Anisotropic superconducting gap in transuranium superconductor PuRhGa$_5$: Ga NQR study on a single crystal

Hironori SAKAI$^1$, Yo TOKUNAGA$^1$, Tatsuya FUJIMOTO$^1$, Shinsaku KAMBE$^1$, Russell E. WALSTEDT$^1$, Hirosi YASUOKA$^1$, Dai AOKI$^2$, Yoshiya HOMMA$^2$, Etsuji YAMAMOTO$^1$, Akio NAKAMURA$^1$, Yoshinobu SHIKAWA$^{1,2}$, Kunihisa NAKAJIMA$^3$, Yasuo ARAI$^3$, Tatsuma D. MATSUDA$^1$, Yoshiinori HAGA$^1$, Yoshichika ŌNUKI$^{1,4}$

$^1$Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, JAPAN
$^2$Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, JAPAN
$^3$Department of Nuclear Energy System, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, JAPAN
$^4$Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, JAPAN

69,71Ga NMR/NQR studies have been performed on a single crystal of the transuranium superconductor PuRhGa$_5$ with $T_c \simeq 9$ K. We have observed a $^{69}$Ga NQR line at $\sim 29.15$ MHz, and assigned it to the $4i$ Ga site using the NMR results. The $^{69}$Ga NQR spin-lattice relaxation rate $1/T_1$ shows no coherence peak just below $T_c$, but obeys a $T^3$ behavior below $T_c$. This result strongly suggests that PuRhGa$_5$ is an unconventional superconductor having an anisotropic superconducting gap. The gap amplitude $2\Delta_0(T \to 0) \simeq 5k_B T_c$ and the residual density of states $N_{res}(T = 0)/N_0(T = T_c) \simeq 0.25$ have been determined assuming a simple polar function of the form $\Delta(\theta, \phi) = \Delta_0 \cos \theta$, where $\theta$ and $\phi$ are angular parameters on the Fermi surface.

KEYWORDS: PuRhGa$_5$, Superconductivity, Ga NQR

The recent discovery of Pu-based superconductors PuTGa$_5$ (T=Co, Rh) has stimulated interest in further experiments on transuranium compounds. A lot of attention is now focused on these Pu heavy-fermion compounds, which have relatively high superconducting (SC) transition temperatures, i.e., $T_c \simeq 18$ K (PuCoGa$_5$) and $T_c \simeq 9$ K (PuRhGa$_5$). The PuTGa$_5$ systems belong to a large family of “115 compounds”, which all crystallize in the same quasi-two-dimensional structure. In this family, the Ce115 isomorphs CeT'In$_5$ (T'=Co, Ir, Rh),$^{3-5}$ which are well-known 4f heavy fermion systems with antiferromagnetic tendencies, show d-wave superconductivity with relatively low $T_c$ values: $T_c=0.4$ K and 2.3 K for CeIrIn$_5$ and CeCoIn$_5$, respectively.$^{6-9}$ On the other hand, the U115$^{10-12}$ and Np115$^{13-16}$ compounds usually show itinerant magnetic order or Pauli paramagnetism, but up to now have not shown any superconductivity. Band calculations$^{17,18}$ and de Haas-van Alphen experiments$^{10,14,15,19,20}$ have

*E-mail address: piros@popsvr.tokai.jaeri.go.jp
revealed that An115 (An=U, Np, Pu, ...) compounds often have cylindrical Fermi surfaces, reflecting a quasi-two-dimensional character.

To elucidate the relatively high $T_c$ values exhibited by PuTGa$_5$, it is important to determine the pairing symmetry, which reflects the SC pairing mechanism. Nuclear Magnetic Resonance (NMR and NQR) is a microscopic probe well-suited to this task. In particular, the $T$ dependence of NQR (zero-field) spin-lattice relaxation rates ($1/T_1$) can provide crucial information regarding the SC pairing symmetry. In this letter, we report $^{69,71}$Ga NMR/NQR experimental results above and below the SC transition in PuRhGa$_5$.

