Observation of ^{105}Pd NMR and NQR signals in the heavy-fermion superconductor UPd_2Al_3

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(Received 11 November 1996; revised manuscript received 13 February 1997)

^{105}Pd NMR and NQR measurements have been performed both in the normal and in the superconducting states for the heavy-fermion superconductor UPd_2Al_3. The magnitude of the internal field at Pd is found to be about 3 kOe (at 4.2 K) in the antiferromagnetically (AF) ordered state. The nuclear spin-lattice relaxation rate, $1/T_1$, in UPd_2Al_3 is nearly temperature, T, independent in the paramagnetic state up to 60 K, successively diverges at Néel temperature associated with the critical slowing down of U magnetic moments, and then decreases markedly in the AF ordered state, which is well explained by a localized moment picture. These results have shown that Pd atoms are nonmagnetic, in which $4d$ electrons couple very weakly to U moments. In the superconducting state, $1/T_1$ decreases in proportion to T^3 down to 0.5 K with no coherence peak just below T_C, which indicates the occurrence of anisotropic superconductivity having line nodes in the superconducting energy gap. The coexistence of the AF ordering and the anisotropic superconductivity in UPd_2Al_3 could unambiguously be confirmed. [S0163-1829(97)04022-8]

The interplay between superconductivity and magnetism in the heavy-fermion (HF) superconductor is a fascinating subject. In particular, the presence of antiferromagnetic (AF) spin fluctuations has led to the prediction that an unconventional Cooper pair state with non-s-wave symmetry, mediated by an antiferromagnetic electron-electron coupling mechanism, is realized in these systems. The coexistence of the AF ordering and the superconductivity is not rare in HF systems. Among them, UPd_2Al_3 occupies a unique position, since the magnitude of the ordered moments, $0.85\mu_B$,[1] is the largest in HF superconductors. This system undergoes an AF transition at Néel temperature, $T_N=14.5$ K, followed by a superconducting transition at $T_C=2$ K corresponding to the highest critical temperature reported to date for HF superconductivity.[1] The magnetic structure of UPd_2Al_3 in the AF ordered state, which consists of ferromagnetic c planes stacked antiferromagnetically along the c axis, was determined by a neutron diffraction.[2] In this structure, Pd ions are located on the ferromagnetic sheets, and Al ions at the interlayer site of the U-Pd layers. So, it is of great interest to study UPd_2Al_3 from the microscopic points of view for an understanding of the interplay of the magnetism and the superconductivity in HF system. For this purpose, the ^{27}Al nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) studies were previously performed, which showed that the superconductivity is anisotropic having line nodes in the superconducting energy gap.[3] On the contrary, little information for the magnetic property was obtained from ^{27}Al NMR-NQR because of the local symmetry of Al site in which the transferred hyperfine fields from U moments are canceled. Hence, ^{105}Pd NMR was desired to perform for the better understanding the system. However, the measurement is generally hard to perform owing to the very small gyromagnetic ratio γ and the rather large quadrupole moment Q. Indeed, no ^{105}Pd NMR/NQR signals have been observed except a Pd metal with the face centered cubic lattice. Recently, we have succeeded in observing ^{105}Pd NMR and NQR signals in UPd_2Al_3. In this paper, we report the results of ^{105}Pd NMR and NQR studies which provide the information of the electronic states of Pd ions and also that of U moments through the nonvanishing transferred hyperfine field.

