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Sb-NQR probe for superconducting properties in the Pr-based filled-skutterudite compound $PrRu_4Sb_{12}$

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We report the electronic and superconducting properties in the Pr-based filled-skutterudite superconductor $PrRu_4Sb_{12}$ with $T_c = 1.3$ K via the measurements of nuclear-quadrupole-resonance frequency ν_Q and nuclear-spin-lattice-relaxation time T_1 of Sb nuclei. The temperature dependence of ν_Q has revealed the energy scheme of Pr^{3+} crystal electric field 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 $(1/T_1T)_{\rm Pr} = $const is valid, with $[(1/T_1T)_{\rm Pr}/(1/T_1T)_{\rm La}]^{1/2} \sim 1.44$, where $(1/T_1T)_{\rm La}$ is for $LaRu_4Sb_{12}$. These results are understood in terms of a conventional Fermi-liquid picture in which the Pr-$4f^2$ 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 $2\Delta/k_BT_c = 3.1$. These results demonstrate that $PrRu_4Sb_{12}$ is a typical weak-coupling *s*-wave superconductor, in strong contrast with the heavy-fermion superconductor $PrOs_4Sb_{12}$ that is in an unconventional strong coupling regime. The present study on $PrRu_4Sb_{12}$ highlights that the Pr-$4f^2$-derived nonmagnetic doublet plays a key role in the unconventional electronic and superconducting properties in $PrOs_4Sb_{12}$.

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Filled-skutterudite compounds ReT_4Pn$_{12}$ (Re = rare earth; T = Fe, Ru, and Os; Pn = pnictogen) show rich properties. $PrRu_4P_{12}$ and $PrFe_4P_{12}$ show a metal-insulator transition and undergo an anomalous heavy-fermion (HF) state, respectively, whereas $PrRu_4As_{12}$, $PrRu_4Sb_{12}$, and $PrOs_4Sb_{12}$ exhibit a superconducting (SC) transition.[1–4] Bauer *et al.* reported that $PrOs_4Sb_{12}$ shows HF behavior and superconducts at $T_c = 1.85$ K. It is the first Pr-based HF superconductor.[4] 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 Γ_3 nonmagnetic doublet.[4,5] In the Pr-based compounds with the Γ_3 ground state, electric quadrupolar interactions play an important role. In analogy with a quadrupolar Kondo model,[6] it was suggested that the HF-like behavior exhibited by $PrOs_4Sb_{12}$ may have something to do with a Pr-$4f^2$-derived quadrupolar Kondo lattice. An interesting issue to be addressed is what role do Pr-$4f^2$-derived quadrupolar fluctuations play in relevance with the onset of the superconductivity in this compound.

Meanwhile, Kotegawa *et al.* have reported the Sb-NQR results that evidence the HF behavior and the unconventional SC property in $PrOs_4Sb_{12}$.[7] 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 $Pr^{3+}(4f^2)$-derived ground state. The analysis of T_1 suggests the formation of HF state below ~ 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 the 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 $PrOs_4Sb_{12}$ looks like an *isotropic* HF superconductor—it may indeed argue for Cooper pairing via quadrupolar fluctuations. Also, $PrRu_4Sb_{12}$ 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 $LaRu_4Sb_{12}$ with $T_c = 3.58$ K.[3] It can be informative to compare $PrRu_4Sb_{12}$ with $PrOs_4Sb_{12}$ and the related La-based superconductors as shown in Table I.[8]

