Neutron scattering study on magnetic ordering in a partially rare-earth filled skutterudite \( \text{Pr}_x\text{Fe}_4\text{Sb}_{12} \)

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Abstract. Neutron scattering studies reveal that a crystal-field-splitting ground state of \( \text{Pr}^{3+} \) \( 4f^2 \) electrons in a partially filled \( \text{Pr}_x\text{Fe}_4\text{Sb}_{12} \) \((x < 1)\) is a triplet. A magnetically ordered structure below 4 K consists of both magnetic moments at the Pr and Fe sites, in contrast to the \( x = 1 \) system without any magnetic ordering due to the \( 4f \)-electron singlet ground state.

1. Introduction
Among rare-earth-filled skutterudite compounds, magnetic ordering sensitive to the Pr-ion filling fraction \( x \) for \( \text{Pr}_x\text{Fe}_4\text{Sb}_{12} \) has been studied [1, 2, 3]. No magnetic ordering takes place in a fully filled system \((x = 1)\), in which a singlet ground state for \( \text{Pr} 4f \)-electron crystal-field splitting (CF) was exemplified by inelastic neutron scattering [4]. On the other hand, partially filled compounds \((x = 0.7 \sim 0.9)\) undergo magnetically ordering transitions with ferromagnetic character below 4 K [1, 2]. The earlier inelastic neutron scattering study for \( x = 0.73 \) proposed that a CF ground state is a magnetic triplet [5]. The magnetic moments of the Fe \( 3d \) electrons are suggested to contribute to the paramagnetic susceptibility. Thus, the magnetic behaviors in \( \text{Pr}_x\text{Fe}_4\text{Sb}_{12} \) are supposed to arise from an interplay between the Pr and Fe ions. In the present study, we revisit a CF level scheme in the partially filled system by measuring temperature evolution of absolute neutron-scattering cross sections. We also carried out neutron diffraction experiments to shed further insight into the magnetic structure that has not fully been solved yet.

2. Experimental procedure
Samples were synthesized by the Sb self-flux method [2]. Magnetic properties were measured by a SQUID magnetometer, after confirming crystal structures by a powder X-ray diffraction. Neutron scattering studies were performed at JRR-3, JAERI (Tokai, Japan). Structure of the single crystalline sample at 6 K was determined at the four-circle diffractometer FONDER. Magnetic excitations and magnetic structures were investigated at the triple-axis spectrometer TOPAN. For the latter, both polarized and unpolarized neutrons were used.
3. Results and analysis

Inelastic neutron scattering data for the polycrystalline sample are shown by symbols in Fig. 1. The results were obtained by subtracting background intensity evaluated from data for LaFe$_4$Sb$_{12}$, and by evaluating the absolute scattering function $S(E)$ using intensity from a standard vanadium sample. The samples by the same synthesis procedure show hysteresis behaviors of magnetization measured at 2 K (data from the single-crystal sample will be shown later). It is consistent with the previously reported system. The filling factor of the present sample could not be determined precisely by the powder diffraction techniques. Lines represent results of a least-squares fitting analysis based on the CF Hamiltonian for $T_h$ space group for the Pr sites [6]. This analysis succeeds in reproducing quantitatively the temperature variation of the spectra with the set of parameters $W = 0.13$ meV, $x = 0.479$, and $y = 0.285$. The level scheme is $\Gamma_4^{(2)}$ (0 meV) - $\Gamma_1$ (2.4 meV) - $\Gamma_4^{(1)}$ (10.3 meV) - $\Gamma_{23}$ (10.7 meV). The scale factor for a ratio of calculated $S(E)$ to the experimental result is around 1.3, which is close to the ideal.

**Figure 1.** Symbols represent the measured spectra. Lines are the fitting analysis. Origin for each temperature set is shifted by 0.01.

