Odd-Parity Superconductivity with Parallel Spin Pairing in UPt_3: Evidence from ^{195}Pt Knight Shift Study

H. Tou,[1] Y. Kitaoka,[1] K. Asayama,[1] N. Kimura,[2] Y. Ōnuki,[2,3] E. Yamamoto,[3] and K. Maezawa[4]
[1]*Department of Material Physics, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan*
[2]*Department of Physics, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan*
[3]*Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11, Japan*
[4]*Faculty of Engineering, Toyama Prefectural University, Toyama 939-03, Japan*
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The temperature dependence of the ^{195}Pt Knight shift, K, for the high quality single crystal UPt_3 has been measured down to $T = 28$ mK in applied magnetic fields parallel and perpendicular to the hexagonal c axis. No change of K's has been found across the superconducting transition temperature T_c down to 28 mK regardless of the crystal directions and independent of the superconducting multiphases. It is demonstrated that UPt_3 is the odd-parity superconductor with *parallel spin pairing* following the direction of the magnetic field in a range of 4.4–15.6 kOe without an appreciable pinning of the order parameter to the lattice. [S0031-9007(96)00830-7]

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Extensive experimental efforts have been devoted to elucidate the characteristic feature of the unconventional superconductivity in UPt_3. Especially, much interest is drawn to a rich variety of its superconducting natures exhibiting the multicomponent H (magnetic field) and T (temperature) phase diagram. Three superconducting phases denoted as A, B, and C phases meet each other at a tetracritical point [see Figs. 3(a) and 4(a)] [1–3]. Furthermore, a power law behavior for the low temperature thermodynamics such as ultrasound attenuation [4], NMR relaxation rate [5], specific heat [6,7], and penetration depth [8], suggested an unusual superconducting order parameter (OP) with the energy gap vanishing on the Fermi surface. A possibility of the odd-parity of the Cooper pairing was suggested from the NMR [5] and the muon spin rotation (μSR) [9] experiments, which pointed to an invariance of the Pt and μ^+ Knight shifts below T_c. It cannot, however, be ruled out *completely* that the invariance of the Pt Knight shift for the polycrystal sample [5] is not associated with the odd-parity, but with the *spin-orbit scattering* [10] due to impurities and/or defects. Although the invariance of the μ^+ Knight shift on the single crystal UPt_3 in a clean limit was instructive, the result only along the c axis was not sufficient to get a decisive insight into the OP. This is because χ_s would be reduced along a certain direction below T_c even for an odd-parity superconductor if the OP was pinned to the lattice owing to the strong spin-orbit (SO) coupling [11]. Actually, various phenomenological scenarios interpreting the superconducting multiphase diagram have predicted the decrease of χ_s either in the basal plane [12] or along the c axis [13] for the strong SO coupling, whereas no decrease was predicted along any crystal direction for the weak SO coupling [14]. A crucial experiment to identify a possible OP representation is thus to measure the T dependence of χ_s along *all crystal directions*.

Absence of the precise measurement of the Knight shift on the high quality UPt_3 *free* from the *spin-orbit scattering* [10] has allowed another room for the two-component *d-wave* model based on accidentally degenerate two independent OP with even parity, e.g., of the A_{1g} and the E_{1g} representations [15,16]. In the *d-wave* scenarios, it is evident that χ_s should be reduced below T_c in the clean limit due to the singlet nature of the OP.

In addition, another underlying issue is that the antiferromagnetic (AF) order with a small magnetic moment of $\mu_s = 0.02\mu_B/U$ below the Néel temperature $T_N = 5$ K is not yet fully established from other measurements, except for the neutron scattering experiment [17]. In fact, previous NMR measurements [5,18,19], as well as macroscopic ones, failed to prove the AF order. Nevertheless the symmetry breaking field (SBF) associated with the AF order is crucial for the odd-parity scenarios [12–14] in explaining the superconducting multiphase diagram by lifting the degeneracy of the unconventional OP with multicomponents.