A single crystal of PuRhGa$_5$ has been prepared using the Ga flux method. The dimensions of the single crystal are $1 \times 2 \times 3$ mm$^3$. This crystal has been attached with varnish to a silver cap for thermal contact, coated with epoxy resin, and sealed tightly in a polyimid tube in order to avoid radiation contamination. The sealed sample was then mounted into an rf coil. NQR/NMR measurements have been carried out in the temperature range 1.5-300 K using a phase-coherent, pulsed spectrometer, which has been installed in the radiation controlled area. $T_1$ was measured for the Ga NQR lines using the saturation-recovery method. The recovery of nuclear magnetization $M(t)$ from a saturation pulse comb was single-exponential type, $\{M(t) - M(\infty)\}/M(\infty) \propto \exp(-3t/T_1)$, in the whole temperature range. The superconductivity of PuRhGa$_5$ has been reported to be influenced by self-radiation damage due to spontaneous $\alpha$ decay, i.e., $T_c$ decreases gradually with $dT_c/dt \simeq -0.2 \sim -0.5$ K/month. Accordingly, in order to study the superconductivity of PuRhGa$_5$, brief and timely experimental measurements are required. In our experiments, the bulk $T_c$ was determined by both in situ ac susceptibility ($\chi_{ac}$) measurements using the rf coil, and the sudden decrease of the NQR signal intensity, as mentioned below. $T_c$ was found to be 8.5 K in zero field at the starting point of the present experiments, which was one month after the synthesis of the single crystal. All the NMR/NQR experiments reported here were conducted within a single month.

PuRhGa$_5$ crystalizes in the tetragonal HoCoGa$_5$ structure with lattice parameters of $a =$
Spin Echo Amplitude (arb. unit)
92
91
90
89
88
H0 (kOe)
θ ~ 0º
θ ~ 0º
θ ~ 3º
θ ~ 5º
Spin Echo Amplitude (arb. unit)
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
H0 (kOe)
(a) PuRhGa5 at 10 K at a frequency of 84.1 MHz, with the applied field (H0) parallel to the c axis. Spectral assignments are denoted by arrows, and the zero-shift positions 69,71K = 0 are also indicated. The two NMR lines near 69,71K = 0 originate from residual Ga flux. (b) Enlarged spectra around 90 kOe at a same frequency of 84.1 MHz at different angles (θ) between H0 and the c axis.

Figure 2 shows a field-swept NMR spectrum in the normal state at T = 10 K and a frequency of 84.1 MHz, with H0 parallel to the c-axis. This spectrum is well explained if we associate two sets of lines to 69Ga(2) and 71Ga(2) sites, where each set has a center line and two quadrupolar satellite lines denoted by arrows in Fig. 2. Since the Ga(2) sites have a lower local symmetry than the Ga(1), with four-fold axial symmetry, each center line lies at an asymmetric position between the satellites. This is due to the second-order quadrupolar effect.

The Knight shift (K), electric field gradient parameter (νEFG \equiv e^2 Q/2h), and asymmetry parameter (η) of the Ga(2) site have been estimated from second-order perturbation theory, where eQ is nuclear quadrupole moment and eq is the largest electric field gradient.22 The calculated K, νEFG, and η at 10 K are K \approx 0.19 \%, 69νEFG = 28.2 MHz, 71νEFG = 17.4 MHz, and η \approx 0.42, respectively. Here, the ratio 69νEFG/71νEFG \approx 1.6 is consistent with that of the nuclear quadrupole moments \( \frac{69Q}{71Q} \approx 1.59 \). These values of νEFG and η for Ga(2) sites are similar to those of the U11523 and Np11524,25 families, e.g., 69νEFG and η at the same site are 27.5 MHz and 0.2 for UPtGa5, and \~27.3 MHz and \~0.29 for NpCoGa5, respectively.

