Impurity Scattering and Triplet Superconductivity in UPt_3

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Substitution of rare earths (R), Th, and Zr for U in UPt_3 depresses the superconducting transition temperature T_c at an initial rate $(\Delta T_c/x)$, where x is the impurity concentration, that increases linearly with increasing residual resistivity ρ_0, indicating that the primary pair breaking mechanism is impurity potential scattering. The scaling of $(\Delta T_c/x)$ with ρ_0 is strong evidence for anisotropic superconductivity in UPt_3. The absence of a correlation of $(\Delta T_c/x)$ with the de Gennes factor of the R ions suggests that the superconducting order parameter in the A phase of UPt_3 has odd parity.

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Existing experimental data provide convincing evidence for unconventional superconductivity in heavy fermion materials [1,2]. The anisotropic order parameter describing an unconventional superconductor can have internal spin and orbital degrees of freedom whose degeneracy can be lifted by a symmetry breaking field. The strongest evidence of this in the heavy fermion superconductor UPt_3 is provided by the zero field specific heat, which reveals a clear splitting of the superconducting transition near $T_c \approx 0.5$ K by ~ 60 mK (Ref. [3]) and the existence of multiple superconducting phases in the H-T plane [4].

In UPt_3, specific heat, ultrasound, penetration depth, and thermal conductivity data, all taken together, suggest an order parameter with a nodal line along the equator and nodal points at the poles [1,2]. Consistent with the nodal structure, several theories based on a lifting of degeneracy of the superconducting order parameter by the antiferromagnetic order ($T_N = 5$ K) have been proposed to explain the split transitions in zero field and the multicomponent H-T phase diagram of UPt_3. Refs. [5–10] give compelling arguments in favor of an order parameter belonging to the two-dimensional (i.e., orbitally degenerate) E_1 or E_2 representation of the D_{6h} space group, leading, in the strong spin orbit coupling limit, to a two component pairing function. The singlet spin phases of the E representation have been the most successful in accounting for key experimental results for UPt_3; however, they fail to explain the crossing of the phase boundaries in the H-T plane for $H \| c$ as observed experimentally [4,11].

The anisotropic critical field $H_{c2}(T)$ data also reveal an unusual convergence and crossing of the phase lines for $H \| c$ and $H \| a$ at low temperatures [12], apparently reflecting the absence of paramagnetic limiting of H_{c2} for $H \| a$. This has been shown to be consistent with an odd-parity theory [13] based on a single component of the triplet with up-down pairs, which is as sensitive to magnetic pair breaking as a singlet superconductor. Ref. [14] presents an alternative scenario that assumes weak spin orbit coupling and is based on an order parameter belonging to a one-dimensional representation (no orbital degeneracy) with spin triplet pairing. In this case, the pairing function is described by a three-component order parameter, of which each component corresponds to a spin direction, and is therefore less sensitive to magnetic pair breaking. This approach can explain the isotropy of the H-T phase diagram for various applied field directions. In addition, both muon spin relaxation [15] and nuclear magnetic resonance [16] measurements yield no change in the Knight shift in the superconducting state, in support of an odd-parity order parameter. Clearly, no single theory has yet been able to account for all the experimental data on UPt_3, indicating the need for further experimental and theoretical work. In this Letter, we report measurements of the depression of T_c of UPt_3 by rare earth (R), Th, and Zr impurities. The results are in sharp contrast to predictions based on the pair breaking theory for impurities in conventional superconductors (i.e., s wave), providing further evidence for anisotropic superconductivity in UPt_3. Furthermore, the absence of a dependence of the depression of T_c on the de Gennes factor of the R impurities suggests that the superconducting order parameter in the A phase of UPt_3 has odd parity.

The polycrystalline samples used in this study were prepared by arc melting appropriate amounts of UPt_3 and $U_{0.95}R_{0.05}Pt_3$ (R = rare earth, Zr, and Th) in an argon atmosphere and annealing in a 150 torr argon atmosphere at 800 °C for ten days. X-ray diffraction analysis showed that all samples are single phase. In this work, T_c is defined as the onset of the superconducting transition in the ac magnetic susceptibility χ_{ac}.

