Nonunitary Spin-Triplet Superconductivity in UPt$_3$: Evidence from ^{195}Pt Knight Shift Study

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^{195}Pt Knight shift (KS) measurements covering the superconducting multiple phases for major field (H) orientations have been carried out on the high-quality single crystal UPt$_3$. For $H > 5$ kOe, the KS does not change below the superconducting transition temperature T_c down to 28 mK, regardless of major crystal orientations, which provides evidence that the odd-parity superconductivity with the *parallel spin pairing* is realized. By contrast, the KS *decreases* below T_c for $H_b \parallel b$ axis and $H_b < 5$ kOe and for $H_c \parallel c$ axis and $H_c < 2.3$ kOe, whereas the KS for $H_a \parallel a$ axis is T independent across T_c down to $H_a \sim 1.764$ kOe. These novel findings entitle UPt$_3$ as the first spin-triplet odd-parity superconductor including a *nonunitary* pairing characterized by the two-component **d** vector like $\mathbf{d}_b + i\mathbf{d}_c$ at low T and low H. [S0031-9007(98)05803-7]

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Extensive experiments have provided convincing evidence for the unconventional nature of the superconducting (SC) state in UPt$_3$ [1]. Especially, the SC double transition and multiple phases (A, B, C phases) in the H (magnetic field)-T (temperature) plane point to internal degrees of freedom in a Cooper pair [2]. Several scenarios to explain the multiple phases in UPt$_3$ have been put forth. A controversy, however, lies in whether the nearly degenerate SC transition temperatures (T_{c1}, T_{c2}) arise either from the pseudospin part (spin scenario) [3,4] or the orbital part (orbital scenario) [5,6] of the Cooper pair. All scenarios have assumed that the degeneracy is broken by the antiferromagnetic (AF) ordering detected by the neutron scattering experiment [7].

A possibility of the odd parity of the Cooper pair was suggested from the NMR [8] and the μSR [9] experiments, which pointed to T-independent Pt and μ^+ Knight shifts below T_c. In our previous paper [10], we reported the precise ^{195}Pt Knight shift (KS) measurements on the high-quality single crystalline UPt$_3$ as follows: No NMR anomalies associated with the AF ordering were observed near and below $T_N = 5$ K, suggesting that it is not a static order but AF spin fluctuations. In the SC state, the KS above 5 kOe does not change across T_c down to $T = 28$ mK regardless of the field orientations and the SC multiple phases. These novel results have revealed that UPt$_3$ is the odd-parity superconductor with the *parallel spin pairing* and the pinning of the order parameter does not take place above ~5 kOe.

In the anisotropic superfluid state in ^{3}He, the triplet order parameter is described by $\hat{\Delta}(\mathbf{k}) = i[\mathbf{d}(\mathbf{k}) \cdot \sigma]\sigma_y$ in terms of the **d** vector [11]. The magnetic field forces to align the **d** vector perpendicularly to H and even stabilize the nonunitary triplet state, i.e., A_1 phase characterized by the $\mathbf{d}_x + i\mathbf{d}_y$ for $H \parallel z$ axis. By contrast, in heavy fermion superconductors (HFS), the spin-orbit coupling (SOC) felt by the Cooper pair have been believed to be strong enough to lock a **d** vector to the crystal lattice. In a quantitative level, the previous experiment clarified that the strength of the SOC is relatively weaker than ~5 kOe in a measure of the field. It was, however, kept in our mind that a **d** vector may be locked to the lattice at lower fields.

In spite of many experimental and theoretical efforts, it is still an underlying issue to identify possible spin-triplet states, e.g., **d** vectors corresponding to the multiple A, B, and C phases. In order to complete the understanding for the odd-parity pairing state in UPt$_3$, further accurate Knight shift experiments at low fields are repeatedly required on a high-quality single crystal.

In this Letter, we report further precise measurements of the ^{195}Pt Knight shift in the SC state down to the lowest field of ~1.764 kOe and temperature of 28 mK. Two single crystals with typical dimensions of $2 \times 2 \times 5$ mm^3 (#3s) and $1 \times 1 \times 4$ mm^3 (#4) with their lengths parallel to the hexagonal [0001] and $[1\bar{1}00]$ axes, respectively, were used. Hereafter, the hexagonal $[11\bar{2}0]$, $[1\bar{1}00]$, and [0001] axes are denoted as a, b, and c axes [see Fig. 5(d)], and field orientations, Knight shifts, and the components of **d** vector are denoted as H_i, K_i, and $\mathbf{d}_i$ with $i = a$, b, and c, respectively. We emphasize that the present samples are in a clean limit with the residual resistivity ratio of $RRR \sim 510$ and the transport mean free path of $l_{tr} \geq 2000$ Å [12]. Therefore, the *spin-orbit scattering* due to impurity was, in fact, ruled out [10].