It should be noted here that the above assignment of Ga(2) NMR lines has been confirmed further by the field orientation dependence (θ) of the spectra in Fig. 2(b), where θ is an angle
between $H_0$ and the $c$ axis. As seen in Fig.2(b), a small increase of $\theta$ causes a splitting of each NMR line. If these lines were ascribed to Ga(1) sites, such a splitting could not be expected, because the Ga(1) sites remain equivalent under any applied field. The $^{69,71}$Ga(1) NMR signals are very weak due to a short $T_2$, and not seen in Fig.2(a) under this experimental condition.

Next, we turn to the zero-field NQR experiments. The $^{69}$Ga(2) NQR spectrum of the single crystal has been observed at $\nu_Q \simeq 29.15$ MHz as shown in Fig.3. Here, the value of $\nu_Q$ is consistent with the expected frequency, $\nu_Q = \nu_{EFG} \sqrt{1 + \eta^2/3}$, extracted from $\nu_{EFG}$ and $\eta$ in the NMR results. The narrow NQR line width ($\sim 20$ kHz) assures us that this sample is still of good quality, i.e., broadening effects due to defects and/or impurities are not serious at this point. The temperature dependence of $\nu_Q$ is shown in the inset of Fig.3. The value of $\nu_Q$ increases gradually as temperature decreases from 300 K, and saturates below $\sim 50$ K. The slight temperature dependence of $\nu_Q$ is caused by that of $\nu_{EFG}$, because the value of $\eta$ is found to be temperature-independent from NMR results. Note that the $^{71}$Ga(2) NQR line has been observed concurrently at the frequency of 18.38 MHz at $T = 10$ K.

$T_1$ has been measured for both $^{69}$Ga(2) and $^{71}$Ga(2) NQR lines in order to clarify the $T_1$ process. The ratio $^{69}T^{-1}/^{71}T^{-1}$ of data so obtained is found to be nearly equal to $^{69,71} \gamma_n^2/\gamma_n^2$ below $\sim 150$ K, where $\gamma_n$ denotes the nuclear gyromagnetic ratio. This indicates that the magnetic dipole relaxation mechanism is dominant over quadrupolar relaxation, at least in the low temperature range. The inset to Fig.4 shows the result of in situ $\chi_{ac}$ measurements. Here, this measurement was performed before and after NQR $T_1$ measurements. The onset $T_c$ was determined to be 8.5 K from $\chi_{ac}$ data, where the distribution of $T_c$ was estimated to be less than $\sim 0.5$ K. In the duration of a single week to obtain NQR $T_1$ data, the onset $T_c$ was unchanged within less than $\sim 0.1$ K. It is noted that the NQR signal intensity was weakened suddenly below 8.5 K, because the rf pulse was attenuated due to the Meissner effect.

Figure 4 shows the temperature dependence of $1/T_1$ obtained for the $^{69}$Ga(2) NQR line. In
the normal state from $T_c$ to $\sim 30$ K, $1/T_1$ is approximately proportional to $T$, i.e., Korringa-like behavior associated with typical coherent Fermi liquid state. The values of $1/T_1$ above $\sim 30$ K fall below Korringa-like behavior, which is thought to be related to a reduction in the coherence of the Fermi liquid state. This Korringa-like behavior is also confirmed by preliminary high-field NMR $T_1$ measurements at $H_0 \sim 110$ kOe ($\parallel c$), where $T_c$ is suppressed down to $\sim 4$ K. The present $T_1$ results suggest that the SC state in PuRhGa$_5$ sets in after a Fermi liquid state is established below $\sim 30$ K. Further discussion of $T_1$ in the normal state will be presented elsewhere.

In the SC state, we have found that $1/T_1$ shows no coherence peak just below $T_c$, but decreases $\propto T^3$ as $T$ decreases, as seen in Fig.4. Besides, a deviation from $T^3$ behavior is also observed for $T$ well below $T_c$. The $1/T_1$ behavior we found cannot be explained in terms of a fully open SC gap with s-wave symmetry. These results strongly suggest that PuRhGa$_5$ has an anisotropic gap in the SC state. We can reproduce the behavior of $1/T_1$ under the assumption of $d$-wave symmetry with line nodes, which is widely accepted to be realized in the Ce115 family. This calculation has been done in the following way: An anisotropic gap function is assumed as a polar function $\Delta(\theta, \phi) = \Delta_0 \cos \theta$, where $\theta$ and $\phi$ mean angular parameters on
the Fermi surface, and the temperature dependence of $\Delta_0$ is assumed to be BCS-like. Then, the temperature dependence of $1/T_1$ below $T_c$ has been calculated from the following integral,

