21a1

New electronic states in 115 compounds

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We report the topology of the Fermi surface and the corresponding cyclotron effective mass in $CeTIn_5$ and $AcTIn_5$ (T: transition metal and Ac : U, Np, Pu) with the tetragonal structure via the de Haas-van Alphen experiments and the energy band calculations. These compounds possess the quasi-two dimensional electronic state, namely the nearly cylindrical Fermi surface. The Fermi surface properties of a heavy Fermion superconductor $CeCoIn_5$ were compared to those of an antiferromagnet $CeRhIn_5$ under pressure. Figure 1 indicates a drastic change of the electronic states in $CeRhIn_5$ from a $LaRhIn_5$-like Fermi surface ($P < P_c$) to a $CeCoIn_5$-like Fermi surface ($P > P_c$), which occurs at $P_c \simeq 2.35\,\mathrm{GPa}$ [1]. The characteristic quasi-two dimensional electronic states are also demonstrated in antiferromaents $UPtGa_5$ and $NpRhGa_5$. We also note a change of the electronic states in an antiferromagnet $CeIn_3$ with the cubic structure under pressure, comparing it with those of $LaIn_3$, $ThIn_3$, UIn_3, $NpIn_3$ and $PuIn_3$.

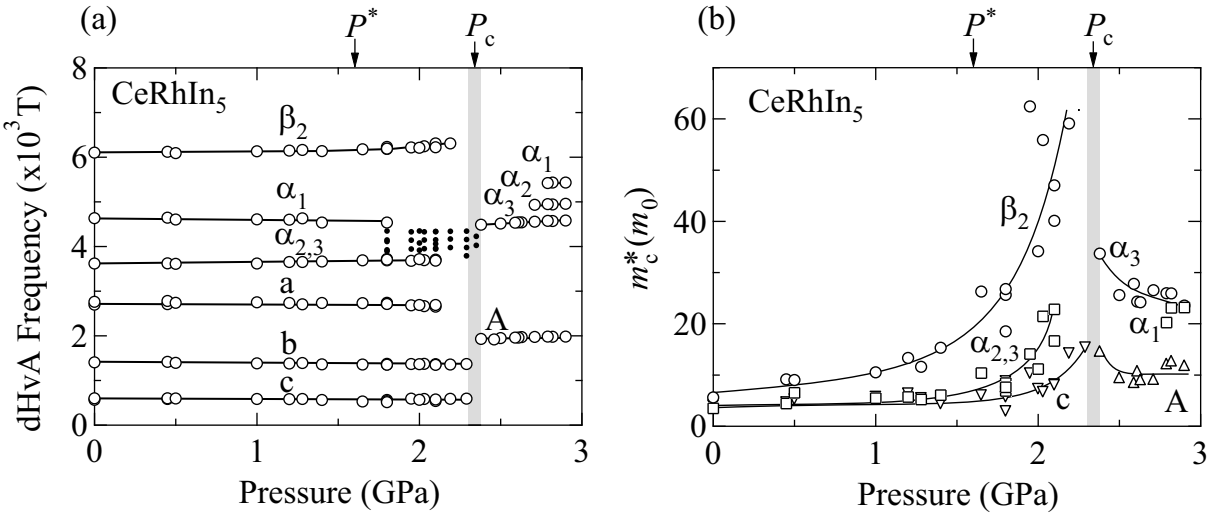

Figure 1: Pressure dependence of (a) the dHvA frequency and (b) the cyclotron mass in $CeRhIn_5$.

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21a2

Tuning Unconventional $PuMGa_5$ and $CeMIn_5$ Superconductors

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The discovery of superconductivity at $T_c = 18.5$ K in $PuCoGa_5$ and at $T_c = 9$ K in $PuRhGa_5$ has generated renewed interest in Pu-based intermetallic compounds. The thermodynamic properties of $PuMGa_5$ (M=Co, Rh), such as specific heat jump at T_c, are consistent with an electronic specific heat coefficient $\gamma \sim 50$-100 mJ/mol-K^2 indicating moderately heavy fermion behavior in these materials. The normal and superconducting states of these two Pu-based superconductors are remarkably similar to those of the well-known heavy-fermion $CeMIn_5$ (M=Co, Rh, Ir) superconductors, in which superconductivity is mediated by antiferromagnetic spin fluctuations. In particular, structural tuning of superconductivity, as evidenced by the linear variation of transition temperature with the tetragonal lattice parameters, plays a major role in the optimization of T_c within the $PuMGa_5$ and $CeMIn_5$ families of superconductors. In addition, we present electrical resistivity and nuclear spin lattice relaxation measurements on $PuMGa_5$ that indicates a single (spin-fluctuation) energy scale dominates the physical properties, suggesting that spin fluctuations control both the superconducting and normal states. These results are taken as evidence that there exists a continuum of energy scales within this mechanism of magnetically mediated superconductivity over at least two orders of magnitude, from millikelvins to ~100 K, suggesting that novel superconducting materials with transition temperatures greater than 100 K may yet be discovered. We also show that an itinerant/localized crossover of the 5f electrons occurs near $PuCoGa_5$ in the $ACoGa_5$ (A=U, Np, Pu, Am) series, similar to what is observed in the actinide elements.

21a3

New superconducting phase $PuTGa_5$ and related compounds

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The recent discovery of superconductivity [1] at a high transition temperature, Tc=18.5 K, in the plutonium-based compound $PuCoGa_5$ has ignited a tremendous interest in this new material [2-10]. Prior to this discovery, no Pu-based compound was known to exhibit superconductivity. Moreover, among the known actinide or lanthanide superconductors one rarely finds a material with a T_c over 2 K. From this perspective, $PuCoGa_5$ can be regarded to have an astonishingly high transition temperature and the nature of the superconducting pair formation has been a point of special focus. Most recently, experimental studies, employing nuclear magnetic and quadrupolar resonance (NMR, NQR), proved that indeed $PuCoGa_5$ and the related superconducting compound $PuRhGa_5$ are unconventional, spin-singlet, d-wave type superconductors [9,10]. These latest findings definitely categorize $PuCoGa_5$ and $PuRhGa_5$ as most exceptional and intriguing materials, yet, many important questions are still open. In particular, the electronic structure of $PuCoGa_5$ and the role played by the Pu 5f electrons are not understood.

In order to shed light on the key parameters in these compounds, different approaches to tune their superconducting properties were undertaken [11,12]. The homologue pure An-compounds (An = Np, Am) and diluted systems by doping either the Pu site or the transition metal site - i.e. $(Pu_{1-x}An_x)CoGa_5$ and $Pu(Co_{1-x}T_x)Ga_5$ respectively - were investigated. In a second rather unique approach, the tuning induced by the self-damage effects resulting from the ^{239}Pu decay was studied.

In this presentation, we propose a summary of the results obtained and their contribution to our present understanding of the magnetic and superconductivity behaviors in this fascinating class of materials.

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21p1

From Skutterud to Japan — the discovery and exploitation of skutterudite-bearing cobalt ore at Modum, Norway

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When cobalt ore was discovered on the farm Skuterud in 1772, the Danish-Norwegian king grasped the possibility of breaking the monopoly of the Kurfürsten of Saxony (later Germany) of the precious blue pigment used in luxury goods like fine china (porcelain). The king thus initiated exploitation of the ore and the building of a chemical plant, but soon technical problems rose. For centuries ultramarine had been the colour of pharaos and kings. After the Egyptian technology of blue colour production was lost, the only source of ultramarine was for centuries lapis lazuli from Afghanistan. In Saxony, however, they succeeded in inventing a production technique of blue pigment from cobalt ore. It was a well kept secret guarded with the threat of death penalty, as the pigment was more valuable than gold. While Saxony both had a long tradition of mining and the technology of producing ultramarine pigment from cobalt ore, no such skills were found in Denmark-Norway. The Modum factory even applied industrial espionage to get access to the technology, and at last succeeded in employing an experienced colour chemist from Hessen (Germany). But the production of the finest quality of blue pigment was not successful until the king had lost the war on Napoleon's side, renounced Norway, and the factory at Modum eventually was taken over by private German owners in 1822. **Friedrich Roscher**, of a family involved in glass and pottery production in Dresden, became in charge of the chemical factory, whereas the 23 years old **Karl-Friedrich Böbert**, educated in mining and geology, became the director of the mines. Until then the ore had been mined in open pits, but Böbert started underground mining. He set long-time goals and tirelessly searched to improve the mining techniques, social reforms and education of the workers and their families.

In 1833, the 20 years old German chemist **Theodor Scheerer** was employed on the night shift in the blue colour factory. By studying mineral samples from the Skutterud mines he found that the ore consisted of three cobalt minerals. One was the pure cobalt sulphide *cobaltite*, the second a cobalt-rich variety of the mineral arsenopyrite which he called *danaite*, while the third was an unknown species. This had previously been noted by Breithaupt (1827) who called it Tesseralkies due to its hexagonal cleavage. Scheerer determined its chemical composition to be $CoAs_3$ and called the new mineral Arsenikkobaltkies (1837). Later the new mineral was named **Skutterudite** by Haidinger (1845 b) after the place where it was first found. Scheerer also studied some ore samples found further north which proved to contain nickel, a new metal discovered by the Swedish mineralogist von Cronstedt in 1751. Scheerer described the world's first nickel mineral, which is now called *pentlandite*. He was also a pioneer in the exploitation of nickel ore that made Norway the world's leading nickel producer between 1860 and 1890 with 40 mines and 7 nickel plants.