Initially, $\chi_{ac}(T)$ measurements were performed on $U_{1-x}M_xPt_3$ with M = Zr, Ce, Gd, Lu, and Th, for various values of x. The resultant curves of T_c vs x are shown in Fig. 1 (for clarity, the data for R = Zr have been omitted). Except for Ce, the curves are nearly linear, with initial slopes varying significantly. The $T_c(x)$ curve for Zr (not shown) initially follows the behavior exhibited by Gd to $x \approx 0.3$ at.%, then develops positive curvature and crosses above the Th line at $x \approx 0.5$ at.%. Two points are worthy of note: First, Th impurities are much more

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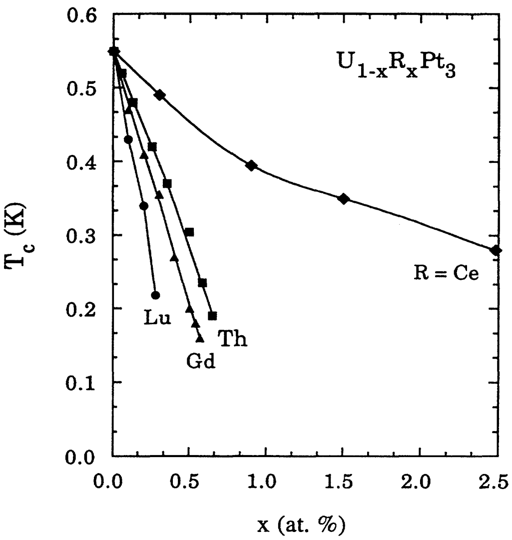

FIG. 1. Superconducting transition temperature T_c vs impurity concentration x for $U_{1-x}M_xPt_3$ with M = Lu, Gd, Th, and Ce. The solid lines are guides to the eye.

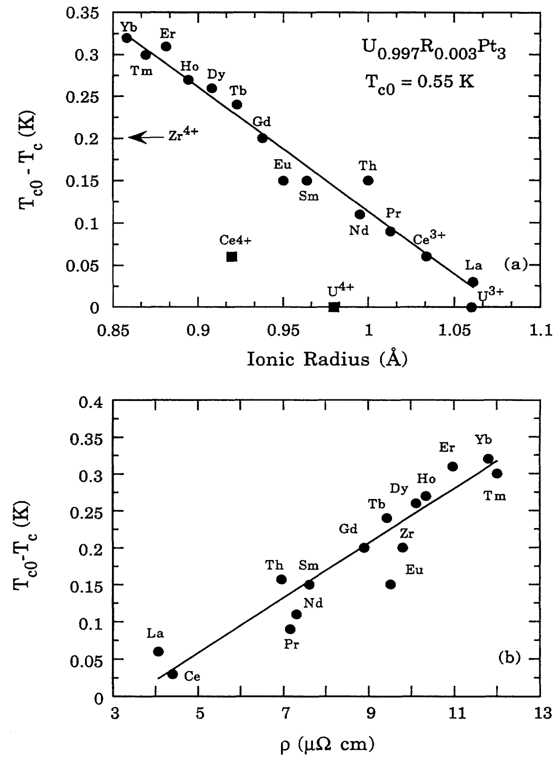

FIG. 2. (a) T_{c0}-T_c vs M ionic radius for $U_{0.997}M_{0.003}Pt_3$ compounds, where M = rare earth (except Pm and Lu), Th, and Zr. T_{c0} is the superconducting transition temperature of UPt_3. (b) T_{c0}-T_c vs residual resistivity ρ_0 for the same compounds as in Fig. 2(a).

effective in suppressing superconductivity in UPt_3 than in $CeCu_2Si_2$ and UBe_{13} and, second, the depression of T_c due to Ce impurities is surprisingly small. The T_c's for Gd lie close to the Th and Lu $T_c(x)$ curves, suggesting no particular effect on superconductivity in UPt_3 from the $4f$ electron local moments, similar to what was observed in rare-earth doped UBe_{13} [17].

