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Spin-triplet superconductivity in $PrOs_4Sb_{12}$ probed by muon Knight shift

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We report a muon spin rotation study in single-crystalline samples of the heavy fermion superconductor $PrOs_4Sb_{12}$. The muon Knight shift is independent of temperature passing through T_c down to 20 mK at 3 and 17 kOe, indicating that the local spin susceptibility does not decrease in the superconducting state. This result is evidence that spin-triplet superconductivity is realized in $PrOs_4Sb_{12}$.

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I. INTRODUCTION

Unconventional superconductivity in strongly correlated electron systems reveals new perspectives of superconductivity. In general, superconductivity can be classified into two categories, spin singlet (even parity) or spin triplet (odd parity) from the viewpoint of the electron spin pairing state of a Cooper pair. A few compounds have been reported to be spin-triplet superconductors, for example the d-electron system Sr_2RuO_4,[1] and the $5f$-electron systems UPt_3 (Ref. 2) and UNi_2Al_3.[3] Since these spin-triplet superconductors have been found in strongly correlated electron systems, electron correlation should be playing a crucial role in the mechanism of spin-triplet pairing. Up to now, no spin-triplet superconductivity has been reported in $4f$-electron systems to our knowledge.

The discovery of superconductivity in the heavy fermion, filled-skutterudite compound $PrOs_4Sb_{12}$ has attracted much attention due to its novel properties.[4,5] $PrOs_4Sb_{12}$ is the first known example of a Pr-based heavy fermion superconductor exhibiting unconventional superconductivity. The crystalline-electric-field (CEF) ground state of the localized f electron has been confirmed to be a nonmagnetic Γ_1 singlet state.[6–8] Recently, the existence of a field-induced antiferroquadrupolar ordered phase was proved by neutron scattering experiments.[6,9] This phase lies close to the superconducting phase, and, therefore, it is argued that quadrupole fluctuations play an important role for the electron pairing mechanism in the superconducting phase.

One of the central issues for this compound is the symmetry of the superconducting order parameter. An isotropic energy gap is suggested from the exponential dependence of penetration depth versus temperature seen in previous muon spin rotation (μSR) experiments.[10] In Sb nuclear quadrupolar resonance measurements, the absence of a Hebel-Slichter peak and non-T^3 behavior of the inverse relaxation time T_1^{-1} suggest either a full gap or point nodes.[11] The magnetic field direction dependence of the thermal conductivity reveals that the symmetry of the superconducting gap $\Delta(k)$ is different between the high-field region ("A phase") and the low-field region("B phase").[12] Surface inductance measurements have revealed a T^2 behavior of the superfluid density, suggesting point nodes.[13] A most intriguing phenomenon has been observed in our previous zero-field μSR measurements. We found that a tiny internal field appears in the superconducting phase, indicating time-reversal-symmetry breaking in the superconducting order parameter.[14] It is difficult to understand all these findings systematically. To solve this puzzling problem, a determination of the pairing symmetry of the Cooper pair is quite an important issue.

Knight shift studies provide crucial information about the pairing symmetry of Cooper pairs. Since a muon has spin 1/2, one can deduce the Knight shift without any complication due to an electric field gradient (EFG). This feature is a great advantage of a muon Knight shift over nuclear magnetic resonance (NMR) in ^{121,123}Sb ($I=5/2,7/2$), in which the EFG is a major hindrance in determining the resonance frequency. In particular, the EFG strongly depends on temperature near T_c,[11] obstructing NMR Knight shift analysis. In this Rapid communication, we report on muon spin rotation experiments on single-crystalline $PrOs_4Sb_{12}$. We have found that the muon Knight shift, determined without ambiguity due to the EFG, is invariant with temperature on passing through T_c at 3 and 17 kOe, suggesting a spin-triplet superconductivity.

II. EXPERIMENT

Single-crystalline specimens of $PrOs_4Sb_{12}$ were grown by the Sb-flux method, as described elsewhere,[15] using raw materials of 99.99% Pr, 99.9% Os, and 99.9999% Sb. Clear de Haas–van Alphen oscillations observed in one of the crystals[15] are indicative of their high quality. Small (~1 mm) crystals were aligned so that the muon spins rotated in the (001) plane. For the measurements below 2 K, the specimens were glued with GE7031 varnish to a silver cold finger in the dilution refrigerator. Above 2 K, since no silver cold finger was used, a background-free signal was obtained. Magnetic fields of 1, 3, and 17 kOe were applied along the [001] direction of the crystals. Conventional μSR measurements under transverse field (TF) were carried out at the M15 beamline of TRIUMF, Vancouver, Canada.