Under the leadership of Böbert, Roscher and Scheerer the blue colour factory at Modum reached its golden age in the 1830s, when it had become Norway's largest employer with

1300 workers and 2000 inhabitants around the mines in the hill Skutterudåsen. The chemical factory was regarded the most high-technological plant in Europe at that time. Due to the supreme quality of the pigment, Modum held 80 % of the world marked, and it was exported to the whole world including Japan that was closed for free trade at that time. In 1839 Theodor Scheerer left for Germany to complete his doctoral thesis, and after that he served some years as a university professor in Kristiania (former name on Oslo) until he was appointed professor in mineralogy and metallurgy at the Acedemy of Mining in Freiberg, the most prestigious center of mineralogy, chemistry and natural science in Europe.

Figure 1: The mining area at Skutterud, Modum (top: around 1860, bottom: recent). The large heaps of stones in the background have been taken out of the open pits further to the left.

21p2

Mixed Rare Earth (Mischmetal) Skutterudites - A Route to Low Thermal Conductivity?

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Significant interest in ternary skutterudites $RE_yT_4X_{12}$ with RE = rare earth, T = Fe, Co, Rh, Ru, . . and X = P, As, Sb, stems from the fact that skutterudites are potential candidates for thermoelectric applications. Depending on the carrier concentration of a particular skutterudite, Seebeck values above $150\mu V/K$ can be observed. Besides, ternary skutterudites are outstanding with respect to their low thermal conductivity, which approaches the theoretical limit. As a matter of fact, the dramatically diminished $\lambda(T)$ values are associated with an exceptionally large thermal parameter of the loosely bound rare earth elements, corresponding to a "rattling" (i.e., soft phonon mode) of these atoms in an oversized cage. Our previous studies on Pr- or Yb-based Fe/Ni-substituted skutterudites evidenced remarkably high Seebeck coefficients approaching $220\mu V/K$. Thus, the aim of the present work is the optimization of the thermoelectric properties of a corresponding Fe/Ni-based skutterudite phase filled by mischmetal. Mischmetal is a random mixture of several light rare earth elements, and is supposed to introduce additional phonon scattering and thus may contribute to a further reduction of thermal conductivity, keeping (i) the high Seebeck coefficient and (ii) a good electrical conductivity. Although the essential parameters for synthesis are known from our previous experimental know-how, optimization is necessary as each rare earth element adopts its specific filling level in the skutteridite phase and by this influences the electron structure at the Fermi-level, which in turn can be balanced via slight adjustment of the Fe/Ni substitution. Mischmetal (MM) was introduced in Skutterudites to reduce thermal conductivity via phonon-scattering on the mischmetal atoms rattling in the voids of an ordered crystal structure. Compounds from the solid solution $MM_y(Fe_{1-x}Ni_x)_4Sb_{12}$ were synthesized by both arc-melting and reaction sintering. From Rietveld refinements isotypism was determined in all cases with the (partially filled) $La_yFe_4P_{12}$ (Skutterudite)-type, space group $Im-3$ (No. 204). The X-ray refinements served to derive the MM-content in the samples. Electron microprobe measurements were made to establish the final Fe/Ni content in the alloys. These investigations confirmed a systematic trend for the MM-occupancy in the parent lattice, revealing a gradual decrease of the MM-content from y=1.0 ($MM_{0.1}Fe_4Sb_{12}$) to y=0 for the equi-atomic composition $Fe_2Ni_2Sb_{12}$. This dependency correlates with the thermal stability of the ternary compounds: a true ternary compound forms for $MMFe_4Sb_{12}$, whilst a stable skutterudite compound already exists for MM-free $Fe_2Ni_2Sb_{12}$. Optimization of thermoelectric properties via Fe/Ni-substitution and degree of filling of the void by MM was monitored by measurement of the thermoelectric parameters of the alloys including Seebeck-coefficient, electrical and thermal conductivity.

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21p3

Magnetic and thermoelectric properties of AT_4Sb_{12} (A = Ca, Sr, Ba; T = Fe, Ru, Os)

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Alkali-metal- and alkaline-earth-filled skutterudites AFe_4Sb_{12} (A = Na, K, Ca, Sr, Ba) are attracting much attention because the compounds with monovalent Na and K are itinerant ferromagnets while those with divalent Ca, Sr, and Ba are nearly ferromagnetic systems [1-3]. In the latter, the presence of Fe $3d$ derived flat bands near the Fermi level is manifested in the rather large value of the specific heat coefficient $\gamma = 100$ mJ/K^{2}mol. The characteristic temperature of spin fluctuations was estimated to be 50 K from the maximum in both the magnetic susceptibility χ and thermopower [3]. At lower temperatures, the $(1/T_1T)_{spin}$ measured by Sb NQR in AFe_4Sb_{12} (A=Sr, Ba) goes to zero, which is however unexpected in nearly ferromagnetic systems [4].

In order to understand the unusual magnetic properties of the Fe compounds, we have studied the magnetic and thermoelectric properties of the Ru and Os compounds AT_4Sb_{12} (A = Sr, Ba; T = Ru, Os) [5]. The dense samples were prepared by the spark-plasma sintering method. As is shown in the figure, the χ of the Ru compounds is negative. This diamagnetic behavior is consistent with the small γ value of 10 mJ/K^{2}mol. The magnitude of χ for the Os compounds is one tenth of that of the Fe compounds and its temperature dependence is much weaker compared with the Curie-Weiss behavior. We note that $\chi(T)$ is describable by the form predicted for a strongly coupled electron-phonon system [6,7]. The moderately high value of $\gamma = 45$mJ/K^{2}mol indicates the presence of a large density of states derived from Os $5d$ states near the Fermi level.

The analysis of the thermal conductivity measurements shows that the lattice thermal conductivity κ_{ph} for the Os compounds does not show a peak near 50 K and its value is much smaller than those of the Fe- and Ru-counterparts. This unusual behaviour of κ_{ph} is attributed to the phonon scattering by localized vibrations of A^{2+} ions in the oversized cage of Os_4Sb_{12}. We propose that the strong electron-phonon interaction in the presence of tunneling states is the origin for the shoulder observed in the electrical resistivity around 100 K.

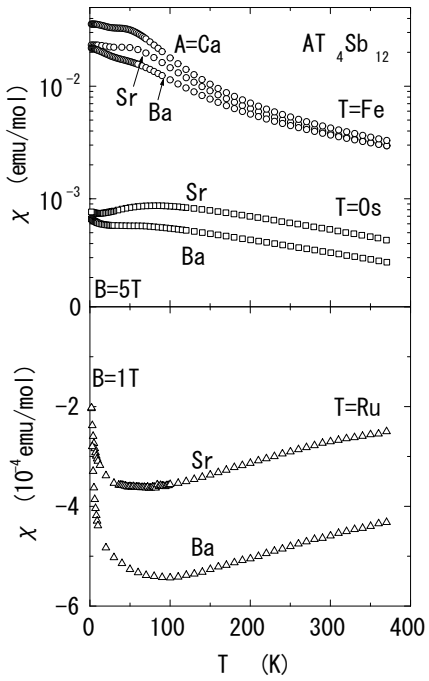

Figure 1: Temperature dependence of the magnetic susceptibility.

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21p4

High Spin Polarization in the Ferromagnetic Alkali-Metal Filled Skutterudites

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The class of compounds known as the filled skutterudites shows a large variety of phenomena of present interest ranging from metal-insulator transitions to unconventional superconductivity and heavy fermion behavior. In the following, we will concentrate on the magnetic and transport properties of the materials with iron-antimony host in which case the magnetic properties are influenced in great measure by the charge of the filler ion. It has been shown [1,2] that monovalent cations (Na^{1+}, K^{1+}) result in weak itinerant ferromagnetic materials with a Curie temperature $T_C \approx 85\,K$.

Here, we present point-contact Andreev reflection (PCAR) measurements [3] performed on KFe_4Sb_{12} and $NaFe_4Sb_{12}$ polycrystalline samples at 2.8 K. Mechanically cut sharp tips of different superconducting materials, Nb and Pb, were used. The transport spin polarization P_t was extracted from the spectra by fitting a Blonder-Tinkham-Klapwijk theory modified to incorporate the effect of spin polarization. We obtained high intrisic values of P_t: 67% for KFe_4Sb_{12}, and 60% for $NaFe_4Sb_{12}$. Thus, these two compounds introduce a new class of materials with a large degree of spin polarization and itinerant electron magnetism. PCAR measurements were also conducted on $CaFe_4Sb_{12}$, the structurally closest but non-ferromagnetic homologue.

These experimental results are compared to those of band structure calculations in which we find an almost fully polarized DOS at the Fermi level E_F for KFe_4Sb_{12}. The spin-up electrons can be assigned mainly to two bands (Fermi surfaces) of almost pure Fe-3*d* character. There is only one band of strongly mixed Sb 5*p*–Fe 3*d* character crossing E_F in the spin-down channel. Two possible mechanisms may lead to reduced experimental values of P_t with respect to the calculated ones: Firstly, weak itinerant ferromagnetism is usually accompanied by large spin fluctuations. In particular, the spin-lattice relaxation rate $1/T_1$ of $NaFe_4Sb_{12}$ is well described by Moriya's spin fluctuation theory for itinerant ferromagnets [4]. Secondly, the Fermi velocity v_F has differently weighted influence on the measured P_t depending on the nature of the point contact (ballistic or diffusive).