The quality of the starting materials for the polycrystalline UPd_2Al_3 sample was $3N$-U, $4N$-Pd, and $5N$-Al. The appropriate amounts of constitutions were arc-melted in argon atmosphere, successively annealed at 900 °C for 5 days. T_C of the sample measured by ac susceptibility was 1.75 K, which is slightly lower than the maximum value of 2.0 K in UPd_2Al_3 reported by another group. Our NMR and NQR studies were carried out by using a phase-coherent-type pulsed spectrometer. The spurious signal from the rf pulse was removed by alternating the rf phases of both $\pi/2$ and π pulses in the spin echo sequence. The NMR spectrum was measured by recording the spin-echo intensity as a function of external field. A superconducting magnet with a maximum field of 15 T was used for NMR measurements. The Knight shift K was determined with respect to ^{105}Pd resonance in Pd metal ($K=4.10\%$ at 4.2 K). In UPd_2Al_3, the transverse component of the susceptibility with respect to the hexagonal c axis $\chi_\perp$ is much larger than the longitudinal component $\chi_\parallel$.[4] Then the microcrystals in the powder specimen easily align with c axis perpendicular to the external field $H_{\rm ext}$. The nuclear spin-lattice relaxation time, T_1, was measured by monitoring the recovery of nuclear magnetization after the saturation pulses. The ^{105}Pd NMR and NQR measurements over the temperature, T, range above 1.3 K were performed in a ^{4}He cryostat, and below 1.3 K in a ^{3}He-^{4}He dilution refrigerator.

Figures 1(a) and 1(b) indicate the ^{105}Pd NMR spectra obtained in randomly oriented microcrystals at 17 K (paramagnetic state) and 4.2 K (AF state), respectively. The spectrum shown in Fig. 1(c) was obtained in aligned (c axis $\perp$ $H_{\rm ext}$) microcrystals. Each NMR spectrum consists of the center line and the satellites induced by the first-order quadrupole effect. As seen in Figs. 1(a) and 1(b), any significant broadening of the line width associated with the appearance

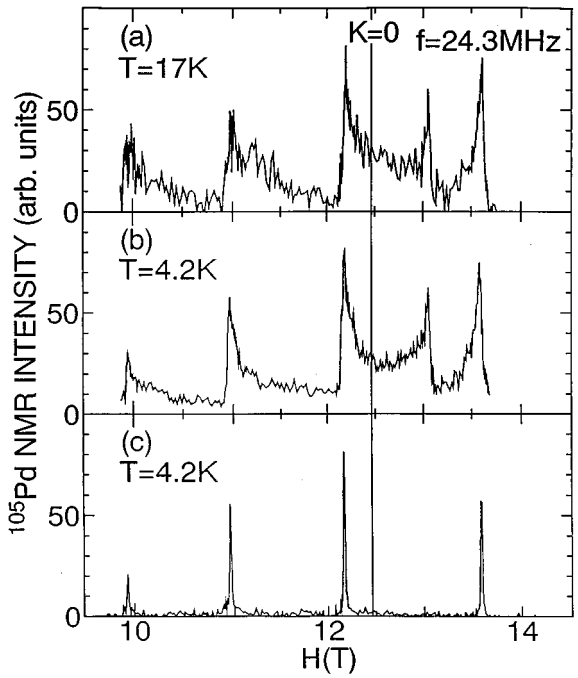

FIG. 1. ^{105}Pd NMR spectra obtained in randomly oriented at 17 K (a) and at 4.2 K (b) and aligned (c axis $\perp H_{\rm ext}$) microcrystals at 4.2 K (c).

of the AF ordering was not observed. The magnitude of the electric quadrupole interaction, $\nu_Q(^{105}\mathrm{Pd})$, was deduced to be about 5 MHz from the separation of the first-order satellites of the randomly oriented powder pattern spectrum, and also the direction of the maximum electric field gradient (V_{ZZ}) was deduced to be the hexagonal c axis from the spectrum for the aligned microcrystals. The T dependence of the Knight shift, $K_\perp$ (c axis $\perp$ $H_{\rm ext}$), obtained from the spectrum is plotted in Fig. 2, and is also plotted against $\chi_\perp$ in the inset of the figure with T as an implicit parameter. $K_\perp$ varied nearly proportional to $\chi_\perp$ with a hyperfine coupling constant

