Detection of a Spin-Triplet Superconducting Phase in Oriented Polycrystalline U_{2}PtC_{2} Samples Using ^{195}Pt Nuclear Magnetic Resonance

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Detection of a spin-triplet superconducting phase in oriented polycrystalline U_2PtC_2 samples using ^{195}Pt nuclear magnetic resonance

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Nuclear magnetic resonance (NMR) measurements on the ^{195}Pt nucleus in an aligned powder of the moderately heavy-fermion material U_2PtC_2 are consistent with spin-triplet pairing in its superconducting state. Across the superconducting transition temperature and to much lower temperatures, the NMR Knight shift is temperature independent for field both parallel and perpendicular to the tetragonal c-axis, expected for triplet equal-spin pairing superconductivity. The NMR spin-lattice relaxation rate $1/T_1$, in the normal state, exhibits characteristics of ferromagnetic fluctuations, compatible with an enhanced Wilson ratio. In the superconducting state, $1/T_1$ follows a power law with temperature without a coherence peak giving additional support that U_2PtC_2 is an unconventional superconductor. Bulk measurements of the AC-susceptibility and resistivity indicate that the upper critical field exceeds the Pauli limiting field for spin-singlet pairing and is near the orbital limiting field, an additional indication for spin-triplet pairing.

The competition between the localized and itinerant nature of the $5f$ electrons in heavy fermion uranium superconductors leads to a rich variety of electronic and magnetic properties in these materials. One such uranium compound U_2PtC_2, discovered 45 years ago [1], has been known to be superconducting with a transition temperature $T_c = 1.47$ K, without magnetic order. A general measure of the local or itinerant nature of f electron materials is based on the inter-atomic spacing and, for uranium, this distance is $d_{U-U} \approx 3.6$ Å[2]. Below this limit, f-bands overlap, electrons tend to be itinerant, and phonon-mediated superconductivity can be supported, as for example in U_6Fe [3]. Above this limit, however, f electrons tend to be more localized and electronic correlations in narrow bands of hybridized f and ligand states become important, possibly leading to unconventional superconductivity as is the case for the heavy-fermion UPt_3 [4]. U_2PtC_2 with $d_{U-U} = 3.52$ Å is intermediate to these extremes [5], leaving to question the nature of superconductivity in this material. In fact, early experiments of muon-spin resonance [6] and pressure-dependent resistivity[7] have shown initial indications of an unconventional superconducting state. Nevertheless, the microscopic details of the superconducting and electronic properties are largely unknown to date, likely due to the difficulty of making high quality samples.

Here, we report the first ^{195}Pt NMR measurements of U_2PtC_2 to determine the microscopic details of the normal and superconducting (SC) states. We find evidence for strong ferromagnetic fluctuations in the normal state from a modified Korringa law and Wilson ratio. Additionally, the NMR shift is temperature independent in the SC state and, from bulk measurements, the upper critical field is much larger than the BCS Pauli limiting field for spin-singlet superconductivity, both consistent with spin-triplet superconductivity. Superconductivity near ferromagnetism has been found in only a few uranium compounds, namely UGe_2 (SC under pressure) [8], URhGe [9], and UCoGe [10], all with $d_{U-U} \approx 3.5$ Å. These materials order ferromagnetically in addition to their superconductivity, and have an upper critical field that exceeds the Pauli limiting value [9–11]; whereas, UCoGe also has a temperature-independent spin shift, K_s, in its SC state [12]. U_2PtC_2 is similar to these materials with regard to the temperature-independent shift and upper critical field, although it is distinct in that it has strong ferromagnetic fluctuations rather than static ferromagnetic order.