In an attempt to identify the pair breaking mechanism responsible for the depression of T_c in doped UPt_3, we prepared a series of samples with fixed concentrations of M ions, $U_{0.997}M_{0.003}Pt_3$, and measured the resultant depression of T_c, $\Delta T_c = T_{c0} - T_c$, where T_{c0} is the T_c of UPt_3. The results of this study are shown as ΔT_c vs ionic radius of the M substituent in Fig. 2(a) and as ΔT_c vs residual resistivity ρ_0, measured at $T = 1.2$ K, in Fig. 2(b). A new and unexpected result shown in Fig. 2(a) is the linear increase of ΔT_c with decreasing size of the impurity ion. This behavior is not incidental since the same effect was also observed in another series with $x = 0.5\%$. The ionic radii were taken from Ref. [18] and correspond to a trivalent M ion, except for Ce, Zr, and Th, where they represent a tetravalent M ion. The data in Fig. 3(a) exhibit some scatter, which could be an indication of competing phenomena. Zirconium is anomalous and does not follow the behavior set by the rare earth and Th impurities; its ΔT_c is equal to that of Gd, but the ionic radius of Zr^{4+} is too small (0.79 Å) and falls outside the range of the plot as indicated by the arrow. The solid circles (squares) for M = Ce and U for pure UPt_3 represent hypothetical points assuming trivalent (tetravalent) ions. The trend of the data in Fig. 3(a) is clearly consistent with both Ce and U being in a trivalent state in UPt_3, in agreement with band structure calculations. Another striking result is evident in Fig. 2(b), which reveals a linear correlation of ΔT_c with the residual resistivity ρ_0. The ΔT_c vs ρ_0 data in Fig. 2(b) show more scatter than the corresponding ΔT_c vs ionic radius data in Fig. 2(a). We attribute this to the different preferential orientations of the sample crystallites which have strong resistivity anisotropy and/or the difficulty of measuring precisely the sample geometrical factor. A similar correlation between T_c and residual resistivity has been observed in the heavy fermion superconductor UPd_2Al_3 doped with Y, Gd, and Ni [19].

It is well known that magnetic impurities act as pair breakers in s-wave superconductors and lead to a rapid depression of T_c due to the exchange interaction $\Im$ between the spins of the impurity ions and conduction electrons [20]. On the other hand, nonmagnetic impurities do not affect the thermodynamic properties of s-wave superconductors and, in turn, do not result in a significant variation of T_c. This is known as Anderson's theorem [21] and is essentially due to the exact cancellation of the impurity normal and anomalous contributions to the self energy due to the pairing potential of electrons. In unconventional superconductors, the order parameter is anisotropic as a consequence of Cooper pairs forming in states of finite relative angular momentum, similar to superfluid ^{3}He. In this case, Anderson's theorem does not hold because the anomalous contribution to the self energy vanishes and even nonmagnetic impurities break superconducting electron pairs and

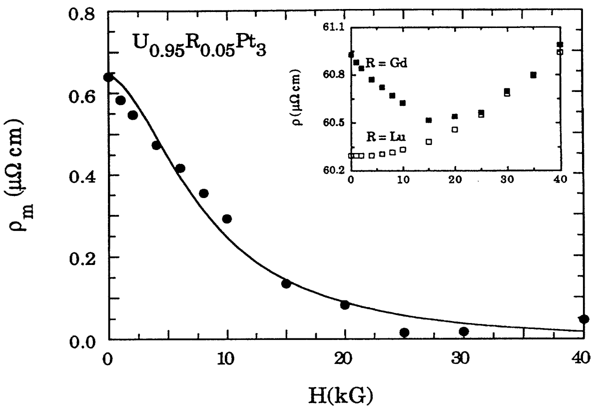

FIG. 3. Magnetic field dependence of the spin-disorder resistivity $\rho_m = \rho(U_{0.95}Gd_{0.05}Pt_3) - \rho(U_{0.95}Lu_{0.05}Pt_3)$, measured at $T = 0.6$ K. The solid line is a least squares fit to Eq. (1). Inset: ρ vs H for $U_{0.95}R_{0.05}Pt_3$ with R = Gd or Lu measured at $T = 0.6$ K.

suppress superconductivity [22]. The strong pair breaking effect of nonmagnetic impurities in UPt_3 observed in this study provides, therefore, evidence in support of unconventional (i.e., non-s-wave) superconductivity in UPt_3. This result is consistent with the unusual superconducting properties and conclusions reached in previous measurements of T_c depressions [23,24] in UPt_3 doped with Y, Th, Pd, Ir, and Au.

