Crystal field excitations in PrFe$_4$Sb$_{12}$ synthesized under high pressure

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Abstract. In the filled skutterudite PrFe$_4$Sb$_{12}$ with high Pr-site filling fraction synthesized under high pressure, the bulk properties indicate a singlet ground state of the crystal field (CF) and no phase transition at low temperature, in contrast to the reported magnetic ordering in the samples with relatively low filling fraction. In order to clarify the CF states in PrFe$_4$Sb$_{12}$ microscopically, we have performed the inelastic neutron scattering experiment on the PrFe$_4$Sb$_{12}$ synthesized under high pressure. The CF level scheme obtained from the results is $\Gamma_1 (0 \text{ meV}) - \Gamma_4 (2.3 \text{ meV}) - \Gamma_23 (11.4 \text{ meV}) - \Gamma_{23} (18 \text{ meV})$. Furthermore, it is found that the singlet-triplet states in low energy region have large off-diagonal matrix elements of quadrupoles, indicating the similarity of the CF states in the heavy fermion superconductor PrOs$_4$Sb$_{12}$.

1. Introduction
Filled skutterudites RT$_4$X$_{12}$ (R = rare earth, T = transition metal, X = pnictogen) crystallize in a body-centered-cubic structure (space group Im3). R ions occupy 2a site inside of an icosahedral cage which is formed by 12 X ions and the site symmetry of R ions is the point group $T_h$ which has no four-fold axis. These compounds have attracted much interest because of a variety of low temperature properties, such as, heavy fermion behavior, multipole ordering and unconventional superconductivity, which appear only by changing constituent elements due to this unique crystal structure.

Among the filled skutterudites, recently the influence of the filling fraction of R ion on the physical properties has been argued, especially in Sb-based filled skutterudites with a large pnictogen cage [1]. PrFe$_4$Sb$_{12}$ is the representative case in which the influence of the filling fraction clearly appears in the low temperature properties. In PrFe$_4$Sb$_{12}$ with high Pr-site filling fraction synthesized under high pressure, no phase transition has been observed down to 0.15 K and the bulk properties indicate that the low-lying crystal field (CF) level scheme consists of a singlet ground state and a triplet first excited state with energy gap of 1.9 meV [2]. Evidence for the singlet ground state is given by the specific heat measurement which shows absence of residual entropy under magnetic fields. These are in contrast to the reported magnetic ordering...
around 5 K and magnetically degenerated CF ground state in the samples with relatively low filling fraction synthesized at ambient pressures [3, 4, 5, 6], but in agreement with the singlet ground state reported in Ref. [7]. In order to obtain the microscopic information of the CF states in PrFe$_4$Sb$_{12}$ with high Pr-site filling fraction, therefore, we have performed the inelastic neutron scattering experiment on the PrFe$_4$Sb$_{12}$ synthesized under high pressure.

2. Experimental

We synthesized 8.19 g of polycrystalline samples of PrFe$_4$Sb$_{12}$ under high pressure of 4 GPa. The detailed synthesis condition is described in Ref. [2]. For estimation of the phonon background for PrFe$_4$Sb$_{12}$, we also synthesized 8.98 g of LaFe$_4$Sb$_{12}$ as a reference compound by the same procedure. The inelastic neutron scattering experiment was done by using the time-of-flight chopper spectrometer HET at the ISIS spallation neutron source with incident energies ($E_i$) of 11 meV and 40 meV. The energy resolutions at zero energy transfer are 0.54 meV and 2.8 meV (full width at half maximum), respectively. Each sample was filled under helium gas atmosphere into an aluminum container and mounted in a closed cycle refrigerator. The observed scattered intensity was converted into absolute units by normalizing the measured intensity to that from a standard vanadium sample. The phonon background of PrFe$_4$Sb$_{12}$ for the low-angle detector bank was estimated by subtracting the scaled intensity of PrFe$_4$Sb$_{12}$ measured at the high-angle detector bank and the scaling factor was estimated from the ratio of the measured intensity at the high-angle detector bank to the intensity at the low-angle detector bank obtained from the measurements on the reference compound LaFe$_4$Sb$_{12}$.

3. Results and discussion

![Figure 1](image-url)

Figure 1. Energy spectra of PrFe$_4$Sb$_{12}$ measured with $E_i = 11$ meV and 40 meV at low-angle detector bank at lowest temperature 5 K after subtracting of the phonon background. The lines are the Gaussian fit to the data.

Figure 1 shows energy spectra of PrFe$_4$Sb$_{12}$ measured with $E_i = 11$ meV and 40 meV at low-angle detector bank at lowest temperature 5 K after subtracting of the phonon background. We found two clear inelastic peaks at 2.3 meV and 11.4 meV. The intensity of these two peaks decreases with increasing wave vector and temperature, as expected for magnetic excitations from the CF ground state. The peak position of the former excitation is slightly higher than the energy splitting of 1.9 meV between the singlet ground state and the triplet estimated by the
bulk measurements [2]. The integrated intensity of two peaks was obtained by fitting the peaks
with Gaussians, as denoted by lines in Fig. 1. The obtained linewidths for the two peaks are
1.4 meV and 4.2 meV, which are larger than the instrumental resolutions, indicating the mixing
between 4f electrons and conduction electrons. The ratio of integrated intensity of the peak at
2.3 meV to the peak at 11.4 meV was found to be 4.9 ± 0.1.