Our polycrystalline samples were arc melted then annealed for approximately one month resulting in a $RRR \approx 30$ with a residual resistivity of $\rho_0 \approx 10$ $\mu\Omega$cm. A comprehensive account of the physical properties has been published elsewhere.[13] To perform NMR experiments, a polycrystalline sample was powdered, mixed with stycast 1266 epoxy in a 1:1 ratio, poured into a teflon cup, and aligned along a radial direction of the cup in a field of 9 T for 24 hours until the epoxy cured. The grain

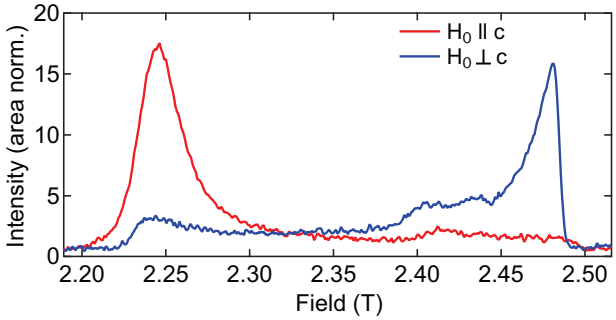

FIG. 1. The ^{195}Pt NMR field swept aligned powder spectra for $\mathbf{H}_0 \parallel \hat{c}$ (red) and $\mathbf{H}_0 \perp \hat{c}$ (blue) normalized by the spectral area taken at a carrier frequency of $\omega_0 \approx 23$ MHz, at a temperature $T = 1.8$ K. The U_2PtC_2 aligned powder spectra show an angular dependence consistent with an anisotropic NMR shift and successful alignment.

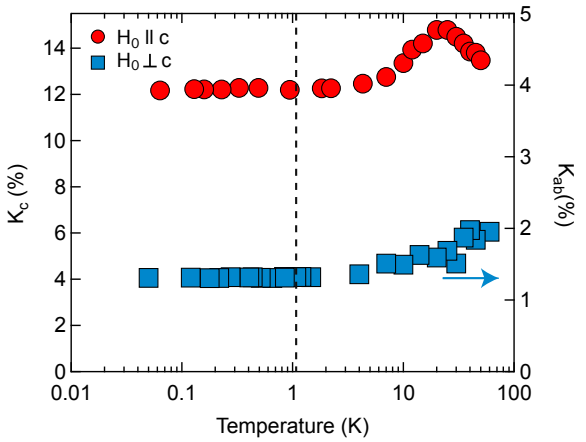

FIG. 2. The NMR shift in both the normal and superconducting states for $\mathbf{H}_0 \parallel \hat{c}$ and $\mathbf{H}_0 \perp \hat{c}$. In the normal state, the shifts for both orientations follow the bulk susceptibility down to a characteristic temperature $T^* = 25$ K. At temperatures $T^* > T > T_c$ the shift deviates from the bulk susceptibility, and in the superconducting state, $T_c(H_0) \approx 1.1$K, the shift becomes temperature independent.

size of the oriented powder was smaller than the rf penetration depth which should significantly reduce the eddy current heating of the NMR pulses. The sample used for NMR had a U_2PtC_2 mass of $m \approx 70$ mg. The ^{195}Pt NMR spectra were taken by the field sweep method, at fixed resonant frequency, using a typical $\pi/2 - \tau - \pi$ Hahn echo pulse sequence. ^{195}Pt spin-lattice relaxation time (T_1) measurements were taken by an inversion recovery sequence at the peak of the spectrum for both orientations. AC-susceptibility measurements were taken *in situ* by recording the detuning of the NMR resonant circuit as a function of magnetic field and temperature, from which H_{c2} and T_c were deduced respectively.

With the external field along the alignment axis, $\mathbf{H}_0 \parallel \hat{c}$, and perpendicular to the alignment axis, $\mathbf{H}_0 \perp \hat{c}$, at a carrier frequency $\omega_0 \approx 23$ MHz, there are well defined peaks for each orientation indicating successful alignment, as shown in Fig. 1. There are minor components with small spectral weight which retain a powder like pattern indicating a small fraction of misaligned crystallites. There are also small features near the peak for $\mathbf{H}_0 \perp \hat{c}$ that are orientation independent, and which may be associated with a secondary phase. Despite these slight imperfections in the spectra, NMR is selective in that measurements of the shift, K, or T_1 can be made at the peak of the spectrum for each orientation and, therefore, are independent of misaligned or impurity components.