The localized character of $4f$ electrons, namely, the closeness of the respective Fermi surfaces with those in $LaRu_4Sb_{12}$ and $LaOs_4Sb_{12}$, has been confirmed in $PrRu_4Sb_{12}$ and $PrOs_4Sb_{12}$ based on the de Haas–van Alphen (dHvA) experiment.[8,9] On the contrary, the mass enhancement in $PrRu_4Sb_{12}$ is much smaller than in $PrOs_4Sb_{12}$. For $PrOs_4Sb_{12}$, the CEF ground state was inferred to be the non-Kramers Γ_3 doublet carrying quadrupole moments, whereas the ground state for $PrRu_4Sb_{12}$ was inferred to be the Γ_1 singlet.[3,10] Recently, however, there have been several reports that are consistent with the CEF ground state for $PrOs_4Sb_{12}$ being the Γ_1 singlet.[11–13] On the comparison in T_c with the La compounds, the two compounds have different trends; T_c for $PrOs_4Sb_{12}$ is higher than that for La compounds, which is unusual if we take into account that $PrOs_4Sb_{12}$ contains the magnetic element Pr ion. These remarkable differences in the underlying CEF level scheme and hence electronic and SC characteristics between $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$ may be ascribed to an intimate change in the hybridization strength of the Pr-4f state with conduction electrons comprising respective Os_4Sb_{12} and Ru_4Sb_{12} cages. In this context, it is needed that further light is shed on 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 $PrRu_4Sb_{12}$ and $LaRu_4Sb_{12}$

TABLE I. Comparison of the superconducting critical temperature T_c, superconducting specific-heat jump ΔC divided by T_C ($\Delta C/T_C$), Sommerfeld coefficient and effective mass m_c^* in ReT_4Sb_{12} (Re = La, Pr, T = Ru, Os) (Ref. 8).

	$PrOs_4Sb_{12}$	$LaOs_4Sb_{12}$	$PrRu_4Sb_{12}$	$LaRu_4Sb_{12}$
T_C (K)	1.85	0.74	1.3	3.58
$\Delta C/T_C$(mJ/K^2 mol)	500	84	110	82
Sommerfeld coefficient (mJ/K^2 mol)	350–750	36, 56	59	37
m_c^*/m_0 for γ branch	7.6	2.8	1.6	1.4

via the measurements of NQR frequency ν_Q and nuclear-spin-lattice-relaxation time T_1 of Sb nuclei.

Single crystals of $PrRu_4Sb_{12}$ and $LaRu_4Sb_{12}$ were grown by the Sb-flux method.[3] The observed dHvA oscillations in both compounds confirm the high quality of the samples.[9] Measurement of ac susceptibility confirmed the SC transitions at $T_c = 1.3$ K and 3.5 K for $PrRu_4Sb_{12}$ and $LaRu_4Sb_{12}$, 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 $T = 0.24$–240 K using a ^{3}He-^{4}He dilution refrigerator.

Figure 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 spins $I = 5/2$(^{121}Sb) and 7/2 (^{123}Sb) have natural abundances 57.3% and 42.7%, and nuclear gyromagnetic ratios $\gamma_N = 10.189$ and 5.5175 MHz/T, giving rise to two and three NQR transitions, respectively. Figure 1(b) indicates the T dependencies of $\nu_Q(T)$ derived from the ^{123}Sb-$2\nu_Q$ transition in $PrRu_4Sb_{12}$ and $LaRu_4Sb_{12}$. The inset indicates $\delta\nu_Q(T) = \nu_Q(T)_{\rm Pr} - \nu_Q(T)_{\rm La}$, which subtracts the common effect due to lattice expansion in both the 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 $\delta\nu_Q(T) = \nu_Q(T)_{\rm Pr} - \nu_Q(T)_{\rm La}$ in $PrOs_4Sb_{12}$ 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 $PrRu_4Sb_{12}$. This is almost consistent with the analysis of susceptibility and resistivity.[3,10]

