega|^r$ at low ω . These anomalies may be observed experimentally at sufficiently low temperatures. In this context, it is interesting to note that a sharp peak in C/T has been observed in the heavy fermion superconductor UPt_3 at 18 mK.⁴⁶ This peak is present at roughly the same position also in the normal state at magnetic fields $B \geq B_{c2}$, as might be expected in a situation where the Kondo temperature is significantly smaller than the critical temperature. If such an interpretation of the measurement of Schuberth *et al.* in these terms is correct, we would expect the size of the peak to scale with other measures of the defect

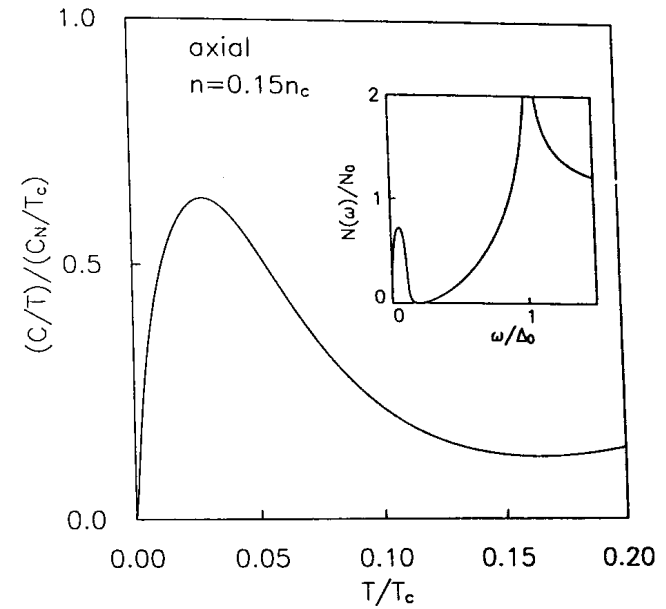


Fig. 10. The low- T part of C/T in the axial state. Note the sharp resonance in the density of states at low energies (the inset).

concentration, such as T_c and the size of the specific heat jump, in different samples. We note, however, that fields of order 1 Tesla would normally destroy a many-body resonance of the usual magnetic type.

We now discuss the low-temperature response functions of the superconductor in the presence of Kondo impurities, which have not to our knowledge been previously calculated in the strongly interacting Fermi liquid regime of interest. The effect of Kondo impurities on the electromagnetic response has been calculated in the phenomenological t -matrix approach mentioned above, and used to analyze experiments on heavy fermion and high- T_c superconductors with impurities, but no microscopic theory is available. The London penetration depth is obtained from $\lambda = [-(4\pi/c)K(0,0)]^{-1/2}$, where $K(0,0)$ is the electromagnetic response kernel. The kernel is given by the linear response formula

$$K''(0, \Omega_m) = -\frac{3e^2 T}{2mc} \int_{-\infty}^{\infty} d\epsilon \sum_n \text{Tr} \langle \hat{k}_i \hat{k}_j G(k, \omega_n) G(k, \omega_n - \Omega_m) \rangle_k \quad (4.6)$$

In the static limit, $\Omega_m \rightarrow 0$, the kernel becomes

$$K^{ij}(0, 0) = -\frac{6\pi e^2 T}{mc} \sum_n \int \frac{d\Omega}{4\pi} \hat{k}_i \hat{k}_j \frac{\Delta^2(k)}{(\Delta^2(k) + \tilde{\omega}_n^2)^{3/2}} \quad (4.7)$$

where the integral represents the angular average. Here we specialize again to the $N=2$ case. The temperature dependence of $(\lambda^{11})^{-2}$ in the polar state, which corresponds to the component of the superfluid density within the plane containing the line of zeroes of the order parameter, is shown in Fig. 11. The low- T behavior changes from linear to quadratic upon doping. A similar result was obtained earlier^{41,47} within the phenomenological theories. The results for $T_k \simeq T_c$ are qualitatively very similar to those shown. Finally, λ^{-2} at $T=0$ along the main axes of symmetry for the axial and the polar state as a function of impurity concentration is presented in Fig. 12. We note that the largest component of the penetration depth scales in the case of line nodes as $\lambda(n)/\lambda_L(0) - 1 \sim n^{1/2}$ at low concentrations,⁴⁸ and $\lambda^{-2}(n) \sim \log(n_c/n)$ close to the critical concentration. Similar suppression of the superfluid density was calculated for a d-wave order parameter