**Figure 2.** Measured magnetization curves of the sample used for the neutron diffraction studies.

| $\lambda$ = 1.24 Å, Reliable Factor $R = 0.0528$ |
|-----------------------------------------------|
|          | Pr  | Fe  | Sb |
| occupation | 0.895(82) | 1   | 1  |
| coordinate $x_c$ | 0   | 0.25 | 0  |
| coordinate $y_c$ | 0   | 0.25 | 0.3362(2) |
| coordinate $z_c$ | 0   | 0.25 | 0.1600(2) |
| $B$ [Å$^2$] | 1.05(32) | 0.295(47) | 0.382(50) |

**Table 1.** Structural parameters determined by the single-crystal diffraction using FONDER. The parameters with error magnitudes in the parentheses were adjusted in the analysis, and the others were fixed.

**Figure 3.** Blue circles are the measured result of magnetic structure factors. Red squares are the fitted result for the depicted model.
value of unity. On the other hand, the CF scheme for the fully filled compound is \( \Gamma_1 (0 \text{ meV}) - \Gamma_1^{(2)} (2.3 \text{ meV}) - \Gamma_1^{(1)} (11.4 \text{ meV}) - \Gamma_{23} (18 \text{ meV}) \), parameterized with \( W = 0.230 \text{ meV}, x = 0.398 \) and \( y = 0.101 \) [4]. The low-lying CF-level sequence in the present partially filled compound is reverse from the fully filled compound, and the \( \Gamma_{23} \) level is located at the energy lower than the fully filled one.

In Table 1, we summarize the structural parameters for the synthesized single-crystal sample determined from the data by FONDER. The Pr-ion fraction was determined to be \( x = 0.89 \). Magnetization up to 5.5 T of this sample, shown in Fig. 2, is the same as in the previously reported data [2]. Small hysteresis in the low magnetic-field region, shown in an upper part, is also consistent with the reported ferromagnetic behavior. Therefore, neutron diffraction was performed for investigating a magnetic structure of this sample. We observed very tiny magnetic reflection peaks from this sample below around 4 K, superimposed on the nuclear diffractions. A rocking-curve profile at the reciprocal-lattice point 200 by subtracting intensities at 5 K from those at 1 K is shown in an inset of Fig. 3. The determined magnetic structure factors for the three reflections at 1 K are plotted in Fig. 3. The dependence on the scattering vector magnitude \( Q \) deviates from that expected for a uniform ferromagnetic structure obeying a monotonic curve of the magnetic form factor. As discussed before, both of the magnetic moments at Pr and Fe are anticipated to play a role in the magnetic ordering. We took into account a simple model based on anti-parallel arrangement of the magnetic moments at the Pr and Fe sites, as shown in the structure picture of Fig. 3. The present structure factors results are well reproduced by the magnetic moments 0.29\( \mu_B \) at the Pr site and 0.19\( \mu_B \) at the Fe site.

Polarized neutron diffractions were measured at a magnetic field 1 T applied along the [001] axis and 1.8 K. The observed flipping ratios \( I_{\text{off}} / I_{\text{on}} \) at the selected reflection points are plotted against \( Q \) in Fig. 4, where \( I_{\text{off}} \) or \( I_{\text{on}} \) represent the peak intensities for the incident neutron spins parallel or anti-parallel to the magnetic field applied to the sample, respectively. The data are well reproduced by the Pr magnetic moments of \( \sim 0.79 \mu_B \) being parallel to the magnetic field, as shown in the inset. The Fe magnetic moments do not contribute to the observed flipping ratios. They might flop toward the direction perpendicular to the magnetic field, and have zero magnetic structure factors for the measured reflections. The net magnetization value \( \sim 0.79 \mu_B \) per chemical formula unit for 1 T is close to the magnetization. Because no additional magnetic reflection appears, the magnetic unit cell is identical with that of the crystal structure.