Figures 1(a) and 1(b) show the T dependence of ^{195}Pt NMR spectra for $H_a \sim 1.764$ and $H_b \sim 1.943$ kOe, respectively. In the normal state, the full width at half maximum of the spectrum is as narrow as ~5.9 Oe being the narrowest to date in the HFS's. As seen in the figure, a peak in the spectrum shifts below T_c to a

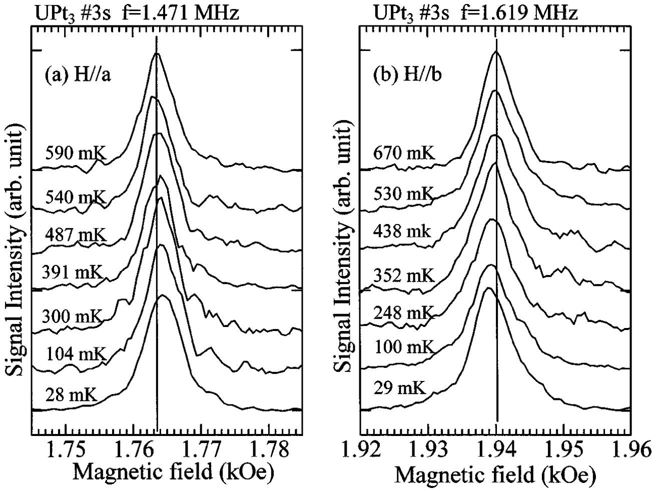

FIG. 1. T dependence of the ^{195}Pt NMR spectra for (a) $H_a \sim 1.764$ kOe at $f = 1.471$ MHz and (b) $H_b \sim 1.943$ kOe at $f = 1.619$ MHz.

high field by $\sim$1 Oe for H_a, whereas to a lower field by $\sim$1.8 Oe for H_b and H_c, respectively. Noting that the hyperfine coupling constant is negative irrespective of crystal orientations [10], it turns out that the shift for H_a is dominated by the SC diamagnetic field, $H_{\rm dia}$. Contrary to this, the significant decrease of the spin part in the KS is observed for H_b and H_c. Even at the lowest T and H, the obtained spectrum remains slightly asymmetric with an increase by $\sim$1.5 Oe in the linewidth, suggesting that the magnetic field penetrates uniformly.

Under $H_{c2} \sim 20$ kOe $\gg H \gg H_{c1} \sim 10$ Oe and a vortex spacing ($d \sim 1050$ Å at $H \sim 2$ kOe) extremely smaller than the London penetration depth ($\lambda >\sim 7000$–11 000 Å [9,13]), the square root of the second moment, $\sqrt{\Delta H^2}$, of the NMR spectrum, which is a good measure of the SC diamagnetic contribution, is estimated as $\sqrt{\Delta H^2} = (B/\sqrt{4\pi})(d/\lambda)[1 + (2\pi\lambda)^2]^{-1/2} \sim \phi_0/(\lambda^2\sqrt{16\pi^3}) \leq 1.9$ Oe by using $\lambda > 7000$ Å, where $\phi_0 = hc/2e$ is the flux quantum [14]. This is comparable with the increase by $\sim$1.5 Oe in the linewidth for H_a, H_b, and H_c at the lowest T and H. Furthermore, a direct calculation by using the relation of $H_{\rm dia} = -H_{c1}\ln(\beta e^{-1/2}d/\xi)/\ln\kappa$ [15] yields $H_{\rm dia} \sim -1.9$ Oe. Here we used the value of $H_{c1} \sim 1$ mT, $\beta = 0.381$ for the triangular lattice, $d \sim 1050$ Å, and $\kappa \sim 100$ [16]. These considerations allow us to estimate $H_{\rm dia}$ to be as small as ~ -1.5 Oe at respective lowest field from the increase in the linewidth below T_c.