In spite of many experimental and theoretical efforts, an identification for the OP remains unresolved yet. In order to unravel unconventional natures of the superconducting state in UPt_3 and its relation to the presence of the AF order, further experiments are repeatedly required on a high quality single crystal.

In this Letter, we report the first precise measurements in the superconducting state of the ^{195}Pt Knight shift on high quality single crystals with the hexagonal c axis parallel and perpendicular to the magnetic field. Detailed preparation techniques for single crystal ingots of UPt_3 were reported elsewhere [20]. The double peaks structure corresponding to A and B phases was confirmed to occur at $T_{c1} \sim 0.58$ K and $T_{c2} \sim 0.53$ K, respectively, from the specific heat experiment. The residual resistivity ratio of RRR ~ 510 and the transport mean free path of $l_{\rm tr} \geq 2000$ Å from the de Hass–van Alphen (dHvA) experiment ensure that the sample quality is sufficiently

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good [20]. Two single crystals with typical dimensions of $2 \times 2 \times 5$ and $1 \times 1 \times 4\ \mathrm{mm}^3$ with their lengths parallel to the hexagonal [0001] and $[10\bar{1}0]$ axes, respectively, were employed [20]. The NMR measurement was carried out by using a conventional phase coherent type of home-made pulsed spectrometer and a ^{3}He-^{4}He dilution refrigerator with a solenoid type of superconducting magnet. The NMR spectrum was obtained by the Fourier transform technique of spin-echo signal. In the normal state, the surface region with a thickness as small as $\sim 2\ \mu$m is available for the observation of NMR signal, which is enough to extract a bulk effect. Temperature was monitored by a RuO_2 thermometer calibrated by the NMR intensity and the T_1 measurement of the high quality platinum powder.

Figures 1(a) and 1(b) show the ^{195}Pt-NMR spectra at $T = 1$ K and 28 mK, respectively, and $\simeq$4.7 kOe for $H \parallel [11\bar{2}0]$ (hereafter denoted as H_a). The full width at half maximum (FWHM) of the spectrum of $\sim$9.5 Oe is very narrow, guaranteeing the high quality of the single crystal from a microscopic viewpoint. Eventually, the Knight shift was measured very precisely with typical experimental errors of $\pm 0.02\%$ and $\pm 0.03\%$ for $H_a \simeq 11$ and $\simeq$4.5 kOe, respectively. In fact, a negatively *increased* small shift of $\sim$4.2 Oe was well resolved below T_c as seen from the spectrum at 28 mK, associated with the superconducting diamagnetic shielding current. The diamagnetic shift was compatible with the estimation of $\sim$6.4 Oe from the relation of $H_{\mathrm{dia}} = H_{c1} \ln(H_{c2}/H)/\ln \kappa$, with the value of $H_{c1} \sim 2$ mT, $H_{c2} \sim 2.2$ T, $H \sim 0.47$ T, and $\kappa \sim 100$. All these results, especially no appreciable broadening of the FWHM at 0.47 T well below T_c, ensure that the magnetic field penetrates rather uniformly in the superconducting state, since the London penetration depth ($\lambda > 7000$ Å) is extremely larger than a mean distance, d among vortices ($d \sim 690$, 490, and 400 Å at $H \sim 5$, 10, and 15 kOe, respectively), and a possible fraction of the normal state within vortex cores amounts to only $(\xi/d)^2 \sim (3\text{–}8)\%$ of the whole due to the smaller coherence length ($\xi \simeq 100\text{–}120$ Å) than d.

