Evidence for Unconventional Strong-Coupling Superconductivity in $PrOs_4Sb_{12}$: An Sb Nuclear Quadrupole Resonance Study

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We report Sb-NQR results which evidence a heavy-fermion (HF) behavior and an unconventional superconducting (SC) property in $PrOs_4Sb_{12}$ with $T_c = 1.85$ K. The temperature (T) dependence of nuclear-spin-lattice-relaxation rate, $1/T_1$, and NQR frequency unravel a low-lying crystal-electric-field splitting below $T_0 \sim 10$ K, associated with $Pr^{3+}(4f^2)$-derived ground state. In the SC state, $1/T_1$ shows neither a coherence peak just below T_c K nor a T^3-like power-law behavior observed for *anisotropic* HF superconductors with the line-node gap. The *isotropic* energy gap with its size $\Delta/k_B = 4.8$ K seems to open up across T_c 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.

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A class of Ce- and U-based intermetallic compounds reveals a crossover from a high-temperature localized to a low-temperature heavy-fermion (HF) state in which f electrons are delocalized with enormous effective mass and are remarkable to undergo a superconducting (SC) transition with a line-node gap, indicative of the Cooper pairing of heavy fermions with an angular momentum greater than zero. It is widely believed that the superconductivity in these materials is mediated by magnetic fluctuations.

Recently, the HF-like behavior or a quadrupolar ordering has been reported in $PrInAg_2$ [1], $PrFe_4P_{12}$ [2–5], and $PrPb_3$ [6–9]. In these compounds, the ground state of a Pr^{3+} with $4f^2$ in a crystal electric field (CEF) scheme is believed to be the Γ_3 nonmagnetic doublet with the electric quadrupolar moments for a total angular momentum $J = 4$ state. The quadrupolar moments interact with the charges of conduction electrons, leading to the HF-like behavior or the quadrupolar ordering in these Pr-based compounds. In fact, $PrPb_3$ shows an antiferroquadrupolar ordering in the Γ_3 ground state at 0.4 K [6–9]. In $PrInAg_2$, a broad peak in specific heat is identified as a Kondo anomaly, having an enhanced electronic specific heat coefficient $\gamma \sim 6.5$ J/mol K^2 [1]. Likewise, the filled-skutterudite compound $PrFe_4P_{12}$ shows the HF-like behavior with a large mass of $m^* \sim 70 m_e$ [2] under a magnetic field and undergoes an anomalous transition at 6.4 K at zero field, indicative of a quadrupolar ordering [3–5]. Note that the large values in C/T for these compounds are due not only to such low-energy degrees of freedom as either magnetic or quadrupolar fluctuations, but also to the Schottky anomaly originating from some low-lying CEF splitting.

Meanwhile, Bauer *et al.* reported the observation of HF behavior and superconductivity at $T_c = 1.85$ K in the filled-skutterudite compound $PrOs_4Sb_{12}$ that is the first Pr-based HF superconductor [10,11]. Its HF state was inferred from the jump in the specific heat at T_c, the slope of the upper critical field near T_c, and the electronic specific heat coefficient $\gamma \sim 350$–500 mJ/mol K^2. The magnetic susceptibility, thermodynamic measurements, and inelastic neutron scattering experiments revealed the ground state of the Pr^{3+} ions in the cubic CEF to be the Γ_3 nonmagnetic doublet [10–12]. In the Pr-based compounds with the Γ_3 ground state, the quadrupolar interactions play an important role. In analogy with the quadrupolar Kondo model [13], it was suggested that the HF-like behavior exhibited by $PrOs_4Sb_{12}$ may be relevant to a quadrupolar Kondo lattice. An interesting issue to be addressed is what the role of Pr^{3+}-derived quadrupolar fluctuations plays in relevance with the onset of the superconductivity in this compound.

In this Letter, we report the observation of unconventional SC property probed by the nuclear-spin-lattice-relaxation time, T_1, in $PrOs_4Sb_{12}$ through ^{121,123}Sb nuclear quadrupolar resonance (NQR) experiments at zero field. Single crystals of $PrOs_4Sb_{12}$ were grown by the Sb-flux method as described elsewhere [14]. Measurements of electrical resistivity and ac susceptibility confirmed a SC transition at $T_c = 1.85$ K. The observation of the de Haas–van Alphen oscillations ensures the high quality of the samples [14]. For the ^{121,123}Sb NQR measurements, the single crystals were crushed into powder.