Figures 2, 3, and 4 display the T dependence of the KS for H_a (K_a), H_b (K_b), and H_c (K_c), respectively. Here, the KS is defined by the first moment of each spectrum without any correction arising from the SC diamagnetic shift. Figure 5 indicates schematically the multiple phase diagram obtained from other measurements on the same single crystals [17] and the H and T region where the KS does decrease as mapped by the shadow area. The spin part in the KS decreases to zero at $T = 0$ and is unchanged across T_c in the case of $\mathbf{d} \parallel H$ and $\mathbf{d} \perp H$, respectively, in the analogy with the superfluid ^{3}He. To determine the spin structure in the Cooper pair, hence, enables us to identify respective $\mathbf{d}$ vectors in the multiple phases as follows:

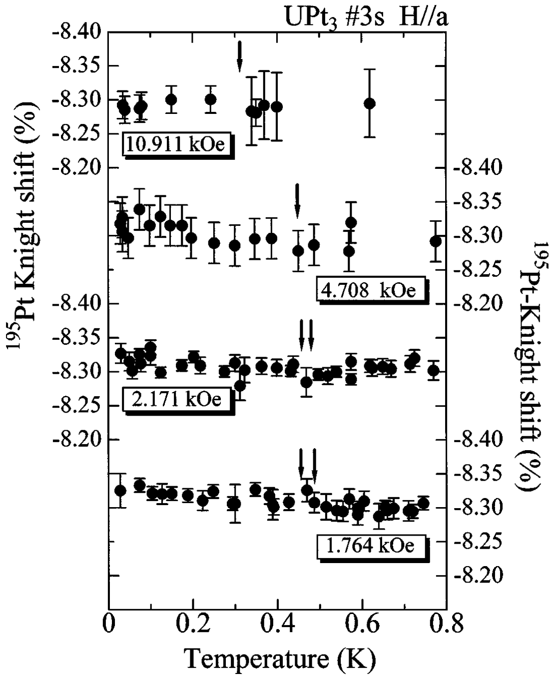

FIG. 2. T dependence of the ^{195}Pt K_a at the various magnetic fields for $H_a \parallel a$ axis. Arrows (↓) show T_{c1} and T_{c2}.

(1) K_a, K_b, and K_c do not change below T_c in the field range of 5–15.6 kOe regardless of crystal orientations. In the C phase for H_a and H_b and the B and C phases for H_c, the spin susceptibility due to the Cooper pair is the same as that in the normal state, namely, the $\mathbf{d}$ vector rotates so that $\mathbf{d} \perp H$ or it is kept as $\mathbf{d} \perp H$.

(2) $|K_b|$ decreases below T_{c1} for $H_b < 5$ kOe, but $|K_a|$ increases for $H_a < 5$ kOe by an amount comparable to $H_{\rm dia}$. The latter means that the spin part in K_a is almost unchanged across T_c for H_a. Since $\mathbf{d} \parallel b$ axis in the A and B phases, the Cooper pair spin vector is in the a-c plane perpendicular to the b axis.

(3) K_c is unchanged across T_{c1} for $H_c < 2.3$ kOe. This result and (2) mean that the spin vector in the A phase follows the field in the a-c plane perpendicular to the b axis. The A phase is hence characterized by the single component $\mathbf{d}_b$ vector.

(4) The decrease in $|K_c|$ occurs below T_{c2} for $H_c < 2.3$ kOe: $|K_c|$ decreases markedly by a slight field reduction for H_c from 2.299 to 2.141 kOe. This means that the spin vector rotates from the c axis to the a axis in the B phase in fields lower than $H_{c,\rm pin} \sim 2.3$ kOe. By incorporating that K_a is almost unchanged across T_c, whereas both $|K_b|$ and $|K_c|$ decrease, it is concluded that the Cooper pair spin vector is spontaneously pinned to the a axis at low T and H. It turns out that the B phase at low T and low H is a *nonunitary state* characterized by the two-component $\mathbf{d}$ vector whose relative phase is $\pi/2$, e.g., $\mathbf{d}_b + i\mathbf{d}_c$ locked to the b and c axes.