In Fig. 2, the temperature dependences of K^a and K^c for H_a and $H \parallel [0001]$ (hereafter denoted as H_c), respectively, are displayed by solid and open circles together with the data (+) reported previously on oriented grains for H_a [5]. The T dependences of $K^a(T)$ and $K^c(T)$ measured up to 11 and 50 K (see the inset of Fig. 2), respectively, were consistent with the data reported so far [5,19]. In a quasiparticle band picture, the Knight shift is composed of two contributions as $K^{a,c}(T) = K_s^{a,c}(T) + K_{\mathrm{VV}}^{a,c}$. $K_s(T)$ is the spin part of the Knight shift and related to the T dependent susceptibility, $\chi_s(T)$ as $K_s^{a,c}(T) = A_{\mathrm{hf}}^{a,c}\chi_s^{a,c}(T)/N_A\mu_B$, which is generated by the pseudospin polarization of quasiparticle bands near the Fermi level, i.e., the intraband effect. Here $A_{\mathrm{hf}}^{a,c}$ is the hyperfine coupling constant, N_A is Avogadro's number, and μ_B the Bohr magneton. $K_{\mathrm{VV}}^{a,c}$ consists of the T independent *Van Vleck* susceptibility originating mainly from the mixing effect with other bands distributed over a higher energy region than the Fermi level, i.e., the interband effect, and of the orbital contribution of Pt $5d$ electrons. It is evident from their marked T dependences that both $K^a(T)$ and $K^c(T)$ are dominated by the spin contribution. In fact, both $K^a(T)$ and $K^c(T)$ have been confirmed to be well scaled to the susceptibility measured [21] in the applied magnetic field parallel to the hexagonal c axis, $\chi_{\mathrm{obs}}^c(T)$, and to the basal plane, $\chi_{\mathrm{obs}}^a(T)$. The hyperfine coupling constants were estimated as $A_{\mathrm{hf}}^a \simeq -84.9$ and $A_{\mathrm{hf}}^c \simeq -70.8 kOe/\mu_B$. In f-electron systems with the strong intra-atomic SO coupling, the general procedure to separate the T independent part of the shift from the measured one is not yet established as in $3d$-electron

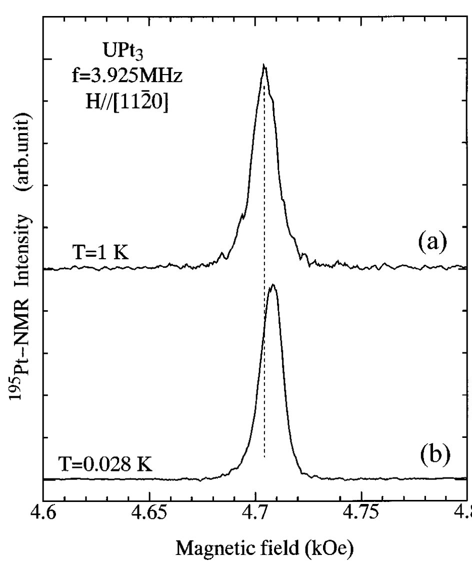

FIG. 1. ^{195}Pt-NMR spectra at (a) 1 K and (b) 28 mK for $H \parallel [11\bar{2}0]$ (H_a) at $f = 3.925$ MHz ($H \simeq 4.7$ kOe).

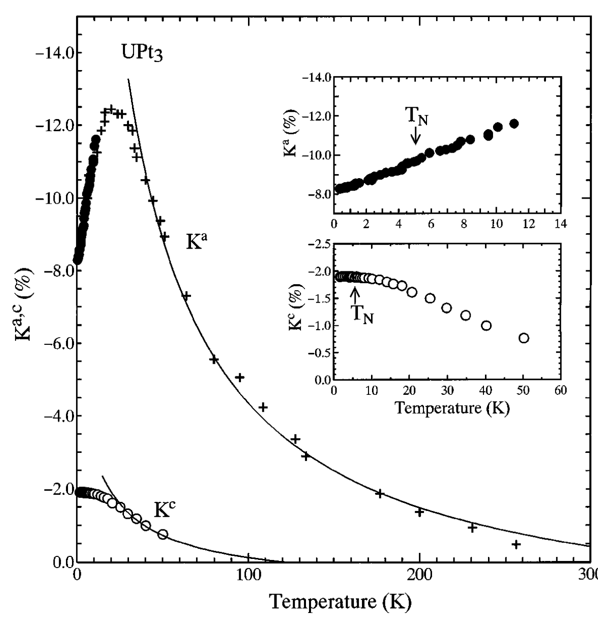

FIG. 2. Temperature dependences of ^{195}Pt K for $H \parallel [11\bar{2}0]$ (H_a) and $H \parallel [0001]$ (H_c), and of the data (+) on oriented grains reported previously [5].

