Novel features in the filled skutterudites containing rare earth elements with plural number of 4f-electrons


aDepartment of Physics, Tokyo Metropolitan University, Tokyo 192-0397, Japan
bFaculty of Integrated Arts and Sci., The University of Tokushima, Tokushima 770-8502, Japan
cAdvanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
dInstitute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan
eDepartment of Physics, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan
fDepartment of Physics and Astronomy, University of California, Riverside, California 92521, USA

Abstract

Wide varieties of strongly correlated electron phenomena are performed on the stage of “filled skutterudite structure”. Especially when one of the players contains plural number of 4f electrons, the orbital degrees of freedom play a major role as a new type of nonmagnetic and/or weak-magnetic phenomena. Several examples found in Pr- and Sm-based filled skutterudites are introduced in relation with the μSR experiments.

Keywords: filled skutterudite; heavy fermion; multipole; crystal field; c-f hybridization; μSR;

1. Introduction

The filled skutterudite compounds (RT₄X₁₂: R= rare earth, actinoide, alkaline and alkaline earth; T= Fe, Ru, Os and Pt, and X= P, As, Sb and Ge) exhibit various attractive features depending on the constituent elements R, T and X [1-6]. It is recognized that the enhanced hybridization between conduction electrons and 4f electrons (c-f hybridization) compared to the ordinary crystal structures is indispensable to realize most of those novel features. The strong c-f hybridization is clearly reflected in the Kondo-insulating behavior which was found in many of the Ce-based filled skutterudites. The reason why the c-f hybridization is highly enhanced in the filled skutterudites could be intuitively inferred from its unique crystal structure shown in Fig. 1, belonging to the space group Im₃, T₅, #204. Especially in the rare earth systems with plural number of 4f-electrons, the unique crystal structure (Fig.1) realizes novel highly correlated electron

Corresponding author. Tel.: +81-42-677-2507; fax:+81-42-677-2507; e-mail: sato@phys.metro-u.ac.jp.

** Present address: Department of Physics, University of Maryland, College Park, Maryland 20742-4111, USA
phenomena such as unusually heavy Fermion masses in PrFe₃P₁₂ and SmOs₄Sb₁₂, unexpected for the ordinary crystal structures. Why such strong electron correlation is realized in the filled skutterudite? One of the reasons is in the large coordination number (twelve X) which leads to effectively large c-f hybridization, even if the hybridization strength between each pair of R and X is small.

Another indispensable parameter controlling the f-electrons’ behaviors in RT₁₂ is an extra term \(-[O^2_6 - O^6_6]\) in the crystalline electric field (CEF) Hamiltonian given by the Stevens’ operators \(O^i_j\), which appears due to the different local symmetry \(T_h\) of R site compared to the ordinary \(O_h\) [7]. In the CEF Hamiltonian of \(T_h\) symmetry, for example, the ground state multiplet \(^2H_4\) of Pr³⁺ ion is split into a singlet \(\Gamma_1\), a doublet \(\Gamma_2\) and two triplets \(\Gamma_4^{(1)}\) and \(\Gamma_4^{(2)}\). Most important consequence of the extra term is that \(\Gamma_4\) and \(\Gamma_5\) in \(O_h\) are mixed into \(\Gamma_4^{(1)}\) and \(\Gamma_4^{(2)}\) states in \(T_h\).

In most of the nonmagnetic (or weakly magnetic) ordered states competing with heavy fermion (HF) state, some hidden parameters associated with 4f-electrons other than the ordinary magnetic dipole are believed to play key roles from the very beginning. Prior to the skutterudite research, “nonmagnetic ordered phase” found in several materials such as UR₆Si₂ has been one of the important subjects in the highly correlated electron systems [8]. However, the progress to clarify the “hidden order parameter” is very slow, since the ways to identify the parameter are usually so limited. In the filled skutterudite family, there have been found quite a few “hidden ordered phases” which have been intensively investigated by various experimental techniques; neutron scattering, NMR, elastic constant, specific heat, etc. Among them, the role played by the μSR technique is remarkable. In this article, the novel features found in Pr- and Sm-based filled skutterudites will be briefly reviewed in correlation with the information given by the μSR techniques.

