論文内容の要旨

論文題目　New Transition Metal Pnictide Superconductors

（新規遷移金属ニクタイド超伝導体）

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1. Introduction The discovery of the iron pnictide superconductor in 2008[1] has opened a new route to high transition temperature (T_c) superconductivity. Comparing iron pnictides with high-T_c cuprates, we notice that they share common characteristics in terms of their "crystal structures" and "electronic phase diagrams". Iron pnictide superconductors include two-dimensional (2D) FePn (Pn: pnictogen atom) layers separated by ionic layers as illustrated in the inset of Fig. 1. Their physical properties are thus highly two-dimensional, as in cuprate superconductors containing 2D-CuO_2 planes. Concerning the latter, superconductivity in both systems emerges by suppressing magnetic orderings of the parent compounds. The electronic phase diagram of iron pnictide superconductors remarkably resembles those of cuprates as depicted in Fig. 1. The correlated metallic state neighboring a competing electronic ordering is believed to be a promising playground for unconventional superconductivity. The search for such superconductivity has been limited mostly within TM oxides or heavy fermion systems. The discovery of high-T_c superconductivity in

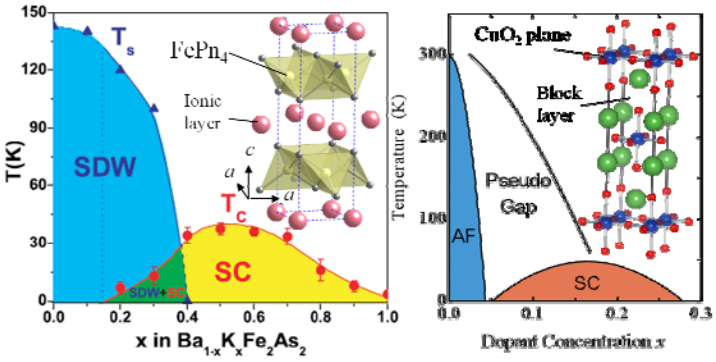

Figure 1 Electronic phase diagrams of iron pnictide superconductor[2] and high-Tc cuprate. The insets show crystal structures of representative superconductors such as $BaFe_2As_2$ and $(La, Sr)_2CuO_4$.

iron pnictides might enlighten that transition-metal (TM) pnictides can be a new research field for the purpose. However, the exploration of new superconductors, triggered by the discovery of LaFeAs(O,F), has so far concentrated mostly on compounds including iron. We have therefore explored new superconductors in TM pnictides without iron.

2. Objective This study aims at exploring new unconventional superconductors in TM pnictides, from the viewpoints of "2D crystal structure" and "superconductivity in the vicinity of a competing phase". First, we have focused on TM pnictides with a $ThCr_2Si_2$-type structure (dubbed as 122 structure), which is isostructural to iron-based superconductor (Ba, K)Fe_2As_2[3]. This structure is quite flexible, and a variety of TM pnictides have been reported to crystallize in this structure. We can investigate a systematic evolution of physical properties by changing TM elements within the same 122 pnictides. Next, we have searched for superconductivity in the vicinity of a competing ordered state. As a candidate for this purpose, we employed RuPn where a novel metal-insulator transition (MIT) was discovered. We aim at realizing unconventional superconductivity in RuPn by suppressing the electronic ordered state.

3. Superconductivity in Transition-Metal Pnictides with a $ThCr_2Si_2$-type crystal structure $BaRh_2P_2$, $BaIr_2P_2$ and $SrIr_2As_2$ We discovered three new superconductors with a 122 structure, $BaRh_2P_2$, $BaIr_2P_2$ and $SrIr_2As_2$. The evidence for superconductivity can be found in the magnetizations and the resistivities at low temperatures, shown in Fig. 2(a), (b). Clear resistance drops to zero were observed, accompanied by a large diamagnetic signal indicative of superconductivity around 1.0 K, 2.1 K and 2.9 K for $BaRh_2P_2$, $BaIr_2P_2$ and $SrIr_2As_2$, respectively. In the electronic specific heat data shown in Fig. 2(c), clear jumps were seen at T_c, hallmarking the bulk superconductivity. This discovery demonstrates the presence of superconductivity over a broad range of transition metal pnictides with a 122 structure from Fe to Ir, enabling a systematic investigation of the superconducting properties by tuning the electronic structures.