systems. Here, in order to assign a possible value of K_s in UPt_3, we try to estimate K_{VV} tentatively. Above the effective Fermi temperature, $T_F^* \sim 20$ K for UPt_3 estimated from a large γ value of 420 mJ/mole K^2, $K_s(T)$ due to the pseudospin polarization is anticipated to exhibit the Curie-Weiss-like behavior approximately, whereas the interband effect may give rise to a minimum value, K_{VV}, as far as the heavy-fermion band picture is maintained. Accordingly, the measured shift is described by $K_{\rm obs}^{a,c}(T) = C^{a,c}/(T + \theta^{a,c}) + K_{VV}^{a,c}$. Actually, as indicated by the solid lines in Fig. 2, the Knight shift data above 30 K can be fitted by the above formula with $\theta^a = 19.5$ and $K_{VV}^a \sim +1.95\%$, and $\theta^c = 15$ and $K_{VV}^c \sim +0.7\%$. It should be noted that K_{VV} is positive, and hence the absolute value for the spin part is larger than the measured one and estimated as $K_s^a(T_c) \sim -10.25\%$ and $K_s^c(T_c) \sim -2.61\%$ from $K_s^{a,c}(T_c) = K_{\rm obs}^{a,c}(T_c) - K_{VV}^{a,c}$.

The precise measurement of the Knight shifts provides crucial clues to identify the AF order below 5 K. In $U(Pt_{0.95}Pd_{0.05})_3$, which orders antiferromagnetically below 5 K with the same spin arrangement as in UPt_3 [17], it was shown that the staggered moment of $\mu_s = 0.6\mu_B$ produced the internal hyperfine field, $H_{\rm int}$ of 45 kOe/μ_B at Pt nuclei from the Pt NMR experiment in the zero field [22]. By scaling, the staggered moment of $0.02\mu_B$ in UPt_3 is estimated to induce the internal field of $H_{\rm int} \simeq 1.5$ kOe at Pt nuclei below $T_N = 5$ K. However, the T dependences of the Knight shift and the FWHM do not reveal any anomaly around $T_N = 5$ K, excluding a static long-range AF ordering.

In Figs. 3 and 4, the respective T dependences of the Knight shifts for H_a and H_c are displayed together with the schematic phase diagram in UPt_3 for each crystal direction. Figures 3(b) and 4(b) indicate the Knight shifts for the C phase at $H_a \simeq 11$ kOe and $H_c \simeq 15.6$ kOe, respectively, while Figs. 3(c) and 4(c) are for the B phase at $H_a \simeq 4.7$ kOe and $H_c \simeq 4.4$ kOe and $\simeq$10 kOe, respectively. As clearly seen in the figures, the Knight shifts do not decrease below T_c regardless of the crystal directions and of the superconducting B and C phases.

Generally for even-parity superconductors in the clean limit, the spin susceptibility, χ_s, below T_c is expressed by $\chi_s = -4\mu_B^2 \int_0^\infty N_s(E)[\partial f(E)/\partial E]dE$ [23], where $N_s(E)$ and $f(E)$ are the density of states at the Fermi level in the superconducting state and the Fermi distribution function. For the *d-wave* scenarios with either E_{1g} or A_{1g} representation, $\chi_s(T)$ should decrease to zero below T_c in the clean limit as shown by solid lines in Fig. 5, where $\Delta(\theta) = 2\Delta_0 \sin\theta \cos\theta$ for E_{1g} is assumed with $2\Delta_0 = 3.5k_BT_c$.