$$\frac{1}{T_1} = \frac{2}{k_B T} \int \left( \frac{N_s(E)}{N_0^2} \right)^2 \theta, \phi \langle f(E) - f(E) \rangle dE,$$

where $N_s(E) = N_0 E / \sqrt{E^2 - \Delta(\theta, \phi)^2}$ with $N_0$ being the density of states (DOS) in the normal state, $f(E)$ is the Fermi distribution function, and $\langle \cdots \rangle_{\theta, \phi}$ means the angular average over the Fermi surface. From the best fit of the experimental data to this calculation, we evaluate the SC gap $2\Delta_0(T \rightarrow 0) \approx 5k_B T_c$ with a residual DOS ($N_{\text{res}}/N_0 \approx 0.25$) in the SC state. This gap estimate is similar to that of CeIrIn$_5$ with $T_c \approx 0.4$ K, while it is smaller than that of CeCoIn$_5$, i.e., $2\Delta_0(0) \approx 8k_B T_c$ with $T_c \approx 2.3$ K. In the high-$T_c$ cuprates, the value of $2\Delta_0(0)$ often reaches $10k_B T_c$. PuRhGa$_5$ would be classified as an intermediate-coupling superconductor.

The finite residual DOS in the $d$-wave SC state is mostly caused by potential scattering associated with nonmagnetic impurities, distortion, and contamination with a secondary phase etc. In Pu compounds, the influence of unavoidable potential scattering coming from self-radiation damage is also expected. In the literature, the relation between the size of the residual DOS and the reduction rate of $T_c$ has been calculated based on an anisotropic SC model, where the scattering is treated in the unitarity (strong) limit. Using the relation with $N_{\text{res}}/N_0 \approx 0.25$ observed in our sample, we can obtain $T_c/T_{c0} \approx 0.94$, where $T_{c0}$ is the intrinsic value of $T_c$ without potential scattering effects. We can estimate the maximum (intrinsic) $T_{c0} = 9.0$ K using the $T_c = 8.5$ K in our sample observed a month after synthesis. This $T_{c0}$ is consistent with the observed $T_c$ just after synthesis. The aging effect on the residual DOS in the SC gap will be an interesting effect to study in Pu-based superconductors.

In summary, we have succeeded in $^{69,71}$Ga NMR/NQR measurements for the Ga(2) site of transuranium superconductor PuRhGa$_5$. The $^{69,71}$Ga(2) NQR lines have been found at frequencies consistent with an analysis based on NMR results. The NQR $1/T_1$ in the SC state shows no coherence peak just below $T_c$, but obeys a $T^3$ behavior below $T_c$. Such a result is strong evidence that PuRhGa$_5$ is an unconventional superconductor with an anisotropic SC gap. Assuming a $d$-wave symmetry, the SC gap $\Delta_0(0) \approx 5k_B T_c$ with $N_{\text{res}}/N_0 \approx 0.25$ has been evaluated. To determine the parity of SC pairing in PuRhGa$_5$, Knight shift measurements are in progress.

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-Added note. After completion of this paper, an NMR/NQR study on the closely related compound PuCoGa$_5$ by Curro et al., has appeared. It is useful to note some contrasting points in the behavior of these two Pu superconductors. First, the $T_1$ results of Curro et al., are also analyzed in terms of $d$-wave superconductivity, finding a SC gap value $2\Delta_0 \approx 8k_B T_c$ (c.f.,
5k_B T_c for PuRhGa_5). Secondly, the T-variation of (T_1 T)^{-1} for PuCoGa_5 shows a monotonic increase right down to T_c, whereas the Rh isomorph shows a Korringa-like behavior below \sim 30 \text{ K}. 
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