Effects of Co Substitution on the Magnetic Excitation in Heavy Fermion Compound PrFe$_4$P$_{12}$

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We performed measurements of specific heat and inelastic neutron scattering on Pr(Fe$_{1-x}$Co$_x$)$_4$P$_{12}$ to investigate the effects of *d*-electron doping on the heavy fermion (HF) state and non-magnetic order state of PrFe$_4$P$_{12}$. The ordered state is suppressed by the Co substitution. A Schottky type behavior in the specific-heat appears at 8 K, in contrast with the undoped system. The inelastic neutron spectrum of the Co substituted system is composed of several sharp inelastic peaks, in contrast with the quasi-elastic spectrum in the HF phase of PrFe$_4$P$_{12}$. The experimental results indicate that the Co substitution induces localized 4f electrons of Pr ions with suppression of the HF state and the exotic ordering.

KEYWORDS: PrFe$_4$P$_{12}$, heavy fermion, neutron scattering, specific heat

1. Introduction

The filled-skutterudite compounds RT_4X_{12} (*R*: rare-earth metal, *T*: transition metal, *X*: pnictogen) have attracted much attentions for a long time due to their various electronic phenomena [1,2]. Numerous experimental and theoretical studies demonstrated that these properties are associated with strong correlation effect between the 4f-electron state of rare-earth ions and the conduction electrons. Typical phenomena are the metal-nonmetal transition of PrRu$_4$P$_{12}$ [3] and the heavy-fermion (HF) superconductivity of PrOs$_4$Sb$_{12}$ [4]. The 4f-electron states are very sensitive to atomic compositions. For example, the 4f-electron crystal field (CF) ground state of Pr$_x$Fe$_4$Sb$_{12}$ depends on the Pr-filling fraction [5,6,7], and the reentrant behavior of metal-nonmetal transition is caused by the atomic substitution for PrRu$_4$P$_{12}$ [8,9]. In this paper, we focus on PrFe$_4$P$_{12}$ to investigate the effects of Co substitution on the ordered state and the HF state.

PrFe$_4$P$_{12}$ shows $-\ln T$ dependence of electrical resistivity between 30 and 100 K, as well as a large electronic specific heat coefficient of 1.4 J/(K^2 mol) with an effective electron mass of 81m_0 [10,11]. These results indicate that PrFe$_4$P$_{12}$ is an unusual

Pr-based HF compound. This material undergoes an unconventional phase transition at T_A = 6.5 K and zero magnetic field. No magnetic reflections were observed in the powder neutron diffraction measurement below T_A [12]. On the other hand, a structural modulation dominated by the Fe-ion displacements was demonstrated by the x-ray diffraction experiments [13]. This modulated structure gives rise to two inequivalent configurations of the Fe ions around the Pr-ion sites, which corresponds to the transformation from the body-centered-cubic to the simple-cubic structure. The magnetic-field-induced antiferromagnetic (AFM) reflections were observed by neutron diffraction experiments indicating an antiferro(AF)-type ordering of $4f$ electrons of Pr ions [14,15].

In our previous inelastic neutron scattering experiments for the polycrystalline and single crystal samples [16,17], the distinct evolution of the $4f$-electron state through the phase transition was observed. The spectra are composed of the broad quasielastic response in the HF state and the shape inelastic peaks at 1.5 and 3.0 meV in the ordered state. The quasielastic spectrum originates from the hybridization between the $4f$ and conduction electrons. The recent theoretical study suggested the staggered ordering of the Kondo-singlet sites and the localized CF singlet sites below T_A [18,19]. This theory concluded that a magnetic spectrum consists of a lower energy sharp peak due to the well-localized CF excitation and a slightly broader peak in the higher-energy range, which explained the experimentally observed spectrum. The inelastic peak at 1.5 meV is attributed to the localized f-electron sites whose CF scheme is Γ_1 (0 meV) - $\Gamma_4^{(1)}$ (1.48 meV) - Γ_{23} (2.60 meV) - $\Gamma_4^{(2)}$ (15.9 meV).