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21p5

Superconductivity in $CeIrIn_5$ under chemical and hydrostatic pressures: ^{115}In-NQR study

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We report the result of ^{115}In nuclear-quadrupole-resonance (NQR) measurements on heavy-fermion superconductor $CeIrIn_5$ under chemical and hydrostatic pressures. We have found that the Rh substitution for Ir makes antiferromagnetic (AFM) spin correlations enhance strongly and at the same time increases a superconducting (SC) transition temperature from $T_c = 0.4$ K for $CeIrIn_5$ up to 1.2 K for $CeRh_{1-x}Ir_xIn_5$ with $x = 0.7$. The temperature dependence of nuclear spin-lattice relaxation rate for $x = 0.7$ has revealed the development of AFM spin fluctuations as if the system approaches an AFM ordered state and a significant increase of SC energy gap. It is this AFM spin fluctuations to mediate a strong coupling anisotropic superconductivity with the line node. By contrast, the application of pressure suppresses markedly the AFM spin fluctuations. Nevertheless, T_c increases up to 0.8 K at 2.1 GPa, that is twice larger that $T_c = 0.4$ K at $P = 0$. It seems that the multiple mechanisms work to increase T_c in $CeIrIn_5$. Relevant with the respective mechanisms for increasing T_c under the presence and absence of AFM spin fluctuations, a reason why T_c is unexpectedly reduced at $x = 0.9$ is suggested to be relevant with a crossover from the former to the latter SC state.

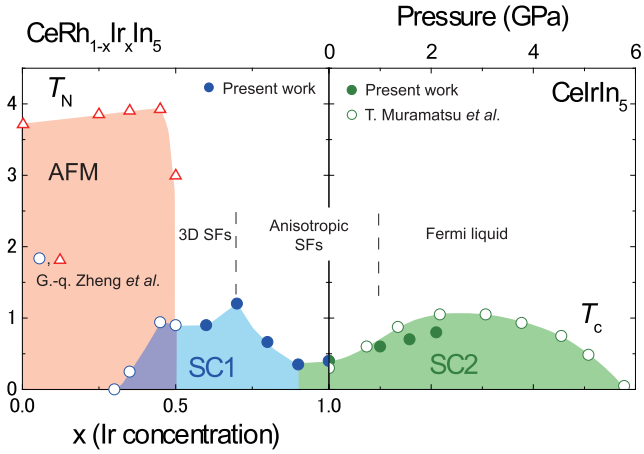

Figure 1: Phase diagram for antiferromagnetism and superconductivity in $CeIrIn_5$ under chemical and hydrostatic pressures. Open circles and triangles for $CeRh_{1-x}Ir_xIn_5$ and open circles for $CeIrIn_5$ are referred from Ref.[2] and [3], respectively.

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21p6

Low temperature - high field superconducting state in $CeCoIn_5$: various probes

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21p7

NMR Study of the FFLO State in $CeCoIn_5$

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A myriad of fascinating properties have been proposed for unconventional superconductors in the presence of a strong magnetic field. Among the possible exotic superconducting (SC) phases, a spatially nonuniform SC state originating from the paramagnetism of conduction electrons has become a subject of intense theoretical investigation after the pioneering work by Fulde and Ferrel, and as well as Larkin and Ovchinnikov (FFLO) in the mid-1960's. In the FFLO state, a pair-breaking due to the Pauli effect is reduced by the formation of a new pairing state $(k \uparrow, -k + q \downarrow)$. As a result, a new SC state with spatially-oscillating order parameter and spin polarization should appear in the vicinity of upper critical field, H_{C2}.

In this context, a newly-discovered heavy electron superconductor $CeCoIn_5$ has aroused great interest, as recent measurements revealed that a second order phase transition takes place at $T^*(H)$ within the SC state in the vicinity of H_{C2} with H parallel to the ab-plane at low temperature. While these experimental results make the FFLO scenario a very appealing one for $CeCoIn_5$, there is no direct experimental evidence so far which verifies the spatially nonuniform SC state expected in the FFLO state. Therefore, a powerful probe of the quasiparticle excitations in the high field SC phase is strongly required to shed light on this subject. NMR is particularly suitable for the purpose, because NMR can monitor the low energy quasiparticle excitations sensitively.

Here we present ^{115}In-NMR studies of the heavy-fermion superconductor $CeCoIn_5$. In the vicinity of H_{C2}, the NMR spectrum exhibits a dramatic change below $T^*(H)$ which well coincides with the position of reported anomalies in specific heat and ultrasound velocity. The spectrum which we observed in the high field SC phase is quite unique. We simulate the spectrum by a model with a spatially modulated superconducting energy gap. On the basis of the analysis, we are able to establish a clear evidence of the spatially-inhomogeneous SC state at high field and low temperatures, as expected in the FFLO state. The present results provide the first microscopic evidence for the occurrence of a spatially inhomogeneous SC state expected in the FFLO state. The NMR spectrum also indicates that the vortex core structure of $CeCoIn_5$ appears to be markedly different from that of ordinary superconductors.

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22a1

Rattling phase transition in the superconducting β-pyrochlore oxide KOs_2O_6

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Recently, a new class of transition metal oxide superconductors have been found, which are β-pyrochlore oxides, AOs_2O_6, with A = Cs,[1] Rb,[2, 3] and K.[4] The superconducting transition temperatures T_c are 3.3 K, 6.3 K, and 9.6 K, respectively, much higher than T_c = 1.0 K for a previously known α-pyrochlore oxide superconductor, $Cd_2Re_2O_7$.

The mechanism of superconductivity in these β-pyrochlore oxides has been studied extensively thus far. A few experimental lines of evidence indicating the possibility of unconventional superconductivity were reported. One is the large upper critical field H_{c2} found in KOs_2O_6, and the others are the results of two resonance experiments: μSR experiments by Koda *et al*. on KOs_2O_6 suggested the presence of an anisotropic order parameter,[5] which is in contrast to previous experimental results on $Cd_2Re_2O_7$ revealing an isotropic gap. In NMR experiments on ^{39}K and ^{87}Rb nuclei, Arai *et al*. found a tiny coherence peak in $1/(T_1T)$ below T_c for $RbOs_2O_6$, while no peaks were found for KOs_2O_6, which strongly suggests that unconventional superconductivity is realized, particularly in KOs_2O_6.[6] In contrast, there are a few reports insisting that the superconductivity of $RbOs_2O_6$ is of the conventional BCS type.[7] Although the basic pairing mechanism of superconductivity must be virtually common to all the β-pyrochlore oxides, the phenomenological properties seem to be quite different among the members. In particular, KOs_2O_6 with the highest T_c is distinguished from the others, exhibiting various unconventional features.

Another interesting finding in the β-pyrochlore oxides is that an alkali metal atom lying in an oversized cage made of OsO_6 octahedra exhibits 'rattling' behavior similar as reported in filled skutterudite or clathrate compounds with low thermal conductivity and thus a large thermoelectric efficiency. We found an anomalously large atomic displacement parameter for the A atom in structure refinements and low-energy Einstein phonons in specific heat measurements. Particularly, the smallest K atom shows the largest rattling. Possibly related to this, we found a first-order phase transition at 7 ~ 8 K below T_c only for KOs_2O_6.

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22a2

Ultrasonic investigation of rattling and tunneling in clathrate compounds

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We preset the recent ultrasonic investigation on the rattling and tunneling of off-center oscillator in clatherate compounds $R_3Pd_{20}Ge_6$ (R=La, Ce, Pr, Nd) and filled skutterudite $PrOs_4Sb_{12}$. It has been found that the transverse C_{44} mode in $R_3Pd_{20}Ge_6$ (R=La, Ce, Pr, Nd) and the $(C_{11}$-$C_{12})/2$ mode in $PrOs_4Sb_{12}$ revealed an appreciable frequency dependence of thier elastic constant and ultrasonic attenuation around 10-30 K. [1,2,3] This ultrasonic dispersion indicates species of the charge fluctuation associated with the rattling motion of the off-center oscillator of the rare-earth ion filled in the cage; the Γ_5 symmetry in $R_3Pd_{20}Ge_6$ and Γ_3 symmetry in $PrOs_4Sb_{12}$. The relaxation time of the thermally activated rattling exhibits the Arrhenius-type temperature dependence of $\tau = \tau_0 \exp(E/k_BT)$ with the attempt time $\tau_0 = 2.5 \times 10^{-12} \sim 3.1 \times 10^{-11}$ s and an activation energy $E = 70 \sim 225$ K. It is remarkable that the heavy Fermion compounds of $Ce_3Pd_{20}Ge_6$ and $PrOs_4Sb_{12}$ exhibit the appreciable softening of attempt frequency $\hbar\omega = \hbar/\tau_0 = 1.5$ K in comparing to the $\hbar\omega = \hbar/\tau_0 = 24$ K of a simple metal $La_3Pd_{20}Ge_6$. This result implies that the coupling of the off-center oscillation to conduction electrons with heavy mass reduces the energy of the off-center oscillator in the cage.

The properties associated with the off-center tunneling state are observable only at low temperatures, where the thermally activated rattling dies out. The elastic constant of C_{44} of $La_3Pd_{20}Ge_6$ shows a remarkable softening below 3 K down to 20 mK, which follows as $C_{44} = C_{44}^0(T - T_C)/(T - \Theta)$ with $\Theta = -338.044$ mK and $T_C = -337.970$ mK. [3] This low temperature softening of C_{44} shows that the charge fluctuation of the triply degenerate Γ_5 off-center tunneling state is relevant even at low temperatures down to 20 mK. The low-temperature softening of $(C_{11} - C_{12})/2$ above the superconducting point $T_C = 1.85$ K in $PrOs_4Sb_{12}$ also suggests the charge fluctuation of the doubly degenerate Γ_3 off-center oscillator, which may participate in the formation of the heavy Fermion quasi-particle and its superconductivity of $PrOs_4Sb_{12}$. [4,5]

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22a3

Microcalorimetry under pressure in heavy fermion matter

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Focus is given on the (T, P) phase diagram on different heavy fermion matter using ac microcalorimetry apparatus developed in Grenoble : the pressure can be tuned in situ at low temperature ($T = 0.4$ K) up to 16 GPa. The examples cover:

- insulator metal transition and magnetism of SmS and SmB_6
- hidden order and superconductivity of URu_2Si_2
- pressure evolution of the double superconducting transition of $PrOs_4Sb_{12}$: intrinsic or extrinsic ?
- comparison between Ce and Yb heavy fermion: $YbRh_2Si_2$ versus $CeRh_2Si_2$
- competition of antiferromagnetism and superconductivity in $CeRhIn_5$: superconductivity description on both side of the quantum first order transition ($P^* = 2$ GPa)

This last study has been extended in magnetic field with the observation of a field reentrance of long range magnetism above P^* *i.e* in the high pressure initial clean d wave state. The possible consequence on the high field superconducting state of $CeCoIn_5$ is discussed (FFLO or not).