Evidently, the invariance of the spin shift below T_c requires the OP with either an odd-parity with *parallel spin pairing* keeping the same magnitude of the spin susceptibility as in the normal state or an even-parity affected by impurity-induced *spin-orbit scattering*. For the latter case, the spin-orbit scattering mean free path, l_{SO}, is estimated to be less than $\sim$10 Å from the formula [10] of $K_s/K_n \simeq 1 - 2l_{SO}/\pi\xi_0$ for $l_{SO} \ll \xi_0$ by using

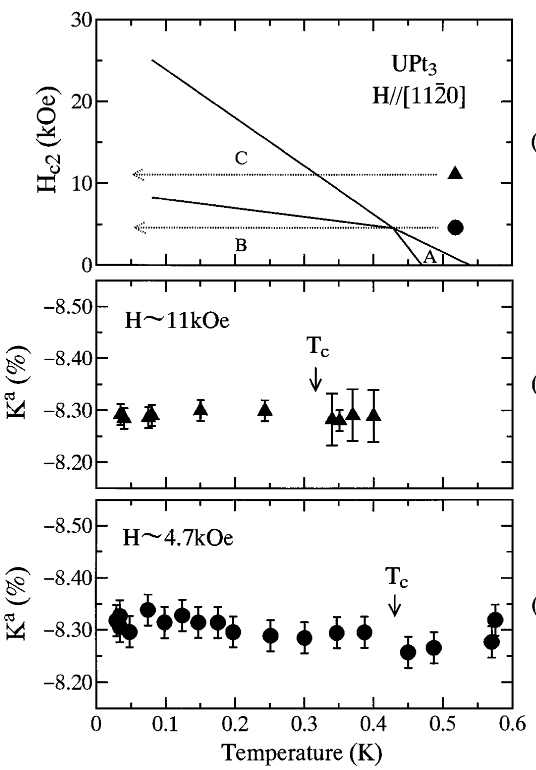

FIG. 3. (a) Schematic H-T phase diagram for $H \parallel [11\bar{2}0]$ (H_a). Temperature dependences of ^{195}Pt K for H_a at (b) $\simeq$11 kOe (C phase) and (c) $\simeq$4.7 kOe (B phase) below and near T_c.

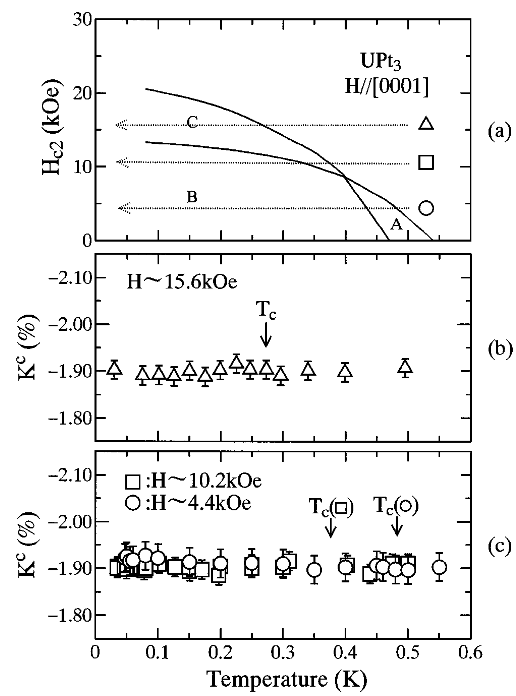

FIG. 4. (a) Schematic H-T phase diagram for $H \parallel [0001]$ (H_c). Temperature dependences of ^{195}Pt K for H_c at (b) $\simeq$15.6 kOe (C phase) and (c) $\simeq$10.2 kOe (B phase) and $\simeq$4.4 kOe (A and B phases) below and near T_c.