For a field swept spectrum, the NMR shift, K, can be expressed as the resonance field relative to that expected for the bare gyromagnetic ratio of the nucleus, $^{195}\gamma/2\pi$= 9.171 MHz/T, at fixed frequency ω_0, as $K = \frac{\omega_0/\gamma - H_{res}}{H_{res}}$, where H_{res} is the resonant field of maximum spectral intensity. The shift is the sum of components such that $K = K_s(T) + K_o$, where $K_s = A\chi_s(T)$ is the spin shift equal to the hyperfine coupling constant A times the temperature-dependent electronic spin susceptibility at the Fermi surface $\chi_s(T)$, and K_o is the orbital shift which is proportional to the temperature independent Van Vleck susceptibility. As shown in Fig. 2, in the normal state, the shift for $\mathbf{H}_0 \parallel \hat{c}$ increases from $T = 50$ K down to a characteristic temperature $T^* = 25$ K, below which it decreases down to T_c. For $\mathbf{H}_0 \perp \hat{c}$, the shift monotonically decreases from high temperature down to T_c. For both field directions, there is no detectable change in the spectrum upon cooling below T_c.

By plotting $K(T)$ vs the bulk susceptibility $\chi(T)$, Fig. 3, with temperature as an implicit parameter, A and K_o can be found by a linear fit, as the slope and the y-intercept respectively. Here, the $K - \chi$ plot deviates from linearity for $T < T^* = 25$ K for both orientations. This Knight shift anomaly is a common feature among the heavy fermion materials [14]. Using data from the temperature region where $K \propto \chi$, we find A_c =101.2 $\pm$ 6.9 kOe/μ_B and $K_{o,c} = 3.64 \pm 0.72$ % for $\mathbf{H}_0 \parallel \hat{c}$, while for $\mathbf{H}_0 \perp \hat{c}$, $A_{ab} = -38.9 \pm 14.0$ kOe/μ_B and $K_{o,ab} = 4.46 \pm 0.97$ %.

In the SC state, for a singlet superconductor in the clean low-field limit, K_s should decrease below T_c down to the value of K_o as $T \to 0$ K. For U_2PtC_2, below T_c and along both orientations, K_s is temperature independent, Fig. 2. However, it is important to compare the temperature independence of the measured shift to the expected temperature dependent behavior of a singlet superconductor. By considering the total shift K and the orbital

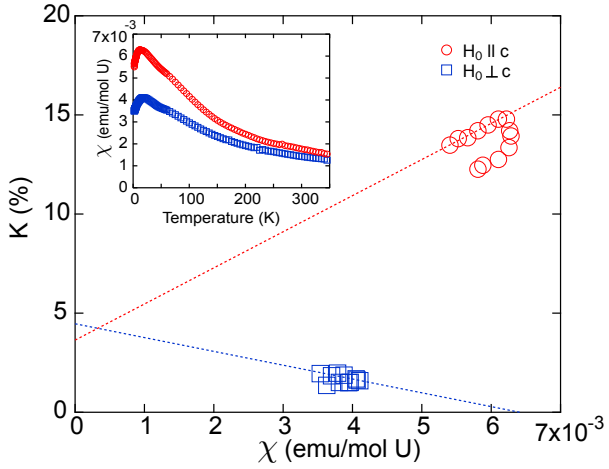

FIG. 3. The K-χ plot for both $\mathbf{H}_0 \parallel \hat{c}$ and $\mathbf{H}_0 \perp \hat{c}$. (Inset) The bulk susceptibility measured by SQUID magnetometry for both orientations. χ was determined from the difference in magnetization measured in fields of 4 and 5T.