22a4

Lu-dilution studies of $YbRh_2Si_2$

Z. Fisk, S. Maquilon

Specific heat, magnetic susceptibility and electrical resistivity data is presented across the alloy system (Yb/Lu)Rh_2Si_2. This data differs from similar dilution studies in Ce-based systems with which some comparison is made.

22a5

Molecular solids - model systems for exploring interacting electrons near critical points

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Solids, made up of molecular units containing open shell transition metal ions or stable organic π-radicals, provide flexible building block systems for exploring correlated electrons in reduced dimensions. As part of an interdisciplinary research program at Frankfurt University, a variety of molecular materials has been synthesized and investigated in detail. Among these are hydroquinone-based transition metal coordination compounds forming low-dimensional quantum spin systems with tuneable material parameters. An especially interesting feature of these molecular quantum magnets is the moderate exchange coupling constants J, weak enough for laboratory magnets to tune the systems across field-induced quantum critical points. Likewise, molecular metals formed by the combination of stable organic π-radicals with suitable inorganic linkers have proved to be excellent model systems for studying the interplay of strong electron-electron and electron-phonon interactions in low dimensions. Of particular interest are the quasi-2D charge transfer salts of the κ-$(ET)_2Cu[N(CN)_2]Z$ (Z = Br, Cl) family where transitions between various symmetry broken states such as Mott-insulator, antiferromagnet, anomalous metal and superconductor can be induced by small variations of chemical (substitution) or physical (pressure, temperature or magnetic field) parameters. In the talk we will discuss examples from both classes of molecular-based materials. Particular emphasis is placed on (i) a Cu(II) coordination polymer where a pronounced acoustic anomaly has been observed near the saturation field and identified as a generic property of the antiferromagnetic $S = 1/2$ Heisenberg chain [1], (ii) a 3D-coupled Cu(II)-dimer system where a field-induced phase transition has been found, reminiscent of the observations made in $TlCuCl_3$, where it has been interpreted as a Bose-Einstein condensation of magnons [2], as well as (iii) the anomalous metallic state and its interrelation with superconductivity for the κ-$(ET)_2X$ compounds [3].

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22p1

Global Phase Diagram of Magnetic Heavy Fermions

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A Kondo lattice system displays a number of quantum phases, with their distinctive Fermi surfaces. I will discuss the global magnetic phase diagram[1], and how local quantum criticality[2] naturally fits into this phase diagram. The role of frustration will be emphasized. The experimental signatures of these phases and critical points will also be presented. These include the Fermi surface evolution, Hall effect[3], thermoelectrical transport, magnetic dynamics, and thermodynamical ratios such as the Grüneisen ratio[4]. Finally, the combined effects of disorder and frustration will be briefly considered.

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22p2

Magnetism and superconductivity in heavy-fermion systems close to quantum criticality

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Magnetic order can continuously be suppressed to $T_{\mathrm{N}} = 0$ at a magnetic quantum phase transition (QPT) as a function of a non-thermal control parameter. In the vicinity of the QPT unusual low temperature behavior is observed in macroscopic properties, e.g. non-Fermi-liquid behavior or the appearance of superconductivity. We report on extensive neutron scattering and muon spin rotation (μSR) experiments in different heavy-fermion compounds to investigate the antiferromagnetic order and the magnetic excitation spectrum close to a QPT. In the case of $CeCu_2Si_2$ the experiments focused on the interplay of antiferromagnetism and superconductivity, while in $YbRh_2Si_2$ the magnetic excitations and critical spin fluctuations above the ordering temperature will be presented.

In a first set of experiments we demonstrated that the magnetic order in $CeCu_2Si_2$, initially called A phase, is determined by the nesting properties of the Fermi surface [1]. Subsequently we performed experiments on $CeCu_2Si_2$ single crystals exhibiting both, antiferromagnetism and superconductivity (A/S-type). The experiments give clear evidence that in A/S-type $CeCu_2Si_2$ (with $T_{\mathrm{N}} > T_c$) superconductivity expels antiferromagnetic order at low temperatures and both phenomena do not coexist on a microscopic scale. Furthermore, the transition from antiferromagnetism at higher temperature to superconductivity at low temperatures is first order in nature even in zero magnetic field with the occurrence of phase separation around the transition.

So far the experiments in $YbRh_2Si_2$ have been restricted to powder. In initial measurements we identified the crystalline electric field (CEF) level scheme with a ground state doublet and three excited states at $0 - 200 - 290 - 500\,\mathrm{K}$ [2]. The large splitting to the first excited state indicates that the non-Fermi-liquid behavior at low temperatures does not depend on CEF excitations and is entirely determined by the properties of the ground state doublet. The spin fluctuations above T_{N} show a critical slowing down when lowering the temperature. However, they cannot be modelled by a simple relaxation ansatz, but by a distribution of different relaxation rates. These results will be discussed in comparison with thermodynamic properties.

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22p3

Conventional or Unconventional? What transport can tell us about the nature of metallic quantum criticality

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Quantum critical points in metals have been studied experimentally in considerable detail over the past decade. These experiments have tested the beautiful marriage of quantum mechanics and the statistical physics of phase transitions that was pioneered by John Hertz [1]. These experiments have revealed a fascinating richness of behaviour from unusual power-laws seen at the quantum critical point to superconductivity and mysterious "hidden order" phases. One of the key puzzles that has emerged is the number of examples of materials (usually heavy fermion metals) which do not seem to fit the predictions of Hertz' theory and its subsequent refinements. These "unconventional" quantum critical metals include $CeCu_{6-x}Au$ and this material in particular has motivated a number of theoretical important ideas as to what physics must lie beyond the ideas of Hertz to explain the data. This has recently been briefly reviewed [2].

One suggestion has been that a magnetic quantum phase transition in a heavy fermion metal coincides with the collapse to zero temperature of a Kondo scale. This Kondo scale separates two regimes. One is the local moment regime – where the *f*-electrons are localized and the conduction electrons alone contribute to the Fermi volume. The other is the heavy fermion metal – where the conduction electrons and *f*-electrons combine to form a heavy electron fluid whose Fermi volume counts both species. It has been predicted that a quantum critical point of this form should be characterized by a jump in the Fermi volume [3]. We have studied the transport properties through this transition by considering a model proposed by Senthil et al. [4] which contains such a transition (albeit without a magnetic phase transition). We find that the discontinuous change in the Fermi volume at the critical point leads to discontinuities in the conductivity. However the heavy fermion metallic state may be thought of as "gossamer"-like in that its frequency response recovers that of the local-moment metal at a frequency which also tends to zero at the quantum critical point [5].

Discontinuities in transport may seem to be a diagnostic for this type of "unconventional" quantum critical point. However, we have also shown that the collapse of an energy scale at a conventional density wave quantum critical point can also lead to discontinuities in transport when a magnetic field is applied [6]. The origin of this lies in a breakdown of weak-field magneto transport because of the cusps induced in the Fermi surface at the transition. This results in a magneto resistance which is non-analytic in magnetic field (proportional to $|B|$) on the ordered side of the transition. Such behaviour has recently been observed in the small gap metal $Ca_3Ru_2O_7$ [7]. We show how magnetic breakdown and disorder will round the discontinuity.

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23a1

Strongly correlated electron phenomena in Pr-based filled skutterudite compounds

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The filled skutterudite compounds MT_4X_{12} (M = alkali metal, alkaline earth, lanthanide, actinide; T = Fe, Ru, Os; X = P, As, Sb) display a variety of strongly correlated electron phenomena including superconductivity, magnetic order, quadrupolar order, valence fluctuations, heavy fermion behavior, non-Fermi liquid behavior, and metal-insulator transitions. In this talk, we focus on the Pr-based filled skutterudites (i.e., M = Pr) and describe recent experiments on the systems $PrOs_4Sb_{12}$, $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ and $PrOs_4As_{12}$. Of particular interest is the heavy fermion compound $PrOs_4Sb_{12}$ which exhibits unconventional strong coupling superconductivity below a superconducting critical temperature T_c = 1.85 K. The unconventional superconducting state breaks time reversal symmetry and apparently consists of several distinct superconducting phases, some of which may have point nodes in the energy gap. Magnetic and quadrupolar excitations between the Pr^{3+} singlet ground state and a low-lying triplet first excited state split by $\sim$ 7 K as a result of the crystalline electric field may be responsible for the heavy fermion behavior and unconventional superconductivity in $PrOs_4Sb_{12}$. Various measurements have revealed the existence of a high field ordered phase in $PrOs_4Sb_{12}$ between 4.5 T and 16 T and below $\sim$ 1 K that has been identified with antiferroquadrupolar order. In contrast, the compound $PrRu_4Sb_{12}$, which has a $T_c \approx 1$ K, displays conventional isotropic BCS superconductivity. In the $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ system, increasing the Ru concentration x results in a monotonic increase in the splitting between the singlet ground state and triplet first excited state to $\sim$ 70 K at x = 1, a minimum in the T_c vs x curve at x $\approx$ 0.6, and an apparent change in the nature of the superconductivity from unconventional to conventional BCS at x $\approx$ 0.2. The compound $PrOs_4As_{12}$ undergoes transitions at 2.3 K and 2.2 K in zero-field into two ordered phases, one of which appears to be antiferromagnetic in nature. The two ordered phases in $PrOs_4As_{12}$ can be suppressed to 0 K with magnetic fields of 2 T and 3.2 T. The temperature and field dependence of the specific heat and electrical resistivity indicate that $PrOs_4As_{12}$ is a Kondo lattice system with a small Kondo temperature T_K of $\sim$ 1 K and an electronic specific heat coefficient of $\sim$ 200 mJ/mol K^2.

