Sb-NQR probe for superconducting property in the Pr-based filled skutterudite compound PrRu$_4$Sb$_{12}$

M. Yogi$^1$, H. Kotegawa$^1$, Y. Imamura$^1$, G. -q. Zheng$^1$, Y. Kitaoka$^1$, H. Sugawara$^2$, H. Sato$^2$

$^1$Department of Physical Science, Graduate School of Engineering Science, Osaka University, Osaka 560-8531, Japan and $^2$Graduate School of Science, Tokyo Metropolitan University, Minami-Ohsawa 1-1, Hachioji, Tokyo 192-0397, Japan

(Dated: January 9, 2022)

We report the electronic and superconducting properties in the Pr-based filled-skutterudite superconductor PrRu$_4$Sb$_{12}$ with $T_c = 1.3$ K via the measurements of nuclear-quadrupole-resonance (NQR) frequency $\nu_Q$ and nuclear-spin-lattice-relaxation time $T_1$ of Sb nuclei. The temperature dependence of $\nu_Q$ has revealed the energy scheme of Pr$^{3+}$ crystal electric field (CEF) that is consistent with an energy separation $\Delta_{CEF} \sim 70$K between the ground state and the first-excited state. In the normal state, the Korringa relation of $\nu_Q$ is valid, with $[(1/T_1)_{\nu_Q}/(1/T(T))_{La}]^{1/2} \sim 1.44$ where $(1/T(T))_{La}$ is for LaRu$_4$Sb$_{12}$. These results are understood in terms of a conventional Fermi liquid picture in which the Pr-4$f^2$ state derives neither magnetic nor quadrupolar degrees of freedom at low temperatures. In the superconducting state, $1/T_1$ shows a distinct coherence peak just below $T_c$, followed by an exponential decrease with a value of $2\Delta/k_B T_c = 3.1$. These results demonstrate that PrRu$_4$Sb$_{12}$ is a typical weak-coupling s-wave superconductor, in strong contrast with the heavy-fermion superconductor PrOs$_4$Sb$_{12}$ that is in an unconventional strong coupling regime. The present study on PrRu$_4$Sb$_{12}$ highlights that the Pr-4$f^2$-derived non-magnetic doublet plays a key role in the unconventional electronic and superconducting properties in PrOs$_4$Sb$_{12}$.

PACS numbers: 71.27.-a, 76.60.-k

Filled-skutterudite compounds Re$_4$Ru$_4$Sb$_{12}$ (Re = rare earth; T = Fe, Ru and Os; Pu = pnictogen) show rich properties. PrRu$_4$P$_{12}$ and PrFe$_4$P$_{12}$ show a metal-insulator transition and undergo into an anomalous heavy-fermion (HF) state, respectively, whereas PrRu$_4$As$_{12}$, PrRu$_4$Sb$_{12}$ and PrOs$_4$Sb$_{12}$ exhibit a superconducting (SC) transition. Bauer et al. reported that PrOs$_4$Sb$_{12}$ shows HF behavior and superconducts at $T_c = 1.85$ K. It is the first Pr-based HF superconductor. Its HF state was inferred from the jump in the specific heat at $T_c$, the slope of the upper critical field $H_{c2}$ near $T_c$, and the electronic specific-heat coefficient $\gamma \sim 350 - 500$ mJ/mole K$^2$. Magnetic susceptibility, thermodynamic measurements, and inelastic neutron scattering experiments revealed the ground state of the Pr$^{3+}$ ions in the cubic crystal electric field (CEF) to be the $\Gamma_3$ nonmagnetic doublet. In the Pr-based compounds with the $\Gamma_3$ ground state, electric quadrupolar interactions play an important role. In analogy with a quadrupolar Kondo model, it was suggested that the HF-like behavior exhibited by PrOs$_4$Sb$_{12}$ may have something to do with a Pr-4$f^2$-derived quadrupolar Kondo lattice. An interesting issue to be addressed is what role of Pr-4$f^2$-derived quadrupolar fluctuations plays in relevance with the onset of the superconductivity in this compound.