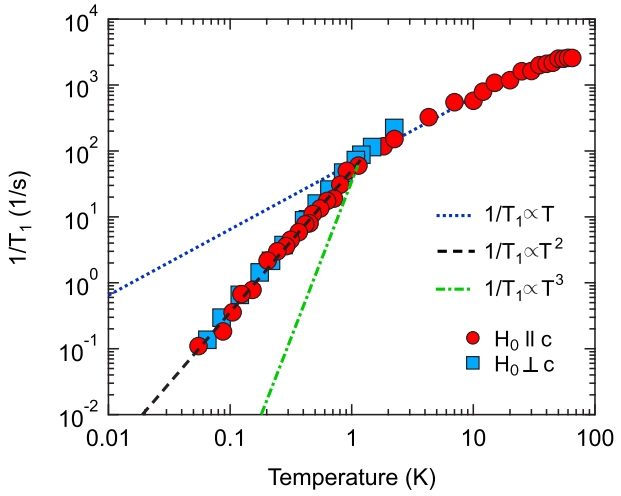

FIG. 4. The spin lattice relaxation rate in the normal and superconducting states for $\mathbf{H}_0 \parallel \hat{c}$ (red, circles), and in the superconducting state for $\mathbf{H}_0 \perp \hat{c}$ (blue, squares). Dashed lines indicate power law temperature dependences.

shift K_o found from the normal state, the magnitude of the spin shifts in the SC state are $K_{s,c}(T \leq T_c) = 8.63$ % and $K_{s,ab}(T \leq T_c) = -3.15$ %. These expected values of K_s are much greater than the linewidth of the spectra accounting for an uncertainty of less than 0.2 %. Furthermore, this uncertainty is greater than the shift expected due to magnetic shielding or the linewidth broadening due to the vortex state, but much less than K_s. The temperature independence of the spin component of the shift below T_c is a strong indication of an equal spin-pairing, spin-triplet state for which the susceptibility is expected not to change below T_c. Furthermore, the absence of temperature dependence in the superconducting state along both directions implies that the orientation of the equal spin-pairing state is not locked to a single crystal axis, rather it is free to rotate, indicating a minimal effect of spin-orbit coupling [15].

In principle, it is possible that strong spin-orbit scattering could suppress the temperature dependence of the spin shift [16] as $K_{sc}/K_{normal} = 1 - 2l/\pi\xi_0$ for $l < \xi_0$ in the strong scattering limit, where l is the electron mean free path and ξ_0 is the Ginzburg-Landau (GL) coherence length. However, for a U_2PtC_2 sample with $\rho_0 = 10$ $\mu\Omega$cm, $l = 580$ Å[6]. The upper critical field, determined from the AC-susceptibility as described below, gives $\xi_0 = 57$ Å. Thus, we conclude that, since $\xi_0 \ll l$, our U_2PtC_2 sample is in the clean limit and spin-orbit scattering cannot account for the temperature independence of K_s in the SC state. Additionally, to assess the effect of rf-heating due to NMR pulses, spectra were measured as a function of transmitted power attenuation over three decades of power at $T = 200$ mK. The shift for both orientations was found to be independent of power; thus, we conclude that the temperature-independent K_s is not due to heating the sample to temperatures $T \gtrsim T_c$.