This research was supported by the US Department of Energy under Grant No. FG02-04ER46105 and the National Science Foundation under Grant No. DMR 0335173.

23a2

Novel Superconductivity in the Skutterudite $PrOs_4Sb_{12}$: Sb-NMR/NQR studies

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Since the discovery of the the Pr-based heavy fermion superconductivity in a filled skutterudite $PrOs_4Sb_{12}$ [1], extensive experimental studies have been carried out so far. The magnetic properties of this material have been well explained by a crystal electric field (CEF) model for single-ion Pr $4f^2$ states. Recent experiments have shown that the low-lying singlet-triplet scheme leads to a field induced antiferro-quadrupole ordered state at high fields after the superconductivity disappears [2]. Thus, much attention has been devoted to elcidate the most foundamental questions such as the properties of these two phases and their mutual relations in $PrOs_4Sb_{12}$.

In order to investigate the physical properties of $PrOs_4Sb_{12}$ from microscopic viewpoints, we have performed Sb-NMR/NQR measurements on single crystal $PrOs_4Sb_{12}$ with $T_c = 1.85$ K. From the field angle dependence of Sb-NMR measurements at $T = 5$ K, we identified the observed NMR lines corresponding to three different Sb sites with asymmetric EFG tensors [3]. We also found that NQR parameters (η and ν_Q) exhibit unusual T dependence, providing evidence for the multipole degree of freedom of Pr $4f^2$ states [4]. We also measured the T dependence of the Sb Knight shift below T_c. Sb Knight shift stays constant upon cooling through T_c. Considering all the NMR/NQR results together, present NMR/NQR results strongly suggest that an odd-parity spin-triplet sate is realized in $PrOs_4Sb_{12}$.

We are grateful to M. Yogi, Y. Kitaoka, G.-q. Zheng, H. Kotegawa and Y. Aoki for help with part of these experiments, and to H. Harima, R. Shiina, S. Takagi, and O. Sakai for theoretical help.

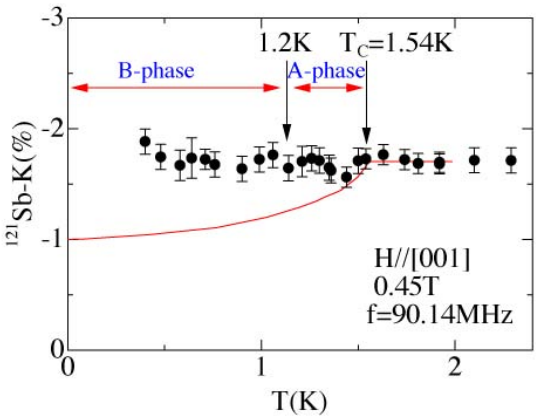

Figure 1: Temperature dependence of the ^{121}Sb-Knight shift below 2K.

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23a3

Muon spin rotation and unconventional superconductivity in $PrOs_4Sb_{12}$ and its alloys

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Muon spin relaxation (μSR) experiments have been carried out in the $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ and $Pr_{1-y}La_yOs_4Sb_{12}$ alloy systems, to investigate the magnetic field distribution in zero field and in the mixed state of these unconventional superconductors. Transverse-field muon spin relaxation rates in the mixed state yield the inhomogeneous distribution of the magnetic field in the vortex lattice [1]. The width of this distribution (or, equivalently, the superconducting penetration depth $\lambda(T)$ extracted from fits to the distribution function) shows little temperature dependence for temperatures below $0.5T_c$, suggesting that $\lambda(T)$ is temperature-independent at low temperatures [2]. In contrast, radiofrequency measurements of the surface magnetic field penetration in the Meissner state [3] yield a stronger (T^2) temperature dependence of $\lambda(T)$, indicative of point nodes in the gap. A similar discrepancy exists in superconducting Sr_2RuO_4 which, like $PrOs_4Sb_{12}$, breaks time-reversal symmetry (TRS) below T_c, but no discrepancy is found in a number of non-TRS-breaking superconductors. The origin of this disagreement is not known, but mechanisms other than diamagnetic screening have been proposed for magnetic field distributions in both the vortex state and in the Meissner-state surface penetration region.

The spontaneous local magnetic field H_{loc} found below T_c in earlier zero-field μSR studies of the end compound $PrOs_4Sb_{12}$ [4] is strong evidence for time-reversal symmetry breaking (TSRB) by the superconducting transition. With Ru doping we observe a rapid suppression of H_{loc} to $\sim$zero for $x = 0.1$, whereas with La doping H_{loc} remains finite up to at least $y = 0.4$ where it is suppressed to about half its value in $PrOs_4Sb_{12}$. No spontaneous field is observed in the end compounds $PrRu_4Sb_{12}$ and $LaOs_4Sb_{12}$, both of which appear to be conventional BCS superconductors. Thus Ru doping is considerably more effective than La doping in suppressing TSRB superconducting pairing in $PrOs_4Sb_{12}$. Band structure calculations [5] yield predominantly Sb- and Os-derived wave functions at the Fermi surface, and our results suggest the hybridized Os d-electron contribution to the band structure participates strongly in superconducting pairing in this compound. In particular, distortion of the Sb icosahedron by randomly-sited Ru ions may be a source of the strong effect of Ru doping.

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23a4

Superconductivity in $PrOs_4Sb_{12}$: on the double transition and multiband effects

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The skutterudite heavy-fermion compound $PrOs_4Sb_{12}$ has attracted much attention notably because it shows signs of unconventional behavior : possibly point nodes of the gap [1] and a double transition in the specific heat. We show results on newly grown samples which indicate that samples with high residual resistivity ratio (≈ 30) and very sharp transition width in the specific heat may show only one transition, at the lowest temperature ($T_c \approx 1.75K$).

All results show that when two transitions are present, the highest is always inhomogeneous even when the specific heat transition is sharp. This cast serious doubts on a possible intrinsic origin of the double transition. Thermal conductivity (κ) on the sample with just one transition confirms the previous measurements [2] on a rather inhomogeneous sample which showed that multiband effects dominate its low field-low temperature behavior. On the other hand, they do not detect an anomaly that could confirm the phase diagram obtained by magneto-thermal transport [1]. The low temperature behavior of the κ of the new sample shows a T^3 behavior, quite different from the T^2 behavior of the previous sample [2]. It attests also the high sample quality, as no residual term is detected (see figure 1).

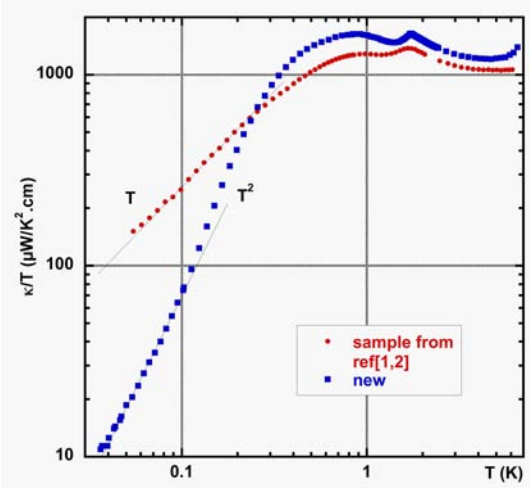

Figure 1: Comparison of κ of the sample from references [1] and [2] with the new sample showing just one transition in specific heat: it has no residual term, and a low temperature T^3 behavior. But this term is of the order expected for the phonon thermal conductivity, so conclusion on the gap nodes from $\kappa(T)$ is still not possible on this new sample.

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23a5

Evolution of superconducting and heavy fermion properties in $Pr_{1-x}La_xOs_4Sb_{12}$

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La doping provides a convenient means of studying the new unconventional heavy fermion superconductor $PrOs_4Sb_{12}$ [1] since it does not alter the lattice constant nor crystalline electric field spectrum. The specific heat discontinuity ($\Delta(C/T)$) at T_c of $Pr_{1-x}La_xOs_4Sb_{12}$ shows a dramatic concentration dependence and indicates that heavy fermion character is suppressed between $x = 0$ and 0.3.[2] On the other hand T_c changes almost linearly with x, indicating lack of a direct link between the enhancement of T_c and m^*. We have searched for an additional confirmation of this strong dependence of m^* on x by measuring the specific heat of $Pr_{1-x}La_xOs_4Sb_{12}$ in small magnetic fields. dH_{c2}/dT has a similar dependence on x as $\Delta(C/T)$ at T_c, with the same characteristic concentration of about 0.3. The positive curvature in dH_{c2}/dT, suggested to be due to two band superconductivity [3], is absent for $x \geq 0.2$. This positive curvature seems to be characteristic of concentrations exhibiting two superconducting transitions.

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23a6

Roles of Multipoles and Excitons in Superconductor $PrOs_4Sb_{12}$

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abstract

The variety of physics in the filled skutterudite compounds is realized by changing the combination of RT_4X_{12} (R is a rare-earth or U; T is one of transition metals: Fe, Ru or Os; X is a pnictogen: P, As or Sb). The rich physics is expected to be understandable by a simple model containing a few parameters such as crystal-field parameters for rare-earth ions and exchange couplings of the f-electron states with conduction electrons. Among them we focus on $PrOs_4Sb_{12}$ that is the first superconductor of Pr-based metallic compounds. In the present study, we discuss a possibility of exciton-mediated mechanism as an origin of this superconductivity [1].

