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Exotic behaviours in the Pr-based filled skutterudites

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Abstract

The exotic features of the Pr-based filled skutterudites are reviewed based on the electronic transport properties, specific heat and de Haas–van Alphen experiments, putting the emphasis on $PrFe_4P_{12}$ and $PrOs_4Sb_{12}$. As references, the experiments on the related La- and Ce-filled skutterudites are also examined and discussed. Compared to their La reference compounds, the Fermi surface is very similar in $PrOs_4Sb_{12}$, suggesting the well localized character of 4f electrons, while it looks largely different in $PrFe_4P_{12}$. For the cyclotron effective mass, both $PrFe_4P_{12}$ and $PrOs_4Sb_{12}$ exhibit a strong enhancement, in reasonable agreement with the large specific heat coefficient.

1. Introduction

The filled-skutterudite compounds ($RETr_4Pn_{12}$: RE = rare earth, Tr = Fe, Ru, Os and P = pnictogen) synthesized by Jeitschko and Braun [1] have recently attracted much attention from two viewpoints: i.e., purely scientific interest in the unusual properties particularly exhibited by Pr-based skutterudites [1–9], and their large potential as thermoelectric materials for the next generation [10–12]. Among them, Pr-based skutterudites are especially interesting, since they exhibit fruitful features unexpected as Pr-based compounds resulting from the unique crystallographic structure. In ordinary Pr compounds, the 4f level is situated far below the Fermi energy (EF), leading to the weaker c–f hybridization compared to the Ce compounds. In the filled skutterudites, however, the large coordination number (of 12 pnictogens surrounding RE) fully compensates it.

As strongly correlated f-electron systems, only Ce compounds with f^1 configuration (along with the hole analogue Yb compounds with f^{13} configuration) are reasonably well understood, according to the long and intense research works, which naturally leads the researcher's interest to the f^2 systems [13]. Several U compounds exhibiting interesting features related to the highly

Table 1. Ground state of light rare earth skutterudites. (a, lattice constant for RE = La; SC, superconducting; semi-C, semiconducting; semi-M, semimetallic; NMO, non-magnetic order; FM, ferromagnetic; AFM, antiferromagnetic; MI, metal–insulator transition; HF, heavy fermion; NFL, non-Fermi liquid.)

RE	La	Ce	Pr	Nd
$REFe_4P_{12}$	SC	Semi-C	NMO	FM
$a = 7.8316$	4.1 K	0.107 eV	6.5 K	2 K
$RERu_4P_{12}$	SC	Semi-C	MI	FM
$a = 8.0561$	7.2 K	0.074 eV	62 K	1.6 K
$RERu_4Sb_{12}$	SC	Semi-M	SC	FM
$a = 9.2774$	3.4 K	NFL	1.1 K	1.3 K
$REOs_4Sb_{12}$	SC	Semi-C	HF-SC	FM
$a = 9.3081$	0.74 K	1 meV	1.85 K	0.8 K

correlated $5f^2$ electrons have been found, while few highly correlated phenomena such as $4f^2$ systems have been reported in Pr compounds. That is ascribed to the more localized character of the 4f electrons.

In the $RETr_4Pn_{12}$ with a small lattice constant, the strong hybridization resulting from the large coordination number realizes exotic behaviours such as the metal–insulator transition in $PrRu_4P_{12}$ [2], the extraordinary heavy electrons and mysterious low field ordered phase (LOP) in $PrFe_4P_{12}$ [3–5] and heavy fermion superconductivity in $PrOs_4Sb_{12}$ [6–9], which are unusual as Pr compounds. For Ce compounds such as $CeRu_4P_{12}$ and $CeFe_4P_{12}$, the stronger c–f hybridization leads to the Kondo semiconducting behaviours [14, 15]. In contrast, for $RERu_4Sb_{12}$ with larger lattice constants than $RETr_4P_{12}$, the anomalous hybridization effect does not appear in $PrRu_4Sb_{12}$ but was observed in $CeRu_4Sb_{12}$ due to the weaker c–f hybridization [16–19].

We have been systematically investigating the filled skutterudites with light rare-earth elements for Tr = Fe and Ru and Pn = P and Sb whose high quality single crystals were successfully grown [3–5, 8, 9, 19–22]. Their reported attractive properties have been summarized in table 1. One of the most reliable tests to examine such interesting behaviours is the de Haas–van Alphen (dHvA) experiment. We have succeeded in observing dHvA in four La-based, one Ce-based, three Pr-based and one Nd-based skutterudites so far [4, 9, 19–22]. In this paper, exotic features in the filled skutterudites revealed by the electronic transport and the specific heat measurements are introduced, putting the emphasis on Pr-based compounds. The main features are further discussed based on the dHvA experiments.

