Rh-substitution effect on 4f-electron states in multipole ordered phase of PrRu$_4$P$_{12}$

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Abstract. We have performed inelastic neutron scattering and magnetic susceptibility measurements on Pr(Ru$_{1-x}$Rh$_x$)$_4$P$_{12}$ (0 ≤ $x$ ≤ 0.15), in which the antiferro-multipole ordering of PrRu$_4$P$_{12}$ is gradually suppressed with increasing $x$. The saturation of magnetic susceptibility at low temperature suggests that all the 4f-electron ground states are singlet for $x$ ≥ 0.03, in contrast to the triplet and singlet ground states in the ordered phase of PrRu$_4$P$_{12}$. Neutron experiments show the presence of two types of crystal field (CF) level schemes: a temperature-dependent one similar to one of those observed in PrRu$_4$P$_{12}$ as signatures of the ordering, and an additional temperature-independent one indicating the existence of Pr ions which do not contribute to the ordering. Rh-substitution seems to have two effects: a local effect causing temperature-independent CF levels of Pr ions, and a wide-range effect causing switch of ground state. The ordering in low Rh-content compounds arises from the inequivalent CF level schemes that allow conserving the antiferro-type ordering pattern of multipoles through thermal excitation, despite the common ground state in compounds with $x$ ≥ 0.03.

1. Introduction
Phase transitions by ordering the charge and magnetic moment have been studied in various materials over a long period of time. These two degrees of freedom of electrons are described as monopoles and dipoles. Recently, higher-rank multipole ordering in some rare earth compounds has been the focus of a great number of investigations. The quadrupole ordering in CeB$_6$ [1] is a typical example, and Ce$_{0.7}$La$_{0.3}$B$_6$ was found to exhibit octupole ordering [2]. Orbital orderings in some transition metal oxide compounds also have been studied extensively, relative to the multipole ordering. The properties of higher-rank multipoles have recently been investigated in rare earth filled skutterudites with body-centered cubic structure.

Among them, PrRu$_4$P$_{12}$ shows a metal-nonmetal transition at $T_{MI}$=63 K without any distinct anomaly in magnetic susceptibility [3]. This transition is accompanied by a structural modulation, characterized by the wave vector $q_0$=(1 0 0) [4] close to the nesting vector of its Fermi surface [5]. Thus, Peierls type mechanism was proposed to explain the transition at first. However, the isostructural system LaRu$_4$P$_{12}$, which has the same nesting property, does not exhibit metal-nonmetal transition [6,7]. Moreover, the role of hybridization between f electrons of Pr and p electrons of P ($p$-f hybridization) has been pointed out from a structural point of view as Pr ions lie in P$_{12}$ atomic cages. Recently, neutron scattering experiments have revealed an

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arrangement of two inequivalent, temperature-dependent, crystal field (CF) level schemes with modulation vector $q_0$, without loss of the local cubic point group symmetry at Pr-sites \[8, 9\]. These phenomena can be explained by the antiferro-hexadecapole ordering of 4$f$ electrons based on strong $p$-$f$ hybridization \[10\]. Due to the Fermi surface nesting property at $q_0$, the staggered ordering of hexadecapole is thought to open the insulating gap.

In Rh-doped compounds Pr$(Ru_{1-x}Rh_x)_4P_{12}$, the phase transition was shown to be gradually suppressed as Rh content increases \[11\]. To investigate the Rh-substitution effect on the ordering, especially on the 4$f$-electron states, we have carried out inelastic neutron scattering and magnetic susceptibility measurements of Pr$(Ru_{1-x}Rh_x)_4P_{12}$ with $x=0$ to 0.15.

2. Experiments

Magnetic susceptibility measurements were carried out using MPMS by Quantum Design. Inelastic neutron scattering experiments were performed at the triple axis spectrometers TOPAN (final neutron energy fixed at $E_f=13.5$ meV) and HER ($E_f=4.98$ meV) installed at the JRR-3 reactor of JAEA in Tokai, Japan. Rh-substituted samples Pr$(Ru_{1-x}Rh_x)_4P_{12}$ for $x=0, 0.01, 0.03, 0.05$ and 0.15 were synthesized using the Sn-flux method \[12\]. $x$ represents the stoichiometric ratio of Rh to Ru in starting materials. The skutterudite structure was confirmed for all the samples using x-ray powder diffraction. Polycrystalline samples were used for all experiments.

3. Results

3.1. Magnetic susceptibility

Figure 1 shows the temperature dependence of magnetic susceptibility for Pr$(Ru_{1-x}Rh_x)_4P_{12}$. In PrRu$_4$P$_{12}$, quoted from a published article \[8\], it diverges at 0 K which is explained by the magnetic $\Gamma_{1}(2)$ triplet ground state at one of the two Pr-sites \[8\]. With increasing Rh-substitution, this diverging behavior is gradually suppressed ($x \leq 0.01$) and finally becomes a saturating behavior, which is consistent with the result of a previous independent study \[11\]. The observation of the saturation indicates that the Pr 4$f$ triplet ground state changes into the nonmagnetic singlet $\Gamma_1$ due to Rh-substitution, so that the van Vleck type susceptibility behavior appears in the lower temperature range. Hence, in Pr$(Ru_{1-x}Rh_x)_4P_{12}$ with $x=0.03, 0.05$ and 0.15, all the Pr ions have a singlet ground state, in contrast with PrRu$_4$P$_{12}$ which shows staggered triplet and singlet ground states of Pr ions.