In this compound the low-lying crystal-field states of Pr form a pseudo-quartet consisting of Γ_1 singlet ground and $\Gamma_4^{(2)}$ triplet excited states. The dispersive crystal-field excitations (excitons) have been detected experimentally. Considering both magnetic and nonmagnetic couplings of conduction electrons with the pseudo-quartet, we determine the effective interaction between conduction electrons and the pseudo-quartet states. The nature of exchange processes is related closely to a_u and t_u components of the conduction electrons that correspond to the molecular orbitals of an Sb_{12} cage surrounding a Pr ion. By the second-order perturbation in the exchange coupling, Cooper pairing interactions are derived both for singlet and triplet superconductivities.

We find that the T_h symmetry, which is a unique feature of the filled skutterudite compounds, plays an important role in realizing a triplet superconducting state. As a candidate for the superconductivity in $PrOs_4Sb_{12}$, we propose a nonunitary triplet state (e.g., $\Gamma_{4x} + i\Gamma_{4y}$) with twofold symmetry which agrees most naturally with the gap structure observed in the low field phase. We also discuss anisotropy of spin susceptibility reflecting the T_h symmetry of gap functions to give useful information to Knight-shift measurements (see Table 1).

Table 1: Possible types of gap functions under the T_h symmetry ($\omega = e^{\pm i2\pi/3}$).

pairing state	gap function	spin susceptibility
(a) Γ_1	T_h	$\chi_{xx} = \chi_{yy} = \chi_{zz}$
(b) $\Gamma_{23,\mathrm{I}},\ \Gamma_{23,\mathrm{II}}$	D_{2h}	$\chi_{xx} \neq \chi_{yy} \neq \chi_{zz}$
(c) $\Gamma_{23,\mathrm{I}} \pm i\Gamma_{23,\mathrm{II}}$	T_h	$\chi_{xx} = \chi_{yy} = \chi_{zz}$
(d) $\Gamma_{4x},\ \Gamma_{4y}\ , \Gamma_{4z}$	D_{2h}	$\chi_{xx} \neq \chi_{yy} \neq \chi_{zz}$
(e) $\Gamma_{4y} \pm i\Gamma_{4z},\ \Gamma_{4z} \pm i\Gamma_{4x},\ \Gamma_{4x} \pm i\Gamma_{4y}$	D_{2h}	$\chi_{xx} \neq \chi_{yy} \neq \chi_{zz}$
(f) $\Gamma_{4x} \pm \Gamma_{4y}\ \pm \Gamma_{4z}$ (fourfold degeneracy)	D_{3d}	$\chi_{xx} = \chi_{yy} = \chi_{zz}$
(g) $\Gamma_{4x} \pm \omega\Gamma_{4y}\ \pm \omega^2\Gamma_{4z}$ (eightfold degeneracy)	D_{3d}	$\chi_{xx} = \chi_{yy} = \chi_{zz}$

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23p1

Multipole order and $4f$-electron dynamics in Pr skutterudites

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Nature of multipole orders and $4f$-electron dynamics are discussed for Pr skutterudites from a theoretical point of view. The origin of rich ordering phenomena is ascribed to the narrow crystalline electric field (CEF) splitting which results from competition between the point-charge interaction and hybridization between $4f$ and conduction electrons [1]. In all cases of anomalous phenomena in $PrFe_4P_{12}$, $PrRu_4P_{12}$ and $PrOs_4Sb_{12}$, the relevant states consist of a singlet and a triplet which together form a pseudo-quartet ground state. The pseudo-quartet can lead to Kondo effect due to exchange interactions with conduction electrons provided the van-Vleck type coupling is strong enough between the singlet and the triplet. Different character of the triplets explains the presence of the Kondo effect in $PrFe_4P_{12}$, and its absence in $PrOs_4Sb_{12}$. We present exemplary theoretical results for dynamics which are relevant to neutron scattering, electrical resisitivity and NMR [2].

By taking the minimal model for $PrFe_4P_{12}$ with antiferro-quadrupole (AFQ) and ferro-type intersite interactions for dipoles and octupoles between nearest-neighbors, we have been able to reproduce the overall feature of the multiple ordered phases [3] in the mean-field theory [4]. The AFQ order with the Γ_3-type symmetry is found to be stable only as a mixture of O_2^0 and O_2^2 components. On this basis we shall discuss the lattice distortion [5], and the single-crystal NMR spectrum [6] which cannot be explained in terms of the dipole field due to induced antiferromagnetic moment at Pr sites. We shall interpret the unique metal-insulator transition which accompanies the drastic rearrangement of CEF levels as well as the lattice anomaly in $PrRu_4P_{12}$ [7] in terms of order parameter which transforms as a scalar in the point-group symmetry [8,9]. The scalar is a combination of hexadecapole and hexacontatetrapole (rank 6) multipoles.

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23p2

Magnetism and thermoelectric features of skutterudites $Pr(Fe, Ni, Co)_4Sb_{12}$

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Filled skutterudites have become well known for their elevated values of the Seebeck coefficient and their reduced thermal conductivity, placing this class of materials into the group of potential candidates for thermoelectric applications. Besides their promising thermoelectric performance, Pr-based skutterudites exhibit a particular rich variety of interesting physics. Ground state properties in these systems are governed by the $Pr-4f$ electrons, resulting in different types of magnetic order, heavy fermion behaviour and superconductivity.

In this paper we review magnetic properties of $Pr(Fe, Ni, Co)_4Sb_{12}$ as derived from specific heat, magnetisation, neutron diffraction and μSR studies and present the relevant transport quantities of this series. It is found that throughout the whole concentration range of $Pr(Fe, Ni, Co)_4Sb_{12}$ the Seebeck coefficient revealed values exceeding 60 μV/K at 300 K and reaching a maximum of more than 200 μV/K in $Pr_{0.21}Fe_{2.5}Ni_{1.5}Sb_{12}$. Measurements of temperature dependent electrical resistivity and thermal conductivity served to calculate the thermoelectric figure of merit.

In addition, our interest is directed to magnetic ordering, its development with the transition metal substitution within this series and crystal electric field effects dominating the physical properties.

Work supported by the Austrian FWF, P16370 and by COST P16 .

23p3

Anomalous Field-insensitive Heavy-fermion State in $SmOs_4Sb_{12}$

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Specific heat C and electrical resistivity ρ measurements have revealed an unconventional heavy-fermion (HF) state in $SmOs_4Sb_{12}$ single crystals [1,2]. The largely-enhanced electronic specific-heat-coefficient ($\gamma = 0.82$ J/K^{2}mol) and the T^2 coefficient of ρ (A) do not show any significant decrease in applied fields, in contrast with ordinary Ce-based HF compounds, suggesting an unconventional nonmagnetic origin of the heavy-quasiparticle formation. The T dependences of several transport properties suggest the characteristic temperature of $T^* \sim 20$ K, which is consistent with $T_1(T)$ in Sb-NQR results [3]. Quite large low-T Seebeck coefficient S and the γ value satisfy an empirical relation reported for a wide range of Fermi liquid compounds [4]. The negative sign of S suggests dominant virtual charge fluctuations of $4f^5$-$4f^6$, i.e., Sm^{3+}-Sm^{2+}, in consistency with recent XAS measurements [5]. Several remarkable features, i.e., the strongly-suppressed Kadowaki-Woods ratio $A\gamma^{-2}$ (indicative of multiply-degenerate quasiparticles [6]), weak magnetic anisotropy in the HF state, and an extremely weak ferromagnetic ordering appearing below 3 K probably originating in the itinerant quasiparticles, will be discussed.

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23p4

Realization of a magnetically robust heavy Fermion due to an off-center motion of ions: A model of $SmOs_4Sb_{12}$

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Among skutterudite compounds, $SmOs_4Sb_{12}$ is attracting much attention. The reasons why this material is so fascinating are that (1) the heavy Fermion behavior, the low temperature specific heat coefficient $\gamma = 820\mathrm{mJ}/(\mathrm{mol}\cdot\mathrm{K}^2)$, is robust against a magnetic field up to 8-14T [1][2], and (2) the frequency dependence of the ultrasonic velocity is observed at around 13K [3] which is also observed in a heavy Fermion superconductor $PrOs_4Sb_{12}$ [4][5]. By these experimental observations, it is expected that the rare Earth element, Sm or Pr ion, moves in a flat potential or possibly an off-center one in the Sb-cage and interacts with conduction electrons via its charge fluctuation, leading to a multilevel Kondo effect. From recent experimental results in various skutterudite compounds, it became to be realized that the so-called rattling motion does not occur in Ru compounds, the reason of which might be related to the deep 4d-orbital of Ru, i.e., the d-electron rarely appears on the Fermi surfaces and the Fermi surfaces are formed mainly by the pnictogen (Sb_{12}) molecular orbital with A_{1u} symmetry.

As a simple model of these off-center systems, we investigate an impurity four-level system in which an ion has four off-center positions around the origin and interacts with conduction electrons with the partial-wave components [6]. In this configuration, irreducible representations of the ion are Γ_1^+ (singlet), Γ_3^+ (singlet) and Γ_5^- (doublet). Those of bare energy levels are estimated as $E_{\Gamma_1^+} < E_{\Gamma_5^-} < E_{\Gamma_3^+}$ for the case of nearest neighbor hoppings. Using perturbative and numerical renormalization group methods, we obtain the effective Hamiltonian of the orbital pseudospin-1 Kondo system in the case of spinless conduction electrons. The pseudospin 1 is constructed as $S_z = \pm 1 : \Gamma_{5\pm}^-$ and $S_z = 0 : \Gamma_1^+$. The corresponding pseudospins of the conduction electron are $p_\pm$-wave and s-wave. As a result, we obtain an enhanced γ without any sensitivity to a magnetic field. We think the heavy effective mass observed in $SmOs_4Sb_{12}$ is related to such kinds of orbital Kondo effect. This orbital scenario gives a good explanation also for the reason why no rattling motion is observed in Ru compounds. This is because it is difficult for the conduction electrons to interact with the ion except a simple potential scattering in Ru compounds, in which there is (approximately) only A_{1u} molecular orbital as the conduction electrons forming the Fermi surface. Then, the dissipation might not occur in Ru compounds, which means no frequency dependence occurs in the ultrasonic velocity.