Meanwhile, Kotegawa et al. have reported the Sb-NQR results which evidence the HF behavior and the unconventional SC property in PrOs$_4$Sb$_{12}$. The temperature ($T$) dependencies of nuclear-spin-lattice-relaxation rate, $1/T_1$ and nuclear-quadrupole-resonance (NQR) frequency unraveled a low-lying CEF splitting below $T_0 \sim 10$ K, associated with the Pr$^{3+}$(4$f^2$)-derived ground state. The analysis of $T_1$ suggests the formation of HF state below $T \sim 4$ K. In the SC state, $1/T_1$ shows neither a coherence peak just below $T_c = 1.85$ K nor a $T^3$ like power-law behavior observed for anisotropic HF superconductors with line-node gap. An isotropic energy-gap with $\Delta/k_B = 4.8$ K is suggested to open up already below $T^* \sim 2.3$ K. It is surprising that PrOs$_4$Sb$_{12}$ looks like an isotropic HF superconductor – it may indeed argue for Cooper pairing via quadrupolar fluctuations. Also, PrRu$_4$Sb$_{12}$ was reported to undergo a SC transition at $T_c = 1.3$ K from the measurements of the electrical resistivity and specific heat as well as LaRu$_4$Sb$_{12}$ with $T_c = 3.58$ K. It can be informative to compare PrRu$_4$Sb$_{12}$ with PrOs$_4$Sb$_{12}$ and the related La-based superconductors as shown in Table 1.

The localized character of 4$f$ electrons, namely the closeness of the respective Fermi surfaces with those in LaRu$_4$Sb$_{12}$ and LaOs$_4$Sb$_{12}$, has been confirmed in PrRu$_4$Sb$_{12}$ and PrOs$_4$Sb$_{12}$ based on the de Haas-van Alphen (dHvA) experiment. On the contrary, the mass enhancement in PrRu$_4$Sb$_{12}$ is much smaller than in PrOs$_4$Sb$_{12}$. For PrOs$_4$Sb$_{12}$, the CEF ground state was inferred to be the non-Kramers $\Gamma_3$ doublet carrying quadrupole moments, whereas the ground state for PrRu$_4$Sb$_{12}$ to be the $\Gamma_1$ singlet. Recently, however, there are several reports that are consistent with the CEF ground state for PrOs$_4$Sb$_{12}$ being the $\Gamma_1$ singlet. On the comparison in $T_c$ with the La compounds, the two compounds have different trend; $T_c$ for PrOs$_4$Sb$_{12}$ is
higher than that for La compounds, which is unusual if we take into account that PrOs$_4$Sb$_{12}$ contains the magnetic element Pr ion. These remarkable differences in the underlying CEF level scheme and hence electronic and SC characteristics between PrOs$_4$Sb$_{12}$ and PrRu$_4$Sb$_{12}$ may be ascribed to an intimate change in the hybridization strength of Pr-4f state with conduction electrons comprising of respective Os$_4$Sb$_{12}$- and Ru$_4$Sb$_{12}$-cage. In this context, it is needed that further light is shed upon the SC and electronic characteristics in the Pr-based superconductors.

In this paper, we report the normal and SC properties in the filled-skutterudite compound PrRu$_4$Sb$_{12}$ and LaRu$_4$Sb$_{12}$ via the measurements of NQR frequency $\nu_Q$ and nuclear-spin-lattice-relaxation time $T_1$ of Sb nuclei.

Single crystals of PrRu$_4$Sb$_{12}$ and LaRu$_4$Sb$_{12}$ were grown by the Sb-flux method. The observed dHvA oscillations in both compounds confirm the high quality of the samples. Measurement of ac-susceptibility confirmed the SC transitions at $T_c = 1.3$ K and 3.5 K for PrRu$_4$Sb$_{12}$ and LaRu$_4$Sb$_{12}$, respectively. The single crystal was crushed into powder for Sb-NQR measurement. The $^{121,123}$Sb-NQR measurements were performed using the conventional saturation-recovery method at zero field ($H = 0$). The NQR-$T_1$ measurement was carried out using the NQR transition $2\nu_Q$ at the $T$ range of $T = 0.24$ K - 240 K using a He$^3$-He$^4$ dilution refrigerator.