Figure 1(a) displays ^{121,123}Sb-NQR spectra for two Sb isotopes at 4.2 K. ^{121}Sb (^{123}Sb) with natural abundance 57.3% (42.7%) has the nuclear spin $I = 5/2$ (7/2) and the nuclear gyromagnetic ratio $\gamma_N = 10.189$ (5.5175) (MHz/T), and exhibits two (three) NQR transitions. The nuclear electric quadrupole interaction is represented as $\mathcal{H}_Q = \frac{e^2qQ}{4I(2I-1)}\{[3I_z^2 - I(I+1)] + \eta(I_x^2 - I_y^2)\}$, where eq gives the component along the principle z axis of the EFG, which is determined by

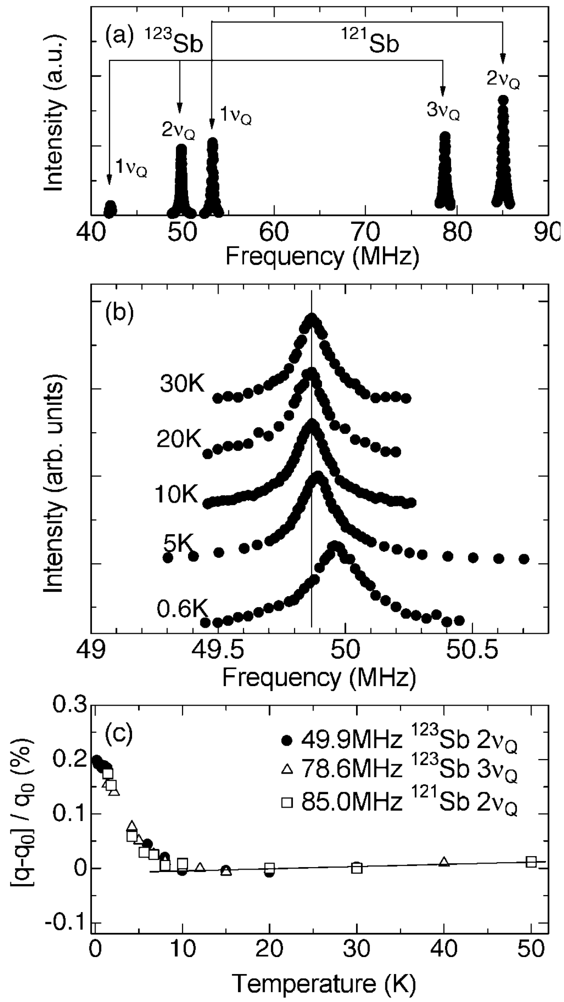

FIG. 1. (a) ^{121}Sb and ^{123}Sb-NQR spectra in PrOs$_4$Sb$_{12}$. The respective electric quadrupole frequencies are estimated as $^{121}\nu_Q \sim 44.2$ MHz and $^{123}\nu_Q \sim 26.8$ MHz, and an asymmetry parameter as $\eta \sim 0.46$. (b) T dependence of the NQR spectrum for the $2\nu_Q$ of ^{123}Sb. The peak in the spectrum shifts significantly to the high frequency upon cooling below $T_0 \sim 10$ K. (c) T dependence of the relative change in the electric field gradient (EFG), $[q(T) - q_0]/q_0$ at the Sb nuclei. Here $[q(T) - q_0]/q_0 = [\nu_Q(T) - \nu_0]/\nu_0$ with the ν_0 at 10 K.