The quality of samples is the most important starting point in a reliable discussion of new exotic phenomena. High quality single crystals were grown by the ordinary Sn-flux method for the phosphides and the Sb-self-flux method for antimonides [1], using high purity elements, 4 N (99.99% pure) RE, 4 N Tr and 6 N pnictogen. The residual resistance ratio (RRR) is basically over 1000 for both phosphides, while RRR for $RERu_4Sb_{12}$ ($REOs_4Sb_{12}$) is smaller but is at least over 100 (50).

2. Exotic phenomena in the bulk properties and their de Haas–van Alphen examination

Firstly, the richness of the physical properties in the Pr-based filled skutterudites is reflected in the temperature dependence of electrical resistivity normalized at 300 K as shown in figure 1. $PrRu_4P_{12}$ exhibits a metal–insulator transition at $T_{MI} \sim 62$ K [2]. The resistivity for $PrFe_4P_{12}$ shows Kondo-like—ln T—dependence at higher temperatures, and exhibits a phase transition

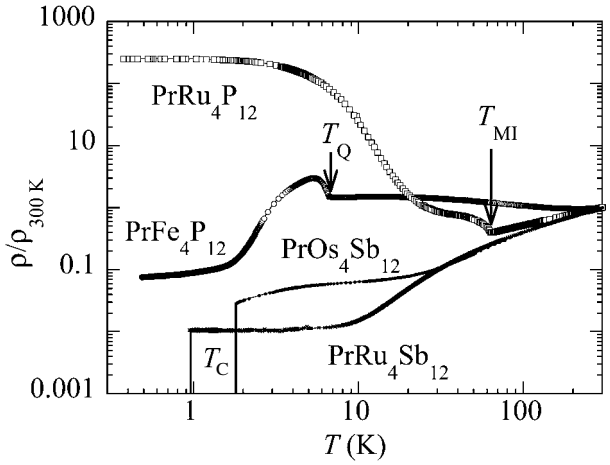

Figure 1. Temperature dependence of electrical resistivity for the Pr-based filled skutterudites. T_{MI}, MI transition temperature; T_Q, transition temperature to the LOP; T_C, superconducting temperature.

at $T_Q \simeq 6.5$ K with a non-magnetic origin. As an origin of the transitions for the two compounds, some kind of quadrupolar ordering related to the Fermi surface (FS) nesting is inferred. ρ for both $PrRu_4Sb_{12}$ and $PrOs_4Sb_{12}$ follows ordinary metallic behaviour down to T_C where both show a superconducting transition. The superconductivity for the former is ordinary BCS type, while the latter is the first Pr-based heavy fermion superconductor and is thought to have some exotic origin [6, 7].

2.1. The small lattice constant systems $PrRu_4P_{12}$ and $PrFe_4P_{12}$

For $RERu_4P_{12}$, dHvA experiments have been performed only on $LaRu_4P_{12}$ [22], since the strongest c–f hybridization leads both RE = Ce and Pr to be semiconducting at low temperatures. For $LaRu_4P_{12}$, a band structure calculation predicts small nearly spherical FSs that are absent in $PrRu_4P_{12}$. The existence of these small FSs is thought to be the reason why the MI transition is only observed in $PrRu_4P_{12}$, since both compounds have a large, almost the same, quasi-cubic FS with an effective nesting vector $\boldsymbol{q} = (1, 0, 0)$ [23, 24]. Many dHvA branches have been observed in $LaRu_4P_{12}$; however, no such spherical FS(s) has been detected, indicating that the FS nesting alone cannot explain the MI transition in $PrRu_4P_{12}$.

