Evidence for Point Nodes in the Superconducting Gap Function in the Filled Skutterudite Heavy-Fermion Compound PrOs$_4$Sb$_{12}$: $^{123}$Sb-NQR Study under Pressure

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We report $^{123}$Sb nuclear quadrupole resonance (NQR) measurements of the filled skutterudite heavy-fermion superconductor PrOs$_4$Sb$_{12}$ under high pressures of 1.91 and 2.34 GPa. The temperature dependence of NQR frequency and the spin-lattice relaxation rate $1/T_1$ indicate that the crystal-electric-field splitting $\Delta_{CEF}$ between the ground state $\Gamma_1$ singlet and the first excited state $\Gamma_4^{(2)}$ triplet decreases with increasing pressure. The $1/T_1$ below $T_c = 1.55$ K at $P = 1.91$ GPa shows a power-law temperature variation and is proportional to $T^5$ at temperatures considerably below $T_c$, which indicates the existence of point nodes in the superconducting gap function. The data can be well fitted by the gap model $\Delta(\theta) = \Delta_0 \sin \theta$ with $\Delta_0 = 3.08k_B T_c$. The relation between the superconductivity and the quadrupole fluctuations associated with the $\Gamma_4^{(2)}$ state is discussed.

KEYWORDS: PrOs$_4$Sb$_{12}$, superconductivity, NQR, pressure

The filled skutterudite compound PrOs$_4$Sb$_{12}$ is the first praseodymium (Pr)-based heavy-fermion superconductor with $T_c = 1.85$ K. The heavy-electron mass has been confirmed by the large specific heat jump $\Delta C/T_c \sim 500 \text{mJ}/(\text{K}^2\text{mol})$ at $T_c$. The superconductivity has been the focus of discussions. Although the superconducting gap function is isotropic. Previous nuclear-quadrupole-resonance (NQR) measurements of the filled skutterudite heavy-fermion superconductor PrOs$_4$Sb$_{12}$ under high pressures of 1.91 and 2.34 GPa. The temperature dependence of NQR frequency and the spin-lattice relaxation rate $1/T_1$ indicate that the crystal-electric-field splitting $\Delta_{CEF}$ between the ground state $\Gamma_1$ singlet and the first excited state $\Gamma_4^{(2)}$ triplet decreases with increasing pressure. The $1/T_1$ below $T_c = 1.55$ K at $P = 1.91$ GPa shows a power-law temperature variation and is proportional to $T^5$ at temperatures considerably below $T_c$, which indicates the existence of point nodes in the superconducting gap function. The data can be well fitted by the gap model $\Delta(\theta) = \Delta_0 \sin \theta$ with $\Delta_0 = 3.08k_B T_c$. The relation between the superconductivity and the quadrupole fluctuations associated with the $\Gamma_4^{(2)}$ state is discussed.
ments were carried out at the $\pm 3/2 \leftrightarrow \pm 5/2$ transition (hereafter, $2\nu_Q$ transition for short) of the $^{123}\text{Sb}$ nucleus. Figure 1 shows the increase in the $2\nu_Q$ resonance frequency below $T = 25$ K for various pressures. $T_0$ is the temperature at which the $2\nu_Q$ resonance frequency increases abruptly. Since the electrical field gradient (EFG) is predominantly determined by the on-site charge distribution, the NQR frequency is a good measure of the population of the ground/excited state. Indeed, in both PrOs$_4$Sb$_{12}$ and PrRu$_4$Sb$_{12}$, $T_0$ is in good agreement with $\Delta_{CEF}/k_B$. More recently, it has been suggested that the temperature dependence of NQR frequency can be accounted for by the EFG associated with the hexadecapole moment of the $\Gamma^{(2)}_4$ state. Therefore, the increase in the NQR frequency below $T_0$ indicates that the depopulation of the $\Gamma^{(2)}_4$ state occurs below this temperature. As seen in Fig. 1, $T_0$ shifts to lower temperatures $T_0(P) \sim 7.5$ and 5 K at $P = 1.91$ and 2.34 GPa, respectively (also see Fig. 1 inset). These results provide evidence that $\Delta_{CEF}$ decreases with increasing pressure.