III. RESULTS AND DISCUSSION

Before describing the muon Knight shift measurements, we first describe our penetration depth measurements using weak TF μSR. The penetration depth is a crucial parameter

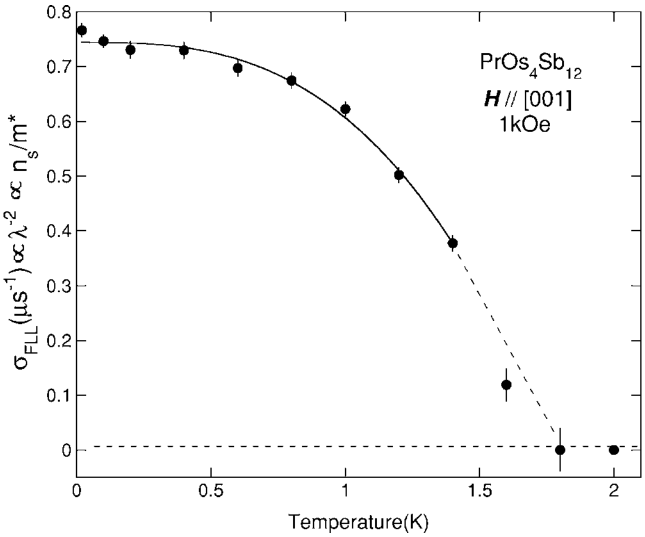

FIG. 1. Temperature dependence of the relaxation rate σ_{FLL} under a transverse magnetic field of 1 kOe in $PrOs_4Sb_{12}$. Solid lines indicate the power-law relation determined by fitting from 0.02 to 1.6 K.

for an exact determination of the muon Knight shift, as mentioned later. Furthermore, an anisotropy in the superconducting gap has been suggested and the penetration depth also might be anisotropic. Thus, measurements by using the present single-crystalline specimen are necessary for the exact determination of Knight shift. In the mixed state of a type-II superconductor, an applied magnetic field ($H_{c1} < H < H_{c2}$, with H_{c1} and H_{c2} being the lower and upper critical fields, respectively) induces a flux line lattice (FLL), and the internal magnetic field distribution is mainly determined by the magnetic penetration depth (λ). At 1 kOe, applied in the same direction as for the Knight shift measurements, the damping rate of the spin precession signal increases with decreasing temperature below the superconducting transition temperature T_c, reflecting the formation of the FLL. In such a situation, the muon spin relaxation can be represented approximately by a simple Gaussian relaxation, namely,

$$G_x(t) = A_s \exp\left(-\frac{1}{2}\sigma_s^2 t^2\right)\exp[-(\Lambda t)^{\beta}]\cos(\omega_s t + \phi) + A_b \exp(-\Lambda_b t)\cos(\omega_b t + \phi), \quad (1)$$

where the first term corresponds to the signal from the specimen and the second term to that from the silver backing plate. The relaxation rate given by $\exp[-(\Lambda t)^{\beta}]$, where $\Lambda = 0.376(8)\ \mu s^{-1}$ and $\beta = 1.14(4)$ at 2.0 K, originates from random nuclear dipolar fields and the dynamic behavior of the f electrons, which was also observed in zero field (ZF).[14] The internal field distribution probed by muons is a convolution of the field distribution in the normal state (σ_n) and that due to the FLL ($\sigma_{FLL}, \sigma_s^2 = \sigma_n^2 + \sigma_{FLL}^2$). Note that the relaxation rate of the silver backing (Λ_b) is negligibly small. For fitting the data in the superconducting state, we fixed Λ and β to the values determined at 2.0 K. Figure 1 shows the temperature dependence of σ_{FLL} at 1 kOe, where σ_{FLL} increases with decreasing temperature below T_c. In an isotropic superconductor with a hexagonal FLL, the second moment ($\langle \Delta B^2 \rangle$) is approximately given by[16]

$$\langle \Delta B^2 \rangle = \sigma_{FLL}^2/\gamma_\mu^2 \approx 7.5 \times 10^{-4}(1-h)^2[1 + 3.9(1-h)^2]\Phi_0^2 \lambda^{-4}, \quad (2)$$

where γ_μ is the gyromagnetic ratio of the muon, $h = H/H_{c2}$, and Φ_0 is the magnetic flux quantum. From these relations, λ is estimated to be 426(3) nm at 0.02 K under $H = 1$ kOe. This value is larger than the one obtained by using a powdered specimen,[10] suggesting anisotropy in λ. As shown in Fig. 1, λ^{-2} ($\propto n_s/m^*$, the superfluid density divided by the effective carrier mass) increases with decreasing temperature, where the curvature is weaker than the case for an isotropic BCS superconductor. The solid line in Fig. 1 indicates that $\Delta\lambda^{-2} = \lambda(0)^{-2} - \lambda(T)^{-2} \propto T^n$, where the best-fit value of $n = 2.9(3)$ is obtained by using the data between 1.6 and 0.02 K, which is smaller than in the previous experiment [3.6(2)].[10]