4. Discussion

As demonstrated by the simple collinear model for the zero magnetic field condition, the spontaneous magnetization is 0.47\( \mu_B / \text{f.u.} \), dominated by the Fe-site magnetic moments (the number of the Fe sites is four times as large as the Pr one). The ordered magnetic moment 0.29\( \mu_B \) at the Pr site is smaller than the eigenvalue of 1.52\( \mu_B \) for the \( \Gamma_1^{(2)} \) ground state. The suppression of the magnetic moment is thought to be due to fluctuation even at 1 K induced by the Pr-site randomness, since the neutron-diffraction intensity does not show a saturation behavior even at 1 K. On the other hand, under the magnetic field of 1 T, the magnetization of \( \sim 0.79 \mu_B \) is explained only by the Pr-site magnetic moments aligning along the applied magnetic

![Figure 4. Blue circles are the polarized-neutron flipping ratios. Red circles are the calculated result for the model in an inset.](image-url)
field without distinct contribution of the Fe sites. Recently, the magnetically ordered structure below 18 K for an isomorphic material PrFe$_{4}$As$_{12}$ was reported [8]. For 0.5 T applied along the [001] axis at 2 K, a magnetic moment of 1.59$\mu_B$ for the Pr ion directs along the magnetic field, and that of 0.56$\mu_B$ for the Fe ion tilting from the [001] axis by 79 degrees. This magnetic structure composed of the almost perpendicular moments is very similar to the present case in Pr$_{0.89}$Fe$_{4}$Sb$_{12}$ at 1 T and 1.8 K.

The CF ground state for Pr 4$f$ electron switches from the singlet in the fully filled materials to the triplet in the partially filled materials. The concentration of Pr-site vacancy by 11% in the present sample means almost one vacancy in the five unit cells. It is not sufficient for changing uniformly point-charge potential at the Pr sites. It was reported that the CF scheme is sensitive to the hybridization of 4$f$ with conduction electrons. PrRu$_4$P$_{12}$ shows the 4$f$ electron multipole ordering on the metal-nonmetal transition [9], and PrOs$_4$P$_{12}$ shows the CF level shift with temperature [10]. The shift of the CF levels with temperature in these materials is 1 - 3 meV, which is close to the ground state switch from $x = 1$ to $x = 0.89$ for Pr$_{x}$Fe$_{4}$Sb$_{12}$. Thus, the lack of the Pr sites in Pr$_{x}$Fe$_{4}$Sb$_{12}$ may induce the uniform switch in the CF ground state, with the assistance of a spatially extent effect through the hybridized conduction band.

The magnetic moments of the Fe 3$d$ electrons are commonly present in the skutterudite materials composed of Fe and Sb. Almost the same magnitudes of the effective magnetic moment per Fe site were evaluated from the high-temperature magnetic susceptibilities: $\mu_{eff}^{Fe} = 0.68\mu_B$ for $x = 1$ [3], 0.60$\mu_B$ for our $x = 0.89$ sample, 0.69$\mu_B$ for $x = 0.87$ [2], and 0.59$\mu_B$ for LaFe$_4$Sb$_{12}$ [7]. On the other hand, the fully filled $x = 1$ system for Pr$_x$Fe$_4$Sb$_{12}$ does not undergo any ordering phase transition only by the Fe magnetic moments [3]. Thus, the magnetic ordering in the skutterudite composed of Fe and Sb is given by the interplay between the magnetic moments at Pr and Fe sites. Recently, a microscopic theory for the inter-site interaction between the transition-metal and rare-earth sites in skutterudite was proposed on the basis of the $d$-$f$ hybridization effect between these atoms [11]. It concludes that a ferrimagnetic ordering is enhanced for the triplet CF ground state, which is consistent with the observation Pr$_x$Fe$_4$Sb$_{12}$.

5. Summary
The combination of the magnetic moments of Fe and those due to the relevant threefold CF ground state of Pr is necessary for the ferrimagnetic ordering below 4 K in Pr$_x$Fe$_4$Sb$_{12}$.

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