2. Brief review on the key members of the filled skutterudites

2.1. Novel superconductivity in PrOs₄Sb₁₂

PrOs₄Sb₁₂ is the first Pr-based heavy fermion superconductor found by B. Maple and coworkers [3], and has been most intensively investigated among all the filled skutterudite compounds, since it exhibits unconventional features both in the superconducting (SC) state and in the normal state [3, 9]. The specific heat jump of \(\sim 500\text{mJ/Kmole}\) at \(T_c \sim 1.85\text{ K}\) undoubtedly shows the main role of heavy fermions in this SC-state. The reasonably enhanced effective mass up to \(7.6 \text{ m}_0\) has been directly confirmed in the de Haas-van Alphen experiment [10]. It should be noted that a unique feature of this material, i.e., 4f-electrons remain localized down to lower temperatures below \(T_c\), was confirmed in the same dHvA experiment, in contrast with the itinerant nature of f-electrons in the reported Ce- and U-based

![Fig. 2. H-T phase diagram for PrOs₄Sb₁₂ determined by specific heat, magnetization and magnetoresistance measurements.](image-url)
The reported features on this material are too rich to be described in a limited space, even if we concentrate on the superconducting properties. Hence, we briefly describe only some of the important results given by μSR experiments, and please refer to ref.[9] on the remaining subjects on this material.

One of the most striking features is the sudden appearance and evolution of the tiny internal magnetic field below \( T_c \) probed by zero-field μSR measurements in Fig. 3 [13]. Note that no such spontaneous field has been found in reference superconductors LaOs\(_4\)Sb\(_{12}\) and PrRu\(_4\)Sb\(_{12}\) in the filled skutterudite family, although the measurements were made in the same condition [9]. The development of the spontaneous internal field across \( T_c \) is clearly seen as a sharp increase of the width of the internal field distribution \( \Delta \) below \( T_c \) in Fig. 3, although it is hard to judge \( \Delta \) starts to increase whether at \( T_{c1} \) or at \( T_{c2} \). The estimated averaged internal field is \( \approx 10^{-4} \) T at 0 K. It should be noted that widely accepted example for the system realizing such an internal magnetic field accompanying Cooper pair creation is only Sr\(_2\)RuO\(_4\) until now.[14]

The NMR Knight shift measurement is known to be a powerful tool to evaluate the parity of superconducting phase in unconventional superconductors, however, very weak hyperfine coupling in applied fields hampers the application of this technique to PrOs\(_4\)Sb\(_{12}\). Recently, Higemoto et al. applied the muon Knight Shift to PrOs\(_4\)Sb\(_{12}\), and have detected no evident change of the muon Knight shift across \( T_c \), suggesting the spin-triplet superconductivity is realized in this material [15]. On the SC gap structure, there remain serious discrepancies among the experimental techniques. For example, on the magnetic penetration depth \( \lambda(T) \), data obtained by a μSR study under 20 mT transverse field shows an exponential \( T \) dependence consistent with a fully opened gap [16], while those by a 21-MHz tunnel-diode oscillator with ac field less than 4 \( \mu \)T shows a \( T^2 \)-dependence consistent with the point-node scenario [17].

At the moment, neither the symmetry of the SC order parameter nor the nodal structure in the energy gap is yet settled. However, recently recognized multiband superconductivity appears to be a clue to solve the problems. One can say that the superconductivity in PrOs\(_4\)Sb\(_{12}\) is neither the “ordinary” conventional nor “ordinary” unconventional type.

2.2. Metal-insulator transition and temperature dependent CEF-level crossing in PrRu\(_4\)P\(_{12}\)

PrRu\(_4\)P\(_{12}\) exhibits a metal-insulator (MI) transition \( T_{MI} \approx 63 \)K [18]. The absence of evident anomaly in magnetic susceptibility (\( \chi \)) and the insensitivity of specific heat to magnetic fields at \( T_{MI} \) indicate the nonmagnetic origin of the transition. Theoretically, the antiferro-hexadecapole-ordering has been proposed for the low temperature ordered state, based on the experimentally required cubic invariance of the Pr-site symmetry [19]