Since the density of states of Fe $3d$ electrons have a very sharp peak close to the Fermi level according to the band calculation study [20], we expect that d-electron doping may influence the structure of the Fermi surface which is responsible for the HF state and the non-magnetic ordered phase of $PrFe_4P_{12}$. Therefore, the polycrystalline samples of $Pr(Fe_{1-x}Co_x)_4P_{12}$ were synthesized to investigate the effects of Co-substitution using specific heat and inelastic neutron scattering measurements.

2. Experimental Procedure

Polycrystalline samples of $Pr(Fe_{1-x}Co_x)_4P_{12}$ were synthesized by the Sn-flux method. The concentration x of Co presents the starting compositions prior to the synthesis. The crystal structures were confirmed by powder x-ray diffraction experiments. Specific heat was measured by the Physical Properties Measurement System (PPMS). Inelastic neutron scattering experiments were carried out at the cold-neutron disk-chopper spectrometer AMATERAS installed at the beam line BL14 in Materials and Life Science Experimental Facility of the Japan Proton Accelerator Research Complex (J-PARC) [21]. The measurements were preformed by multi E_i method with the incident neutron energies of 6.39, 11.66, and 27.60 meV. Sample temperature was controlled between 5 and 61 K by a helium closed-cycle refrigerator.

3. Results

Figure 1 (a) shows the results of the specific heat divided by temperature C/T of x = 0.05, 0.10, and 0.15. In contrast with the jump in $PrFe_4P_{12}$ no anomaly appears near 6.5 K in all samples, which suggests that the ordered state was suppressed rapidly by the

Co substitution. It is worth mentioning that a broad hump appears approximately at 8 K, and becomes significant with increasing x. The values of C/T for $x = 0.05$ and 0.10 below 4 K approach to 1 J/(K^2 mol) with decreasing temperature, which are slightly lower than that of the undoped system. The C/T of $x = 0.15$ exhibits a clear peak at 8 K, which can be ascribed to a Schottky peak due to the CF splitting levels.
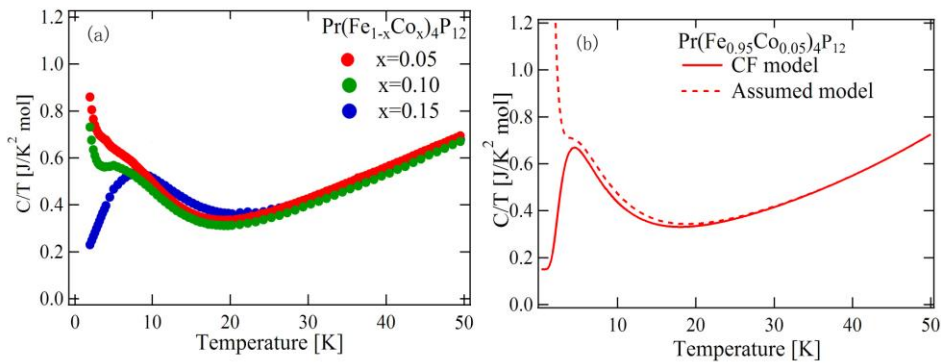

Fig. 1. (Color online) (a) Symbols are experimental results of specific heat divided by temperature C/T. (b) The solid line represents the result considering only the CF scheme under cubic symmetry, and dashed line represents the result based on the assumed splitting of the $\Gamma_4^{(1)}$ and Γ_{23} states.
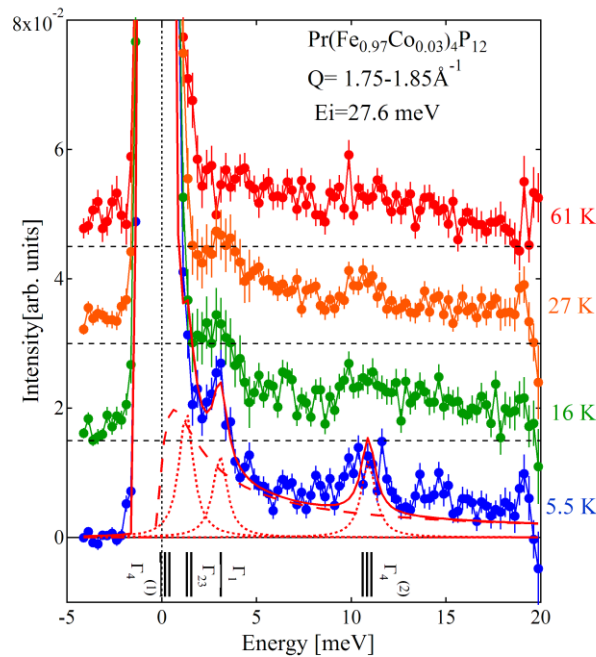