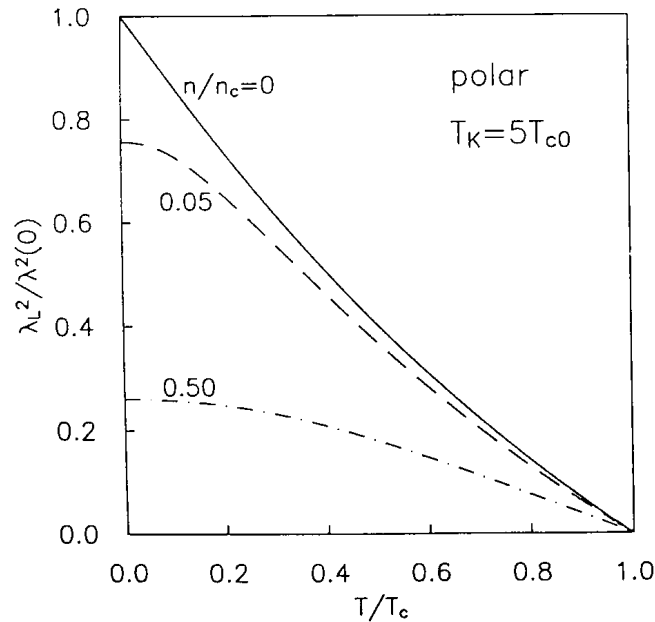


Fig. 11. The inverse square of the penetration depth vs. temperature at several concentrations of impurities in the polar state.

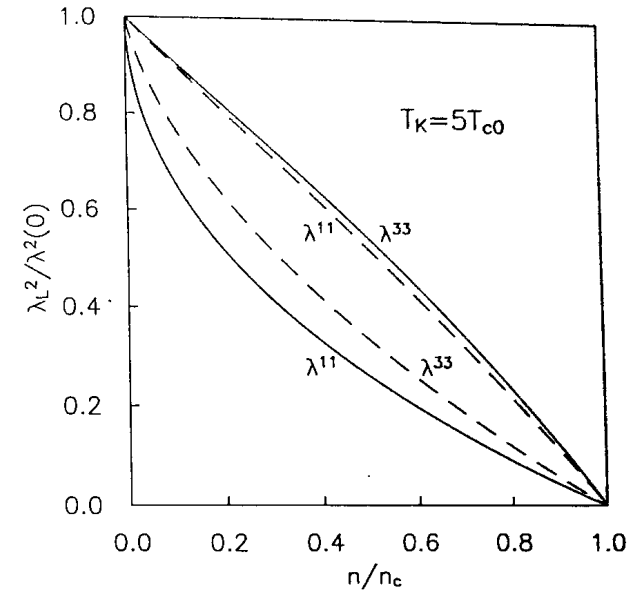


Fig. 12. The inverse square of the $T=0$ penetration depth in the two principal directions as a function of impurity concentration for the polar (full lines) and the axial state (dashed lines).

within a phenomenological theory in Ref. 49. It is clear that both the concentration and temperature dependence of the penetration depth components may be important tests of gap anisotropy.

5. CONCLUSIONS

We have presented a slave boson theory of Kondo impurities in superconductors which has the advantages of being applicable in the Fermi liquid regime and being relatively easy to use in calculating quantities of experimental interest at all temperatures in the superconducting state. The theory has been shown to reproduce all of the qualitative features of the physics found by previous theories for large T_k , and is asymptotically in quantitative agreement with "exact" NRG calculations for the s-wave case. It is furthermore capable of going considerably beyond currently available theories in that practical calculations of superconducting response functions are possible at low temperatures in the superconducting state, and can be easily generalized to the unconventional states of great current

interest in the heavy fermion and high-temperature superconductivity problems.

The single exception to this success is the failure to properly describe the s-wave superconductor at very large impurity concentrations, in that the theory predicts an infinite critical concentration. In practical terms this is quite academic, as all independent impurity analyses will break down due to interimpurity interaction effects long before any putative critical concentration is achieved. Nevertheless, this formal shortcoming of the theory exists and must be addressed. Preliminary analysis of fluctuations about the saddle point has convinced us that the Gaussian fluctuations to the scattering amplitude arising from the slave boson dynamics will be sufficient to induce a critical concentration, in analogy to the works of Matsuura *et al.*²³ and Sakurai,²⁵ and that the theory as it stands is sufficient to describe the Fermi liquid regime everywhere except for very large concentrations in the s-wave case. The difficulty does not arise in the unconventional case.