Initially, the phase diagram has been quite simple compared to PrOs\(_4\)Sb\(_{12}\) and PrFe\(_4\)P\(_{12}\), e.g., almost vertical single line at 63 K. Recently, an additional...
structure has been recognized below ~30 K where \( \rho \) shows a related upturn in addition to the clear kink at \( T_{MI} \) as shown in Fig. 4(a) [20]. Electron diffraction experiments clarified the MI transition to be accompanied by a structural transformation from BCC to simple cubic structure [21], promoted by the nearly perfect Fermi surface nesting condition [22]. However, there remain several unusual behaviors, such as the large negative magnetoresistance at low temperatures, which cannot be understood by the simple CDW scenario. Saha et al. reported zero-field \( \mu \)SR experiment [23], in which they confirmed the absence of any evident change of relaxation rate across \( T_c \) further supporting nonmagnetic origin of the MI transition. In contrast, they found clear enhancement of \( \lambda \), below ~30 K where \( \rho \) shows a clear upturn [20]. This fact is consistent with the temperature dependence of CEF level scheme revealed by the neutron inelastic scattering experiment, where the CEF ground state of one of the two Pr sub-lattice changes from \( \Gamma_1 \) to \( \Gamma_4^{(2)} \) below ~40 K.[24]. That also suggests that the increase of \( \rho \) could not be simply ascribed to the reduction of carrier number. The more detailed studies are necessary to clarify the low temperature behaviors of this material.

2.3. Heavy fermion ferromagnet \( \text{SmFe}_4\text{P}_{12} \)

\( \text{SmFe}_4\text{P}_{12} \) was reported to be the first Sm-based Kondo-lattice compound with a ferromagnetic ground state below \( T_C = 1.6 \) K by Takeda and Ishikawa [25]. Fig. 5(a) shows the temperature dependence of magnetic part of the electrical resistivity \( \rho_m \) evaluated by subtracting the phonon part of electrical resistivity using \( \rho(T) \) for \( \text{LaFe}_4\text{P}_{12} \). \( \rho_m \) shows a peak near 40 K, indicating the formation of the Kondo-lattice with the effective Kondo temperature \( T_K \) ~40 K [25]. Near \( T_C \sim 1.6 \) K, clear anomalies reflecting some phase transition are clearly found in bulk properties as shown in Fig.5 for the magnetic part of specific heat and electrical resistivity. Both the extrapolated specific heat coefficient \( \gamma \sim 0.37 J/K^2\)mole and the coefficient \( A = -0.23 \) \( \mu \)Ωcm/K^2 of the \( T^2 \)-dependence of \( \rho \) indicate the remarkably heavy fermion state, as a Sm-based

Fig. 4. (a) \( H-T \) phase diagram, temperature dependences of (b) electrical resistivity and (c) Muon relaxation late in \( \text{PrRu}_4\text{P}_{12} \) degitized from ref.Saha.

Fig. 5. (a) Temperature dependences of the electrical resistivity, (b) the magnetic part of specific heat and magnetic entropy in \( \text{SmFe}_4\text{P}_{12} \). Inset in (b) shows the field dependence of magnetization at 2K.
compound. In fact, largely enhanced cyclotron effective mass up to \( \sim 9m_0 \) \((m_0: \text{electron's rest mass})\) has been directly detected in the Haas-van Alphen experiment, although the expected heavier mass branches for the 48th open FS has not yet been detected [26].

Until now, four out of eight investigated Sm-based skutterudites were found to show a ferromagnetic order [4]. Among them, the ferromagnetic states both in SmFe\textsubscript{3}As\textsubscript{12} and SmFe\textsubscript{3}Sb\textsubscript{12} are expected to be realized by the cooperative interaction of localized Sm\textsuperscript{3+} and Fe-3d electrons having the high electronic density of states near Fermi level [27]. In fact, the associated magnetism is strong and the full moment of Sm\textsuperscript{3+} plays a role in those ferromagnetisms. In contrast, the magnetization \( M=0.16\mu_B/\text{Sm} \) at 7 T and 2.0K is far less than 0.71 \( \mu_B \) expected for the free Sm\textsuperscript{3+} ion, and the entropy \( \sim 0.15 \text{ J/Kmole} \) at \( T_C \) is far less than \( R \ln 2 \), suggests the novelty of the ferromagnetic state in the ferromagnetic state of SmFe\textsubscript{3}P\textsubscript{12}. To clarify the feature of such delicate ferromagnetic state, it is important to investigate the low magnetic field response. In this case, the NQR experiment is hardly applicable, since \( ^{31}\text{P} \) nucleus has no quadrupole moment. Therefore, Hachitani et al. applied zero field \( \mu\text{SR} \) measurement to this system [28], and have succeeded in observing the increase of relaxation late indicating the development of static internal field below \( T_C \). At the lowest temperature, the oscillation evidencing the bulk ferromagnetism in this material is visible. Based on this result, further investigations to clarify this novel heavy fermion ferromagnet have been in progress.