the charge distribution of conduction electrons around the Sb nuclei. The ratio of the nuclear quadrupolar moment, $^{123}Q/^{121}Q$, was reported as $\sim$1.275 from the NQR measurement of the pure Sb metal [15]. From these spectra, the values of nuclear quadrupole frequency, $^{121}\nu_Q \sim 44.2$ MHz and $^{123}\nu_Q \sim 26.8$ MHz, are deduced for PrOs$_4$Sb$_{12}$ along with an asymmetric parameter $\eta \sim 0.46$. Here $\nu_Q = \frac{3e^2qQ}{2I(2I-1)}$. Figure 1(b) indicates the T dependence of the ^{123}Sb-NQR spectrum arising from the $2\nu_Q$ transition. The peak of the spectrum shifts to a high frequency below $T_0 \sim 10$ K that is shown later to be a characteristic temperature also in $1/T_1$. Since the transitions of $2\nu_Q$ and $3\nu_Q$ are not sensitive to the change in η, almost the same relative variations of EFG, $[q - q_0]/q_0$, against the value q_0 at 10 K are obtained from the $2\nu_Q$ for ^{123}Sb and $2\nu_Q$ and $3\nu_Q$ for ^{121}Sb, using a relation of $[\nu_Q(T) - \nu_0]/\nu_0$ as shown in Fig. 1(c). Here ν_0 is the value of ν_Q at 10 K. The rapid increase in EFG at the Sb site is evident below $T_0 \sim 10$ K. Such a distinct shift is never seen in the isostructual LaOs$_4$Sb$_{12}$ at low T. It is natural to ascribe this increase in EFG to the Pr^{3+}-derived change. This is because the electronic contribution in specific heat divided by T, $\Delta C/T$ revealed a similar T variation to the EFG. It was reported that the rapid increase in $\Delta C/T$ is consistent with the energy scheme of the $4f^2(J = 4)$ state of Pr^{3+} in the CEF; that is, the Γ_3 nonmagnetic doublet is a ground state and the Γ_5 magnetic triplet is a first excited state. The magnetic susceptibility, inelastic neutron scattering, and specific heat revealed the CEF energy splitting of $\Delta_{\rm CEF} = 7$–11 K between these two levels [10–12,16,17]. Therefore, the electric quadrupole moments of this Γ_3 ground state interact with the charges of the conduction electrons in the T range below $T_0 \sim 10$ K because of $T < \Delta_{\rm CEF}$. Thus the significant increase below T_0 in both $\Delta C/T$ and the EFG at the Sb site is indicative of a low-lying CEF splitting below $T_0 \sim 10$ K, associated with the Pr$^{3+}(4f^2)$-derived ground state.

Figure 2 indicates the T dependence of $1/T_1$ measured at $2\nu_Q \sim 48.9$ MHz for ^{123}Sb along with the result in LaOs$_4$Sb$_{12}$ ($T_c = 0.75$ K). T_1 is uniquely determined by the theoretical curve of nuclear magnetization where the value of η is incorporated [18]. In the normal state, a relation of $T_1T =$ const is valid in LaOs$_4$Sb$_{12}$, characteristic for conventional metallic materials. By contrast, the $1/T_1$ in the normal state for PrOs$_4$Sb$_{12}$ is more strongly enhanced than for LaOs$_4$Sb$_{12}$, showing a relaxation behavior similar to Ce-based HF systems reported thus far. Since $1/T_1$ stays a constant in $T = 10$–20 K, the $4f$-electron-derived moments behave as if localized. With decreasing T below $T_0 \sim 10$ K, $1/T_1$ decreases because of $T < \Delta_{\rm CEF}$. In the localized regime at high T, $1/T_1T \propto \chi(T)$, where $\chi(T)$ is a Curie-Weiss-like magnetic susceptibility in the normal state. As a matter of fact, the T dependence of $1/T_1T$, which is shown in Fig. 3, resembles the measured susceptibility [10], which suggests that the Γ_3 is the ground state and the Γ_5 is the first excited state [10,11]. The relaxation behavior is thus consistent with the other experiments suggesting $\Delta_{\rm CEF} = 7$–11 K [10–12,16,17]. In T lower than $\sim$4 K, however, this CEF model is not valid.

