Universal reduction of $T_c$ in strong-coupling superconductors by a small concentration of magnetic impurities

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The first exact calculation of $T_c$ in the presence of a dilute concentration $c$ of uncorrelated magnetic impurities is presented. The shape of $T_c(c)$ is universal, $T_c(c)/T_{c0} = h(c/\lambda_0)/N(0)T_{c0}T_K/T_{c0}$. The detailed shape of $T_c(c)/T_{c0}$ is qualitatively and quantitatively different from that found by previous approximate theories. $T_c(c)$ depends strongly upon the electron-phonon coupling $\lambda_0$. There is no indication of a low-temperature tail of positive curvature for $T_{K}/T_{c0} < 1$, or the associated third transition temperature $T_{c3}$, both predicted by Müller-Hartmann and Zittartz. My results agree well with experimental data.

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 very small concentration of impurities can severely reduce the superconducting transition temperature and even destroy superconductivity. In addition, the depairing potential which the impurities exert on the superconductor must compete with the phonon-mediated pairing potential. Thus the inhibition of $T_c$ must depend upon the relative strength of these potentials. Since the pairing potential is proportional to the electron-phonon coupling strength $\lambda_0$, one might expect the impurities to inhibit most effectively in the weak-coupling limit ($\lambda_0$ small).

Previously, I provided the first exact calculations of $(\partial T_c/\partial c)_c=0$, the initial depression of $T_c$ by a small concentration $c$ of magnetic impurities. For several reasons $T_c(c)$ is also of both experimental and theoretical interest. First, since magnetic impurities strongly inhibit superconductivity, the inhibition of superconductivity is perhaps the most sensitive probe of the magnetic state of the impurities. Second, calculations of $(\partial T_c/\partial c)_c=0$ are not sufficient to distinguish a material with $T_K/T_{c0} \approx 1$ from one with $T_K/T_{c0} \approx 1$, where $T_K$ and $T_{c0}$ are the Kondo and pure host superconducting transition temperatures, respectively. $(\partial T_c/\partial c)_c=0$ can have the same value in both regimes. However, $T_c(c)$ has a qualitatively different structure in the two regimes. Third, when $T_K/T_{c0} < 1$, the system exhibits the most striking and unusual phenomena, that of reentrant superconductivity where for certain values of $c$ the system exhibits two transition temperatures, $T_{c1} > T_{c2}$. Finally, $T_c(c)/T_{c0}$ is universal.

Both superconducting and Kondo impurity systems display universality. The Kondo susceptibility, resistivity, etc., depend only upon the ratio $T/T_K$, so that the universal scale is $T_K$. Universality in the superconducting system is characterized by the law of corresponding states, and the universal energy scale is $T_c$. Thus perhaps it is not surprising that a system of magnetic Kondo impurities embedded in a superconducting host would display universality. In this system the universal scale is the ratio $T_K/T_{c0}$.

Here I present the first exact calculations of $T_c(c)$, the superconducting transition temperature in the presence a small concentration $c$ of uncorrelated impurities. The calculations are made with a novel combination of quantum Monte Carlo simulation and Eliashberg-Migdal perturbation theory. Since I assume the impurities are dilute, I will ignore all diagrams of order $c^2$ and higher, which correspond to correlation between the impurities. The Monte Carlo simulation allows one to account for the Kondo effect in an exact, nonperturbative way, hence the exact nature of this calculation in the dilute limit.

In Fig. 1 I show that the reduction of superconductivity depends strongly upon the electron-phonon coupling $\lambda_0$, with $T_c$ reduced most effectively in the weak-coupling limit. As shown in the inset, curves corresponding to different values of $\lambda_0$ have the same shape, and hence may be scaled to overlap. Note also the reentrant behavior with two values of $T_c$ for some values of $c$. Figure 2 demon-

![Graph](image-url)
strates that for a given $\lambda_0=2.8$, $T_c(T_c)/T_{c0}$ depends only upon $T_K/T_{c0}$. Thus, aside from a scaling of the abscissa demonstrated in Fig. 1, $T_c(T_c)$ is a universal function of $T_K/T_{c0}$.

In Fig. 3, $T_c(T_c)/T_{c0}$ is plotted for various values of $T_K/T_{c0}$. In each case the $T_c(T_c)/T_{c0}$ is either purely concave ($T_K/T_{c0}<1$) or convex ($T_K/T_{c0}>1$), and for $T_K/T_{c0}=1$ is linear. For $T_K/T_{c0}=1$ the superconductivity is reentrant. However, in the entire region $T_K/T_{c0}<1$ there is no evidence for the low-temperature positive curvature tail associated with the third reentrant transition predicted by Müller-Hartmann and Zittartz (hereafter referred to as MHZ).