Fig.1(a) displays the $^{121,123}$Sb-NQR spectra at 4.2 K. Sb nuclei have two isotopes $^{121}$Sb and $^{123}$Sb. The respective nuclear spin $I = 5/2$ ($^{121}$Sb) and 7/2 ($^{123}$Sb) have natural abundance 57.3 and 42.7%, and nuclear gyromagnetic ratio $\gamma_N = 10.189$ and 5.5175 [MHz/$T$], giving rise to two and three NQR transitions, respectively. Fig.1(b) indicates the $T$ dependencies of $\nu_Q(T)$ derived from the $^{123}$Sb-2$\nu_Q$ transition in PrRu$_4$Sb$_{12}$ and LaRu$_4$Sb$_{12}$. The inset indicates $\delta\nu_Q(T) = \nu_Q(T)_{Pr} - \nu_Q(T)_{La}$, which subtracts the common effect due to lattice expansion in the both compounds. $\nu_Q(T)$ reveals a progressive increase upon cooling below $T \sim 70$ K, which is considered to be due to the CEF splitting. Note, as shown in Fig.1(c), that the $\delta\nu_Q(T) = \nu_Q(T)_{Pr} - \nu_Q(T)_{La}$ in PrOs$_4$Sb$_{12}$ was observed to be increased below a temperature comparable to the CEF splitting $\Delta_{CEF} \sim 10$ K between the ground state and the first excited state. From this comparison, $\Delta_{CEF} \sim 70$ K is expected in PrRu$_4$Sb$_{12}$. This is almost consistent with the analysis of susceptibility and resistivity.

Fig.2 presents the $T$ dependencies of $(1/T_1T)$ for PrRu$_4$Sb$_{12}$ and LaRu$_4$Sb$_{12}$. In the normal state, $T_1$ reveals a Korringa relation $(1/T_1T)_{Pr} = 1.73$ (s$K^{-1}$) for PrRu$_4$Sb$_{12}$, being comparable to $(1/T_1T)_{La} = 1.2$ (s$K^{-1}$) for LaRu$_4$Sb$_{12}$. The $1/T_1T = const.$ law deviates at temperatures higher than $\sim 30$K in PrRu$_4$Sb$_{12}$. Since such a deviation is seen in LaRu$_4$Sb$_{12}$ above $\sim 25$K as well, these deviations are not derived by the presence of Pr$^{3+}$ ions, but may be ascribed to a conduction-band derived effect inherent to the filled-skutterudite structure. In the filled-skutterudite structure, a Pr atom forms in a body centered cubic structure, surrounded by a cage of corner-sharing Ru$_4$Sb$_{12}$ octahedra. The cage might begin to stretch with increasing $T$. This stretching motion of cage may be relevant to the decrease in a value of $1/T_1T = const.$ for PrRu$_4$Sb$_{12}$ and LaRu$_4$Sb$_{12}$ and LaRu$_4$Pd$_{12}$. The measurements of the dHvA effect and the electronic specific heat for PrRu$_4$Sb$_{12}$ and LaRu$_4$Sb$_{12}$ revealed that the mass-renormalization effect in the Fermi liquid state is not so significant in PrRu$_4$Sb$_{12}$, suggesting that Pr$^{3+}$-4f$^2$ electrons are well localized in PrRu$_4$Sb$_{12}$. Note that the value of $1/T_1T$ is proportional to the square of the density of states $N(E_F)$ at the Fermi level. Also, it is scaled to a $T$-linear electronic contribution $\gamma$ of specific heat, giving rise to the relation of $(1/T_1T)^{1/2} \propto \gamma$. Therefore, the change in value of $(1/T_1T)^{1/2}$ is directly related to a change of $N(E_F)$ in systems. Corroborated by the fact that the value of $1/T_1T$ in PrRu$_4$Sb$_{12}$ is not so enhanced than that in...
LaRu$_4$Sb$_{12}$ with a ratio of $[(1/T_1 T)_{Pr}/(1/T_1 T)_{La}]^{1/2} = 1.44$, we remark that the Pr$^{+3} - 4f^2$ electrons with $Γ_1$ singlet as the ground state does not play a vital role for electronic and magnetic properties at low temperatures in PrRu$_4$Sb$_{12}$.