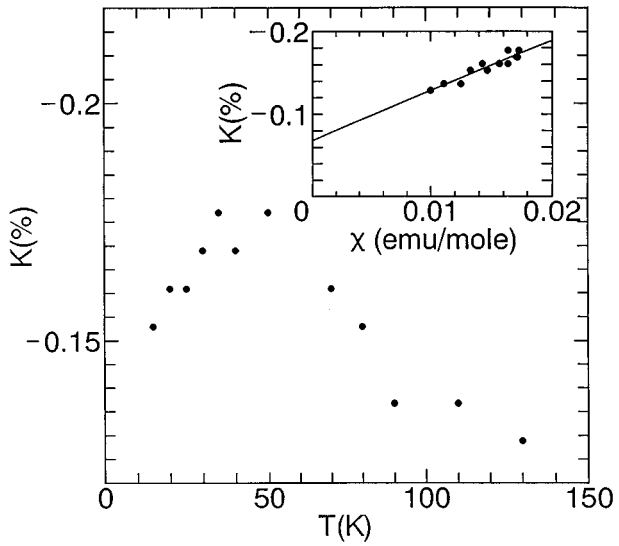

FIG. 2. T dependence of $K(c$ axis $\perp H_{\rm ext})$. In the inset of the figure, K is plotted against $\chi_\perp$.

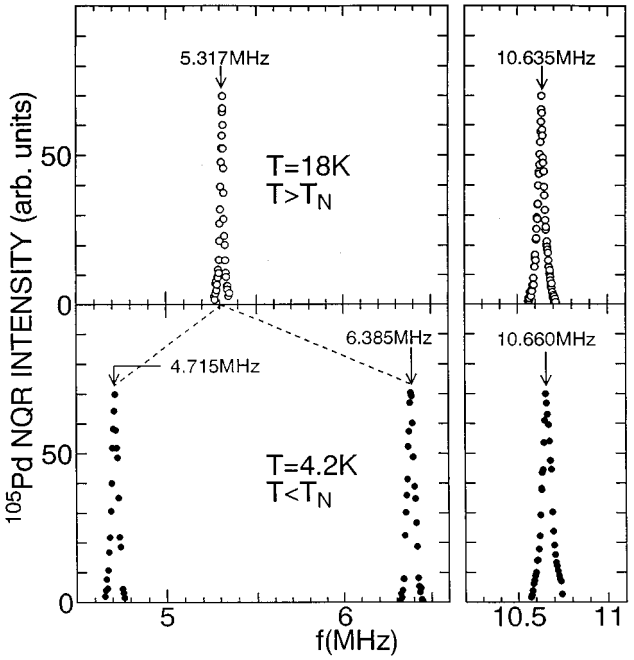

FIG. 3. ^{105}Pd NQR spectra obtained at 18 K (paramagnetic state) and at 4.2 K (AF state).

of 0.3 kOe/μ_B (shown by a line in the inset of the figure). The hyperfine coupling constant of ^{105}Pd is surprisingly small in UPd_2Al_3, which is even smaller than that of ^{27}Al (3.7 kOe/μ_B in the paramagnetic state). The small hyperfine coupling constant of ^{105}Pd represents that there is no significant polarization density of Pd 4d electrons. The hybridization between U 5f and Pd 4d electrons is very weak in this system. This result is consistent with the result of the polarized neutron diffraction experiment by Paolasini *et al.*, in which no spin transfer was found on the Pd atoms,[5] and also consistent with the band structure calculations showing Pd 4d states located too far below the Fermi energy.[6]

Figure 3 shows ^{105}Pd NQR spectra obtained in the paramagnetic state (18 K) and in the AF state (4.2 K). In the paramagnetic state, ^{105}Pd NQR lines were observed at the resonance frequencies of 5.317 and 10.635 MHz. At 4.2 K, the lower frequency resonance line split into two lines which were observed at 4.7 and 6.4 MHz. The NQR spectrum of ^{105}Pd is described by a nuclear spin Hamiltonian which is a sum of electric quadrupole and Zeeman terms with usual notations,[7]

$$\mathcal{H}=\frac{3e^2qQ}{4I(2I-1)}\left(I_Z^2-\frac{1}{3}I(I+1)+\frac{1}{6}\eta(I_X^2-I_Y^2)\right)$$
$$-\gamma_N\hbar(H_\parallel I_Z+H_\perp I_X\cos\alpha+H_\perp I_Y\sin\alpha),$$

