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Present condition of preparation of doped Pr skutterudites

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Replacing T - or X -element by another T - or X -element, Pr skutterudites $\text{Pr}T_4X_{12}$ ($T=\text{Fe}$, Ru , Os and $X=\text{P}$, As , Sb , Bi) drastically change their characteristic physical properties. However, the partial substitution is very difficult especially that of pnictogen atom. In this workshop, we report our trial to prepare partially substituted Pr skutterudites and several topics of them.

1. $\text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_4\text{P}_{12}$

We tried to prepare $\text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_4\text{P}_{12}$ using Sn flux method. In case of $x=1$, single crystals with a size of about 2 mm were obtained, however, in case of $x=2/3$, the crystal size suddenly becomes small, about 0.1 mm. Furthermore, in case of $x=0$, any trace of Pr skutterudite is not obtained. Instead of it, another phase such as PrOs_2 appears. This result may indicate that the decomposition temperature of $\text{PrOs}_4\text{P}_{12}$ is much lower than that of $\text{PrRu}_4\text{P}_{12}$. Furthermore, low solubility of Os in liquid Sn may disturb the growth process of a single crystal.

2. $\text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_4\text{Sb}_{12}$

$\text{PrRu}_4\text{Sb}_{12}$ is thought to be a conventional superconductor, while $\text{PrOs}_4\text{Sb}_{12}$ is a heavy fermion superconductor. Recently, N. A. Frederick *et.al.* succeeded to grow single crystals of $\text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_4\text{Sb}_{12}$. [1] We also succeeded to grow single crystals of $\text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_4\text{Sb}_{12}$ and measured their magnetic susceptibilities which are shown in Fig. 1. Systematic change of the magnetic susceptibilities indicates that the crystal field splitting systematically change from $\text{PrOs}_4\text{Sb}_{12}$ to $\text{PrRu}_4\text{Sb}_{12}$ as suggested in ref.1.

3. $\text{Pr}(\text{Os}_{1-x}\text{Rh}_x)_4\text{Sb}_{12}$

When Os is partially replaced by Rh, the physical properties of $\text{PrOs}_4\text{Sb}_{12}$ is predicted to change. We tried to prepare $\text{Pr}(\text{Os}_{1-x}\text{Rh}_x)_4\text{Sb}_{12}$ with $x=0.1$ and succeeded to grow its single crystals. Judging from the slope of the inverse magnetic susceptibility above 100K, 10% doping of Rh causes to create 10% vacant Pr sites. On the other hand, its magnetic susceptibility at low temperature is rather different from that of non-doped $\text{PrOs}_4\text{Sb}_{12}$ suggesting different crystal field splitting. Nevertheless, Rh-doped $\text{PrOs}_4\text{Sb}_{12}$ shows superconducting transition at the same temperature as that of the non-doped system.

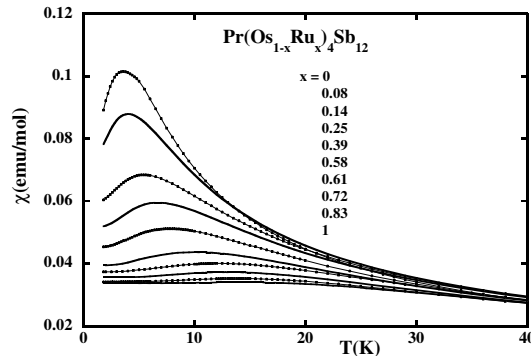


Figure 1: Magnetic susceptibilities of $\text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_4\text{Sb}_{12}$.

[1] N. A. Frederick, T. D. Do, P. -C. Ho, N. P. Buch, V. S. Zapf and M. B. Maple, Phys. Rev. B **69**, 024523 (2004).