Inhibition of Strong-Coupling Superconductivity by Magnetic Impurities: A Quantum Monte Carlo Study

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The first exact calculation of $(\partial T_c/\partial c)_{c=0}$, the initial depression of the superconducting T_c, due to a small concentration, c, of magnetic impurities is presented. $(\partial T_c/\partial c)_{c=0}$ has been calculated from the pair-breaking regime ($T_K/T_{c0} \ll 1$) where the impurities are magnetic, to the pair-weakening regime ($T_K/T_{c0} \gg 1$). I find that $(\partial T_c/\partial c)_{c=0}$ can be expressed as the product of two universal functions $f(\lambda_0)$ and $g(T_K/T_{c0})$, and that, in contrast to previous results, the maximum $|(\partial T_c/\partial c)_{c=0}|$ occurs when $T_{c0} = T_K$, thus resolving a long-standing experimental puzzle.

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It is well known that magnetic impurities have a profound effect upon the properties of superconductors. In the Kondo limit they form a magnetic moment which spin-flip scatters the conduction electrons through an antiferromagnetic coupling. This scattering breaks apart the singlet Cooper pairs which characterize the superconducting state. Thus a small concentration of impurities can severely reduce the superconducting transition temperature[1] and even destroy superconductivity. As the temperature is lowered toward the Kondo temperature, T_K, the scattering rate increases logarithmically. However, as the temperature is lowered further, such that $T \ll T_K$, the conduction electrons screen the impurity moment. Thus one might expect the impurities to inhibit superconductivity most effectively in some intermediate regime.

Here I present the first exact calculation of $(\partial T_c/\partial c)_{c=0}$, the initial depression of the superconducting transition temperature, T_c, by a small concentration, c, of paramagnetic impurities. The calculations are made with a novel combination of quantum Monte Carlo simulations and Eliashberg-Migdal perturbation theory.[2,3] The Monte Carlo simulations allow one to account for the Kondo effect in an exact, nonperturbative way; hence the exact nature of this calculation. It was found that,

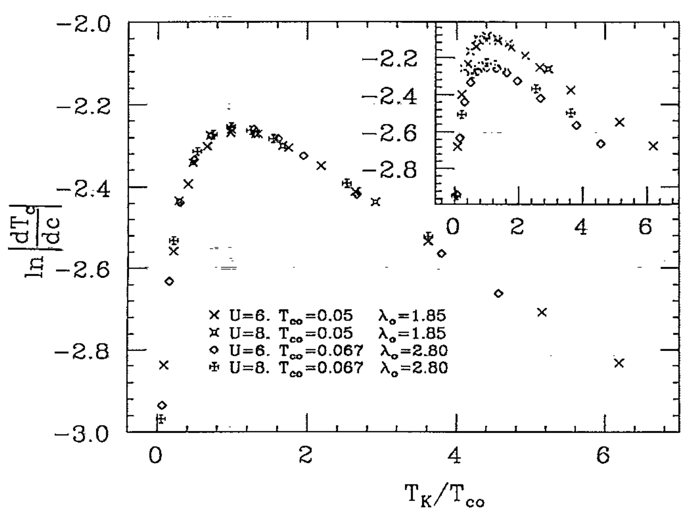

FIG. 1. Rescaled $\ln|(\partial T_c/\partial c)_{c=0}|$ vs T_K/T_{c0}. For each set of data $\omega_0 = 0.25$, but the other parameters were allowed to vary as shown. The data were rescaled by addition of a constant to the ordinate values to obtain the best fit. The unscaled data are shown in the inset. In each case the data can be collapsed to one curve which is a function of T_K/T_{c0}. The maximum inhibition of the transition temperature always occurs when $T_K = T_c$.