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24a1

Probing the Gap Topology of Anisotropic Superconductors by means of Field-Angle Dependent Specific Heat Measurements

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Determination of the angular position of nodes in the superconducting gap structure is of importance in identifying the pairing symmetry of anisotropic superconductors (SCs). We have been performing measurements of the field-angle dependence of the specific heat $C(H, \phi)$ of various anisotropic SCs. By this method, which takes advantage of that quasiparticles under a certain field orientation become Doppler-shifted, direct information about the SC gap is obtained. Dips in $C(H, \phi)$ show the position of gap minima or nodes. In this talk, the results for $CeCoIn_5$, $CeRu_2$ and $PrOs_4Sb_{12}$ will be presented. $CeCoIn_5$ is a d-wave SC and $CeRu_2$ is considered to be an anisotropic s-wave system, whereas the pairing symmetry of $PrOs_4Sb_{12}$ is still in question. In all cases, clear fourfold angular oscillations are observed in $C(H, \phi)$ when the magnetic field is rotated in the (001) plane. Figure 1 shows an example of the data for $PrOs_4Sb_{12}$ obtained at $H = 0.6$ T and $T = 0.3$ K. The fourfold oscillation with minima along the [100] directions was observed in the whole field range below H_{c2} of ∼2.3 T. Difference in the field dependence of the oscillation amplitude among the three systems will be discussed.

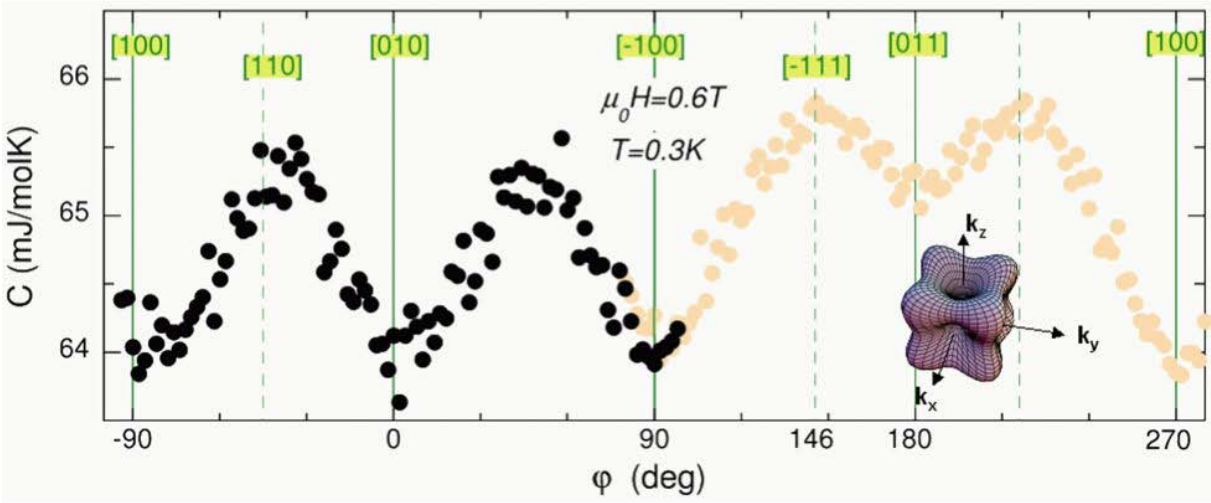

Figure 1: Field-angle dependent measurement on $PrOs_4Sb_{12}$ at 0.6 T. Exemplary, the results in the [100]-[010] plane and [-100]-[011] plane are shown. The inset indicates how the SC gap structure looks like in agreement with our results.

24a2

Anomalous quasiparticle transport and superclean superconducting state of $CeCoIn_5$

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We report on a study of thermal Hall conductivity κ_{xy} in the superconducting state of $CeCoIn_5$. The scaling relation and the density of states of the delocalized quasiparticles, both obtained from κ_{xy}, are consistent with d-wave superconducting symmetry. The onset of superconductivity is accompanied by a steep increase in the thermal Hall angle, pointing to a striking enhancement in the quasiparticle mean free path. This enhancement is drastically suppressed in a very weak magnetic field. These results highlight that $CeCoIn_5$ is unique among superconductors. A small Fermi energy, a large superconducting gap, a short coherence length, and a long mean free path all indicate that $CeCoIn_5$ is clearly in the superclean regime ($\varepsilon_F/\Delta \ll \ell/\xi$), in which peculiar vortex state is expected.

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24a3

Microscopic studies of electronic structure in mixed state in exotic superconductors —-how to identify gap symmetry—-

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There have been known several unconventional superconductors, such as heavy Fermion materials, high temperature cuprates or skutterudites. Yet there are only a few systems in which the pairing symmetry is firmly identified. A difficulty to determine it lies in the fact that decisive experimental methods for its identification are still lacking. We need more spectroscopic tools to analyze the Cooper pair symmetry, which is characterized by the gap structure and the order parameter parity.

For this couple of years we have been working for remedying this situation by considering the electronic structure around a vortex core in the mixed state of these type II superconductors based on microscopic theory [1,2,3,4,5]. It turns out that this study is important because the electronic structure with low lying energies, such as the local density of states, or magnetic field distribution, etc sensitively reflects the underlying pairing symmetry.

In this talk we will cover some of these studies together with topics related to those, which are now under progress.

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24a4

Anisotropic properties of nodal superconductors in the vortex state revisited

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Specific heat and thermal conductivity of nodal superconductors are anisotropic under an applied magnetic field. This directional dependence is rapidly becoming the experimental tool of choice in determining the position of the nodes in the gap. Theoretical understanding of the anisotropy is, however, still incomplete, which hinders developing an unequivocal interpretation of the existing results, and prevents the method from reaching its full potential.

In this talk I will address this problem from two complementary viewpoints. First I will discuss the semiclassical ("Doppler shift", or Volovik) approach, commonly used at low magnetic fields. Two issues under consideration will be the consequences of the spatial inhomogeneities in the thermal conductivity and the implications of the commonly used nodal approximation. I will compare the semiclassical results with those obtained using the Brandt-Pesch-Tewordt approximation, valid at moderate to high fields. I will particularly focus on connecting the experimentally observed minima and maxima with the positions of the nodes, and consider the switching between the two in the H-T phase diagram of model superconductors.

24a5

Heavy-fermion superconductors without inversion symmetry

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A theoretical review on novel phenomena in superconductors without inversion symmetry is presented with particular emphasis on the role of strong electron correlation and the application to the recently discovered heavy-fermion superconductor $CePt_3Si$ [1]. It was discussed by Edelstein and Yip several years ago [2] that noncentrosymmetric superconductors may exhibit nontrivial magnetoelectric effects; i.e. the existence of supercurrent flows induced by an applied magnetic Zeeman field, and supercurrent-flow-driven magnetization. On the basis of the formally exact Fermi liquid theory, I show that the Zeeman-energy-induced paramagnetic supercurrent is not at all affected by electron correlation effects provided that ferromagnetic spin fluctuation is not developed, in contrast with the diamagnetic Meissner current of which the magnitude is much reduced by the mass renormalization effect, and that the existence of strong electron correlation inherent in heavy-fermion supercoductors is crucial for the experimental detection of the magnetoelectric effect [3].

Also, I will make a comment on a possible pairing state realized in $CePt_3Si$, paying special attention to an unusual coherence effect in noncentrosymmetric superconductors which can be observed as the existence of a coherence peak of the nuclear relaxation rate $1/T_1$ even in the case that the superconducting state is dominated by the p-wave pairing [3]. The implication for the recent NMR measurement done by Yogi et al. [4] will be given.

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24p1

Pressure–induced metal–insulator transition in $PrFe_4P_{12}$

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The filled skutterudite $PrFe_4P_{12}$ shows an antiferroquadrupolar (AFQ) ordering at 6.5 K at ambient pressure. We have carried out an electrical resistivity [1] and Hall effect measurements under high pressure and found a band–insulating phase at low temperature above 2.4 GPa as shown in Fig. 1(a). Since $PrFe_4P_{12}$ with Pr^{3+} is an uncompensated metal, it requires a phase transition which doubles the unit cell to be the band insulator. We carried out P-NMR measurement to investigate the insulating state.

Figure 1(b) shows NMR spectra at 3.5 GPa using the powdered single crystalline sample. In the metallic region of 20 K, the spectrum shows a sharp peak, which is similar to ambient pressure. In contrast, two broad peaks appear in the insulating phase at 1.5 K. At 7 K, these two kinds of signals are observed, indicative of the first–order transition accompnying with the phase separation. The splitting width between two peaks in the insulating phase is estimated to be about 2 kOe, which is about 20 times larger than that of AFQ state at ambient pressure. [2] Such large splitting suggests that the internal field exists in the insulating phase. Taking a magnetization in the insulating state into account, an antiferromagnetic ordering might occur in the insulating phase.