Considering that both the residual resistivity ρ_0 and ΔT_c should be directly proportional to the potential scattering rate of the nonmagnetic impurity, the observed linear dependence of ΔT_c on the residual resistivity, i.e., $\Delta T_c \propto \rho_0$, indicates that the pair breaking mechanism responsible for the T_c depression is primarily due to impurity potential scattering. On the other hand, the anomalous correlation between residual resistivity and ionic radius, as inferred from the linearity of ΔT_c with both resistivity and ionic radius, is not well understood. Had each ion been assumed to scatter unitarily, the residual resistivity would be expected to be roughly independent of ionic radius.

The effects of impurities on anisotropic superconductors have been investigated by Maekawa *et al.* [25], Millis *et al.* [26], and Hirschfeld *et al.* [27], who find that the depression of T_c follows the Abrikosov-Gor'kov universal function with a pair breaking parameter that includes both spin flip and potential scattering contributions, i.e.,

$$\ln\left(\frac{T_c}{T_{c0}}\right) = \psi\left(\tfrac{1}{2}\right) - \psi\left(\frac{1}{2} + \frac{\Gamma}{2\pi T_c}\right), \qquad (1)$$

with the scattering $\Gamma = [n \sin^2\delta/\pi N^*(0)]x + (\pi/k_B)N^*(0)\Im^2(g_J - 1)^2 J(J+1)x$; the first and second terms in Γ represent the potential and magnetic scattering rates, respectively, ψ is the digamma function, δ is the scattering phase shift, $N^*(0)$ is the host density of states at the Fermi level for both spin directions, n is the conduction electron density, g_J is the Landé g factor, J is the total angular momentum, and x is the impurity concentration. For small impurity concentrations, the initial depression is then given by

$$-\Delta T_c = \frac{n \sin^2\delta}{4N^*(0)} x + \left(\frac{\pi^2}{4k_B}\right) N^*(0)\Im^2(g_J - 1)^2 J(J+1)x \,. \qquad (2)$$

In other words, magnetic impurities in anisotropic superconductors contribute two terms to the pair breaking parameter, the ordinary potential scattering term, and the spin flip scattering term, which depends on the de Gennes factor $(g_J - 1)^2 J(J+1)$. However, nonmagnetic impurities contribute only the potential scattering term. Therefore, one would expect that for odd parity superconductors, both magnetic and nonmagnetic impurities contribute only the potential scattering term since the Zeeman interaction of the applied field with the superconducting electrons in the equal spin pairing states $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ shift the excitation energies of the single particle states either up or down without breaking the Cooper pair. On the other hand, both magnetic and nonmagnetic impurities are pair breaking for non-s-wave even-parity superconductors. Millis, Sachdev, and Varma [26] have argued that in d-wave superconductors, the pair breaking rate for nonmagnetic impurities is of the same order as that of magnetic impurities.

It is noteworthy that the T_c depression in Fig. 2(b) is not proportional to the de Gennes factor of the R ion, as expected for magnetic pair breaking. This can be attributed either to ineffectual magnetic pair breaking as would occur in spin triplet states or to a relatively small strength of the exchange coupling $\Im$ that would lead to a contribution too small to resolve. To distinguish between these two possibilities, we have measured the magnetoresistance of a $U_{0.95}Gd_{0.05}Pt_3$ sample. How much each unquenched Gd moment couples to the conduction electrons can be estimated from the spin disorder scattering. Shown in the inset of Fig. 3 is a ρ vs H isotherm at 0.6 K for $U_{0.95}Gd_{0.05}Pt_3$, obtained from measurements up to 40 kOe. Magnetoresistance data, taken on a $U_{0.95}Lu_{0.05}Pt_3$ reference sample, were subtracted from those of $U_{0.95}Gd_{0.05}Pt_3$ in order to extract the spin-disorder resistivity ρ_m vs H curve shown in Fig. 3. Using a free electron model, Kasuya [28] has shown that