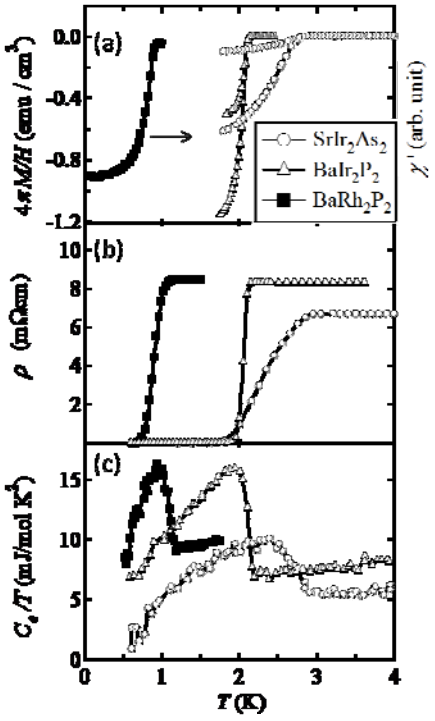

Figure 2 Superconducting transitions of $BaRh_2P_2$, $BaIr_2P_2$ and $SrIr_2As_2$, displaying (a)Meissner signals, (b)zero resistivities, and (c)electronic heat capacities.

From the electronic specific heat coefficients and Pauli paramagnetic susceptibilities, the Wilson ratio R_W were estimated to be 0.98, 1.29 and 0.54 for $BaRh_2P_2$, $BaIr_2P_2$ and $SrIr_2As_2$, respectively. These values are close to or less than 1 expected for free electrons. This sharply contrasts with iron pnictide superconductors where an enhanced Wilson ratio of 11 for LaFeAsO was reported [4], possibly associated with the magnetic instability. The new 122 superconductors thus have totally different superconducting and also normal state properties from those of iron-based ones.

4. Superconductivity in the vicinity of competing ordered state in RuPn TM pnictides were found to be a rich reservoir for superconductivity as evidenced in the 122 compounds. The normal metallic

states away from magnetic or other instabilities give rise to conventional superconductivity unlike iron pnictides. In order to realize exotic and also even higher-T_c superconductivity, we have searched for superconductivity which manifests itself at the critical vicinity to a competing electronic ordering. We discovered a novel MIT in binary pnictides RuPn(Pn = P, As, Sb), and realized superconductivity by suppressing the ordering.

4-1. Metal-Insulator Transition in RuPn RuPn are known to crystallize in a MnP-type orthorhombic (*Pnma*) structure [5, 6], but no physical properties have been reported so far. The Ru atoms are octahedrally coordinated by pnictgen atom. $RuPn_6$ octahedra are connected with sharing edges within *bc*-plane, wheres they have a face sharing network along *a*-axis. As a whole, this structure has a three-dimensional framework.

We discovered a MIT in RuP at 265 K, as shown in Fig.3(a). RuP displays a metallic behavior at high temperatures, while the resistivity markedly increases below the MIT temperature. Simultaneously, the magnetization shows a precipitous drop at the MIT temperature (Fig. 3(b)). The fact that the magnetization drops drastically down to negative values might suggest that paramagnetic moments are quenched into a spin-singlet insulator state. The spin-singlet formations can be found in three-dimensional system such as $Tl_2Ru_2O_7$ [7]. Their spin singlet formations are attributed to the particular orbital orderings which give rise to anisotropic magnetic interactions. The orbital ordering of Ru 4*d* electrons might be also involved in RuP.

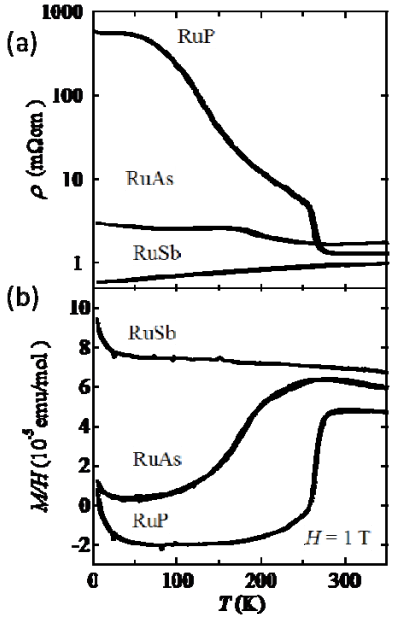

Figure 3 (a), (b) Temperature dependences of resistivity and magnetic susceptibility for RuPn.

RuPn shows a systematic evolution in physical properties by changing Pn atoms. RuP exhibits the sharpest transition, whereas the transition become broader in RuAs and eventually disappears in RuSb. As and Sb have more widely spreading *p* orbitals than P, leading to the enhanced hybridizations between Ru 4*d* and *p* orbitals of pnictogen atoms.

4-2. Superconductivity in Rh doped RuAs We attempted to achieve superconductivity by suppressing the novel ordering found in RuPn with carrier doping. In order to introduce electron carriers, we substituted Ru site with Rh. The Rh doping substantially affected the transition of RuAs. The transition temperatures determined by the local minimum of resistivities decreases systematically with increasing the Rh content as shown in Fig. 4(a). Beyond Rh content of 25 %, the resistivity shows metallic temperature dependence without any upturns. As the low temperature ordering is removed by Rh doping, superconductivity emerges at low temperatures. The superconducting transition is clearly observed for $x = 0.25$ in the resistivity and heat capacity measurements (Fig. 4(b)). The superconductivity was also found in other doping contents. The overall behavior of Rh doped RuAs is summarized in the electronic phase diagram shown in Fig. 4(c). The dome-like superconducting region in the phase diagram looks similar to those in unconventional superconductors such as cuprates and iron pnictides. The superconductivity in $Ru_{1-x}Rh_xAs$, neighboring the spin-singlet ground state might represent unique properties.