The inset of Fig. 2 presents the T dependencies of $(1/T_1)/\gamma_N^2$ at the $2\nu_Q \sim 48.9$ MHz and the $3\nu_Q \sim 78.6$ MHz for ^{123}Sb, and the $2\nu_Q \sim 85.0$ MHz for ^{121}Sb. All the data fall on one curve, demonstrating that the relaxation process is magnetic in origin throughout the measured T range. This result indicates that the ground state is not always in a nonmagnetic regime where the quadrupolar degree of freedom of nonmagnetic doublet Γ_3 is dominant, but Γ_3 might be hybridized with

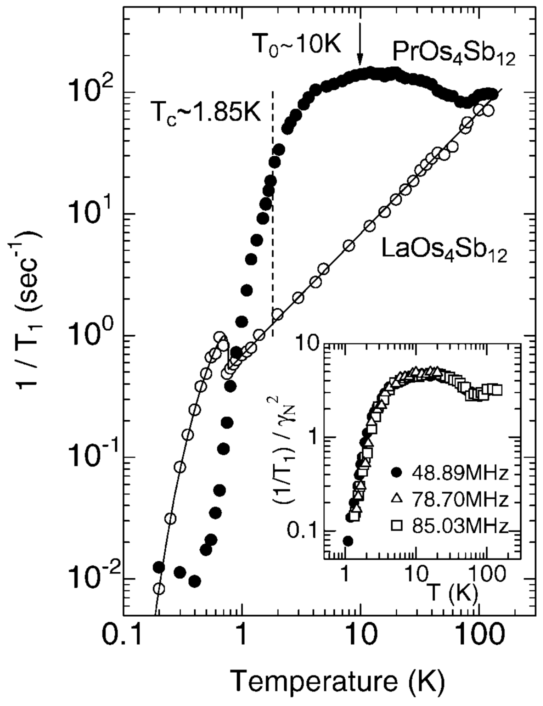

FIG. 2. T dependence of $1/T_1$ at the $2\nu_Q$ transition of ^{123}Sb for $PrOs_4Sb_{12}$ (closed circles) and $LaOs_4Sb_{12}$ (open circles). The inset presents the T dependencies of $1/T_1$'s at the $2\nu_Q$ (48.89 MHz) and $3\nu_Q$ (78.70 MHz) for ^{123}Sb and the $2\nu_Q$ (85.03 MHz) for ^{121}Sb where the respective data are divided by the nuclear gyromagnetic ratio $^{123}\gamma_N^2$ and $^{121}\gamma_N^2$. All these data are consistent with each other, demonstrating the relaxation process is magnetic in origin.

conduction electrons, making the magnetic relaxation channel open even for $T \ll \Delta_{\rm CEF}$. In such a case, the relaxation process at low T may be described in terms of the CEF channel and the quasiparticle's one as follows: $(1/T_1)_{\rm obs} = A \times \exp(-\Delta_{\rm CEF}/k_BT) + B \times 0.7T$, where $1/T_1 = 0.7T$ corresponds to the Korringa relation for $LaOs_4Sb_{12}$. The first term is the CEF contribution arising from the first excited Γ_5 triplet state and the second one the quasiparticle's one due to the hybridization between the Γ_3 state and conduction electrons. The dotted line in the inset of Fig. 3 is a best fit obtained by assuming $\Delta_{\rm CEF}/k_B = 8$ K [16] and $B = 26.7$ below ~4 K. The latter value allows us to estimate that the effective density of state (DOS) for $PrOs_4Sb_{12}$ is ~5.2 times larger than that for $LaOs_4Sb_{12}$, because $1/T_1T$ is proportional to the square of the DOS. This value is quite consistent with the result of $\gamma = 313$–350 mJ/mol K^2 for $PrOs_4Sb_{12}$ [10,17] being 6 times larger than $\gamma = 56$ mJ/mol K^2 for $LaOs_4Sb_{12}$ [19]. It is expected that the heavy-quasiparticle state is realized through mixing between the nonmagnetic Γ_3 doublet state and conduction electrons.