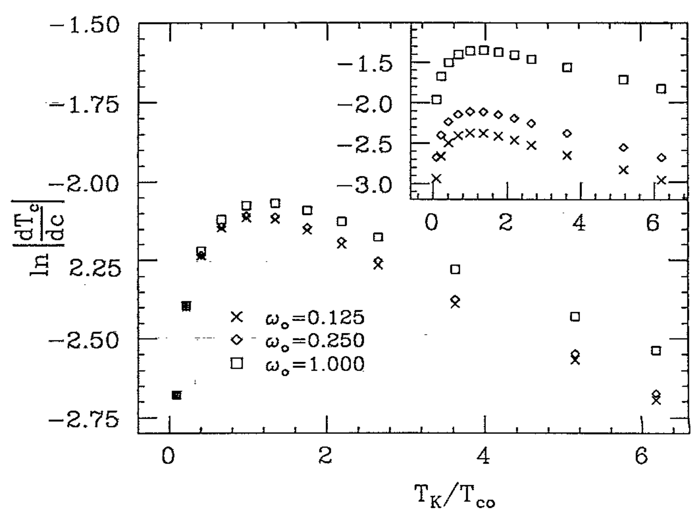

FIG. 2. Rescaled $\ln|(\partial T_c/\partial c)_{c=0}|$ vs T_K/T_{c0} for different values of the host Einstein frequency ω_0, but with all other parameters the same for all curves ($T_{c0} = 0.05$, $U = 6$). The data were rescaled by adding a constant to the ordinate values so that the leftmost points of each curve overlap. For low frequencies $\omega_0 = 0.125$ and $\omega_0 = 0.250$ the curves almost overlap indicating nearly universal behavior. The data corresponding to the higher frequency $\omega_0 = 1.000$ cannot be rescaled to overlap the lower frequency data, indicating that universality is violated at higher frequencies. The unscaled data are shown in the inset.

apart from a scaling factor, $(\partial T_c/\partial c)_{c=0}$ is a universal function of T_K/T_{c0} (see Figs. 1 and 2). The maximum initial depression occurs when $T_K=T_{c0}$ in rough agreement with experiment,[4] but in extreme quantitative disagreement with previous approximate calculations[5-8] which placed the maximum between 5 and 12. I also found that the scaling factor mentioned above is a function of only the electron-phonon coupling strength, λ_0, of the pure superconducting host (see Fig. 3).

Knowledge of the quantitative structure of $(\partial T_c/\partial c)_{c=0}$ is needed to interpret data from experiments where T_K is modified by the application of pressure[4,9] or by changing the type of impurity[10] or the composition of the superconducting host.[11,12] An unequivocal measure of T_K/T_{c0}, and hence T_K, is then obtained by fitting these data to a theoretical curve which gives $(\partial T_c/\partial c)_{c=0}$ as a function of T_K/T_{c0}. However, as shown in Table I, due to the breakdown of the previous theories when $T_K/T_{c0}\approx 1$, the values of T_K obtained in this way are much larger than those estimated from the resistivity data.[4,10,13]

In the model used here, the conduction electrons interact with Einstein phonons with a coupling strength λ_0, and frequency ω_0, resulting in a transition temperature, T_{c0}, of the pure system. This temperature is lowered by a small concentration of Anderson impurities characterized by a hybridization width Δ, an on-site repulsion U, and a Kondo temperature T_K. For the symmetric Anderson model a perturbation expansion gives $T_K=0.364(2\Delta U/\pi)^{1/2}e^{-\pi U/8\Delta}$ (Refs. 14,15). Using standard Eliashberg-Migdal diagrammatic techniques one finds that

$$(\partial T_c/\partial c)_{c=0}=-\frac{T^2\Delta}{N(0)}\sum_n\frac{C_n^2}{|\omega_n|^2}[\mathrm{Im}G_d(i\omega_n)|-\Delta|G_d(i\omega_n)|^2] +\frac{T^4\Delta^2}{N(0)}\sum_{n,m}\frac{C_nC_m}{|\omega_n||\omega_m|}[\Gamma_d(i\omega_n,i\omega_m)-\beta^2|G_d(i\omega_n)|^2\delta_{n,m}],$$

where ω_n and ω_m are fermion Matsubara frequencies at temperature $T=1/\beta$, $N(0)$ is the conduction-band density of states at the Fermi energy, and G_d and Γ_d [16] are the one- and two-particle Green's functions, respectively, for an isolated impurity. The function C_n is obtained from the Eliashberg equation of the pure host lattice. C_n approaches a constant of order unity for $|\omega_n|\ll\omega_0$ and falls off as ω_n^{-2} for $|\omega_n|\gg\omega_0$, thus providing a cutoff for the n and m summations.

The one- and two-particle single-impurity d Green's functions, G_d and Γ_d, are obtained from a Monte Carlo simulation described by Hirsch and Fye.[17] In this simulation the problem is cast into a discrete path-integral formalism in imaginary time, τ_l, where $\tau_l=l\Delta\tau$, $\Delta\tau=\beta/L$, and L is the number of time slices. A discrete Hubbard-Stratonovich transformation, which introduces an Ising field $\sigma(\tau_l)$, is used to make the Hamiltonian quadratic in fermion operators. The fermion degrees of freedom are then integrated out, and one is left with an effective action which is a function of the Ising field. The Monte Carlo algorithm is constructed to provide an important sampling of $\sigma(\tau_l)$. I have taken $\Delta\tau=0.25$ and 0.1875 and studied β values as large as 20, in units where $N(0)=0.25$ and $U\approx 7$. The systematic errors as-