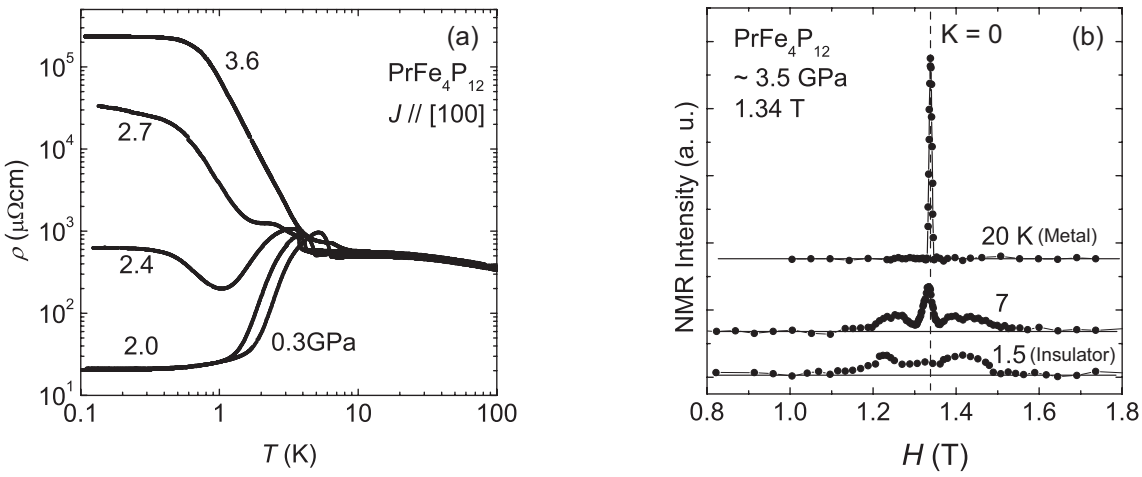

Figure 1: (a) Temperature dependence of resistivity for $PrFe_4P_{12}$ at several pressures. (b) P–NMR spectra at $\sim$ 3.5 GPa using the powdered sample.

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[2] K. Ishida et al., Phys. Rev. B **71**, (2005) 024424.

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Role of p-f Hybridization in the Metal-Nonmetal Transition of $PrRu_4P_{12}$

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$PrRu_4P_{12}$ undergoes a metal-nonmetal transition at $T_{M-I} = 63$ K [1]. It is accompanied with the structural change from $Im\bar{3}$ to $Pm\bar{3}$ due to Ru and P displacements [2,3]. Because the band calculation revealed three dimensional Fermi surface nesting condition with the wave vector $2\mathbf{k}_F \sim \{100\}$ [4], this transition has been suggested to be the charge density wave formation. On the other hand, $LaRu_4P_{12}$ does not show such a metal-nonmetal transition, in spite of the similar Fermi surface structure as in $PrRu_4P_{12}$ [5]. Therefore, $4f$ electrons of Pr ions are naturally expected to play a key role in the transtion.

Our inelastic neutron scattering experiment revealed that the magnetic spectrum at temperatures much lower than T_{M-I} is described as well-defined crystal-field (CF) excitations by the two inequivalent schemes of Pr^{3+} $4f^2$ electrons [6]. With approaching T_{M-I}, the excitation peaks broaden and shift considerably. We also performed polarized neutron diffraction experiments [7]. At the lowest temperature, the two inequivalent CF schemes with Γ_1 and $\Gamma_4^{(2)}$ ground states are located at Pr1 and Pr2 sites surrounded by the smaller and larger cubic Ru-ion sublattices, respectively.

The evolution of CF state can be explained by the p-f hybridization due to the intermediate states of $4f^1$ and $4f^3$ [8]. The density of state at the Fermi level enhanced by the hybridization gives rise to the energy gain by the gap formation under the Fermi surface nesting condition combined with the CF scheme superlattice. $PrRu_4P_{12}$ exhibits a new type of metal-nonmental transition in which the $4f$ electrons play an essential role.

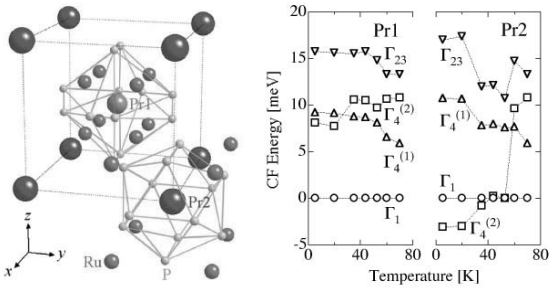

Figure 1: The lefthand figure shows the crystal structure with the location of Pr1 and Pr2 whose CF schemes are shown in the righthand side.

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24p3

Physical properties of $NdOs_4Sb_{12}$ and the effects of Nd substitution on the superconductivity of $PrOs_4Sb_{12}$

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We have investigated single crystals of the filled skutterudite compound $NdOs_4Sb_{12}$ by means of electrical resistivity, magnetization, and specific heat[1]. The experimental results show that $NdOs_4Sb_{12}$ undergoes a ferromagnetic transition at T_{Curie} 1 K. Heavy fermion behavior is inferred from specific heat measurements with $\gamma \sim 520$ mJ/mol-K2, while spin wave excitations are inferred from low temperature resistivity data. Conventional Arrott plot analysis indicates $NdOs_4Sb_{12}$ conforms to mean-field ferromagnetism. Previous studies on $PrOs_4Sb_{12}$ showed that this compound is an unconventional heavy fermion superconductor with $T_c = 1.85$ K. Experimental evidence from zero-field muon spin relaxation and the penetration depth measurements[2,3] suggest that the superconducting pairing in $PrOs_4Sb_{12}$ is spin-triplet (odd parity), which, when considered along with the low T_{Curie} of $NdOs_4Sb_{12}$, implies that $PrOs_4Sb_{12}$ may be near a ferromagnetic quantum critical point. We have performed measurements of zero-field ac magnetic susceptibility and electrical resistivity between 0 T and 8 T for several concentrations in the $(Pr_{1-x}Nd_x)Os_4Sb_{12}$ system. Superconductivity persists up to $x = 0.5$ and the ferromagnetism appears above $x = 0.55$. In the normal state the features related to the antiferroquadrupolar phase are clearly observed up to $x = 0.4$, in contrast to the quick disappearance of the features above $x = 0.05$ in the $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ system.

The superconducting and ferromagnetic phase diagrams in x, T and H are presented.
This research was supported by the U.S. DOE (DE-FG02-04ER46105 and DE-FG52-03NA00068) and the NSF (DMR-0335173). NHMFL is supported by the NSF, the State of FL and the US DOE.

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24p4

Ultrasonic investigation of multipole ordering in $SmRu_4P_{12}$

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Filled skutterudite compound $SmRu_4P_{12}$ has attracted much attention due to its interesting properties. Magnetic susceptibility, specific heat measurements and the series of the lattice parameter for $R Ru_4P_{12}$ (R: rare earth) show that the Sm ion in $SmRu_4P_{12}$ is trivalent with $J = 5/2$ [1]. The multiplet is spilt into quartet Γ_{67} ground state and Γ_5 excited state with the separation of 60 K by the cubic crystalline electric field (CEF) [2].

$SmRu_4P_{12}$ undegoes a Metal-Insulator (M-I) transition at $T_{MI} = 16$ K and a successive phase transition at T_N =14 K [1,2]. We have investigated the elastic properties of $SmRu_4P_{12}$ for both single crystal and polycrystalline samples and reported their strange behavior, so far [3,4]. The temperature dependence of the elastic constants C_{44} and $\frac{1}{2}(C_{11} - C_{12})$ shows a sharp drop at T_{MI} in a zero field. The successive transition at T_N is indistinct in a low field. The anomaly at T_{MI} disappears with the increase of field. A clear softening toward T_N appears in the elastic constants in a high magnetic field. These curious elastic behavior has been well explained by assuming the breakdown of time reversal symmetry (*TRS*) below T_{MI} [5] This is caused by a particular coupling among elastic strains, dipole momenst and octupole moments. The breakdown of *TRS* below T_{MI} was successfully detected by μSR [6]. Recent theory predicts that Sm compound in BCC structure having a suitable CEF energy separation is expected to enhance octupole fluctuations, which lead to an octupolar ordering [7].

We are now examining the octupolar ordering scenario by further ultrasonic measurements. $SmRu_4P_{12}$ resembles systems of antiferro-quadrupolar ordering in the magnetic phase diagram, where the transition temperature increases with field. According to the molecular field theory based on the realistic CEF scheme, such phase diagram is produced by an existence of antiferro-quadrupole interaction in the case of the octupole phase transition. In other word, a hidden antiferro-quadrupole phase should be there nearby. Very recently, we have found an elastic softening above T_{MI} in its temperature dependence under hydrostatic pressure [8]. Such a sign of the subsidiary quadrupole ordering would be a key to detect and investigate invisible octupole ordering.

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24p5

Effect of dynamical Jahn-Teller phonons on multipole properties of filled skutterudites

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In order to clarify exotic multipole properties of filled skutterudites, we evaluate multipole susceptibility for n=1$\sim$5 [1], where n is the local f-electron number, on the basis of a multiorbital Anderson model constructed using the j-j coupling scheme [2,3]. For n=1, magnetic fluctuations dominate over low-temperature electronic properties, while for n=2 and 4, electronic states are dominated by both magnetic and quadrupole fluctuations. For n=3 and 5, octupole fluctuations are found to be significant, depending on the crystalline electric field potential.

By further analyzing the multiorbital multiorbital Anderson model coupled with dynamical Jahn-Teller phonons, we propose a mechanism of non-magnetic Kondo effect [4]. An electron system coupled dynamically with JT phonons has a vibronic ground state with double degeneracy due to clockwise and anti-clockwise rotational modes with entropy of $\log 2$. When a temperature is lower than a characteristic energy to turn the rotational direction, the rotational degree of freedom is eventually suppressed and the corresponding entropy $\log 2$ is released, leading to quasi-Kondo behavior. We discuss possible relevance of the numerical results to electronic properties of filled skutterudites.

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