UNUSUAL SUPERCONDUCTIVITY IN SKUTTERUDITE COMPOUND $PrOs_4Sb_{12}$*

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We report Sb-NQR results, which evidence unusual superconducting (SC) property in a filled-skutterudite compound $PrOs_4Sb_{12}$ with a SC transition temperature, $T_c = 1.8\,K$. The nuclear-spin–lattice relaxation rate, $1/T_1$ have revealed that Pr-derived $4f$ moments behave as if they are localized in a high temperature (T) above $T_0 \sim 10\,K$. The observed NQR-line shift below T_0 suggests the local redistribution of the charges associated with quadrupolar moments of Pr^{3+}. The $1/T_1$ in the SC state has revealed an isotropic energy gap of $\Delta/k_BT_c \sim 2.7$. The absence of the coherence peak, but an exponential decrease in $1/T_1T$ below $T_c = 1.8\,K$ cannot be accounted for by either a conventional s-wave model or an anisotropic SC model with point- or line-node gap, pointing to a new class of unusual superconductivity.

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1. Introduction

Recently, Bauer *et al.* reported the observation of heavy fermion (HF) behavior and superconductivity at $T_c = 1.85\,K$ in a filled-skutterudite compound $PrOs_4Sb_{12}$ which is the first case of Pr-based HF superconductor [1]. 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 $\gamma \sim 500$ mJ/mole K^2. The magnetic susceptibility, thermodynamic measurements, and recent inelastic neutron scattering experiments revealed the

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ground state of the Pr^{3+} ions in the cubic crystal electric field (CEF) to be the Γ_3 non-magnetic doublet [1,2]. 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 [3], it was suggested that the HF-like behavior in $PrOs_4Sb_{12}$ may be relevant to a quadrupolar Kondo lattice. An interesting issue to be addressed is what role of Pr^{3+}-derived quadrupolar fluctuations are relevant with the onset for the superconductivity in this compound.

2. Experimental data and discussion

Nuclear spin-lattice relaxation time (T_1) was measured through the Sb nuclear quadrupolar resonance (NQR) experiment at zero field [4]. Single crystals of $PrOs_4Sb_{12}$ were grown by the Sb-flux method as described elsewhere [5]. Measurements of electric resistivity and ac-susceptibility confirmed a superconducting (SC) transition at $T_c = 1.8\,\mathrm{K}$. For ^{121,123}Sb NQR measurements, the single crystals were crushed into powder.

Fig. 1(a) shows NQR spectrum at several temperature (T) for ^{123}Sb-2ν_Q ($\pm 3/2 \leftrightarrow \pm 5/2$ transition). The peak shifts to higher frequency with decreasing T below $T_0 \sim 10\,\mathrm{K}$. Fig 1(b) indicates T-dependence of $(\nu_Q - \nu_0)/\nu_0$ for ^{123}Sb-2ν_Q, ^{123}Sb-3ν_Q, and ^{121}Sb-2ν_Q, where ν_0 is the value of ν_Q at 10 K. All the data to demonstrate a same T-variation indicate that these shifts are not magnetic but electric in origin. Since such the

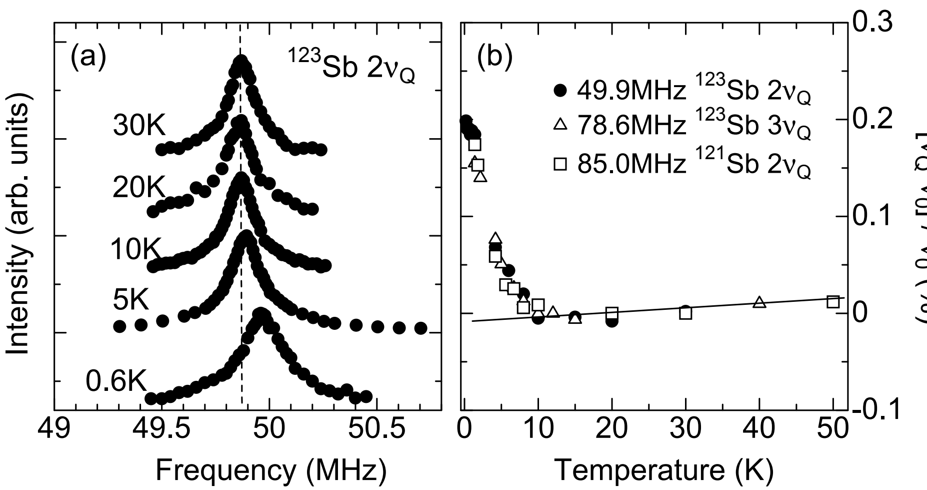

Fig. 1. (a) Sb NQR spectra for several T. The peak shifts at low T. (b) T-dependence of NQR frequency. ν_Q increases gradually below $T_0 \sim 10\,\mathrm{K}$.

large shift in ν_Q is never seen in $LaOs_4Sb_{12}$, it is natural to consider that the quadrupolar fluctuation of Pr-$4f$ moment induces these shifts as the result of a redistribution of conduction electrons. The magnetic susceptibility and inelastic neutron scattering experiments suggested the CEF energy splitting between the ground state (Γ_3) and the first excited state (Γ_5) as $\Delta_{\rm CEF} = 8 \sim 11\,\mathrm{K}$ [1, 2], which almost coincides with $T_0 \sim 10\,\mathrm{K}$.