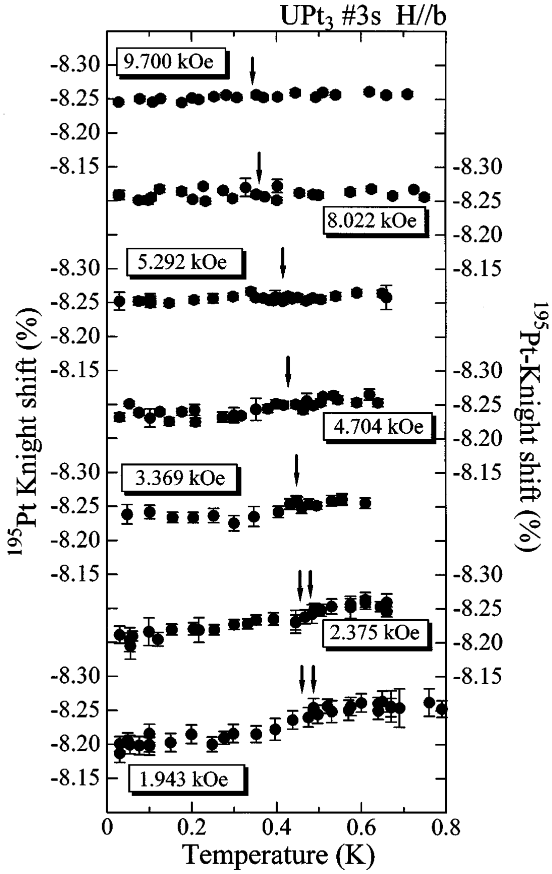

FIG. 3. T dependence of the ^{195}Pt K_b at the various magnetic fields for $H_b \parallel b$ axis. Arrows (↓) show T_{c1} and T_{c2}.

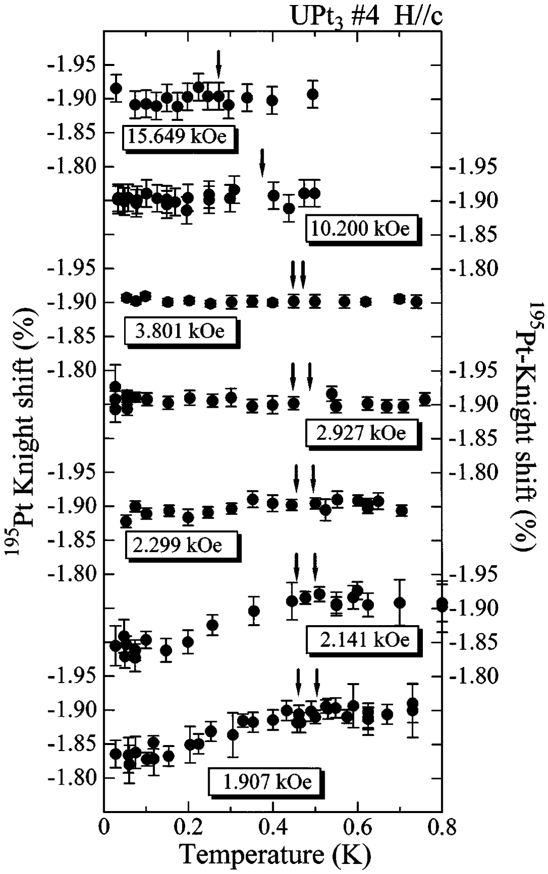

FIG. 4. T dependence of the ^{195}Pt K_c at various magnetic fields for $H_c \parallel c$ axis. Arrows (↓) show T_{c1} and T_{c2}.

(5) As a result, it is reasonable that the C phase possesses a single component $\mathbf{d}_c$ ($\mathbf{d}_a$) vector for $H_{a,b}$ (H_c).

(6) As indicated in Fig. 5(b) for H_b, the decrease in $|K_b|$ almost tunes to the $C \longrightarrow B$ transition in the H variation and the normal to A phase transition in the T variation.

(7) As in Fig. 5(c) for H_c, although the decrease in $|K_c|$ tunes qualitatively to the $A \longrightarrow B$ transition in the T variation, but it does not to the $C \longrightarrow B$ transition $[H_c(CB)]$ in the H variation, taking place at $H_{c,\mathrm{pin}} \sim 2.3$ kOe much lower than $H_c(CB)$.

Contributing insights are obtained from a comparison of the above rich variety of the Knight shift results with the proposed scenarios for the order parameter symmetry in UPt$_3$ so far as follows:

(A) The spin-singlet E_{1g} scenario [6] is ruled out because it predicts an isotropic decrease in the KS which should be independent of the field.

(B) The two dimensional E_{1u} [4] and E_{2u} [5] scenarios for the strong SOC are excluded because the KS in E_{1u} and E_{2u} is predicted to decrease below T_c in the basal plane (in both the a and b axes) and only along the c axis, respectively. From the results of (1) and (7), since the vector rotation from the $\mathbf{d}_c$ to the $\mathbf{d}_a$ in the B phase takes place for $H_c > H_{c,\mathrm{pin}} \sim 2.3$ kOe which is a relatively weak field, any scenario based on the strong SOC fails to interpret the present experiment.

(C) The first proposed spin scenario [3] for the weak SOC seems to be consistent with the result for $H > 5$ kOe [8–10], but is not in accord with the present results below 5 kOe since no decrease in the KS was predicted along any crystal direction.