Figure 2 presents the T dependencies of $(1/T_1T)$ for $PrRu_4Sb_{12}$ and $LaRu_4Sb_{12}$. In the normal state, T_1 reveals a Korringa relation $(1/T_1T)_{\rm Pr} = 1.73\ ({\rm s\,K})^{-1}$ for $PrRu_4Sb_{12}$, being comparable to $(1/T_1T)_{\rm La} = 1.2\ ({\rm s\,K})^{-1}$ for $LaRu_4Sb_{12}$. The $1/T_1T = $ const law deviates at temperatures higher than ~ 30 K in $PrRu_4Sb_{12}$. Since such a deviation is seen in $LaRu_4Sb_{12}$ above ~ 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_4Sb_{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 $PrRu_4Sb_{12}$, $LaRu_4Sb_{12}$, and $LaRu_4P_{12}$.[14] The measurements of the dHvA effect and the electronic specific heat for $PrRu_4Sb_{12}$ and $LaRu_4Sb_{12}$ revealed that the mass-renormalization effect in the Fermi-liquid state is not so significant in $PrRu_4Sb_{12}$, suggesting that Pr^{3+}-$4f^2$ electrons are well localized in $PrRu_4Sb_{12}$.

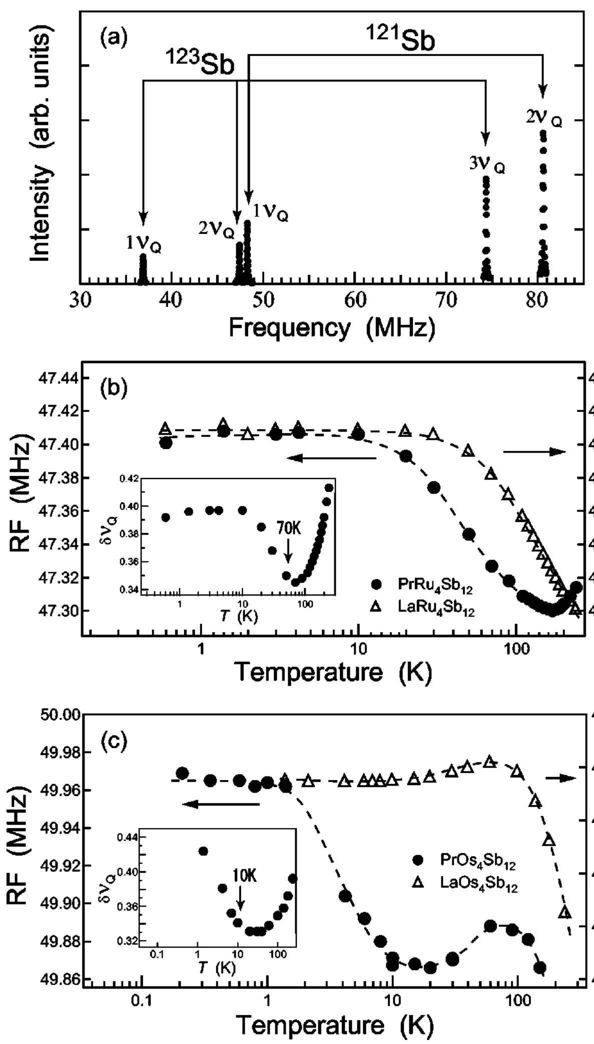

FIG. 1. (a) ^{121}Sb- and ^{123}Sb-NQR spectra in $PrRu_4Sb_{12}$. (b) The temperature dependence of NQR frequency ν_Q for $PrRu_4Sb_{12}$ and $LaRu_4Sb_{12}$ at the ^{123}Sb-$2\nu_Q$ transitions. The inset indicates the Pr-derived contribution in ν_Q, $\delta\nu_Q = (\nu_Q)_{\rm Pr} - (\nu_Q)_{\rm La}$. (c) T dependence of NQR frequency for $PrOs_4Sb_{12}$ and $LaOs_4Sb_{12}$ at ^{123}Sb-$2\nu_Q$ transitions (Ref. 7). The inset indicates $\delta\nu_Q = (\nu_Q)_{\rm Pr} - (\nu_Q)_{\rm La}$.