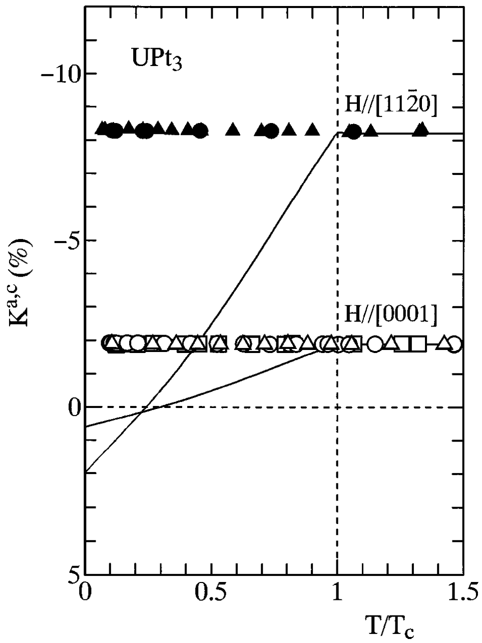

FIG. 5. Temperature dependences of ^{195}Pt K against temperature normalized by T_c with a full scale for the shift. Solid lines indicate the calculations in a clean limit on the assumption of the even-parity d-wave (E_{1g}) model with parameters of $2\Delta_0 = 3.5k_BT_c$ and $\Delta(\theta) = 2\Delta_0 \sin\theta\cos\theta$.

the coherence length, $\xi_0 \sim 100$ Å and the reduction of the Knight shift, $K_s/K_n \simeq 0.96$, assuming that the reduction of the shift would occur within the experimental error of $\pm 0.02\%$. This is, however, inconsistent with a criterion of $l_{SO} \gg l_{tr}$ for the above mechanism because l_{tr} is larger than 2000 Å from the dHvA experiment [20]. We note that the mean free path at low fields is longer than at high fields since an additional scattering mechanism such as the Kondo channel is not anticipated to emerge at low fields because of very low residual resistivities and *positive* magnetoresistances [20]. The *spin-orbit scattering* mechanism based on the *d-wave* scenarios fails to interpret any change of the Knight shifts.

Therefore, an odd-parity superconducting state in the clean limit is most promising in UPt_3. In the two-dimensional E_{1u} [12] and E_{2u} [13] scenarios for the strong SO coupling, χ_s^a in the basal plane and χ_s^c along the c axis were predicted to decrease below T_c, respectively. These two-dimensional scenarios contradict the present results of the Knight shifts below T_c.

In conclusion, the precise Pt Knight shift measurements on the high quality single crystal UPt_3 have unraveled several underlying issues concerning the magnetic and the superconducting characteristics. No NMR anomalies associated with the AF ordering have been observed near or below $T_N = 5$ K, suggesting that the static long-range ordering is ruled out. In the superconducting state, the ^{195}Pt Knight shifts do not decrease at all within experimental error of $\pm 0.02\%$ regardless of the crystal directions and of the superconducting multiphases. These novel results have eliminated the possibilities of both the even-parity superconductor and the odd-parity superconductor with the strong SO coupling. As a result, the unconventional superconductivity of UPt_3 is characterized by the odd-parity with the *parallel spin pairing* keeping the same anisotropy of the spin susceptibility as in the normal state and following the direction of the magnetic field in a range of 4.4–15.6 kOe without an appreciable pinning to the lattice. The present Pt Knight shift study has provided an important clue that the SO coupling for the *pair* is not so strong as to lock the pseudospin degree of freedom in the crystal direction. In this context, the one-dimensional scenario incorporating the SBF for the weak SO coupling [14] seems to be promising. However, since the presence of SBF comes into question from the μSR [24], the previous NMR [5,18,19] and the present NMR results which do not support any static long-range order below 5 K, it is required that the present phenomenological scenarios for UPt_3 are reconsidered by incorporating the novel characteristics of the *parallel spin pairing*.

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