![Figure 1. Results of magnetic susceptibility measurements. Horizontal axis is set to log scale to emphasize low temperature behavior. The applied magnetic field is 0.1 T.](image-url)

3.2. Inelastic neutron scattering

The inelastic spectra of Pr$(Ru_{1-x}Rh_x)_4P_{12}$ with $x=0, 0.03$ and 0.15 obtained at TOPAN are shown in figure 2. In PrRu$_4$P$_{12}$, clear temperature dependencies are observed for the width and position of the CF peak at around 8 meV, which corresponds to the excitation from $\Gamma_1$ singlet ground state to $\Gamma_{4}(2)$ triplet state at one of the two Pr-sites \[8\]. In Pr$(Ru_{0.97}Rh_{0.03})_4P_{12}$,
in addition to a temperature-dependent CF peak similar to the one in PrRu4P12, temperature-independent peaks appear at 2.4 and 11 meV. In Pr(Ru0.85Rh0.15)4P12, temperature-independent peaks remain while the temperature-dependent peak disappears. Figure 3 shows that the integrated intensities of the peak at 2.4 meV increase with increasing Rh concentration x. Considering x-dependence of these peaks, temperature-dependent and -independent peaks originate with different Pr-sites and the latter ones emerge due to Rh-substitution.

Figure 2. Inelastic spectra of (a) PrRu4P12, (b) Pr(Ru0.97Rh0.03)4P12, (c) Pr(Ru0.85Rh0.15)4P12 obtained at TOPAN. Q=2.5*(2π/a) for all the results. The broken lines indicate offset values for each temperature data and the dotted lines indicate temperature-independent peaks. The spectra presented in panels (b) and (c) are normalized by the number of incident neutrons and the mole number of sample.

Figure 3. Integrated intensities of the peak at 2.4 meV as a function of Rh concentration x, obtained from HER measurements. The data are normalized with the number of incident neutrons and the mole number of sample.

4. Discussion

As mentioned in the introduction, the temperature dependency of CF level schemes in PrRu4P12 is considered as a signature of the evolution of the order parameter for antiferro-hexadecapole ordering [10]. Therefore, the temperature-dependent CF level observed in Pr(Ru1−xRx)4P12 would be the remainder of the Pr ions contributing to the ordering. This is consistent with the increment of resistivity below approximately 50 K in the earlier study [11]. Recently, we also confirmed the resistivity upturn below 50 K in our samples with x=0.03 and 0.05, as well as the structural transition with the modulation vector q0 for x=0.01, 0.03, 0.05 [13]. On the other hand, we observed temperature-independent CF peaks, those intensities increase as Rh-substitution increases. This suggests that some of the Pr 4f states are modified by Rh-substitution and do not contribute to the ordering. Therefore, the Pr ions in the Rh-doped sample can be separated into two categories: (1) those with a temperature-dependent CF level scheme forming the antiferro-multipoles ordered state, and (2) those with a temperature-independent CF level scheme, which do not contribute to the ordering.
Taking into account the singlet ground state and excitation peaks at 2.4 and 11 meV, we have roughly estimated the number of the temperature-independent Pr ions, which corresponds to several Pr-sites for each Rh-site. This may be attributed to a local effect of Rh-substitution. Thus, the temperature-dependent Pr-sites are expected to be dominant in samples with lowest Rh-concentrations, and to give rise to the multipole ordered phase. The latter expectation is consistent with the observation of superlattice reflections in Pr(Ru$_{1-x}$Rh$_x$)$_4$P$_{12}$ with $x = 0.01, 0.03$ and $0.05$ at low temperatures, using x-ray diffraction [13].

The saturation in magnetic susceptibility at low temperatures indicates that the triplet ground state of a temperature-dependent Pr-site switches to the singlet one for $x \geq 0.03$. Hence, for Rh-contents higher than 3%, all the Pr ions in Pr(Ru$_{1-x}$Rh$_x$)$_4$P$_{12}$ have the same singlet ground state. This may be attributed to a rather widespread effect of the Rh-substitution. In the ordered phase of Rh-doped compounds with uniform ground state, the staggered pattern of multipoles would arise from inequivalent CF levels occupied by the thermally excited electrons. As temperature decreases, the singlet ground states get predominantly occupied: all the Pr-sites become equivalent, which would lead to the disappearance of the multipole order. This is consistent with the results of x-ray diffraction experiments which reveal a drop of the superlattice reflection intensities in Pr(Ru$_{1-x}$Rh$_x$)$_4$P$_{12}$ with $x = 0.03$ and $0.05$ at lowest temperatures [13].

5. Conclusion
Rh-substitution affects the multipole ordering in PrRu$_4$P$_{12}$ through two kinds of modification of Pr 4f-electron states: a local effect causing the emergence of Pr-sites that do not contribute to the ordering, and a wide-range effect causing switch of ground state in one of two Pr-sites which contribute to the ordering. The role of Ru-site in the ordering should be investigated further, in addition to the $p$-$f$ hybridization effect between Pr and P.

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