Ohmi and Machida have recently put forward a renewed spin scenario, which is successful in assigning the $\mathbf{d}$ vector structure to describe the multiple phases of superconductivity and in identifying the B phase as the *nonunitary spin-triplet* state at low T and low H [18]. Furthermore, they have pointed out that the cause that the $\mathbf{d}$ vector in the A and B phases is locked to the b axis is not due to the SOC, but to the symmetry breaking field associated with the quasielastic AF fluctuations with the staggered polarization vector, $\mathbf{M}_Q$ along the b axis. In order to match the Knight shift results for H_c to the phase diagram, a phenomenological pinning field, $H_{c,\mathrm{pin}}$ along H_c is taken into account so as to reproduce the rotation of the $\mathbf{d}_c$ vector found experimentally. A possible explanation for a microscopic origin of the small pinning field along $H_{c,\mathrm{pin}} \sim 2.3$ kOe should, however, be addressed in future theoretical works.

Finally, we comment on the quasiparticle spin susceptibility. The fraction of the decrease in the KS's, δK_b,

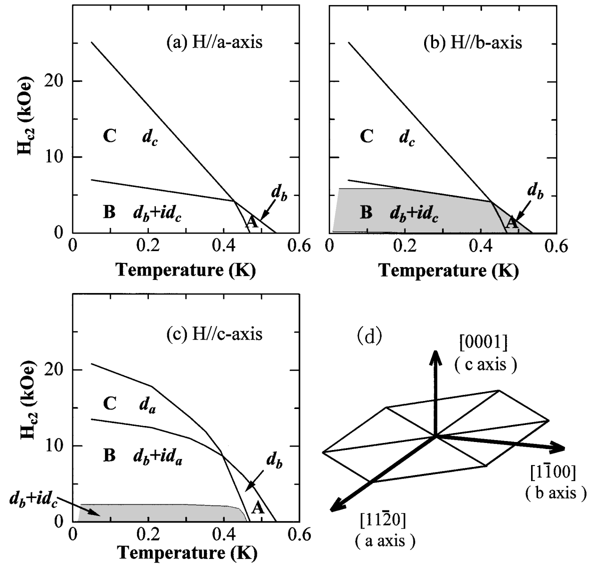

FIG. 5. (a), (b), and (c) indicate respective superconducting multiple phase diagram in UPt$_3$ for H_a, H_b, and H_c obtained from other measurements on the same single crystals. The shadow areas show H and T regions where the KS does decrease. Notice that these areas are not new phases associated with other SC transitions. (d) shows the definition of the hexagonal crystal axes in the present experiment.

and δK_c are nearly isotropic with $\sim$0.07% and $\sim$0.08%, respectively, at the lowest H and T. When $H_{\rm dia} \sim -1.5$ Oe ($\sim -0.08\%$) is taken into account, the spin susceptibility χ_s as $\delta\chi = \chi_s$ is estimated to be ($\sim$0.99 and $\sim$1.26) $\times 10^{-4}$ emu/mole for respective directions perpendicular and parallel to the c axis from the relation of $\delta K = A\delta\chi/(N_A\mu_B)$ with the hyperfine coupling constants of $A_\perp \sim -84.9$ and $A_c \sim -70.8$ kOe/μ_B [10]. These values are by an order of magnitude smaller than the values of measured susceptibility. This anomalously small (pseudo) spin part in the quasiparticle susceptibility may be relevant to the realization of the *nonunitary* spin-triplet pairing in which the *ferromagnetic* spin polarization is spontaneously induced to the a axis.

In conclusion, a complete set of the ^{195}Pt Knight shift data on the high-quality single crystal UPt$_3$ have identified the spin structure of the Cooper pair. From the detailed dependences of the Knight shift on the temperature, magnetic field, and crystal orientation, it has been established that the A and B phases belong to a class of *unitary* and *nonunitary* triplet pairing states characterized by the $\mathbf{d}_b$ and $\mathbf{d}_b + i\mathbf{d}_c$ vectors, respectively, and the C phase may be the *unitary* state described as the $\mathbf{d}_c$ ($\mathbf{d}_a$) vector for $H_{a,b}$ (H_c). The vector rotation from the $\mathbf{d}_c$ to the $\mathbf{d}_a$ for $H_c > 2.3$ kOe has experimentally verified that the spin-orbit coupling felt by the Cooper pair is weak. UPt$_3$ is thus concluded to be the first *spin-triplet odd-parity superconductor* in charged many body systems.

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