Superconducting properties of Pr-based filled skutterudite PrRu$_4$As$_{12}$

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We report on a systematic study of the superconducting characteristics and Pr crystalline-electric-field (CEF) levels of the filled skutterudite PrRu$_4$As$_{12}$ ($T_c = 2.33$ K). The temperature dependences of the upper critical field $H_{c2}$ and the Ginzburg-Landau (Maki) parameter $\kappa_2$ suggest $s$-wave clean-limit superconductivity. The electronic specific heat coefficient $\gamma \sim 95$ mJ/K$^2$mol, which is $\sim 1.5$ times larger than that of LaRu$_4$As$_{12}$, indicates $4f$-originating quasiparticle mass enhancement. The magnetic susceptibility $\chi(T)$ indicates that the CEF ground state is a $\Gamma_1$ singlet and a $\Gamma_4^{(1)}$ triplet first excited state lies at $\Delta_{CEF} \sim 30$ K above. A systematic comparison among PrOs$_4$Sb$_{12}$, PrRu$_4$Sb$_{12}$, PrRu$_4$As$_{12}$, and La-based reference compounds suggests that the inelastic exchange scattering and aspherical charge scattering of conduction electrons from CEF-split $4f$ levels play an essential role in the quasiparticle mass enhancement and in determining the value of $T_c$ in the Pr-based filled skutterudites.

KEYWORDS: Filled skutterudite, PrRu$_4$As$_{12}$, specific heat, susceptibility, superconductivity, crystal electric field

Among heavy-fermion superconductors, the filled skutterudite PrOs$_4$Sb$_{12}$ has attracted considerable attention for its unconventional superconducting (SC) properties.$^1,2$ Some of the characteristic features are broken time-reversal symmetry,$^3$ odd parity,$^4$ possible structure in the SC gap,$^5,6$ multi band superconductivity,$^7$ and adjacent quadruple ordering and its fluctuations (quadruple excitons).$^8-11$ In contrast, PrRu$_4$Sb$_{12}$ is a conventional BCS-type superconductor as suggested by a coherence peak in the NQR spin-lattice relaxation rate $1/T_1$. Systematic understanding for such variety in the SC properties of Pr-based filled skutterudites is one of the important issues (see Table II for a summary of the SC parameters).

It has been pointed out that the crystalline electric field (CEF) level scheme of Pr ions may play an essential role. In the $T_n$ site symmetry, the $J = 4$ multiplet of Pr$^{3+}$ ions splits into four sublevels (quadrupole excitons),$^{12}$ namely, a singlet $\Gamma_1$, a non-Kramers nonmagnetic doublet $\Gamma_2$, and two triplets $\Gamma_4^{(1)}$ and $\Gamma_4^{(2)}$. PrOs$_4$Sb$_{12}$ has $\Gamma_1$ ground state with a $\Gamma_4^{(2)}$ first excited state with the energy separation $\Delta_{CEF} = 8$ K.$^{13,14}$ In contrast, PrRu$_4$Sb$_{12}$ has $\Gamma_1 - \Gamma_4^{(1)}$ levels with $\Delta_{CEF} = 65$ K.$^{15-17}$ The differences in the type of the first excited state and $\Delta_{CEF}$ may be a key reason for the different SC properties.

In this paper, we report the specific heat and magnetic susceptibility measurements of another Pr-based filled skutterudite PrRu$_4$As$_{12}$ to study the SC properties and the CEF level scheme. The results indicate that the superconductivity is of the conventional BCS type with a moderate quasiparticle mass enhancement. A systematic comparison among these Pr-based compounds and their

### Table I. Fractional coordinates and Debye-Waller factors $U_{eq}$ of PrRu$_4$As$_{12}$ determined from the single-crystal x-ray diffraction data.

| atom | site | $x$ | $y$ | $z$ | $U_{eq}$ ($\AA^2$) |
|------|------|-----|-----|-----|---------------------|
| Pr   | 2a   | 0   | 0   | 0   | 1.082(4)           |
| Ru   | 8c   | 1/4 | 1/4 | 1/4 | 0.294(3)           |
| As   | 24g  | 0   | 0.14954(3) | 0.35019(3) | 0.387(5) |

La-based references reveals that inelastic scatterings of conduction electrons from CEF-split $4f$ levels play an essential role for the SC properties and quasiparticle mass enhancement in the Pr-based filled skutterudites.