Next we deal with the SC property. In order to present the T dependence of the quasiparticle part $(1/T_1T)_{\rm qp}$ at low T, the CEF contribution is subtracted from the raw data $(1/T_1T)_{\rm obs}$ as $(1/T_1T)_{\rm qp} = (1/T_1T)_{\rm obs} - (A/T) \times \exp(-\Delta_{\rm CEF}/k_BT)$ with $\Delta_{\rm CEF}/k_B = 8$ K. Figure 4(a) presents the T dependence of $(1/T_1T)_{\rm qp}/(1/T_1T)_{{\rm qp},n}$ below $T = 4.2$ K, where $(1/T_1T)_{{\rm qp},n}$ stays a constant in $T =$ 2.3–4.2 K. Unexpectedly, $(1/T_1T)_{\rm qp}/(1/T_1T)_{{\rm qp},n}$ decreases over *3 orders of magnitude* down to $0.3T_c$ without any trace of coherence peak across T_c. Thus far, most Ce- or U-based HF superconductors are used to show a power-law behavior of $1/T_1 \sim T^3$ at low temperatures, consistent with a line-node SC gap [20,21]. The $(1/T_1T)_{\rm qp}$ in $PrOs_4Sb_{12}$ does not, however, reveal a T^2 dependence as indicated by the solid line in Fig. 4(a). Instead, as presented in Fig. 4(b), it follows an exponential decrease with $\Delta/k_B = 4.8$ K across $T_c = 1.85$ K. A recent μSR experiment also suggests an isotropic energy gap [22]. The estimated large value of a SC gap with $2\Delta/k_BT_c \sim$ 5.2 seems to be relevant with the observation of the large

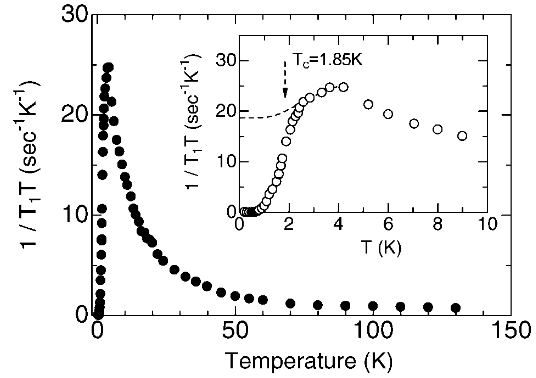

FIG. 3. T dependence of $1/T_1T$ for $PrOs_4Sb_{12}$. The data below ~4.2 K are reproduced by incorporating both the contributions arising from the CEF effect and the formation of heavy quasiparticles (see text). The dotted line in the inset corresponds to the relation of $(1/T_1T)_{\rm obs} = (A/T) \times \exp(-\Delta_{\rm CEF}/k_BT) + 0.7B$. Here $1/T_1T = 0.7$ corresponds to the Korringa relation for $LaOs_4Sb_{12}$. The latter is responsible for the onset of the superconductivity.

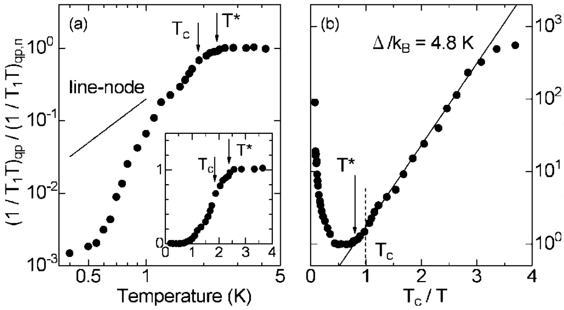

FIG. 4. (a) $(1/T_1T)_{\rm qp}/(1/T_1T)_{{\rm qp},n}$ vs T plots at temperatures lower than $T = 4.2$ K in both logarithmic scales. Here $(1/T_1T)_{\rm qp} = (1/T_1T)_{\rm obs} - (A/T) \times \exp(-\Delta_{\rm CEF}/k_BT)$ with $\Delta_{\rm CEF}/k_B = 8$ K and $(1/T_1T)_{{\rm qp},n} = 0.7B$ (see text). The inset presents the clear decrease in $(1/T_1T)_{\rm qp}$ below $T^* \sim 2.3$ K. (b) Arrhenius plots of $\ln[(T_1T)_{\rm qp}/(T_1T)_{{\rm qp},n}]$ vs (T_c/T) are on a linear line across T_c below $T^* \sim 2.3$ K, giving rise to the large value of isotropic energy gap with $2\Delta/k_BT_c \sim 5.2$.

jump $\Delta C/\gamma T_c \sim 3$ in the specific heat at T_c [17]. From the T dependence of $(1/T_1T)_{\rm qp}$ below $T^* \sim 2.3$ K that is presented in the inset of Fig. 4(a) along with Fig. 4(b), the isotropic SC gap for $\rm PrOs_4Sb_{12}$ across T_c seems to open up already below $T^* \sim 2.3$ K in the normal state. As a possible interpretation for this anomaly, some unconventional strong-coupling effect may give rise to preformed pairs around T^* before a bulk SC transition takes place. Note that this T^* is close to the temperature at which C/T has a peak [17]. However, this interpretation remains still an issue, because other measurements such as the electric resistivity and the static susceptibility do not show any anomaly around T^*.