$$\rho_m = \frac{\pi m^* N_i}{\hbar N N_a{}^2 e^2} N^*(0)\Im^2(g_J - 1)^2 (J - \langle J\rangle) \times (J + \langle J\rangle + 1), \qquad (3)$$

where m^* is the effective mass of the metallic host, N_i is the number of magnetic scattering centers per unit volume, N is the total number of conduction electrons, N_a is the total number of atoms per unit volume, and $\langle J\rangle = JB_J(g_J J\mu_B H/k_B T)$, where B_J is the Brillouin function. In the paramagnetic state, $\langle J\rangle = 0$ and ρ_m is finite. Application of a magnetic field H causes $\langle J\rangle$ to assume a finite value and the spin-disorder resistivity to decrease. When the applied field is strong enough to line up all of the Gd spins, $\langle J \rangle = J$ and $\rho_m = 0$. A least squares fit of the $\rho_m(H)$ data to Eq. (3), represented in Fig. 3 as a solid line, describes the data reasonably well. Assuming that each U atom has three $5f$ electrons, the parameter $N^*(0)\Im^{*2} = 3.8 \times 10^{15}$ states eV is obtained from the fit.

At this point, it is useful to recall that low temperature electron spin resonance (ESR) experiments [29,30] on UBe_{13} and UPt_3 doped with rare earth local moments have revealed little enhancement of the ESR linewidth thermal broadening over the local-moment ESR of a normal metal. This observation has led to conclusions that the local moment substituting at the U site does not couple significantly to the heavy fermion subsystem. One possible reason for this behavior is that, contrary to normal metals, the exchange coupling $\Im$ in heavy fermion systems is renormalized to reflect the indirect coupling between the heavy quasiparticles responsible for superconductivity and the rare earth $4f$ electrons through hybridization with the conduction electrons [31]. Having considered this possibility, we propose that the preceding observation in the ESR linewidth data can be explained by a cancellation of the enhanced density of states $N^*(0)$ by the renormalized exchange coupling $\Im^*$ since the linewidth is proportional to $N^*(0)\Im^*$. Similarly, we assume in our analysis of the spin disorder resistivity that $\Im^*$ is the renormalized coupling constant and that no further renormalization of the extracted $N^*(0)\Im^{*2}$ parameter is necessary. Using this parameter value in Eq. (2) to estimate the paramagnetic pair breaking effect of 0.3% Gd in UPt_3, we obtain, despite the weak coupling between the conduction and $4f$ electrons, $\Delta T_c \approx 0.25$ K, a value that is larger than the measured value, $\Delta T_c = 0.2$ K. This implies that the absence of a dependence of the T_c depression in $U_{0.997}R_{0.003}Pt_3$ on the de Gennes factor is not due to a small value of $N^*(0)\Im^{*2}$, but rather to an ineffective magnetic pair breaking mechanism, a result that suggests an odd-parity triplet superconducting state in UPt_3, consistent with previous μSR (Ref. [15]) and NMR (Ref. [16]) experiments.

To our knowledge, no comprehensive study of impurity effects aimed at determining the parity of the order parameter in UPt_3 has been undertaken, except perhaps for Ref. [24]. In it, Vorenkamp *et al.* suggest even-parity singlet superconductivity in UPt_3 based on the argument that Pd substitution for Pt leads to magnetic pair breaking. Considering, however, the possibility of spin-fluctuation mediated superconductivity in UPt_3, it cannot be excluded that the depression of T_c is due to suppression of the spin fluctuations, as pointed out by the authors. To distinguish between these possibilities requires a comparative study of several magnetic impurities, as performed in our work.

In summary, we have shown that the T_c reduction upon substitution of impurities on the U site in UPt_3 correlates with the residual resistivity as expected for unconventional superconductors in which the energy gap vanishes at points or lines on the Fermi surface. The residual resistivity also has an unexpected linear dependence on the ionic radius of the impurity ion. We argue that the absence of a marked correlation of ΔT_c with the de Gennes factor of the rare earth solute, taken together with the magnetoresistance measurements, suggests an odd-parity triplet-spin pairing type of superconductivity in UPt_3.

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