MHZ first calculated $T_c(T_c)/T_{c0}$ in the dilute impurity limit for all values of $T_K/T_{c0}$ using the Nagaoka approximation. They found that $T_c(T_c)/T_{c0}$ was a universal function of $T_K/T_{c0}$, and was purely concave for $T_K/T_{c0}<1$. However, for $T_K/T_{c0}<1$, $T_c(T_c)/T_{c0}$ has negative curvature for $T_c=T_{c0}$ and positive curvature for low temperatures. They predicted that the superconducting phase transition would be reentrant for $T_K/T_{c0}<1$ displaying three transition temperatures ($T_{c1}>T_{c2}>T_{c3}$). The third transition results from the low-temperature tail of positive curvature in $T_c(T_c)/T_{c0}$ predicted when $T_K/T_{c0}<1$. No experimental evidence for this low-temperature tail or the corresponding $T_{c3}$ has been found. Refinements of the MHZ theory, most notably that by Matsuurara, Ichinose, and Nagaoka (hereafter referred to as MIN) also cast doubt upon existence of a third transition. MIN used an approximate interpolation between the Fermi-liquid regime ($T_K/T_{c0}$) to the regime where the Nagaoka approximation is appropriate ($T_K< T_{c0}$). Both of these calculations (MHZ and MIN) are in the BCS limit, and predict no dependence of $T_c/T_{c0}$ upon $\lambda_0$.

In the model used here the conduction electrons interact with Einstein phonons with a coupling strength $\lambda_0$, and frequency $\omega_0$, resulting in a transition temperature, $T_{c0}$, of the pure system. The transition temperature is lowered by a small concentration of Anderson impurities characterized by a hybridization width $\Delta$, an on-site repulsion $U$, and a Kondo temperature $T_K$. For the symmetric Anderson model a perturbation expansion gives $T_K=0.364 \times (2\Delta U/\pi)^{1/2} e^{-\pi \Delta/2U}$. Calculations of $T_c(T_c)/T_{c0}$ required a combination of Monte Carlo simulation and diagrammatic perturbation theory. In the dilute limit the impurities are uncorrelated, so that each impurity makes an independent contribution to $T_c(T_c)/T_{c0}$. The net contribution is simply $CN$ times the contribution of a single impurity (where $N$ is the number of lattice sites).

Following Owen and Scalapino one can rewrite the Eliashberg equations at $T=T_c$ in terms of a single eigenvalue equation,

$$
\Phi_n = T \sum_p \left[ \frac{\lambda_0 \omega_0^3 \pi}{(\omega_n - \omega_m)^2 + \omega_0^2} + eT \frac{\Delta^2}{\pi N(0)} \sum_p G_p(\omega_n, \omega_m) \right] \Psi_p \frac{\Phi_m}{|\omega_n| |\omega_m|}^{1/2}
$$

$$
- \left( \frac{\pi T \lambda_0}{\omega_n} \sum_m \frac{\omega_0^2}{(\omega_n - \omega_m)^2 + \omega_0^2} + \frac{i e \Delta}{\pi N(0) \omega_n} \right) G_p(\omega_n) \Phi_n ,
$$

(1)
where $\omega_n$ and $\omega_m$ are fermion Matsubara frequencies at temperature $T = 1/\beta$, $N(0)$ is the conduction-band density of states at the Fermi energy, and $Q_d$ and $\Gamma_d$ (Ref. 10) are the one- and two-particle Green's functions, respectively, for the isolated impurity. A transition is indicated ($T = T_c$) when the largest eigenvalue of this equation first becomes 1.

The one- and two-particle single-impurity Green's functions, $G_0$ and $\Gamma_0$, are obtained from a Monte Carlo simulation of the symmetric Anderson model developed by Hirsch and Fye. In this simulation the problem is cast into a discrete path-integral formalism in imaginary time, $\tau$, where $\tau = \pm \beta\tau$, $\Delta < \beta/L$, and $L$ is the number of time slices. I have taken $\Delta = 0.25$ and 0.1875 and studied $\beta$ values as large as 75, $6 < U < 8$, and $0.5 < A < 1.7$.

Larger values of $\beta$ were avoided since the computer time required by the algorithm scales as $L^3$. The systematic errors associated with the finite value of $\Delta$ were estimated to be of order 2% but could be twice that for $\Gamma_0$ at the largest values of $U$ reported here.