To summarize, the electronic and superconducting properties in the Pr-based filled-skutterudite superconductor PrRu$_4$Sb$_{12}$ with $T_c = 1.3$ K were investigated through the measurements of nuclear-quadrupole-resonance (NQR) frequency $ν_Q$ and nuclear-spin-lattice-relaxation time $T_1$ of Sb nuclei. The $T$ dependence of $ν_Q$ has revealed the energy scheme of crystal electric field (CEF) of Pr$^{+3}$ ion that is consistent with an energy separation $Δ_{CEF} \sim 70$K between the ground state and the first-excited level. In the normal state, the Korringa relation of $(1/T_1 T)_{Pr} = const.$ is valid, revealing a comparable value $[(1/T_1 T)_{Pr}/(1/T_1 T)_{La}]^{1/2} \sim 1.44$ with $(1/T_1 T)_{La}$ for LaRu$_4$Sb$_{12}$. These results are understood in terms of the conventional Fermi-liquid picture in which the Pr-4$f^2$ state derives neither magnetic nor quadrupolar degrees of freedom at low temperatures. In the SC state, $1/T_1$ shows a distinct coherence peak just below $T_c$, followed by an exponential decrease with the value of $2Δ/k_BT_c = 3.1$. These results demonstrate that PrRu$_4$Sb$_{12}$ is a typical weak-coupling $s$-wave superconductor, in strong contrast with the heavy-fermion superconductor PrOs$_4$Sb$_{12}$ that is in an unconventional strong coupling regime. The present study on PrRu$_4$Sb$_{12}$ highlights that the Pr-4$f^2$-derived non-magnetic doublet plays a key role for the unconventional electronic and superconducting properties in PrOs$_4$Sb$_{12}$.

We thank Y. Aoki and H. Harima for helpful discussions. This work was supported by the COE Research (10CE2004) in Grant-in-Aid for Scientific Research from the Ministry of Education, Sport, Science and Culture of Japan. One of the authors (H. K.) has been supported by JSPS Research Fellowships for Young Scientists.

1. C. Sekine, T. Uchiumi, and I. Shirotani, Phys. Rev. Lett. 79 (1997) 3218.
2. I. Shirotani, T. Uchiumi, K. Ohno, C. Sekine, Y. Nakazawa K. Kanoda, S. Todo and T. Yagi, Phys. Rev. B 56 (1997) 7866.
3. N. Takeda, M. Ishikawa, J. Phys. Soc. Jpn. 57 (2000) 868.
4. E. D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf, and M. B. Maple, Phys. Rev. B 65 (2002) 100506R.
TABLE I: Comparison of the superconducting critical temperature $T_c$, superconducting specific heat jump $\Delta C$ divided by $T_c$ ($\Delta C/T_c$), Sommerfeld coefficient, and effective mass $m^*_c$ in $RT_4Sb_{12}$ ($R$=La, Pr, T=Ru, Os).

| $T_c$ (K) | $\Delta C/T_c$ (mJ/K$^2$ mol) | Sommerfeld coefficient (mJ/K$^2$ mol) | $m^*_c/m_0$ for $\gamma$-branch |
|----------|-------------------------------|--------------------------------------|-------------------------------|
| PrOs$_4$Sb$_{12}$ | 1.85 | 500 | 350$\sim$750 | 7.6 |
| LaOs$_4$Sb$_{12}$ | 0.74 | 84 | 36, 56 | 2.8 |
| PrRu$_4$Sb$_{12}$ | 1.3 | 110 | 59 | 1.6 |
| LaRu$_4$Sb$_{12}$ | 3.58 | 82 | 37 | 1.4 |