The above conclusion is supported by the pressure effect on the temperature dependence of $1/T_1 T$. Figure 2 shows the temperature dependence of $1/T_1 T$ at $P = 0$ and 1.91 GPa. The pressure effect appears below 4 K. At $P = 0$, the reduction of $1/T_1 T$ results in a peak in the plot of $1/T_1 T$ versus $T$, which is due to the depopulation of the $\Gamma^{(2)}_4$ state below $T_0$. At $P = 1.91$ GPa, the decrease in $1/T_1 T$ occurs at a lower temperature, indicating the decrease in $\Delta_{CEF}$. These results are consistent with the conclusion inferred from the magnetization measurement.\(^{18}\)

We find concomitantly that the temperature of the onset of the superconducting transition decreased with increasing pressure, in agreement with previous reports.\(^2,18\) The inset in Fig. 3 shows the temperature dependence of ac-susceptibility measured using the NQR coil. $T_c$ decreased from 1.85 K at $P = 0$ to 1.55 K at $P = 1.91$ GPa. The main panel of Fig. 3 shows the temperature dependence of $1/T_1$ at $P = 0$ and 1.91 GPa. The ambient-pressure data are in excellent agreement with the data at ambient $P$ cited from literature\(^{13}\) along with the data at ambient $P$ cited from literature\(^{13}\) of the $^{123}\text{Sb}$ NQR ($\pm 3/2 \leftrightarrow \pm 5/2$ transition) at $P = 0$ (solid circles), 1.91 (solid triangles), and 2.34 GPa (open squares) along with the data at $P = 0$ (open circles) by Kotegawa et al.\(^{13}\) Solid, dotted, and dashed arrows indicate $T_0$ at $P = 0$, 1.91, and 2.34 GPa, respectively (see text). The inset shows the pressure dependence of $T_0$.
independent above $T_0$, indicating that the relaxation in the high-temperature region is predominated by the Pr-4$f^2$-derived localized magnetic moments. With decreasing temperature below $T_0$, $1/T_1$ starts to decrease. Below $T_c$, no coherence peak is observed at $T_c = 1.55$ K for $P = 1.91$ GPa, as for $P = 0$. However, the $T$ dependence of $1/T_1$ at high pressure is markedly different from that at ambient pressure. $1/T_1$ at $P = 1.91$ GPa decreases in a power law of $T$ below $T_c$.

In particular, below $T \sim 0.55$ K, $1/T_1$ is proportional to $T^\alpha$, as can be seen more clearly in Fig. 4. We find that a point-nodes model, with a low-energy $(E)$ superconducting density of states (DOS) proportional to $E^2$, can well explain the experimental result. In Fig. 4, the curve below $T_c$ is a fit to the Anderson-Brinkman-Morel (ABM) model.\(^{24, 25}\) Namely,

$$
\frac{T_1(T_c)}{T_1} = \frac{2}{k_B T_c} \int \left( \frac{N_S(E)}{N_0} \right)^2 f(E)[1 - f(E)]dE,
$$

where $N_S(E)/N_0 = E/\sqrt{E^2 - \Delta^2}$ with $\Delta(\theta) = \Delta_0 \sin \theta$. The fit gives $\Delta_0/k_B T_c = 3.08$. The penetration depth data at ambient pressure seem to be consistent with our results.\(^{16}\) However, the $p + h$ model proposed to explain the thermal conductivity would give a $T^3$-like dependence, since the DOS at low-$E$ is linear in $E$, and is therefore not compatible with our data.

It has been proposed that the superconductivity is mediated by the excitons due to the $\Gamma_{1}^{(2)} - \Gamma_{1}$ quartet.\(^{11}\) In such case, $T_c$ would increase when $\Delta_{CEF}$ is reduced. Clearly, our results do not lend a straightforward support to this theory. Further experimental study under higher pressure is highly desirable. Finally, we comment on the different temperature dependences of $1/T_1$ at $P = 0$ and 1.91 GPa. Two possible causes could be responsible. First, the larger gap $\Delta_{CEF}$ may contribute to the reduction of $1/T_1$ below $T_c$ at ambient pressure, which makes the temperature dependence of $1/T_1$ exponential. Second, it may be due to the multiple-band nature of the superconductivity.\(^{27}\) Recent thermal conductivity measurement under a magnetic field suggests the superconductivity at ambient pressure is induced in two different Fermi sheets,\(^{27}\) which may have different symmetry. The sheet in which nodes develop may grow significantly under high pressures.

In conclusion, we have presented the $^{123}$Sb-NQR results on the filled skutterudite heavy-fermion compound PrOs$_2$Sb$_{12}$ at $P = 0$, 1.91, and 2.34 GPa. The temperature dependence of NQR frequency and the spin-lattice relaxation rate $1/T_1$ indicate that the gap $\Delta_{CEF}$ between the ground state $\Gamma_1$ singlet and the first excited state $\Gamma_{2}^{(2)}$ triplet decreases with increasing pressure. At $P = 1.91$ GPa, the temperature dependence of $1/T_1$ below $T_c$ is well explained by the ABM superconducting state, with point nodes in the gap function. To confirm the mechanism showing why $T_c$ decreases with increasing pressure in PrOs$_2$Sb$_{12}$, further NQR measurements under pressure are now in progress.

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