For $PrFe_4P_{12}$, apparent Kondo-like behaviours have been found in the transport properties: the large $-\ln(T)$ term in ρ (figure 1) and the large magnitude of thermoelectric power ($\geqslant -50\ \mu$V K^{-1}) at low temperatures [3], which are quite unusual in Pr-based systems. Under magnetic fields above H_M, where the ordered phase is suppressed, an enhancement of highly correlated electrons is recognized both in the ρ and C/T. The resistivity follows $\rho = \rho_0 + AT^2$ at low temperatures with $A = 3$–$15\ \mu\Omega$ cm K^{-2} depending on the field strength between 4 and 10 T. C/T at 1 K shows a jump from 0.11 to $C/T \sim 1.4$ J K^{-2} mol^{-1} across $H_M \simeq 4$ T, above which it monotonically decreases with increasing H. The field dependences of A and the square of the specific heat coefficient γ^2 also follow the Kadowaki–Woods relation very well with a reasonable value of $A\gamma^2 \simeq 2 \times 10^{-10}\ \Omega$ m mol^2 J^{-1} for $H \parallel \langle 100 \rangle$.

Important information can be obtained from the nuclear Schottky contribution C_N caused mostly by Pr nuclei; i.e., the 4f moment is evaluated to be effectively zero for $H = 0$, indicating the low field ordered state to have non-magnetic origin in consistent with the absence of superlattice peaks in the neutron scattering experiment [5, 26]. As an origin of this ordering, the band

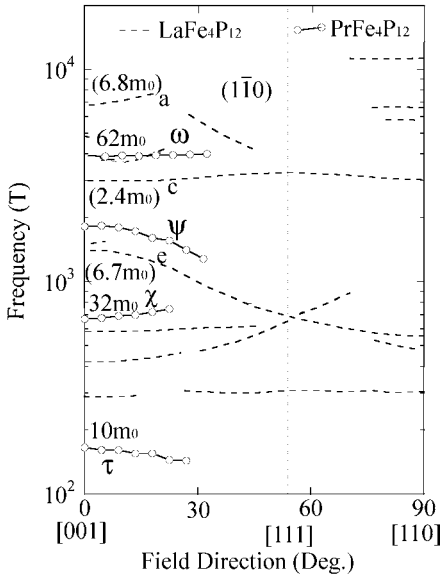

Figure 2. Comparison of the angular dependence of dHvA frequency between $LaFe_4P_{12}$ and $PrFe_4P_{12}$ in the (110) plane. The cyclotron effective mass in parentheses is for $LaFe_4P_{12}$.

structure calculation predicted a lattice distortion caused by an FS nesting with $\boldsymbol{q} = (1, 0, 0)$, which was recently confirmed by a precise x-ray diffraction measurement [25, 27]. The absence of such order in $LaFe_4P_{12}$ along with the theoretical study predicting symmetry lowering Fe-ion displacement accompanied by antiferro-quadrupolar (AFQ) ordering [25] point to the coexistence of the Kondo effect and the long range order in $PrFe_4P_{12}$ both resulting from the quadrupolar interaction. The dHvA experiment is a powerful tool to investigate both the FS change and the mass enhancement.

Figure 2 shows a comparison of the angular dependence of dHvA frequencies between $PrFe_4P_{12}$ and $LaFe_4P_{12}$ in the (110) plane [4]. Below H_M only the τ-branch with a small cross-section has been observed, while above H_M three branches, χ, ψ and ω, have been observed. The important information from the dHvA experiments can be summarized as follows.

(a) A large change in the FS across H_M, probably due to the disappearance of the main part of the FS due to the superzone gap formation, is confirmed.

(b) Even above H_M, there exists an apparent difference in the FS between $PrFe_4P_{12}$ and $LaFe_4P_{12}$.

(c) Extraordinary large mass enhancement as a Pr-based compound, the heaviest mass of 81 m_0 at this stage, has been confirmed. Both the field and angular dependences of the effective mass suggest a mass heavier by more than a factor of three. It should be noted that $m^* \simeq 10\ m_0$ for the τ-branch in the LOP is quite large taking into account its small FS size (0.15% of the BZ size assuming a spherical FS, consistent with the carrier concentration estimated from R_H). In addition, the field effect of mass for this branch is quite small compared to the other branches, suggesting the mass enhancement in the LOP is nonmagnetic in origin.

(d) We have not succeeded in observing the dHvA signal for χ-, ψ- and ω-branches around $\langle 110 \rangle$ and $\langle 111 \rangle$, strongly suggesting a large anisotropic mass enhancement usually unexpected for a cubic crystal structure.