In unconventional superconductors, we have shown that the phenomenological theories of Refs. 37 and 38 will be reproduced by the microscopic theory presented here in the limit $N=2$ and $T_K/T_c \rightarrow \infty$. The decondensation of the slave boson amplitude prevents extension of the theory into the high temperature regime, but qualitatively it is clear that the effect of lowering the Kondo temperature is to sharpen the many-body resonance near the Fermi surface, but lower its weight. Thus the effect of resonant scattering leading to low-energy gapless effects in superconducting thermodynamic and transport properties is reduced. Impurities with larger orbital degeneracy may lead to similar resonances away from the Fermi level, possibly similar to those observed by Maple *et al.*⁵⁰ in specific heat experiments on Pr-doped YBCO.

The effect of Zn and Ni-doping on superconducting properties of YBCO suggests that these two dopants may be described within a traditional Kondo-type picture in conjunction with the theory discussed here. Ni, with spin one, may possibly be treated as a higher-degeneracy scatterer below its Kondo temperature. As we have seen, such an impurity acts as a weak scatterer compared to the $N=2$, $T_K \gg T_c$ resonant scattering case, a possible model for Zn. On the other hand, recent NMR measurements appear to suggest that a moment forms around the Zn site. Within an isolated impurity picture, this would suggest that $T_K \ll T_c$, where the present theory is not applicable. A more plausible explanation, however, is that the local spin correlations induced by a missing Cu must be accounted for, as suggested by Poilblanc *et al.*⁵¹ Further experimental and theoretical work on this problem is clearly essential.

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REFERENCES

1. A. A. Abrikosov and L. P. Gor'kov, *Zh. Eksp. Teor. Fiz.* **39**, (*Sov. Phys. JETP* **12**, 1243 (1961).
2. P. W. Anderson, *J. Phys. Chem. Solids* **11**, 26 (1959).
3. L. S. Borkowski and P. J. Hirschfeld, *Phys. Rev. B* **46**, 9274 (1992).
4. D. Withoff and E. Fradkin, *Phys. Rev. Lett.* **64**, 1835 (1990).
5. W. N. Hardy *et al.*, *Phys. Rev. Lett.* **70**, 399, (1993).
6. Z. X. Shen *et al.*, *Phys. Rev. Lett.* **70**, 1553 (1993); R. J. Kelley, J. Ma, G. Margaritondo, and M. Onellion, *Phys. Rev. Lett.* **71**, 4051 (1993).
7. D. A. Wollman, D. J. van Harlingen, W. C. Lee, D. M. Ginsberg, and A. J. Leggett, *Phys. Rev. Lett.* **71**, 2134 (1993).
8. K. Ishida *et al.*, *Physica C* **179**, 29 (1991); J. A. Martindale *et al.*, *Phys. Rev. Lett.* **68**, 702 (1992); K. Ishida *et al.*, *J. Phys. Soc. Japan* **62**, 2803 (1993).
9. D. A. Bonn *et al.*, preprint (1993).
10. R. Walstedt *et al.*, *Phys. Rev. B* **45**, 10646 (1993).
11. E. R. Ulm, J. T. Kim, and T. R. Lemberger, preprint, (1993).
12. A. V. Mahajan *et al.*, preprint (1994).
13. S. E. Barnes, *J. Phys. F* **6**, 1375 (1976).
14. P. Coleman, *Phys. Rev. B* **28**, 5255 (1983).
15. N. Read and D. M. Newns, *J. Phys. C* **16**, 3273 (1983).
16. For a review of the early literature on this problem, see: E. Müller-Hartmann, in *Magnetism*, vol. V., ed. H. Suhl (Academic Press: New York, 1973), and references therein.
17. H. Shiba, *Prog. Theor. Phys.* **40**, 435 (1968).
18. E. Müller-Hartmann and J. Zittartz, *Z. Physik* **234**, 58 (1970).
19. Y. Nagaoka, *Phys. Rev.* **138A**, 1112 (1965).
20. G. Riblet and K. Winzer, *Solid State Commun.* **9**, 1663 (1971).
21. M. B. Maple, W. A. Fertig, A. C. Mota, L. E. DeLong, D. Wohlleben, and R. Fitzgerald, *Solid State Comm.* **11**, 829 (1972); P. H. Ansari, J. B. Bulman, J. G. Huber, L. E. DeLong, and M. B. Maple, *Phys. Rev. B* **49**, 3894 (1994).
22. H. Shiba, *Prog. Theor. Phys.* **50**, 50 (1973).
23. T. Matsuura, S. Ichinose, and Y. Nagaoka, *Prog. Theor. Phys.* **57**, 713 (1977).
24. K. Yosida and K. Yamada, *Prog. Theor. Phys.* **53**, 1286 (1975).
25. A. Sakurai, *Phys. Rev. B* **17**, 1195 (1978).
26. S. Ichinose, *Prog. Theor. Phys.* **58**, 404 (1977).
27. N. E. Bickers and G. Zwicknagl, *Phys. Rev. B* **36**, 6746 (1987).
28. M. Jarrell, *Phys. Rev. Lett.* **61**, 2612 (1988).
29. O. Sakai, Y. Shimizu, H. Shiba, and K. Satori, *J. Phys. Soc. Japan* **62**, 3181 (1993).
30. P. Schlottmann, *J. Low Temp. Phys.* **47**, 27 (1982).
31. M. B. Maple, L. E. Long and B. C. Sales, in *Handbook on the Physics and Chemistry of Rare Earths*, ed. K. A. Gschneider, Jr. and L. Eyring (North-Holland, 1978).
32. J. Zittartz and E. Müller-Hartmann, *Z. Physik* **232**, 11 (1970).
33. T. Matsuura, *Prog. Theor. Phys.* **57**, 1823 (1977).
34. M. Jarrell, D. S. Sivia and B. Patton, *Phys. Rev. B* **42**, 4804 (1990).