Polycrystalline PrRu$_4$As$_{12}$ samples are synthesized using stoichiometric amounts of 3N(99.9% pure)-Pr, 4N-Ru, and 5N-As powders by the high-pressure and high-temperature method (4 GPa at 900 °C).$^{19}$ Powder x-ray diffraction indicates the inclusion of a small amount of the RuAs$_4$ phase; the maximum peak height of RuAs$_4$ is approximately 10% of that of PrRu$_4$As$_{12}$. The structural parameters of PrRu$_4$As$_{12}$ are determined by single-crystal x-ray diffraction using an imaging plate detector with Mo K$_\alpha$ radiation. A small single crystal with approximate dimensions of $0.10 \times 0.07 \times 0.05$ mm is selected from the ingot. The structural parameters are successfully refined based on the 179 independent reflections with the agreement factor $\sum |F_o| - |F_c|/ \sum |F_o| = 0.023$, where $F_o$ and $F_c$ are the experimental and calculated structure factors, respectively.

Fractional coordinates and Debye-Waller factors ($U_{eq}$) are listed in Table I. The obtained lattice constant of 8.491(4) A agrees with a reported value.$^{20}$ $U_{eq}(Pr)$ is $\sim 3$ times larger than $U_{eq}(Ru)$ and $U_{eq}(As)$. Note that $U_{eq}(Pr)$ in PrRu$_4$As$_{12}$ is larger than that in PrRu$_4$P$_{12}$, indicating larger ther-

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mal vibrations of Pr ions in As$_{12}$ cages, whose size is larger than that of P$_{12}$ cages.

The specific heat $C(H, T)$ is measured by a quasiadiabatic heat pulse method$^{20}$ using a dilution refrigerator equipped with an 8 T SC magnet. The temperature increment caused by each heat pulse is controlled to ~2 % for the usual measurement and to ~0.5 % in limited temperature ranges where the SC transition occurs. The magnetic susceptibility $\chi$ is measured in 1.8 $< T < 300$ K using an SC quantum interference device (SQUID) magnetometer (Quantum Design Inc.).

The temperature dependence of $C/T$ measured in selected magnetic fields is shown in Fig. 1. In zero field, a clear jump appears at the SC transition temperature $T_c = 2.33$ K, which is very close to a resistively determined value of 2.4 K.$^{18}$ With increasing field, $T_c$ shifts to lower temperatures and the size of the jump becomes smaller (for details, see the inset of Fig. 2).

From the $C_\text{el}(T, H)$ data, the upper critical field $\mu_0H_{c2}(T)$ is determined, as shown in the $H$-vs-$T$ phase diagram of Fig. 2. It appears that the $\mu_0H_{c2}(T)$ curve is well reproduced by the Werthamer-Helfand-Hohenberg (WHH) formula for the clean limit$^{23,24}$ with the initial slope $-d(\mu_0H_{c2})/dT|_{T_c} = 0.365$ T/K. This fact indicates that $\mu_0H_{c2}$ is mainly determined by the orbital effect and the spin Pauli paramagnetic effect does not play a dominant role; the Pauli limiting field is $\mu_0H_P = 3.9$ T $\ll \mu_0H_{c2}$. The $T = 0$ value of $\mu_0H_{c2}$ is estimated to be $\sim 0.62$ T by the WHH fitting.

There appears a slight upward deviation in the $\mu_0H_{c2}(T)$ curve below 0.05 T, leading to an enhancement in $T_c$ by 2% in zero field compared with the best-fit WHH curve for $\mu_0H > 0.05$ T. A similar behavior is observed in the case of PrOs$_4$Sb$_{12}$
$^{28}$ and YNi$_2$B$_2$C$^{29}$ indicating that the upward deviation in $T_c$ may come from the multi band effect.

By combining the $\mu_0H_{c2}$ and $\Delta C/T_c$ data, the Ginzburg-Landau parameter (or Maki parameter)$^{30}$ $\kappa_2$ is determined using the thermodynamical relation:

$$\Delta C/T_c = \left[ \frac{d(\mu_0H_{c2})}{dT_c} \right] \times \frac{1}{4\pi(2\kappa_2^2 - 1)\beta_A},$$