The values of $U$, $\Delta$, and $T_c$ were chosen so as to remain in the universal Kondo regime as defined by Krishna, Wilkins, and Wilson, while keeping $U$ small enough, and $\Delta$ and $T_c$ large enough to make the simulation feasible. Thus, in this study I was able to explore a wide range of $T_K/T_c$. I was limited to relatively high $T_c$, and consequently large values of $\lambda_0$ and/or $\omega_0$.

In Fig. 1 $T_c/T_c$ is plotted versus $\tilde{\varepsilon} = e/\epsilon/2\pi) N(0) T_c$ when $T_K/T_c = 1/15$ for several values of $\beta \lambda_0$. The concentration of impurities is normalized in this manner to be consistent with MHZ. Three outstanding features are demonstrated in this figure. First, the depression of $T_c$ depends very strongly upon $\lambda_0$, with the strongest suppression for small $\lambda_0$. This reflects the fact that more tightly bound Cooper pairs are less susceptible to magnetic pair breaking. Second, all three plots share the same universal shape, as shown in the inset where the data for the two smaller values of $\lambda_0$ were scaled to overlap the $\lambda_0 = 2.8$ data set. Any difference in shape is probably due to nonuniversal effects associated with the (unphysically) large values of $\omega_0$ necessary due to the restrictions imposed by the Monte Carlo calculation. I have discussed this effect elsewhere. Third, the superconducting transition is reentrant; for example, when $\lambda_0 = 2.8$, there are two transition temperatures for $\tilde{\varepsilon} = 0.9$.

In Fig. 2 the universal nature of $T_c/T_c$ is demonstrated. Here $T_c/T_c$ vs $\tilde{\varepsilon}$ is plotted for three different values of $T_K/T_c$ when $\lambda_0 = 2.8$. In addition, each plot contains three data sets with values of $\omega_0$, $U$, $\Delta$, chosen to satisfy the stated values of $T_c$ and $T_K/T_c$. Since the sets with the same value of the ratio $T_K/T_c$ overlap, $T_c/T_c$ is a universal function of $T_K/T_c$.

From Figs. 1 and 2 (as well as other data which cannot be displayed due to limitations of space) one may conclude that $T_c/T_c$ is a universal function of the form

$$\frac{T_c}{T_c} = h \left( \frac{c f(\lambda_0)}{N(0) T_c}, \frac{T_K}{T_c} \right).$$

The scaling function $f(\lambda_0)$ is the same as that determined from measurements of $\frac{\partial T_c}{\partial c}$ (Refs. 2 and 3) since

$$N(0)(\partial T_c/\partial c)_{c=0} = \frac{h}{N(0) T_c}.$$  

In Refs. 2 and 3 the function $h'$ is identified as $g(T_K/T_c)$, and in Ref. 3 $(\lambda_0)$ is plotted.

In Fig. 3, $T_c/T_c$ is plotted versus $\tilde{\varepsilon}$ and $T_c/T_c$ when $\lambda_0 = 2.8$. There are three outstanding features of this plot. First, as a function of $T_K/T_c$, $T_c(c)/T_c$ changes continuously from a curve of purely positive curvature ($T_K/T_c > 1$) to one of purely negative curvature ($T_K/T_c < 1$). Second, when $T_K/T_c = 1$, $T_c/T_c$ is linear down to the lowest temperatures simulated. Third, by extrapolating these results to $T_c = 0$ it is possible to estimate the critical concentration of impurities, $c_{c_{crit}}$, necessary to completely destroy the zero-temperature transition. From Fig. 3 the minimum of $c_{c_{crit}}$ occurs when $T_K/T_c \approx \frac{1}{2}$. Due to the necessity of extrapolation it is not possible to fix the minimum $c_{c_{crit}}$ more accurately; however, it is clear that the minimum occurs for $T_K/T_c < 1$.