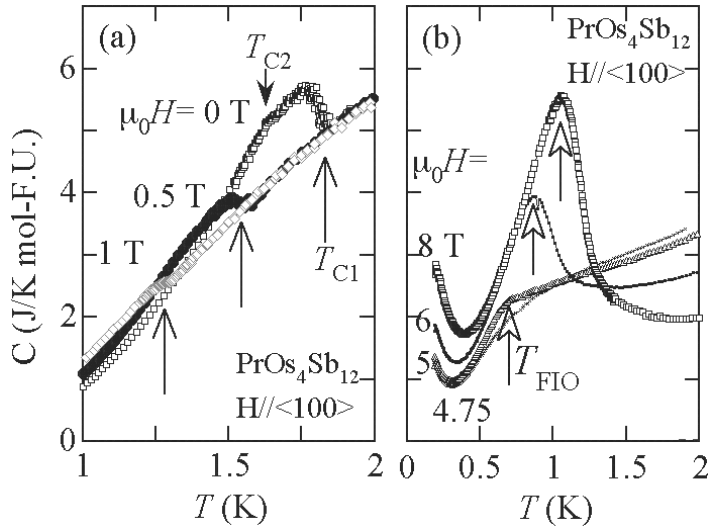

Figure 3. Temperature dependence of specific heat for $PrOs_4Sb_{12}$ under selected magnetic fields. (a) shows the shift of T_C while (b) presents the growth of the FIOP.

Taking these results into account, the drastic reduction of C/T across T_Q is ascribed to the disappearance of the main part of the FS, and the strong enhancement of effective mass also exists in the LOP, that is most likely an AFQ ordering.

2.2. The large lattice constant systems $PrRu_4Sb_{12}$ and $PrOs_4Sb_{12}$

From the systematic trend of the decreasing c–f hybridization with increasing lattice constant estimated from the hybridization gap for the Ce filled skutterudites (table 1), little interesting behaviour has been expected for $PrRu_4Sb_{12}$ and $PrOs_4Sb_{12}$. In fact, $PrRu_4Sb_{12}$ was reported to be a Van Vleck paramagnet exhibiting ordinary superconductivity near 1 K by Takeda and Ishikawa [16]. We have also confirmed the absence of any exotic behaviour characteristic of highly correlated electron systems in the Hall effect and thermoelectric power [19]. Hence, the finding of the first Pr-based heavy fermion superconductivity in $PrOs_4Sb_{12}$ by Bauer *et al* [6] was an unexpected and exciting result for further investigations. They also reported the double-peak structure in the specific heat measurement suggesting a multiple superconducting state [7]. The specific heat result on our sample used for the dHvA experiment is shown in figure 3 [8]. We also found two consecutive anomalies at T_{C1} and T_{C2}, except some difference in the shape and the temperature of the specific heat jumps; i.e., the higher temperature peak is more prominent and the lower temperature peak becomes shoulder-like in the present work. In addition, Aoki *et al* [8] have confirmed a field-induced ordered phase (FIOP) above H_{C2}, the origin of which has not yet been clarified.

The angular dependence of dHvA frequency in the (001) plane is shown in figures 4(a) and (b) for $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$, respectively, along with those for the reference compounds [8, 21]. For $PrOs_4Sb_{12}$, the dHvA signal becomes detectable just above $H_{C2} =$ 2.2 T, suggesting the high quality of the present sample. A faint peak anomaly appears at $H_A \simeq 4.4$ T, which agrees with the phase boundary of the FIOP determined by the specific heat measurement [8]. The α- and β-branches observed over the whole field directions come from closed FSs [9], while the γ-branch observed in a narrow angular region is attributable to a multiply connected FS.