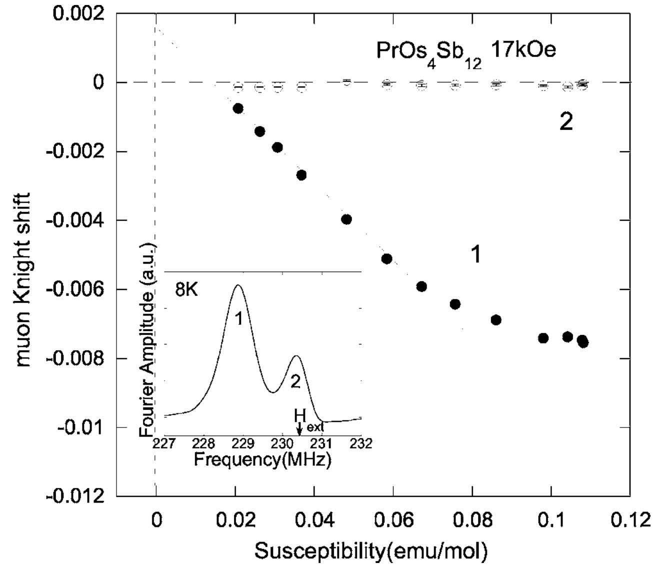

FIG. 2. Muon Knight shift versus susceptibility plot (K-χ plot) at 17 kOe. Inset shows the typical FFT spectrum (at 8 K).

Next, we describe the muon Knight shift measurements. Since the frequency shift is proportional to the magnetic field at the muon site, higher fields are required for an accurate determination of the Knight shift. We have, therefore, measured Knight shifts above 3 kOe. The inset of Fig. 2 shows a typical spectrum of the fast Fourier transform (FFT) of the μSR spectra at 17 kOe in $PrOs_4Sb_{12}$. Here we observed two peaks in the FFT spectra. Since the muon spin relaxation due to the distribution of the Knight shifts (δK) at 3 and 17 kOe, $\gamma_\mu \delta K H$, is larger than that from either Λ or σ_{FLL} in Eq. (1), the relaxation function is no longer expressed by Eq. (1), and the μSR spectra can be represented by simple Gaussians. We fitted the μSR spectra by using a sum of two Gaussian functions, namely,

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$$P(t) = \sum_{i=1,2} A_i \exp(-\sigma_i^2 t^2)\cos(2\pi f_i t + \phi). \tag{3}$$

We defined the muon Knight shift of the ith component K_i as $K_i=(f_i-f_{ext})/(f_{ext})$. Here f_{ext} indicates the external field frequency defined as $f_{ext}=\gamma_\mu B_{ext}/2\pi$, where B_{ext} indicates the external field. The fraction of the ith component is estimated as $A_i/\Sigma A_i$, which is about 70% and 30% for peaks 1 and 2, respectively.

In Fig. 2 (Clogston-Jaccarino plot), the muon Knight shift is plotted against the susceptibility measured in the same field (17 kOe) and direction ($H \parallel [001]$). Above 15 K, a linear relation in the K-χ plot is seen. In general, the muon Knight shift K is expressed as $K(T)=K_s(T)+K_{orb}$, where $K_s(T)$ and K_{orb} are the spin and orbital parts of the Knight shift and K_{orb} is independent of temperature. The spin part of the muon Knight shift is expressed as $K_s=(1/N_A\mu_B)A_{hf}\chi$, where A_{hf} is the hyperfine coupling constant and N_A is Avogadro's number. The estimated $A_{hf,i}$ above 15 K is −648(7) and 2(3) Oe/μ_B for peaks 1 and 2, respectively. A deviation from the linear relation appears below 12 K, probably due to modification in the thermal population of the crystalline-electric-field states of the $4f$ electron, as suggested in $CeCoIn_5$,[17,18] $CeCu_2Si_2$,[19] etc.