\[ \Gamma_{18}^{(1)} \quad 18 \text{ meV} \]
\[ \Gamma_{11.4}^{(1)} \quad 11.4 \text{ meV} \]
\[ \Gamma_{23} \quad 2.3 \text{ meV} \]
\[ \Gamma_{0} \quad 0 \text{ meV} \]

**Figure 2.** The CF level scheme of the eigenvalues of CF Hamiltonian obtained by the peak positions and
the ratio of the integrated intensity in Fig. 1. The levels are labeled by their eigenstates. The vertical dashed lines
denote the allowed dipole transitions for the point group \( T_h \).

\[ H_{\text{CF}} = W \left[ \frac{O_4^0 + 5O_4^4}{60} + (1 - |x|) \frac{O_6^0 - 21O_6^4}{1260} + y \frac{O_6^2 - O_6^6}{30} \right], \quad (1) \]

where \( W, x \) and \( y \) are CF parameters and \( O_l^m \) are Stevens operators. Under the cubic CF for \( T_h \)
symmetry, \( J = 4 \) multiplet of Pr\(^{3+} \) split to \( \Gamma_1 \) singlet, \( \Gamma_{23} \) doublet and \( \Gamma_{4}^{(1)}, \Gamma_{4}^{(2)} \) triplets. The last term in the Hamiltonian of Eq. (1) represents the effect of \( T_h \) symmetry which mixes two triplets \( \Gamma_4(O_h) \) and \( \Gamma_5(O_h) \) under CF with \( O_h \) symmetry. The neutron scattering cross section for CF
excitations is proportional to the square of the off-diagonal matrix elements of magnetic dipoles
between their CF states. Thus, by calculating the dipole matrix elements between the ground
state and the two excited states consistent with the observed peak positions, we examined three
CF parameters which reproduce the data at lowest temperature. The obtained parameters are
\( W = 0.230 \text{ meV}, x = 0.398 \) and \( y = 0.101 \). By using the CF parameters, the eigenvalues and
eigenstates of Eq. (1) are calculated to be \( \Gamma_1 \) singlet (0 meV) - \( \Gamma_{4}^{(2)} \) triplet (2.3 meV) - \( \Gamma_{4}^{(1)} \)
triplet (11.4 meV) - \( \Gamma_{23} \) doublet (18 meV), as shown in Fig. 2. It is readily distinguishable by
the ratio of integrated intensity of the peak that the first excited state is \( \Gamma_{5}(O_h) \)-like triplet.

**Figure 3.** Energy spectra of PrFe\(_4\)Sb\(_{12}\) with \( E_i = 40 \text{ meV} \) at low-angle detector bank for
different temperatures after subtracting of the phonon background. The lines represent the calculated energy spectra based on the obtained CF level scheme in Fig. 2.
15 meV increases with increasing temperature. The temperature dependence of spectra are well reproduced by the obtained CF parameters and can be naturally explained by the decrease of the $\Gamma_1 \rightarrow \Gamma_4^{(1)}$ transition and the increase of $\Gamma_4^{(2)} \rightarrow \Gamma_1$ and $\Gamma_4^{(2)} \rightarrow \Gamma_{23}$ transitions, as denoted by the vertical dashed lines in Fig. 2. This agreement between the experiment and the calculation validates the obtained CF parameters. If the ground state is the triplet as in the case for the low Pr-filling-fraction samples reported in Refs. [3, 4, 5, 6], it should be noted that there must be three CF excitations from the ground state at low temperature because of the selection rule of the dipole transitions for $T_h$ symmetry [8]. However, the measurements at lowest temperature show no evidence of additional peaks above 1 meV.

The low-lying singlet-triplet levels of PrFe$_4$Sb$_{12}$ obtained from the present results is the characteristics in common in PrT$_4$Sb$_{12}$ ($T = $ Fe, Ru and Os). The energy gap of 2.3 meV between the singlet and the triplet is the value intermediate between the paramagnetic PrRu$_4$Sb$_{12}$[9] and the unconventional superconductor PrOs$_4$Sb$_{12}$[10, 11]. On the other hand, the wave function of the $\Gamma_4^{(2)}$ first excited state is very similar to that of PrOs$_4$Sb$_{12}$, that is, the singlet-triplet states of PrFe$_4$Sb$_{12}$ have large off-diagonal matrix elements of electric quadrupoles with $\Gamma_4$ symmetry (corresponding to $\Gamma_5$ symmetry in the point group $O_h$). If the inter-site interaction between Pr$^{3+}$ is strong in PrFe$_4$Sb$_{12}$, such as PrOs$_4$Sb$_{12}$ [10, 12], therefore, it may be also expected that field-induced quadrupolar ordering could occur under high magnetic fields at low temperature due to the level crossing between the singlet and the triplet.

4. Summary
From our inelastic neutron scattering experiment on PrFe$_4$Sb$_{12}$ synthesized under high pressure, we have obtained a direct microscopic information about the CF level scheme in PrFe$_4$Sb$_{12}$ with high filling fraction and the obtained level scheme is $\Gamma_1$ (0 meV) - $\Gamma_4^{(2)}$ (2.3 meV) - $\Gamma_4^{(1)}$ (11.4 meV) - $\Gamma_{23}$ (18 meV). Furthermore, it is found that the low-lying singlet-triplet states have large off-diagonal matrix elements of quadrupoles, indicating the similarity of the CF states in the heavy fermion superconductor PrOs$_4$Sb$_{12}$.

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