2.4. Octupole order in SmRu\textsubscript{4}P\textsubscript{12}

The metal-nonmetal transition at \( T_{\text{MI}}\sim 16K \) accompanied by magnetic anomaly in SmRu\textsubscript{4}P\textsubscript{12} first reported by Sekine et al. attracts much attention [29], since the phase diagram has a feature close to the antiferro-quadrupolar ordering reported in CeB\textsubscript{6}; \( T_{\text{MI}} \) increases with increasing magnetic field. With increasing field, an additional anomaly becomes evident in various physical properties at \( T^* \) below \( T_{\text{MI}} \), shown in Fig. 7 as a \( H-T \) phase diagram. Initially, it was thought to be successive transitions of antiferro-quadrupolar ordering at \( T_{\text{MI}} \) and antiferromagnetic ordering at \( T^* \) [30].

To clarify the origin of the successive transition, various experimental techniques have been applied to this material, such as specific heat, elastic constant, NMR, nuclear resonant forward scattering, etc [31-36]. As a result, the octupole ordering scenario tends to be accepted as an origin of the MI-transition near 16.5 K, although there still remains some controversy in detail. Among them, zero-field (ZF) muon spin

![Fig. 6. ZF-\( \mu\text{SR} \) spectra below and above \( T_C \). The data points are digitized from Fig.5 in ref. [28]. Inset shows the temperature dependence of electrical resistivity near \( T_C \).](image)

![Fig. 7. (a) \( H-T \) phase diagram determined by various technique on polycrystals and the open symbols are anisotropy estimated by the specific heat measurement on a single crystal.(b) Temperature dependence of Muon spin relaxation late in SmRu\textsubscript{4}P\textsubscript{12} digitized from Fig.2 in ref. [35]](image)
relaxation (μSR) measurements played a key role confirming the time-reversal symmetry (TRS) breaking below $T_{MI}$ without any sign of change in muon spin relaxation rate across $T^*$.

2.5. Novel heavy fermion states in PrFe$_4$P$_{12}$ and SmOs$_4$Sb$_{12}$

Finally, the basic features of PrFe$_4$P$_{12}$ and SmOs$_4$Sb$_{12}$ are briefly mentioned, since they are indispensable materials to have a general view on the filled skutterudite compounds [2, 4, 5]. The electrical resistivity in the former exhibits evident −$ln(T)$ dependence down to ~6.5 K below which some nonmagnetic ordered state is realized. When the ordered state is destroyed by magnetic field, a quite anisotropic field induced heavy fermion state is realized. The lower limit value of the Pr-moment (10$^{-3}$μ$_B$/Pr-ion) determined by the ZF and transverse-field μSR measurements is indispensable information, in order to understand the nonmagnetic low-field-ordered state [37].

The heavy fermion state (with $\gamma$ = 800 mJ/K$^2$/mol) in SmOs$_4$Sb$_{12}$, robust against magnetic field and coexistent with a weak ferromagnetic state, is one of the most attractive subjects in the filled skutterudite compounds. The weak ferromagnetic state was confirmed to be an intrinsic bulk ordered state by ZF-μSR, which will be presented in this proceeding [38].

3. Summary

The strong c-f hybridization and the small CEF level splitting allowed by the unique filled skutterudite structure realize varied attractive phenomena through the delicate balance between the strong electron correlation and the 4f-electrons’ degrees of freedom left down to low temperatures. Many of them have nonmagnetic or weakly magnetic nature which is suited to μSR experiments.

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References

[8] For example, p.172 in ref. [2].
[38] Y. Aoki et al., unpublished.