The insets of Figs. 3(a) and 3(b) show the FFT spectra observed using the dilution refrigerator at 17 and 3 kOe. Two distinct peaks are clearly observed. Since the samples are glued on the silver backing plate in the dilution refrigerator, a huge background peak from the silver cold finger is seen at $K \sim 0$ and, therefore, K_2 is difficult to resolve due to the overlap with the background peak. Thus, we focus on the main peak (peak 1 in Fig. 2) in order to discuss the temperature dependence of the Knight shift. A fitting was also done by using a sum of two Gaussians. In Figs. 3(a) and 3(b), the temperature dependence of the muon Knight shift is presented. Below T_c, no enhancement in the peak width is seen at 17 kOe. The frequency shift Δf in the superconducting phase is expressed by $2\pi\Delta f/\gamma_\mu = KH_{ext}+H_{FLL}+H_{dia}$, where H_{FLL} is the difference between the field at the van Hove singularity (corresponding to the field near the saddle point) of the field profile in the FLL state and the external field,[20] and H_{dia} is the magnetic field shifts due to the Meissner diamagnetism. At 3 kOe, we have observed a tiny broadening of the FFT spectra below T_c due to the formation of the flux line lattice. In this case, the peak position in the FFT spectrum shifts to lower frequency. By using the following modified London model,[21] we have made a simulation to estimate the frequency shift due to FLL formation at 3 kOe:

$$B(\mathbf{r}) = B_0 \sum_{\mathbf{K}} \frac{e^{-\mathbf{K}\cdot\mathbf{r}}}{1+K^2\lambda^2} \exp(-K^2\xi^2). \tag{4}$$

Here we use 79° (Ref. 22) and 120 Å (Ref. 4) for the angle of the FLL and the coherence length ξ, respectively. For the penetration depth λ, the value obtained in the previous section is used. By the simulation, the peak position shift due to the FLL is obtained as less than 0.2 Oe. This is negligibly small. The Meissner diamagnetic component H_{dia} is estimated to be about −2.5 Oe at 3 kOe by using the relation $H_{dia}=-H_{c1}\ln(\beta e^{-1/2}d/\xi)/\ln\kappa$,[24] which corresponds to 0.0008 of the Knight shift at 3 kOe. Here we used H_{c1} =23 Oe,[8] β=0.381 for the triangular lattice, κ=35, and the distance between vortices d=893 and 375 Å at 3 and 17 kOe, respectively. The observed value $K(T_c)-K(0.02\text{ K})$ =0.000 63 corresponds to −1.9 Oe at 3 kOe which agrees with the estimated H_{dia}. At 17 kOe, H_{dia} (=−2.1 Oe, corresponding to 0.000 12 of the Knight shift) is negligibly small.

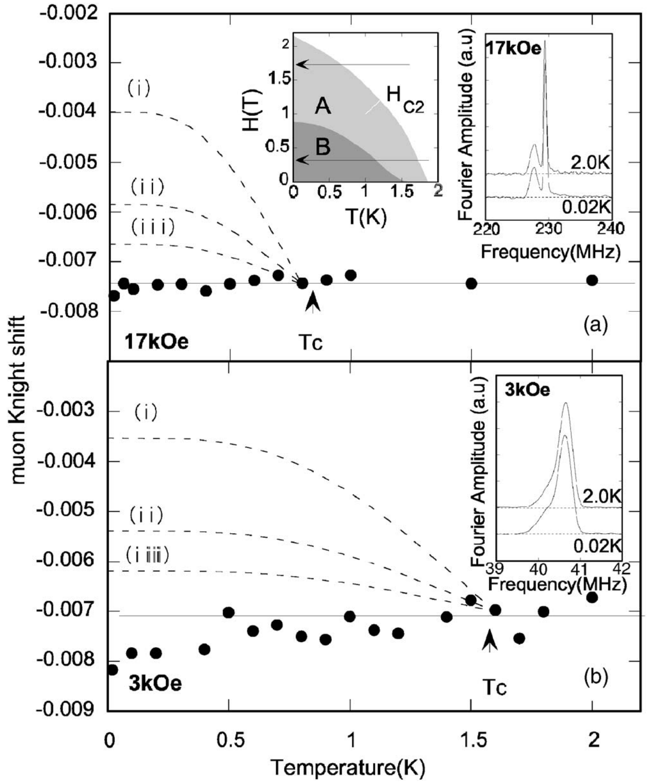

FIG. 3. Temperature dependence of the muon Knight shift for peak 1 at (a) 17 and (b) 3 kOe. The dashed lines are calculations of the temperature dependence expected for the Yosida function and ΔK_s obtained from Eq. (5) with γ=550 mJ/mol K^2 and (i) $4f^2$ configuration ($g_J^2 J_{eff}^2$=12.8), (ii) $\Gamma_1+\Gamma_4^{(2)}$ pseudoquartet state ($g_J^2 J_{eff}^2$ =6.0), and (iii) free electron value ($g_J^2 J_{eff}^2$=3.0). Inset shows the FFT spectra; the large peak is predominantly from the silver sample holder. The phase diagram is also shown and A phase and B phase have the same definition as in Ref. 12.