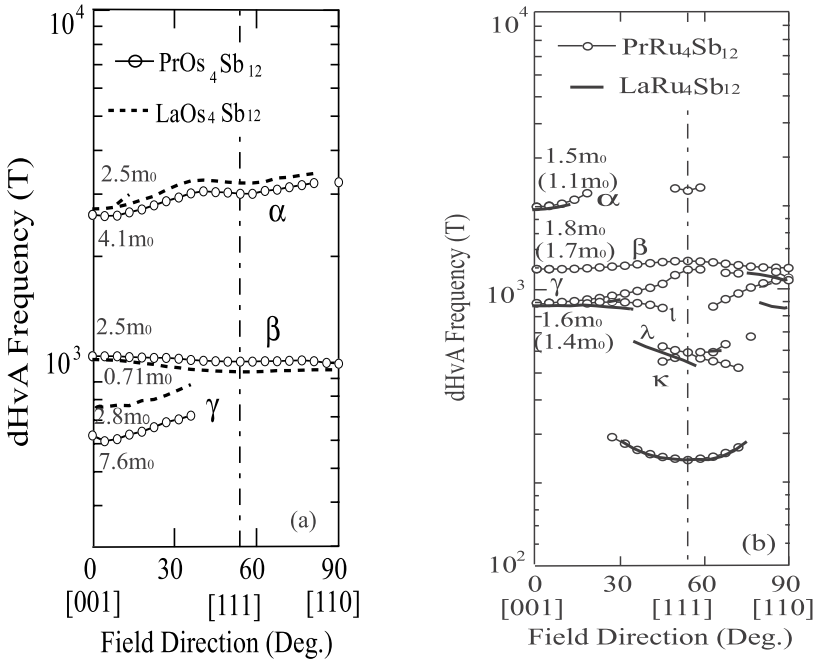

Figure 4. Comparison of the angular dependence of dHvA frequency between (a) $LaOs_4Sb_{12}$ and $PrOs_4Sb_{12}$, and (b) $LaRu_4Sb_{12}$ and $PrRu_4Sb_{12}$. The Greek letters are dHvA branch names for $LaTr_4Sb_{12}$. The numbers near [001] show the cyclotron effective mass. The numbers in the parentheses are for $LaRu_4Sb_{12}$.

On the FS topology, the dHvA branches for both compounds are very close to those for the reference compounds, which indicates the closeness of the FS between Pr- and La-based compounds. Hence, 4f electrons may not have any essential role in the FS formation and are basically localized for both $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$. In fact, the FSs are well reproduced by the band structure calculation assuming 4f electrons to be localized [9].

On the mass enhancement, a clear difference is found between $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$. For $PrRu_4Sb_{12}$, as shown along the [001] direction, the mass enhancement (numbers in parentheses are for $LaRu_4Sb_{12}$) is not so large, consistent with that estimated from the specific heat coefficients. In contrast, in $PrOs_4Sb_{12}$, larger mass enhancements (up to ∼6 times of that for $LaOs_4Sb_{12}$) are evident. The estimated Sommerfeld coefficient of 150 mJ K^{-2} mol^{-1}, assuming multiple spherical FSs, is a factor of two smaller than the experiment (300 mJ K^{-2} mol^{-1}) [28]. However, it should be noted that the mass has been estimated for the larger amplitude (lighter mass) spin-split sub-branches in the present experiment, which tends to underestimate the total mass enhancement. The mass enhancement is apparently larger than those in the ordinary Pr-based compounds except that in $PrFe_4P_{12}$ [4]. Another noticeable feature is the change in T_C by replacing La and Pr in $RETr_4Sb_{12}$; by replacing La with Pr T_C is enhanced to $T_C(\mathrm{Pr})/T_C(\mathrm{La}) \sim 2.5$ for $REOs_4Sb_{12}$ in contrast to the suppression to 0.32 for $RERu_4Sb_{12}$ as usually observed. These facts naturally suggest an important role of 4f electrons in the HF superconductivity in $PrOs_4Sb_{12}$.

For $RERu_4Sb_{12}$, an apparent c–f hybridization effect has been realized in $CeRu_4Sb_{12}$, where the NFL behaviour is suppressed by magnetic field [16]. Above ∼4 T, we have succeeded in observing both the Shubnikov–de Haas oscillations and the ordinary dHvA effect.

The FS is apparently smaller (estimated to be 0.04 holes/fu assuming a spherical FS) than that in $LaRu_4Sb_{12}$. The highly enhanced effective mass for such a small FS indicates it to be a heavy fermion semimetal.

3. Summary

To summarize: a drastic change in the FS across H_M has been confirmed in $PrFe_4P_{12}$, suggesting the recovery of the main part of the FS that disappeared in the LOP due to the superzone gap formation. Even in the field induced HF state, the FS is largely different from that in $LaFe_4P_{12}$. In both states, large electron mass enhancement has been confirmed, consistent with the apparent Kondo-like behaviours in the bulk properties. The FS of $PrOs_4Sb_{12}$ is basically the same as that in $LaOs_4Sb_{12}$, suggesting localized 4f electrons as in $PrRu_4Sb_{12}$. Large mass enhancement has been confirmed in dHvA measurements, though the Sommerfeld coefficient cannot be fully explained in contrast with $PrRu_4Sb_{12}$ showing only minor mass enhancement. Anomalies related to the field induced ordered state have been observed both in the electronic transport properties and dHvA measurements. The FS nesting effect on the MI transition in $PrRu_4P_{12}$ predicted from the band structure calculation has been confirmed, not only by the present dHvA experiment.

Acknowledgments

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