Now we turn to the spin-lattice relaxation rate measurements, $1/T_1$, which probe the imaginary component of the q-dependent dynamic susceptibility, $1/T_1 \propto \sum_q \chi''(q, \omega_0)$. In the high temperature regime, $T > 40$ K, for $\mathbf{H}_0 \parallel \hat{c}$, $1/T_1$ approaches a temperature independent value consistent with local moment behavior [17]. At temperatures $T_c < T < 40$ K, $1/T_1$ is linear with temperature, so called Korringa behavior, which is expected of a heavy Fermi liquid. The modified Korringa law is given by $T_1 T K_s^2 \equiv S\mathcal{K}(\alpha)^{-1}$, where S is the Korringa constant defined as $S = \hbar\gamma_e^2/4\pi\gamma_N^2 k_B$, and $\mathcal{K}(\alpha)$ is an enhancement factor which is equal to 1 for non-interacting electrons, greater than 1 for antiferromagnetic exchange correlations, and less than 1 for ferromagnetic correlations [18]. The Korringa relation should be taken as anisotropic, as evident from the anisotropy of the shifts, such that $T_{1,j} T K_{s,i}^2 \equiv S\mathcal{K}_i(\alpha)^{-1}$ where i is parallel or perpendicular to the crystal $\hat{c}$ direction and j are the directions perpendicular to i, such that $(1/T_1)_\parallel = (1/T_1)_{ab}$ and $(1/T_1)_\perp = 2(1/T_1)_{ab} - (1/T_1)_c$. For U_2PtC_2, we find that $\mathcal{K}_c(\alpha) = 0.076$ and $\mathcal{K}_{ab}(\alpha) = 0.39$ at $T = 2$ K suggesting a strong ferromagnetic exchange enhancement dominant in the $\hat{c}$ direction. It is useful to compare the value for $\mathcal{K}_c(\alpha)$ with the nearly ferromagnetic intermetallic $TiBe_2$ for which $\mathcal{K}(\alpha) = 0.032$ [19].

Additional evidence for ferromagnetic fluctuations comes from the Wilson ratio $\mathcal{R} = \frac{\pi^2 R}{3C}\frac{\chi(0)}{\gamma}$ where R is the ideal gas constant, C is the Curie constant, $\chi(0)$ is the low temperature susceptibility, and γ is the electronic specific heat coefficient. Using $\chi_c(T = 2\text{K}) = 5.6\text{x}10^{-3}$

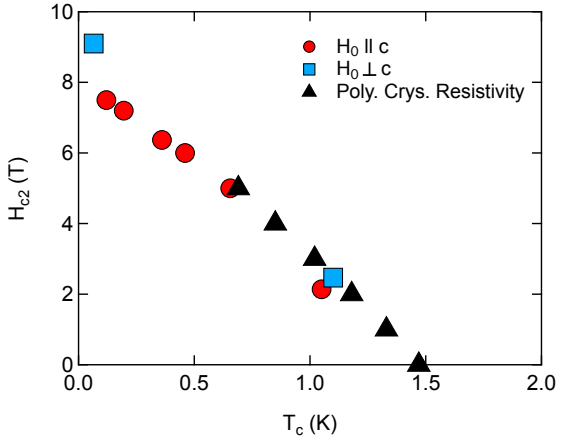

FIG. 5. The upper critical field, H_{c2} - superconducting transition temperature, T_c phase diagram. The orientationally dependent H_{c2} and T_c were measured *in situ* using the NMR coil and turning circuit (red, blue) while the polycrystalline T_c were measured as the midpoint of the resistivity superconducting transition(black, triangle).

emu/mol U, $\chi_{ab}(T = 2\text{K}) = 3.5\text{x}10^{-3}$ emu/mol U and $\gamma = 0.075$ J/mol U K^2 [5], we find that $\mathcal{R}_c \approx 3.3$, and $\mathcal{R}_{ab} \approx 2$, both larger than the expected $\mathcal{R} = 1$ for a heavy Fermi liquid and characteristic of ferromagnetic enhancement of the electronic interactions.

For $T < T_c$, the relaxation rate $1/T_1$ decreases as $1/T_1 \propto T^2$ along both orientations. This is an unusual power law as $1/T_1$ generally decreases below T_c as an exponential for a fully gapped Fermi surface, T^3 for a Fermi surface with line nodes, and T^5 for a Fermi surface with point nodes [20]. We note that the magnetization recovery did not follow a simple exponential law in the SC state, rather a stretched exponential behavior indicating a distribution of relaxation times [21], likely due to misaligned crystallites and the vortex state. The stretching factor became 0.5 at the lowest temperatures and increased with increasing temperature to an unstretched exponential at T_c. A T^2 temperature dependence in both field directions has been predicted theoretically by Ohmi and Machida for a non-unitary spin triplet superconducting state where the spin orientation is free to rotate with the field[22] and may provide an explanation for the peculiar power law. Furthermore, the salient features are that $1/T_1$ does not follow an exponential and there is no evidence of a Hebel-Slichter coherence peak [23] both features expected for a BCS superconductor. With these factors considered, it is likely that U_2PtC_2 does not have a fully gapped Fermi surface, rather a nodal structure, the details of which may become more clear from measurements on single crystals.