In a spin-singlet superconductor, the spin part of the Knight shift decreases below T_c. In the case of d-electron superconductors, the spin part of the Knight shift can be estimated from a K-χ plot. However, in f-electron systems, the Knight shift at low temperatures is possibly dominated by the Van Vleck contribution. Here we use a Fermi liquid relation as the most reliable way of estimating the quasiparticle contribution to the Knight shift and the susceptibility, χ^{qp}, which has been applied successfully for other heavy fermion superconductors,[25]

$$\Delta K_s = A_{hf}\chi^{qp} = A_{hf}\frac{\gamma g_J^2 \mu_B^2 J_{eff}^2}{\pi^2 k_B^2} \times R. \tag{5}$$

We use the electronic specific heat coefficient γ =550 mJ/mol K^2, which is an average of the reported values

(350–750 mJ/mol K).[2,4,5] The CEF level scheme has been accurately determined by a neutron scattering study[6,8] and the effective spin $g_J^2 J_{eff}^2$ can be easily calculated. The Γ_1 singlet ground state and the low-lying $\Gamma_4^{(2)}$ triplet excited state, located only about 8 K from the ground state, are relevant for the heavy fermion (HF) state formation.[23] Therefore, the relevant 4f-electron state can be approximated as a $\Gamma_1+\Gamma_4^{(2)}$ pseudoquartet state at low temperatures, and $g_J^2 J_{eff}^2=6.0$ for the $\Gamma_1+\Gamma_4^{(2)}$ pseudoquartet state should provide a reasonable value. Even if we use the free electron value ($g_J^2 J_{eff}^2=3.0$), the difference is not very large. Since the Wilson ratio R ($2>R>1$) in the heavy fermion state is of the order of unity, we use $R=1$. By using the obtained hyperfine coupling constant for peak 1, we have estimated ΔK_s. In the case of an s-wave state, the temperature dependence of the Knight shift follows the Yosida function.[26] By using the Yosida function and ΔK_s the expected behaviors for the temperature dependence of the Knight shift for an s-wave superconductor are represented by the dotted lines in Figs. 3(a) and 3(b). We have estimated for three cases: the (i) the $4f^2$ configuration ($g_J^2 J_{eff}^2=12.8$), (ii) the $\Gamma_1+\Gamma_4^{(2)}$ pseudoquartet state ($g_J^2 J_{eff}^2=6.0$), and (iii) the free electron value ($g_J^2 J_{eff}^2=3.0$). The cases (i) and (iii) provide the upper and the lower bounds of the s-wave spin susceptibilities, respectively.[27] Compared with these cases, it is clear that the muon Knight shift does not show any reduction below T_c as demonstrated in Fig. 3.[28]

No reduction in Knight shift suggests that spin-triplet (odd-parity) superconductivity is realized in $PrOs_4Sb_{12}$. If the spin-triplet d vector is pinned to a certain direction in the lattice, it is expected that some part of the muon Knight shift could decrease. The absence of such a reduction in the Knight shift even at 3 kOe suggests that the effective spin-orbit coupling is much weaker than 3 kOe, leading to an alignment of the d vector perpendicular to the external field direction. In a previous paper,[14] we have found that the spin or orbital component of the Cooper pairs in $PrOs_4Sb_{12}$ carries a nonzero momentum and generates a hyperfine field at the muon site. Even in the spin-triplet pairing case, there are still two possible sources for the magnetic fields observed in the ZF μSR measurements. Theoretically, several possible pairing symmetries have been discussed. For example, it is argued that a spin-triplet superconductivity can possibly be stabilized by considering an exciton-mediated pairing mechanism in the T_h symmetry.[29] Moreover, a "nonunitary" superconductivity is proposed in Ref. 30, which is one possible state that coincides with our result. However, there are still several candidates for the pairing symmetry. Further experimental and theoretical investigations are required.

IV. CONCLUSION

In conclusion, the muon Knight shift is invariant with temperature on passing through T_c at 3 and 17 kOe down to 20 mK in $PrOs_4Sb_{12}$. This fact implies that the local spin susceptibility along the [001] direction does not change in the superconducting state, indicating spin-triplet superconductivity. The present system is the first 4f-electron system in which spin-triplet superconductivity is realized to our knowledge.

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