where $I=5/2$, $Q=0.8$(b), $\gamma_N/2\pi = 0.195$(MHz/kOe) for ^{105}Pd,[8] $H_\perp$ and $H_\parallel$ mean the perpendicular and parallel components of magnetic field with respect to V_{ZZ}, respectively, and α is an angle between $H_\perp$ and X axis. The asymmetry parameter η for the electric field gradient (EFG) tensor is defined by

$$\eta=(V_{XX}-V_{YY})/V_{ZZ},$$

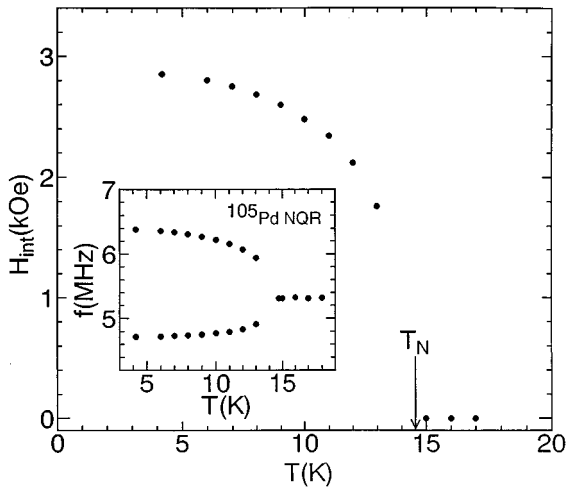

FIG. 4. T dependence of deduced internal field. In the inset of the figure, the T dependence of the lower frequency resonance lines is also shown.

where $|V_{ZZ}|>|V_{YY}|>|V_{XX}|$ is assumed in the principal axis system of EFG. As for V_{ZZ}, we know already from the NMR spectrum that the direction is the hexagonal c axis. The NQR spectrum in the paramagnetic state is simply interpreted by only the electric quadrupole term. The values of the parameters are estimated to be

$$\nu_Q = 3e^2qQ/2I(2I-1)h = 5.317 \text{ MHz} \quad \text{and} \quad \eta = 0.$$

In the AF state, the Zeeman term takes part in the nuclear spin Hamiltonian. By solving the secular equation of the Hamiltonian numerically, the resonance frequencies were evaluated. After some calculations by trial and error, a set of parameters was found to reproduce the peak positions of experimental spectrum. The parameters to explain the resonance lines obtained at 4.2 K are as follows:

$$\nu_Q = 5.317 \text{ MHz}, \quad \eta = 0, \quad H_\perp = 2.9 \text{ kOe}, \quad \text{and} \quad H_\parallel = 0.$$

Thus, an appearance of the internal field perpendicular to the hexagonal c axis could explain the observed spectrum. The T dependence of the separation of two lines below T_N are shown in the inset of Fig. 4, and also the internal field deduced from the spectra at the respective temperatures are shown in Fig. 4. The internal field has nearly the same T dependence as that of the sublattice magnetization of U moments in the commensurate AF ordered state measured by the neutron diffraction experiment.[2,9] But we could not observe the internal field associated with an incommensurate phase which is stable for temperatures $15<T<20$ K observed in the neutron diffraction experiment of polycrystalline UPd_2Al_3.[2]

Next, by using NQR, $1/T_1$ of ^{105}Pd, hereafter referred to $^{105}(1/T_1)$, was measured in zero magnetic field in the T range from 0.5 to 70 K at around 10.65 MHz. When the magnetic interaction governs the nuclear spin-lattice relaxation, the recovery of ^{105}Pd nuclear magnetization $M(t)$ at time t after the saturation pulses is given by the following multi-exponential equation:[10]

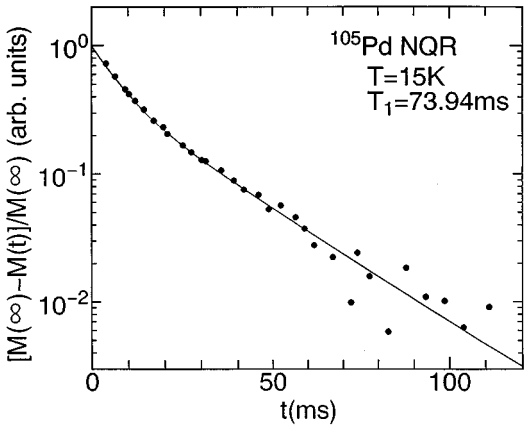

FIG. 5. Typical recovery of $M(t)$ obtained at 15 K after a saturation pulse.