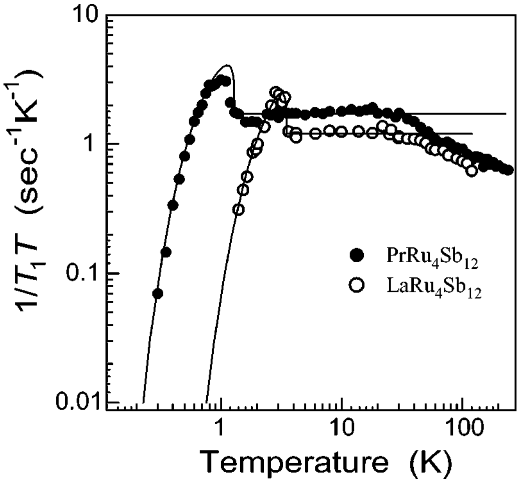

FIG. 2. Temperature dependence of $1/T_1T$ for $PrRu_4Sb_{12}$ and $LaRu_4Sb_{12}$. Solid lines are the fits calculated based on the weak-coupling *s*-wave model assuming a size of isotropic gap $2\Delta/k_BT_c = 3.1$ and 3.6 for $PrRu_4Sb_{12}$ and $LaRu_4Sb_{12}$, respectively.

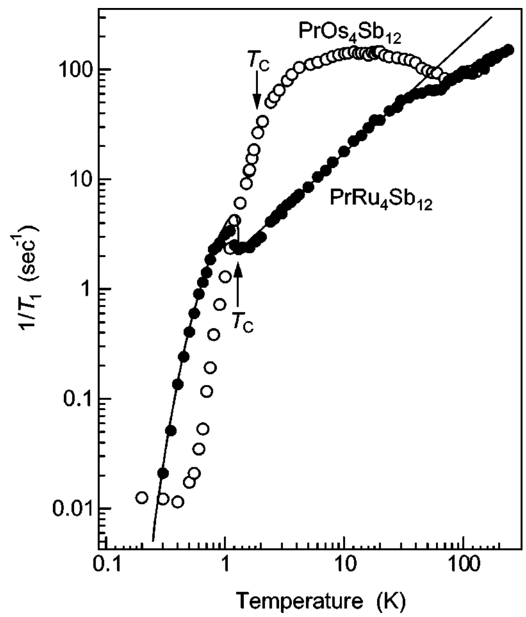

FIG. 3. Temperature dependencies of $1/T_1$ for $PrRu_4Sb_{12}$ and $PrOs_4Sb_{12}$ (Ref. 7). The solid line for $PrRu_4Sb_{12}$ is the fit based on the weak-coupling *s*-wave model with $2\Delta/k_BT_c = 3.1$.

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 γ of specific heat, giving rise to the relation of $(1/T_1T)^{1/2} \propto \gamma$. Therefore, the change in the 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 $PrRu_4Sb_{12}$ is not so enhanced than that in $LaRu_4Sb_{12}$ with a ratio of $[(1/T_1T)_{\mathrm{Pr}}/(1/T_1T)_{\mathrm{La}}]^{1/2} = 1.44$, 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 $PrRu_4Sb_{12}$.

In the SC state for $PrRu_4Sb_{12}$ and $LaRu_4Sb_{12}$, $1/T_1$ shows a distinct coherence peak, followed by an exponential decrease below T_c with an isotropic gap $2\Delta/k_BT_c = 3.1$ and 3.6, respectively. These results demonstrate that $PrRu_4Sb_{12}$ and $LaRu_4Sb_{12}$ are typical weak-coupling *s*-wave superconductors. In Fig. 3 are shown the *T* dependencies of $1/T_1$ for $PrRu_4Sb_{12}$ and $PrOs_4Sb_{12}$. From the comparison in the normal and SC states, it is clear that remarkable differences arise because the quadrupole degree of freedom plays a vital role in $PrOs_4Sb_{12}$, associated with the Pr^{+3}-$4f^2$ derived non-Kramers doublet. It may indeed argue for Cooper pairing via quadrupolar fluctuations.