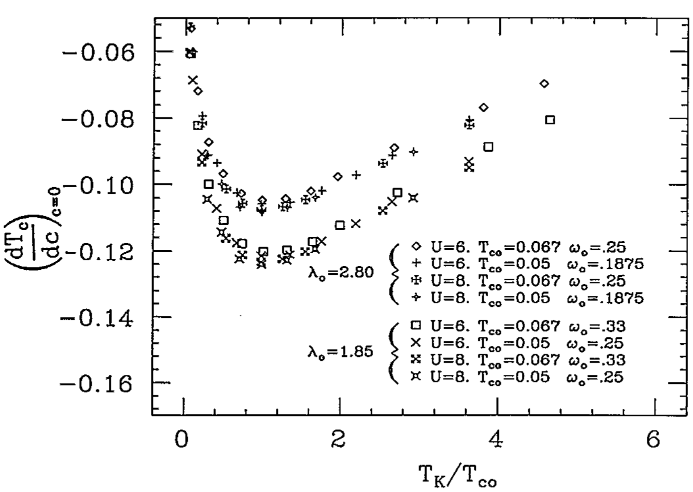

FIG. 3. $(\partial T_c/\partial c)_{c=0}$ vs T_K/T_{c0} with two values of the host Einstein electron-phonon coupling strength λ_0. Notice that each data set falls on one of the two curves, determined by λ_0. $\lambda_0=2.80$ for data on the upper curve, and $\lambda_0=1.85$ for the lower curve. Thus $(\partial T_c/\partial c)_{c=0}$ may be expressed as the product of two universal functions $(\partial T_c/\partial c)_{c=0}=f(\lambda_0)g(T_K/T_{c0})$.

TABLE I. Kondo temperatures, T_K, of Ce impurities in La-Th alloys. The values of T_K in the second and third columns were obtained by fitting the result of MZ and my result (MJ) to $N(0)(\partial T_c/\partial c)_{c=0}$ data reported by Luengo *et al.* (Ref. 11). The values in the fourth column were estimated from the resistivity, $\rho(T)$, data of Peña and Meunier (Ref. 12). T_K was taken as the temperature half way up the logarithmic rise of ρ. The values in parenthesis were estimated by Meunier (Ref. 13) from their own and other data.

% Th	T_K (MZ) (K)	T_K (MJ) (K)	T_K (expt.) (K)
0	1	···	(0.1)
10	5	···	···
15	8	1.1	2.5
20	14	2.1	3.5
25	18	2.6	3.5(<3)
34	55	4.5	4.3
41	96	8.0	5.0($\approx$10)

sociated with the finite value of $\Delta\tau$ were estimated to be typically of order 2% but could be twice that for Γ_d at the largest value of U reported here.

The values of U, Δ, and T were picked so as to remain in the universal Kondo regime as defined by Krishna-murthy, Wilkins, and Wilson,[15] while keeping U small enough, and Δ and T_{c0} large enough to make the simulation feasible. Thus, although I was able to explore a wide range of T_K/T_{c0}, I was limited to relatively high T_{c0}, and consequently large values of λ_0 and/or ω_0.

Figure 1 shows the underlying universal nature of $(\partial T_c/\partial c)_{c=0}$ as a function of T_K/T_{c0} for a wide range of U, T_{c0}, and λ_0, when the host Einstein frequency is held fixed at $\omega_0=0.25$. In this and in all the following plots the density of states of the conduction electrons is fixed at $N(0)=0.25$. The data have been rescaled to overlap the $U=6$, $T=0.067$, and $\lambda_0=2.80$ data by addition or subtraction of a constant to obtain the best fit (the unscaled data are shown in the inset). It is clear that the shape of the curve is universal in that it depends only upon the ratio T_K/T_{c0}. The maximum depression always occurs when $T_K/T_{c0}\approx 1$. The location of this maximum is as much as an order of magnitude lower than that predicted by previous theories which break down as T_K/T_{c0} approaches 1.