Fig. 2. (Color online) Temperature dependence of the inelastic spectra of $x = 0.03$. Each data set is shown with a relative shift of the ordinate. Solid line indicates the calculated results for 5.5 K based on the simple CF model. The broken line represents only the CF-splitting excitation components at 5.5 K. The long dashed line means the quasi-elastic component.

   Figure 2 shows the temperature dependence of the inelastic spectra when $x = 0.03$, in which integrated intensities are within the scattering-vecor range $Q = 1.75 - 1.85$ Å^{-1}, where contribution of the empty cell data was subtracted. Two inelastic peaks were observed at 2.5 and 10 meV for the 5.5 K data, whose intensities decrease with increasing temperature. These sharp peaks are expected to be the CF splitting

excitations, and are in contrast with the spectrum consisting of only quasi-elastic intensity in the HF state of PrFe$_4$P$_{12}$.

Figure 3 shows Q-dependence of the peak intensities in the energy-transfer ranges of $E = 2 - 4$ meV and $E = 10 - 12$ meV at 5.5 and 16 K. The intensities in both energy-transfer ranges distinctly decrease with increasing Q, as shown by symbols. The solid line represents square of the calculated magnetic form factor of Pr^{3+} ion. Discrepancies between the experimental data and the calculations above $Q = 3$ Å^{-1} can be ascribed to the phonon excitations. These results indicate that the observed peaks can be attributed to the CF excitations.
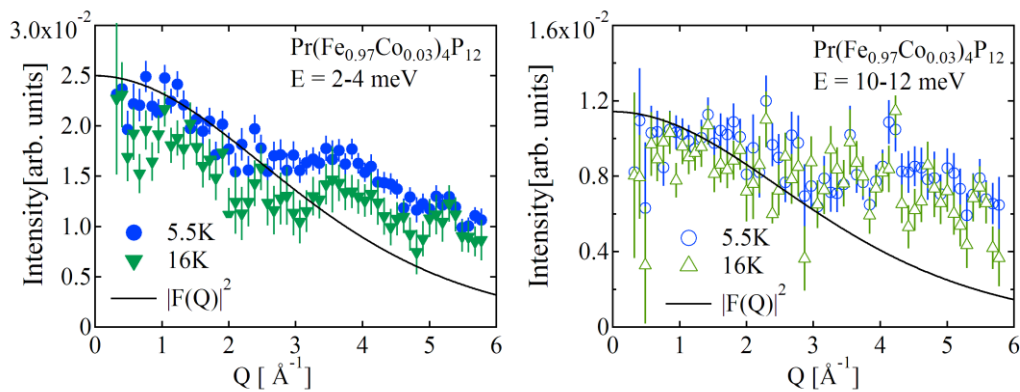

Fig.3. (Color online) Q-dependence of the intensities at $E = 2 - 4$ meV (left) and $E = 10 - 12$ meV (right) at 5.5 and 16 K. The solid line represents square of the magnetic form factor of Pr^{3+} ion.

4. Analysis and Discussion

The spectrum for Pr ion under T_h point group is composed of three inelastic peaks at the most because of the four splitting levels. In addition to the peaks at 2.5 and 10 meV, we expect a peak near 1 meV by taking into account the Schottky peak at 8 K in the specific heat data. We calculated neutron scattering function $S(E)$ and C_{CF} using the CF Hamiltonian for T_h point group [23]. Moreover, a quasielastic component is also taken into account, as for the undoped systems [16, 17]. The specific heat C can be expressed as $C_{CF} + C_{el} + C_{ph}$, where $C_{el} = \gamma T$ and $C_{ph} = \beta T^3$ are contributions from carrier electrons and phonons, respectively.