35. A. Sakurai, *Physica* **86-88 B**, 521 (1977).
36. T. Soda, T. Matsuura, and Y. Nagaoka, *Prog. Theor. Phys.* **38**, 551 (1967).
37. P. J. Hirschfeld, D. Vollhardt, and P. Wölfle, *Solid State Commun.* **59**, 111 (1986).
38. S. Schmitt-Rink, K. Miyake, and C. M. Varma, *Phys. Rev. Lett.* **57**, 2575 (1986).
39. C. M. Varma, *Comments in Solid State Physics* **11**, 221 (1985).
40. K. Miyake, S. Schmitt-Rink and C. M. Varma, *Phys. Rev. B* **34**, 6554 (1986); D. J. Scalapino, E. Loh, and J. E. Hirsch, *Phys. Rev. B* **34**, 8190 (1986); S. R. White, D. J. Scalapino, R. Sugar, N. E. Bickers, and R. Scalettar, *Phys. Rev. B* **39**, 839 (1989); D. Monthoux and D. Pines, *Phys. Rev. Lett.* **69**, 961 (1992).
41. F. Gross *et al.*, *Z. Phys. B* **64**, 175 (1986).
42. L. P. Gor'kov and P. A. Kalugin, *Pis'ma Zh. Eksp. Teor. Fiz.* **41**, 208 (1985).
43. K. Ueda and T. M. Rice, in *Theory of Heavy Fermions and Valence Fluctuations*, eds. T. Kasuya and T. Saso (Springer, Berlin, 1985).
44. P. J. Hirschfeld, P. Wölfle, and D. Einzel, *Phys. Rev. B* **37**, 83 (1988).
45. S. Skalski, O. Betbeder-Matibet, and P. R. Weiss, *Phys. Rev.* **136 A** 1500 (1964).
46. E. A. Schubert, B. Stricker, and K. Andres, *Phys. Rev. Lett.* **68**, 117 (1992).
47. C. H. Choi and P. Muzikar, *Phys. Rev. B* **37**, 5947 (1988).
48. P. J. Hirschfeld and N. Goldenfeld, *Phys. Rev. B* **48** (1993).
49. H. Kim, G. Preosti, and P. Muzikar, *Phys. Rev. B* **49**, 3544 (1994).
50. S. Ghamaty, B. W. Lee, J. J. Neumeier, and M. B. Maple, *Phys. Rev. B* **43**, 5430 (1991).
51. D. Poilblanc, D. J. Scalapino, W. Hanke, *Phys. Rev. Lett.* **72**, 884 (1994).