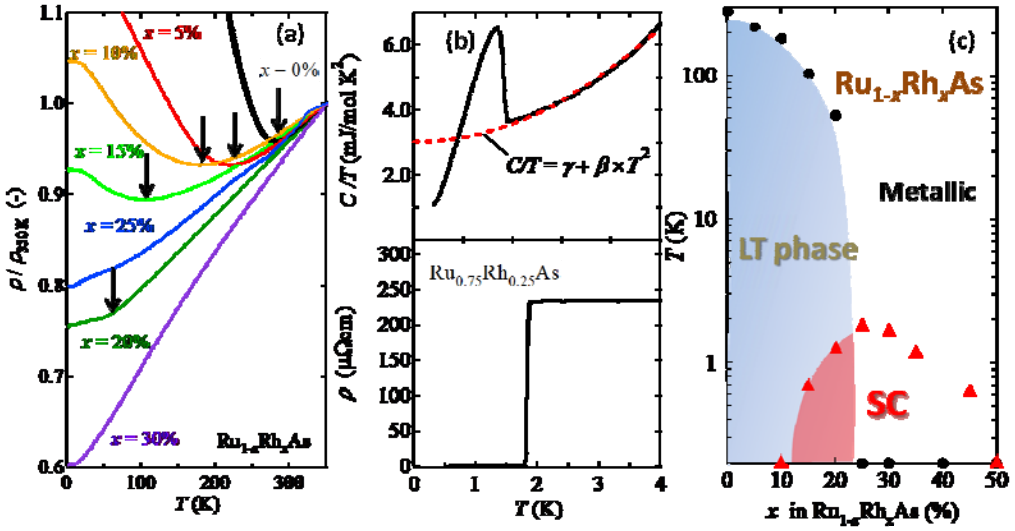

Figure 4 (a)Temperature dependences of resistivity normalized by the value at 350 K for $Ru_{1-x}Rh_xAs$. (b)Superconducting transition of $Ru_{0.75}Rh_{0.25}As$, displaying a heat capacity jump and zero resistivity. (c)Electronic phase diagram as a function of Rh content x in $Ru_{1-x}Rh_xAs$. .

5. Summary and Perspective TM pnictides are newly developing research field for superconductivity triggered by the discovery of iron pnictide superconductors. In this study, we discovered new superconductors focusing on the "2D crystal structures" and "superconductivity in the vicinity of a competing order".

First, the three new superconductors, $BaRh_2P_2$, $BaIr_2P_2$ and $SrIr_2As_2$ were discovered in the 122 structure. This discovery demonstrates the superconductivity prevails in the 122 pnictides. The difference of superconducting properties between non-Fe and iron pnictide superconductors may imply the importance of a competing magnetism to achieve high-T_c. Second, we discovered a MIT in RuPn, likely associated with the spin-singlet formation. The ordered state in RuAs can be easily suppressed by Rh doping, and superconductivity emerges. The electronic phase diagram is fairly similar to that of high-T_c superconductors, which might indicate the unconventional nature of the superconductivity. This study demonstrates that TM pnictides are a fertile playground for searching for new superconductors. The TM pnictides are not only an untouched area, but posse unique properties distinct from oxides or alloys. The study in 122 pnictides shows that TM pnictides can form the same crystal structure in the wide range of TM elements. This enables a systematic evolution of physical properties by tuning electronic configurations. Furthermore, the study in RuPn indicates that the charge, spin and orbital characters of TM metals manifest themselves even in pnictides, as in the prominent TM oxides. The advantage in TM pnictides would be found in the fact that such collective ordered state can be easily suppressed and evolve into a metallic or even superconducting state by simple chemical substitutions. We believe that these characteristic features of TM pnictides provide us with a unique opportunity to explore further new and unconventional superconductors.

[Reference] **[1]** Y. Kamihara *et al.*, J. Am. Chem. Soc. 130 (2008) 3296. **[2]** H. Chen *et al.*, Europhys. Lett. 85 (2009) 17006. **[3]** M. Rotter *et al.*, Phys. Rev. Lett. 101, 1076006 (2008). **[4]** Y. Kohama *et al.*, Phys. Rev. B 78 (2008) 020512. **[5]** S. Rundqvist. Acta Chem. Scandinavica 16 (1962) 287. **[6]** R. D. Heyding et al., Canadian J. of Chem. 39 (1961) 955. **[7]** M. Schmidt et al., Phys. Rev. Lett. 92 (2004) 056402.