When compared to previous approximate results for $T_c/T_c$, my results are qualitatively and quantitatively different. First, to my knowledge, all previous calculations of $T_c(c)/T_c$ are in the weak-coupling limit, and are independent of $\lambda_0$. My results are strongly dependent on $\lambda_0$, as determined by $f(\lambda_0)$, especially when $\lambda_0 < 1$ (Ref. 3) where the impurities inhibit $T_c$ most effectively. Second, as seen in Fig. 3 when $T_K/T_c < 1$, there is no indication of the low-temperature tail of positive curvature predicted by MHZ. For example, in the original work of MHZ for $T_K/T_c = 1$ the curvature of $T_c/T_c$ becomes distinctly positive when $T_K/T_c = 0.3$, whereas in my results the behavior is linear down to the lowest temperatures simulated ($T_c/T_c = 0.06$). Similarly when $T_K/T_c = 1/4$ MHZ predict a transition to positive curvature when $T_c/T_c = 0.2$, and my results maintain negative curvature to the lowest temperature simulated ($T_c/T_c = 0.06$). This tail resulted in a third transition $T_c$ when $T_K/T_c < 1$; however, the appearance of this tail in the original work of MHZ was probably due to the breakdown of the Nagaoka approximation at low temperatures $T_K/T_c > 1$. Third, when $T_K/T_c = 1$ I found that $T_c(c)/T_c$ was purely linear. MHZ found no linear region, and MIN found a region of almost linear behavior for $T_K/T_c \approx 3$.

The qualitative features of my results for $T_c(c)/T_c$ compare well with experimental data. Figure 3 bears a striking resemblance to the experimental results of Huber, Fertig, and Maple (Ref. 2 for (La$_1-x$Th)$_x$Ce. They plot $T_c/T_c$ vs Ce concentration and $x$ ($x = 0.0$, 0.1, 0.25, 0.45, 0.65, 0.80, 1.00). In this material Ce is a nonorbitally degenerate magnetic impurity in a superconducting La-Th alloy host, and $T_K/T_c$ increases monotonically with $x$. Superconductivity is reentrant for small $x$. As $x$ and $T_K/T_c$ increase, the curve $T_c(c)/T_c$ changes continuously from a curve of purely negative curvature, to one of purely positive curvature. The curvature goes through zero when $x = 0.55$, and the minimum value of $c_{c_{crit}}$ falls at $x = 0.45$. Thus there are two unique features of agreement between my results and experiment: The smooth transition from a region of purely positive to negative curvature in $T_c(c)/T_c$ and the minimum value of $c_{c_{crit}}$ occurs for $T_K/T_c$ below the linear region.
Where an independent estimate of $T_K$ is available, a quantitative comparison of theory and experiment is possible. Measurements of the Kondo resistivity for $(\text{La}_{1-x}\text{Th}_x)\text{Ce}$, when $x = 0.25$ ($T_{c0} = 5$ K) suggest that $T_K$ is of order 2.5 K so that $T_K/T_{c0} = 1/2$. A best fit to my results is obtained when $T_K/T_{c0} = 1/5$. In $(\text{LaCe})\text{Al}_2$ Ce acts as a nonorbitally degenerate magnetic impurity in superconducting LaAl$_2$ ($T_{c0} = 3.3$ K). A good fit of this data to my results is obtained when $T_K/T_{c0} = 1/25$. Low-temperature susceptibility and nuclear orientation measurements suggest that $T_K$ is of order 0.1 K, so that $T_K/T_{c0} = 1/33$.

In conclusion, I have made the first exact calculations of $T_c(c)/T_{c0}$ in the dilute (uncorrelated) impurity limit. I have shown that the shape of $T_c(c)/T_{c0}$ is universal,

$$\frac{T_c}{T_{c0}} = \ln \left[ \frac{c f(\lambda_0)}{N(0)T_{c0}} \frac{T_K}{T_{c0}} \right].$$

The detailed shape of $T_c(c)/T_{c0}$ is qualitatively and quantitatively different than that found by previous approximate theories. In contrast to these theories, I find that the depression of $T_c$ depends strongly upon $\lambda_0$, as determined by $f(\lambda_0)$, and is most pronounced in weak-coupling superconductors. $T_c(c)$ changes from a curve of purely positive curvature for $T_K/T_{c0} > 1$ to a curve of purely negative curvature for $T_K/T_{c0} < 1$. There is no indication of a low-temperature tail of positive curvature for $T_K/T_{c0} < 1$, or the associated third transition temperature $T_{c3}$, both predicted by MHZ. The qualitative features of my results agree well with experimental data.

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1M. B. Maple, Appl. Phys. 9, 179 (1976), and references 33 and 39 therein.
10$\Gamma_d$ is defined by

$$\Gamma_d(iv,iv') = \int_0^\infty d\tau_1 \cdots d\tau_4 \exp \left[ iv(\tau_1 - \tau_2) - iv(\tau_3 - \tau_4) \right] \times \langle \langle T d_i(\tau_1) d_i(\tau_2) d_1(\tau_3) d_1(\tau_4) \rangle \rangle,$$

where $d_\sigma$ destroys a spin-$\sigma$ fermion on the impurity site.