where $\beta_A = 1.16$ for a triangular vortex lattice.$^{31}$ The result is shown in Fig. 3. The value of $\kappa_2$ is $\sim 10$ at $T = T_c$ (in zero field) and increases with decreasing temperature.$^{32}$ The behavior of $dk_2/dT < 0$ is again consistent with the negligible Pauli paramagnetic depairing effect mentioned above; for superconductors with a strong Pauli paramagnetic effect, $dk_2/dT > 0$ appears (e.g., CeCoIn$_5$; see Ref. 33). The temperature dependence of $\kappa_2$ is affected by impurity scatterings.$^{34}$ In the clean limit, the theoretical parameter $\kappa_2(T)$ diverges as $T \rightarrow 0$ with $\kappa_2 \propto \sqrt{\ln(T_c/T)}$,$^{30,35}$ as shown in Fig. 3.
first excited state. Note that in the case of a $\Gamma_4^{(2)}$ first excited state, as realized in PrOs$_4$Sb$_{12}$, a maximum should appear in $\chi(T)$. This interpretation agrees with the electronic entropy $S_d(T, H)$ (not shown) calculated from the $\Delta(T, H)$ data. $S_d$ at 8 K is less than 20% of $R \ln 2$, ruling out the possibility of any degenerate ground states. In the measured temperature range, $dS_d/dH$ is always negative. In PrOs$_4$Sb$_{12}$, $dS_d/dH > 0$ is observed below 3 K. This behavior is caused by the Zeeman splitting of the low-lying triplet first excited state at $\Delta_{CEF} = 8$ K. This fact indicates that $\Delta_{CEF} \approx 8$ K for PrRu$_4$As$_{12}$. For a rough estimation of the low-lying CEF level scheme, a least-squares fit has been made based on the O$_h$ Lea-Leask-Wolf scheme (omitting the $O_6^2 - O_6^0$ term characteristic of the $T_h$ site symmetry in the CEF Hamiltonian). The best overall fit of the $\chi(T)$ data (shown by the dashed line in Fig. 4) corresponds to a $\Gamma_1$ ground state with a $\Gamma_4$ ($\Gamma_4^{(1)}$ in $T_h$) triplet excited state at $\Delta_{CEF} \sim 30$ K. For an accurate determination of the overall CEF level scheme, inelastic neutron scattering measurements would be necessary.

Only for LaOs$_4$Sb$_{12}$, among the three systems shown in table II, an enhancement in $T_c$ is caused by the replacement of La by Pr ions. This behavior may be accounted for by considering the predominant type of conduction-electron scatterings from Pr 4f electrons. Fulde et al. have theoretically demonstrated that inelastic aspherical charge scattering (ACS) associated with 4f quadrupole moments leads to an increase in $T_c$, while exchange scattering (ES) decreases $T_c$. For a qualitative discussion, a comparison with the theoretical calculation is made in Fig. 5. For LaOs$_4$Sb$_{12}$, since the first excited state of the replaced Pr ions is $\Gamma_4^{(2)}$ ($\sim \Gamma_5$ in O$_h$ having large off-diagonal quadrupole moments with $\Gamma_1$), the ACS may dominate over the ES. Furthermore, $\Delta_{CEF}/2T_c$(LaOs$_4$Sb$_{12}$) $\sim 5$ happens to be the best condition for the enhancement in $T_c$. On the other hand, in LaRu$_4$As$_{12}$ and LaRu$_4$Sb$_{12}$, the first excited state of the replaced Pr ions is $\Gamma_4^{(1)}$ ($\sim \Gamma_4$ in O$_h$ having large off-diagonal dipole moments with $\Gamma_1$) and the resulting predominant ES will cause a strong pair-breaking effect, thereby decreasing $T_c$.

The quasiparticle mass enhancement is also expected to be caused by the interactions of conduction electrons with low-lying CEF levels. Flude et al. have proposed a model for the mass enhancement due to virtual CEF excitations:

$$\frac{m^*}{m_0} - 1 = (g_J - 1)^2 J_s^2 N_0 \frac{|\langle i | J | f \rangle |^2}{\Delta_{CEF}},$$  \hspace{1cm} (2)
where $g_J$ is the Landé factor, $J_{sf}$ is the exchange integral coupling the conduction electrons to the $f$ electrons, $N(0)$ is the bare conduction electron density of states at the Fermi level, and $⟨j | J_i j⟩$ is the magnetic dipole matrix element calculated using the derived CEF parameters. Figure 6 shows several physical quantities that provide measures of the mass enhancement as a function of $Δ_{CEF}$. There appears a rough trend of $m^*/m - 1 \propto 1/Δ_{CEF}$ in Fig. 6. However, as discussed above for the effect on $T_c$, not only the ES process but also the ACS process should contribute to the mass enhancement with a different prefactor of $1/Δ_{CEF}$. In PrOs$_4$Sb$_{12}$, the importance of quadrupolar degrees of freedom is inferred from a strong correlation between quadrupolar excitons and superconductivity. Further experimental and theoretical studies on the role of quadrupoles in Pr-based filled skutterudites will be needed.

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