The upper critical field, H_{c2}, and T_c were measured on the aligned sample along both orientations by AC susceptibility, and $T_c(H)$ was also determined on polycrystalline samples from resistivity measurements, Fig. 5. The upper critical field from AC-susceptibility is $H_{c2}(T \rightarrow 0)$ = 7.8 (9.2) T for $\mathbf{H}_0 \parallel \hat{c}$ ($\mathbf{H}_0 \perp \hat{c}$), although it should be noted that due to the misaligned crystallites, evident from the spectra, the measured H_{c2} could have errors of approximately 10 %. The initial slope of the upper critical field found from the resistivity measurements is $dH_{c2}/dT_c \approx -10$ T/K. The zero-temperature orbital limiting field can be estimated in the weak coupling limit from the initial slope of H_{c2} by the Werthamer-Helfand-Hohenberg relation as $H_{c2,orb}(0) = 0.693(-dH_{c2}/dT_c)T_c$ [24, 25], which gives $H_{c2,orb}(0) = 10.2$ T for the polycrystalline sample, consistent with the measured values in both orientations. Thus, the GL coherence length can be estimated as $\xi_0 \equiv \sqrt{\Phi_0/2\pi H_{c2,orb}} = 57$ Å, where $\Phi_0 = 2.07\text{x}10^{-15}$ Tm^2 is the flux quantum.

The Pauli paramagnetic limiting field can be estimated from the Clogston-Chandrasekhar relation [26, 27] for spin-singlet pairing $H_{c2,p}(0) = 1.84T_c$ in units of Tesla, which gives a value of $H_{c2,p}(0) = 2.7$ T, i.e. $H_{c2,p} < H_{c2,orb} \approx H_{c2}$. Thus, Pauli limiting, generally associated with spin-singlet pairing, is absent because in U_2PtC_2 as there is no change in spin susceptibility as temperature decreases through T_c and, consequently, the Pauli limiting field goes to infinity. This indicates that the upper critical field is dominated by orbital effects and is additional supporting evidence of spin-triplet pairing.

In summary, for the first time ^{195}Pt NMR and H_{c2} have been measured on an aligned powder sample of the heavy-fermion superconductor U_2PtC_2. In the normal state, K deviates from the bulk χ at a temperature $T^* = 25$ K, typical of heavy-fermion materials. $1/T_1$ goes from a localized T-independent behavior at high temperatures to a Korringa T-linear behavior at lower temperatures. The modified Korringa law shows that U_2PtC_2 is ferromagnetically exchange enhanced, consistent with an enhanced Wilson ratio. In the superconducting state, K_s is temperature independent and unchanged relative to the normal state along both orientations, suggesting spin-triplet superconductivity with spin-orbit coupling too small to lock the equal spin pairs to the crystal lattice. Below T_c, $1/T_1$ follows a T^2 law likely indicative of a nodal gap structure. Further measurements on single crystals are necessary to clarify the orbital component of the superconducting pairs. From AC-susceptibility and resistivity we show that H_{c2} is consistent with the orbitally limiting field and exceeds the spin-singlet Pauli limiting field, which is a further indication of spin-triplet superconducting Cooper pairs. Collectively, these data are compatible with U_2PtC_2 being in a class of spin-triplet superconductors that show a temperature independent K_s below T_c which includes UPt_3 [28], Sr_2RuO_4 [29], UNi_2Al_3[30], and UCoGe [12].

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