Apparently, the anomalous relaxation behavior in $\rm PrOs_4Sb_{12}$ contrasts with a conventional one for an s-wave case that is actually seen in the T dependence of $1/T_1$ for $\rm LaOs_4Sb_{12}$ with $T_c = 0.75$ K in Fig. 2. Remarkably, in this SC state, $1/T_1$ shows the large coherence peak just below T_c, followed by the exponential dependence with the gap size of $2\Delta/k_BT_c \sim 3.2$ at low T. This clearly evidences that $\rm LaOs_4Sb_{12}$ is the conventional weak-coupling BCS s-wave superconductor. In a strong-coupling regime, a significant suppression in the coherence peak was reported in the s-wave superconductor [23]. In the HF superconductor $\rm PrOs_4Sb_{12}$, however, the absence of the coherence peak may be ascribed to the combined effects of a precursory formation of gap in the HF quasiparticle state at temperatures higher than $T_c = 1.85$ K and the large value of SC gap with $2\Delta/k_BT_c \sim 5.2$. These anomalies may arise because the unconventional strong-coupling effect to make pairs is relevant with the quadrupolar degree of freedom.

Although the recent thermal-conductivity experiment suggests a point-nodes gap [24], $1/T_1$ suggests that the existence of any node in the SC gap is absent down to $0.3T_c$. Unfortunately, $1/T_1$ saturates below $0.3T_c$, preventing us to make a more precise distinction on the gap form. It is evident, however, as unraveled in this work that the novel superconductivity takes place under such a situation that the quadrupolar degree of freedom plays a vital role in the formation of quasiparticles at temperatures lower than $\Delta_{\rm CEF} = 7$–11 K. We also remark that $T_c = 1.85$ K for $\rm PrOs_4Sb_{12}$ is much enhanced over $T_c = 0.75$ K for $\rm LaOs_4Sb_{12}$ and, furthermore, the Pr-based superconductor $\rm PrRu_4Sb_{12}$ ($T_c = 1.3$ K), which is characterized by a singlet CEF ground state, is the weak-coupling s-wave superconductor with $2\Delta/k_BT_c \sim 3.1$ [25]. Therefore, it raises a question of what type of pairing interaction is possible in mediating the Cooper pair to cause the unconventional strong-coupling superconductivity in $\rm PrOs_4Sb_{12}$.

In summary, the T dependence of $1/T_1T$ in the new HF superconductor $\rm PrOs_4Sb_{12}$ revealed that the $4f$-derived moments behave as if localized at the higher T than $T_0 \sim 10$ K. Below T_0, the marked increase in NQR frequency at the Sb site and the decrease in $1/T_1$ unraveled a low-lying crystal-electric-field splitting, associated with the $\rm Pr^{3+}(4f^2)$-derived ground state. In the lower T than $\sim$4 K, the relaxation process is well accounted for by incorporating both of the CEF contributions arising from the first excited Γ_5 triplet state and the $(T_1T)_{\rm qp} =$ const contribution from the heavy-quasiparticle state.

In the SC state, $1/T_1$ shows neither the coherence peak just below T_c nor the T^3-like power-law behavior observed for the anisotropic HF superconductors with the line-node gap to date. We highlight that the HF superconductor $\rm PrOs_4Sb_{12}$ reveals the very large and *isotropic* energy gap $2\Delta/k_BT_c \sim 5.2$, indicative of a new type of unconventional strong-coupling regime. It is very surprising to have an *isotropic* heavy-fermion superconductor—it may indeed argue for Cooper pairing via quadrupolar fluctuations.

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