This will alleviate problems encountered in the past, when experimental data were fitted to theory, and unreasonably large values of T_K were inferred which did not agree with those estimated from resistivity data.[4,10,13] This is illustrated in Table I. Here T_K's of Ce impurities in a La-Th alloy are tabulated. In this alloy T_K increases monotonically with Th concentration, x, and $(\partial T_c/\partial c)_{c=0}$ exhibits a peak at $x\approx 0.45$.[11] The second column contains the data of Luengo *et al.*[11] They fitted their data to the result of Müller-Hartmann and Zittartz (MZ)[5] to obtain T_K as a function of x. However, as pointed out by Meunier *et al.*,[13] the values of T_K they obtained are about an order of magnitude larger than those estimated from the resistivity (shown in the fourth column of Table I), even where $T_K/T_{c0}\ll 1$. At first this seems surprising since the MZ result should be corrected when $T_K/T_{c0}\ll 1$. However, the reason for this discrepancy is clear: The data must be fitted to the MZ curve by making the points of maximum initial depression coincide. As I have shown, the MZ theory predicts a point of maximum depression which is an order of magnitude too high. Thus all of the inferred values of T_K are off by a corresponding factor. However, when these data are fitted to the curve in Fig. 1, the values of T_K obtained, and displayed in the third column, are in much closer agreement with the resistivity data.

In Fig. 2, $\ln|(\partial T_c/\partial c)_{c=0}|$ is plotted versus T_K/T_{c0} for a range of ω_0 and corresponding λ_0, while $U=6$ and $T_{c0}=0.05$ are held fixed. The data have been rescaled to overlap the $\omega_0=0.25$ data set by addition or subtraction of a constant. Clearly it is not possible to make the high-frequency data curve overlap the lower frequency curves, indicating that for high frequencies the behavior is nonuniversal.

As discussed above, the Einstein frequency acts as a frequency cutoff, so that higher frequency components of G_d and Γ_d do not effect $(\partial T_c/\partial c)_{c=0}$. However, we can see from the shape of the impurity spectral function, $(1/\pi)\mathrm{Im}[G_d(\omega)]$, that only the low-frequency behavior of the Anderson impurity is universal. For the symmetric Anderson model, it has a universal central Abrikosov-Suhl resonance, and two nonuniversal side peaks located at $\pm U/2$ with widths determined by Δ. Thus when $\omega_0\ll U$ the nonuniversal side peaks will not effect $(\partial T_c/\partial c)_{c=0}$; however, when ω_0 becomes large we will sample the side peaks and see some nonuniversal behavior. This is the case when $\omega_0=1.00$. Note that the behavior becomes less universal when Δ, and hence T_K, increases, thus increasing the width of the side peaks.

Normal superconducting materials, where $\omega_0\ll U$, will not display such nonuniversal effects. In contrast, some mechanisms proposed to explain the new high-T_c compounds will violate this inequality, resulting in nonuniversal effects. For example, in charge transfer mechanisms,[18,19] the characteristic frequency is of the order of an electron volt.

In Fig. 3, $(\partial T_c/\partial c)_{c=0}$ is plotted versus T_K/T_{c0} for different values of all the parameters, but for only two values of the host electron-phonon coupling strength λ_0. The data fall on one of two curves determined by λ_0, with $\lambda_0=2.80$ for the upper curve, and $\lambda_0=1.85$ for the lower curve. The spread in the data on each curve is systematic, because of the finite values of $\Delta\tau$, which becomes worse as β and U increase. Thus the scaling factor discussed above, and used in Fig. 1, is a function of λ_0 only. Within the region explored in this study, $(\partial T_c/\partial c)_{c=0}$ may be expressed as the product of two universal functions $(\partial T_c/\partial c)_{c=0}=f(\lambda_0)g(T_K/T_{c0})$.

In conclusion, I have made the first exact calculation of $(\partial T_c/\partial c)_{c=0}$, and shown that it is a universal function of T_K/T_{c0} multiplied by a scaling function of λ_0. $(\partial T_c/\partial c)_{c=0}$ has been calculated from the pair-breaking regime $(T_K/T_{c0}\ll 1)$ where the impurities are magnetic, to the pair-weakening regime $(T_K/T_{c0}\gg 1)$ where the impurities are nonmagnetic because of the screening of the conduction electrons. The maximum depression always occurs when $T_K/T_{c0}\approx 1$ in quantitative disagreement with previous theories which break down as T_K/T_{c0} approaches 1. It was this large quantitative discrepancy which resulted in an extreme overestimation of Kondo temperatures when data were fitted to these theories. I have shown that when data are fitted to the curves shown here, more reasonable values of T_K are obtained.

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[16]Γ_d is defined by

$$\Gamma_d(i\nu,i\nu')=\int_0^\beta d\tau_1 \cdots d\tau_4 e^{i\nu'(\tau_1-\tau_2)-i\nu(\tau_3-\tau_4)} \times\langle T d_\uparrow(\tau_1) d_\downarrow(\tau_2) d_\downarrow^\dagger(\tau_4) d_\uparrow^\dagger(\tau_3)\rangle ,$$

where d_σ destroys a spin-σ fermion on the impurity site.

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