$$[M(\infty)-M(t)]/M(\infty) = 3/7\exp(-3t/T_1)+4/7\exp(-10t/T_1).$$

Figure 5 shows the recovery of $M(t)$ after the saturation pulse obtained at 15 K. Since the recovery was fitted quite well to the above equation, T_1 could accurately be determined. As can be seen in Fig. 6, $^{105}(1/T_1)$ above T_N is T independent, $1/T_1 = 10\ (\text{s}^{-1})$, which is explained by a localized moment picture. In the model developed by Moriya, the value of $1/T_1$ is expressed as[11]

$$1/T_1 = \sqrt{2\pi}\sum_i (A_i/\hbar)^2 S(S+1)/3\omega_e,$$

where A_i is a hyperfine interaction, and ω_e is the fluctuating frequency of the electron spin system modulated by the RKKY interaction. The crude estimation of $1/T_1$ is the following.

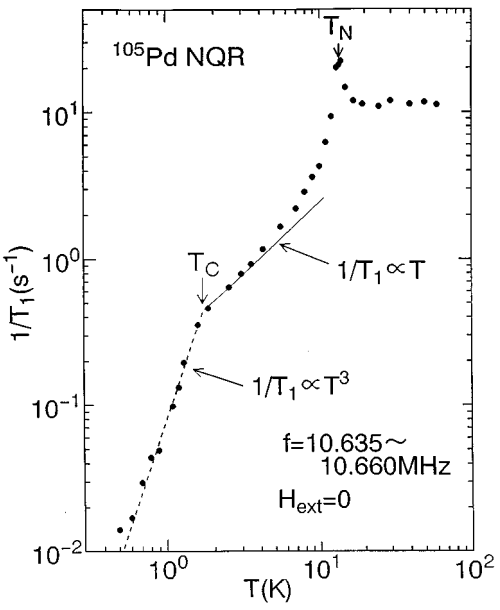

FIG. 6. T dependence of $1/T_1$ of ^{105}Pd obtained by NQR.

The value of ω_e is estimated as 1.9×10^{12} (s^{-1}) by using $\omega_e \approx k_B T_N/\hbar$ with $T_N=14.5$ K. The estimation of A_i for the nonmagnetic site is not simple. In this paper, we estimated it by assuming that the internal field of 2.9 kOe in the AF state was induced by the nearest-neighbor 3 U moments. In this way, we obtained $\omega_n^2 \equiv A_i^2 S(S+1)/\hbar^2 = (2\times10^4)^2$ (s^{-2}), and the value of $1/T_1$ was derived to be 2.56 (s^{-1}), which agreed in order of magnitude with the value obtained by the present experiment. The relatively long T_1 together with the small value of the Knight shift represent that Pd ions are nonmagnetic with the very small polarization of Pd $4d$ electrons in UPd_2Al_3.

Moreover, the divergence of $1/T_1$ was also observed at T_N with the critical slowing down of U magnetic moments. Thus, the relaxation behavior of ^{105}Pd through T_N can be well explained by a localized moment picture of U. It should be noted that not only the size of the U moments but also the fluctuations of the moments are well explained by a localized moment picture. The T dependence of $^{105}(1/T_1)$ near T_N is different from that of ^{27}Al, $^{27}(1/T_1)$, which varies in proportion to T in the paramagnetic state near T_N without critical slowing down phenomenon at T_N.[3] The different T dependence of $1/T_1$ arises from the difference of the crystallographic symmetry of respective sites as mentioned in the former part. Namely, Pd atoms are surrounded ferromagnetically by U moments, while Al atoms are located at site in which the transferred hyperfine fields from U moments are canceled. Consequently, $^{105}(1/T_1)$ is governed by the fluctuations of U moments, while $^{27}(1/T_1)$ is governed by the contribution from the conduction electrons. Below T_N, $^{105}(1/T_1)$ varies nearly in proportion to T, as can be seen in the figure. In the superconducting state, $1/T_1$ has no Hebel-Slichter coherence peak just below $T_C=1.75$ K, and varies in proportion to T^3 at low T, which is a common relaxation behavior of the nuclear spins observed in the HF superconductors. This behavior can be explained by an anisotropic energy gap model of gap zeros on lines at the Fermi surface. To analyze $1/T_1$ quantitatively, we assume the following simple superconducting gap with a line node:

$$\Delta(T)=\Delta_0(T)\cos\theta,$$

where $\Delta_0(T)$ has the T dependence expected in BCS theory. The ratio of $1/T_1$ in the normal and superconducting states, $R\equiv T_{1N}/T_{1S}$, is expressed as

$$R=\frac{2}{k_B T}\int \frac{E^2}{E^2-\Delta^2} f(E)[1-f(E)]dE,$$

where $f(E)$ is the Fermi distribution function. Here, T_{1N} is extrapolated by the relation of T_1T = const. The evaluated R of ^{105}Pd, $^{105}(R)$, together with R of ^{27}Al, $^{27}(R)$, measured previously in the same sample are shown in Fig. 7 as a function of reduced T, T/T_C. As seen in the figure, $^{105}(R)$ and $^{27}(R)$ are on the same line, and a best fit to the observed relaxation data could be obtained by taking $2\Delta_0 = 5.5 k_B T_C$ indicated by the line in Fig. 7. The anisotropy of the superconducting energy gap obtained by NMR is the same at both Al and Pd sites, showing that the single heavy-fermion band sytem sets in the superconducting state. The information of the superconducting energy gap was also obtained from the specific heat C, which varies as $C=\gamma T+BT^3$.[12] This T dependence is explained by an anisotropic superconducting energy gap with point of nodes and residual density of states. Thus, the consistent explanation was not yet obtained between NMR and specific heat measurements. Further study, especially the NQR experiment at lower T, is now in progress to solve the discrepancy.

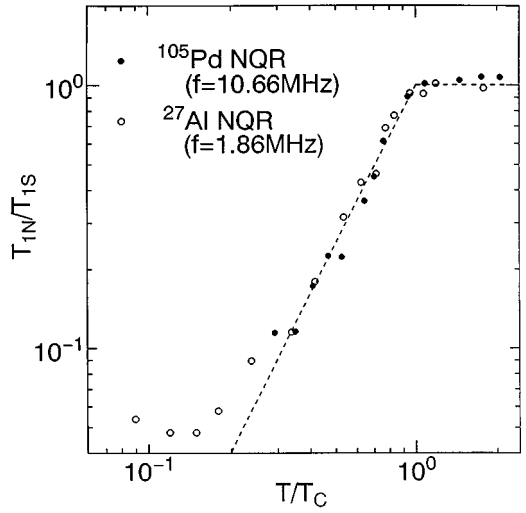

FIG. 7. Dependence of the reduced relaxation rate T_{1N}/T_{1S} on the reduced temperature of T/T_C.

In conclusion, we have succeeded in observing ^{105}Pd NMR and NQR signals in UPd_2Al_3 for a wide T range. The ^{105}Pd NMR/NQR measurements have shown that the electric quadrupole interaction parameters of ^{105}Pd were determined to be ν_Q = 5.317 MHz and η =0, and have also shown that Pd ions are nonmagnetic with very small polarization of a $4d$ electron. In the AF ordered state, the small internal field of about 3 kOe, which is perpendicular to c axis, appears below 14.5 K. The T-independent $1/T_1$ in the paramagnetic state diverges at T_N owing to the critical slowing down phenomenon, and then decreases markedly in the ordered state. In the supercondcuting state, $1/T_1$ varies in proportion to T^3 with no coherence peak just below T_C, indicating the existence of line nodes in the superconducting energy gap. The coexistence of the AF ordering and the anisotropic superconductivity in UPd_2Al_3 could unambiguously be confirmed by this experiment.

This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science and Culture of Japan, and also supported by Hyogo Science and Technology Association.

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