To summarize, the electronic and superconducting properties in the Pr-based filled-skutterudite superconductor $PrRu_4Sb_{12}$ with $T_c = 1.3$ K were investigated through the measurements of 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 CEF of Pr^{3+} ion, which is consistent with an energy separation $\Delta_{CEF} \sim 70$ K between the ground state and the first-excited level. In the normal state, the Korringa relation of $(1/T_1T)_{\mathrm{Pr}} = \mathrm{const}$ is valid, revealing a comparable value $[(1/T_1T)_{\mathrm{Pr}}/(1/T_1T)_{\mathrm{La}}]^{1/2} \sim 1.44$ with $(1/T_1T)_{\mathrm{La}}$ for $LaRu_4Sb_{12}$. These results are understood in terms of the conventional Fermi-liquid picture in which the Pr-$4f^2$ 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 $2\Delta/k_BT_c = 3.1$. These results demonstrate that $PrRu_4Sb_{12}$ is a typical weak-coupling *s*-wave superconductor, in strong contrast with the heavy-fermion superconductor $PrOs_4Sb_{12}$ that is in a unconventional strong coupling regime.[7] The present study on $PrRu_4Sb_{12}$ highlights that the Pr-$4f^2$ derived nonmagnetic doublet plays a key role for the unconventional electronic and superconducting properties in $PrOs_4Sb_{12}$.

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[1] C. Sekine, T. Uchiumi, I. Shirotani, and T. Yagi, Phys. Rev. Lett. **79**, 3218 (1997).

[2] I. Shirotani, T. Uchiumi, K. Ohno, C. Sekine, Y. Nakazawa, K. Kanoda, S. Todo, and T. Yagi, Phys. Rev. B **56**, 7866 (1997).

[3] N. Takeda and M. Ishikawa, J. Phys. Soc. Jpn. **57**, 868 (2000).

[4] E.D. Bauer, N.A. Frederick, P.-C. Ho, V.S. Zapf, and M.B. Maple, Phys. Rev. B **65**, 100506(R) (2002).

[5] M.B. Maple, P.-C. Ho, V.S. Zapf, N.A. Frederick, E.D. Bauer, W.M. Yuhasz, F.M. Woodward, and J.W. Lynn, J. Phys. Soc. Jpn. **71**, 23 (2002).

[6] D.L. Cox, Phys. Rev. Lett. **59**, 1240 (1987).

[7] H. Kotegawa, M. Yogi, Y. Imamura, Y. Kawasaki, G.-q. Zheng, Y.

Kitaoka, S. Ohsaki, H. Sugawara, Y. Aoki, and H. Sato, Phys. Rev. Lett. **90**, 027001 (2003).

[8] H. Sugawara, S. Osaki, S.R. Saha, Y. Aoki, H. Sato, Y. Inada, H. Shishido, R. Settai, Y. Onuki, H. Harima, and K. Oikawa, Phys. Rev. B **66**, 220504(R) (2002).

[9] T.D. Matsuda, K. Abe, F. Watanuki, H. Sugawara, Y. Aoki, H. Sato, Y. Inada, R. Settai, and Y. Onuki, Physica B **312-313**, 832 (2002).

[10] K. Abe, H. Sato, T.D. Matsuda, T. Namiki, H. Sugawara, and Y. Aoki, J. Phys.: Condens. Matter **14**, 11 757 (2002).

[11] Y. Aoki, T. Namiki, S. Ohsaki, S.R. Saha, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **71**, 2098 (2002).

[12] M. Kohgi *et al.*, J. Phys. Soc. Jpn. (to be published).

[13] T. Tayama *et al.* (unpublished).

[14] K. Fujiwara, K. Ishihara, K. Miyoshi, J. Takeuchi, C. Sekine, and I. Sirotani, Physica B **281-282**, 296 (2000).