We propose a CF scheme of $\Gamma_4^{(1)}$ (0 meV) - Γ_{23} (1.29 meV) - Γ_1 (3.07 meV) - $\Gamma_4^{(2)}$ (10.9 meV), which reproduces the observed excitation spectrum as shown by solid line in the Fig. 2. The broken lines represent CF-splitting excitations, and the long dashed line is the quasi-elastic component. The sharp peaks at 2.5 and 10 meV correspond to the excitations between $\Gamma_4^{(1)}$ and Γ_1 and between $\Gamma_4^{(1)}$ and $\Gamma_4^{(2)}$, respectively. The excitation peak from $\Gamma_4^{(1)}$ to Γ_{23} merges with the incoherent elastic peak.

The hump of the specific heat located at 8 K is well reproduced by the CF level scheme together with $\gamma = 0.15$ J/(K^2 mol) and $\beta = 0.00021$ J/(K^4 mol), as shown by solid line in the Fig. 1 (b). The value of γ is approximately 10% of the undoped system, which suggests suppression of the HF behavior. Although the statistical accuracy of the measured spectrum is low, we carried out the spectral analysis by taking into account the multi peak components. The HMHW of quasielastic peak is estimated as 0.75±0.25

meV, which is also smaller than 1.8 meV of pure $PrFe_4P_{12}$. These results indicate that the HF state is not completely suppressed.

We noted that the $\Gamma_4^{(1)}$ magnetic triplet ground state is different from the non-magnetic Γ_1 of the pure $PrFe_4P_{12}$. In case of the Γ_1 ground state, we expect a strong excitation peak to $\Gamma_4^{(1)}$, a very small one to $\Gamma_4^{(2)}$, and no intensity for the excitation to Γ_{23}. This does not agree with the two excitations with the similar intensity at 2.5 and 10 meV. If we assumed quasi-degenerated low-lying levels of Γ_1 and $\Gamma_4^{(1)}$, these inelastic peaks could be reproduced. However, this scheme does not agree with the specific-heat Schottky peak located at 8 K. We could not find any CF level scheme to reproduce the observed data under a constraint of the Γ_1 ground state. The magnetic susceptibility of the Co-substituted system increases with decreasing temperature below 10 K [22]. This observation is accountable by the proposed magnetic ground state. Such switch of the CF scheme induced by the atomic substitution also occurs in $PrRu_4P_{12}$ which exhibits the switch CF ground state from magnetic $\Gamma_4^{(2)}$ to non-magnetic Γ_1 by the Rh-substitution in the nonmetallic phase [24,25]. The sensitive changes of the 4*f*-electron states in the filled-skutterudite compounds are given by the *d*-electron contribution to the Fermi level.

The rapid upturns in the specific heat below 4 K in $x = 0.05$ and 0.10 cannot be explained only by the present CF scheme. This may be explained by split of the $\Gamma_4^{(1)}$ triplet ground state due to local lattice distortion induced by the Co substitution. If we assume that the low-lying $\Gamma_4^{(1)}$ triplet and Γ_{23} doublet states split by 0.2 meV, the upturn is reproduced as shown by dashed line in the Fig. 1 (b). In contrast, no trace of upturn in *C/T* with decreasing temperature was seen in $x = 0.15$. This may be explained by that the higher Co concentration modifies the CF scheme further. As reported previously [22], the magnetic susceptibilities of $x = 0.03$ and 0.05 are enhanced with decreasing temperature below 10 K, although those in high-temperature region are unexpectedly larger. This enhancement seems to be consistent with the triplet ground state. Comparing with the less Co-concentration materials, the smaller magnetic susceptibility in the $x = 0.15$ sample below 10 K seems to be accountable by the nonmagnetic ground state Γ_1 or Γ_{23}. We conclude at this moment that the localized Pr *f*-electron state is stabilized by the Co substitution, and the HF state and the exotic ordered phase below 6.5 K are destroyed by the electron doping.

5. Conclusion

On the basis of specific heat and inelastic neutron scattering experiments, the HF and the ordered states were found to be suppressed by the Co substitution to $PrFe_4P_{12}$. The localized nature of Pr 4*f* electrons emerges with the switch of CF ground state from non-magnetic Γ_1 to magnetic $\Gamma_4^{(1)}$. This variation of electron state suggests that *d* electrons strongly contribute to the properties of $PrFe_4P_{12}$ system.

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