Fig. 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 $LaOs_4Sb_{12}$ ($T_c = 0.75\,\mathrm{K}$). A relation of T_1T = const. is valid in the normal state of $LaOs_4Sb_{12}$, characteristic for conventional metallic materials. In the SC state, $1/T_1$ shows a large coherence peak just below T_c, followed by the exponential T dependence with the gap size of $\Delta/k_BT_c \sim 1.6$ at low T. These results are consistent with $LaOs_4Sb_{12}$ being a conventional weak-coupling BCS s-wave superconductor.

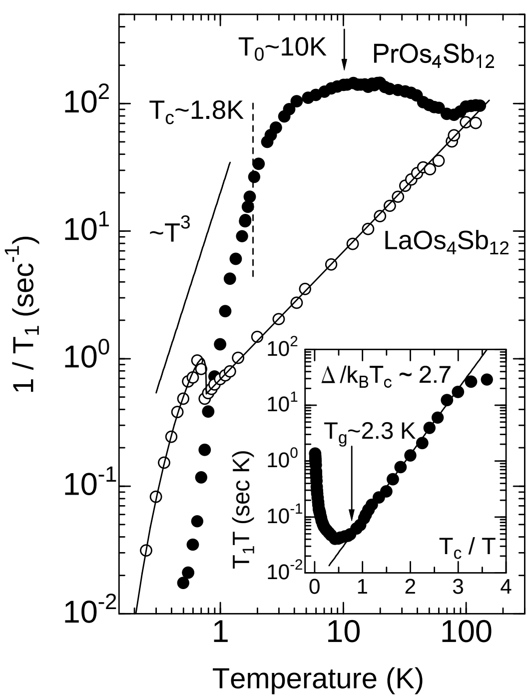

Fig. 2. T-dependence of $1/T_1$ for $PrOs_4Sb_{12}$ and $LaOs_4Sb_{12}$. The inset shows T_1T *versus* T_c/T.

By contrast, the $1/T_1$ in $PrOs_4Sb_{12}$ is strongly enhanced than in $LaOs_4Sb_{12}$, revealing a relaxation behavior similar to Ce-based HF systems reported thus far. Above $T_0 \sim 10\,\mathrm{K}$, the T dependence of $1/T_1$ reveals that the $4f$ electrons behave as if they are localized. However, $1/T_1$ decreases gradually below T_0.

This seems to be consistent with the CEF energy splitting of Pr^{3+} ions of $\Delta_{\mathrm{CEF}} = 8$–$11\,\mathrm{K}$ [1,2]. Magnetic fluctuations are suppressed at temperatures below Δ_{CEF}. In the SC state, T_1T is well fitted by the exponential relation of $T_1T \propto \exp\left(\Delta/(k_{\mathrm{B}}T_{\mathrm{c}})\,(T_{\mathrm{c}}/T)\right)$ with $\Delta/(k_{\mathrm{B}}T_{\mathrm{c}}) = 2.7$ already below $T_{\mathrm{g}} \sim 2.3\,\mathrm{K}$ as shown in the inset, indicating an isotropic energy gap and the existence of pseudogap. However, the absence of the coherence peak just below T_{c} is obvious. This behavior cannot be accounted for by either a conventional s-wave model or anisotropic SC models with point- or line-node gap. The quadrupolar fluctuations might be responsible for a new class of superconductivity.

3. Conclusion

We have measured T_1 of ^{123}Sb in $PrOs_4Sb_{12}$ superconductor with $T_{\mathrm{c}} \sim 1.8\,\mathrm{K}$. $1/T_1$ shows the exponential decrease with $\Delta/(k_{\mathrm{B}}T_{\mathrm{c}}) = 2.7$ below $T_{\mathrm{g}} \sim 2.3\,\mathrm{K}$, indicative of a strong-coupling isotropic gap. However, $1/T_1$ does not exhibit any coherence peak. $PrOs_4Sb_{12}$ differs from a conventional s-wave type and from an unconventional superconductor with the line-node of the gap.

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