Thermodynamic properties of the f-electron-nuclear hyperfine-coupled composite multiplets of Pr ions in filled-skutterudite PrRu$_4$P$_{12}$

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Abstract. It has recently been found that composite multiplets are formed by the hyperfine coupling between the triplet crystalline-electric-field ground state of the 4$f$ electrons and the $^{141}$Pr nuclear spin in Pr ions of the filled skutterudite PrRu$_4$P$_{12}$. Entropy analysis of the characteristic Schottky-type peak structure appearing in the low-temperature specific heat demonstrates that it is actually caused by thermal excitations of not only 4$f$ electrons but also $^{141}$Pr nuclei. The hyperfine coupling constant for Pr ions in nonmetallic PrRu$_4$P$_{12}$ is determined to be $A = +0.050(2)$ K, which is almost the same as in metallic Pr-based compounds. This fact corroborates that the intra-ion hyperfine coupling of Pr ions is independent of the type of material.

1. Introduction

It has recently been found that composite multiplets are formed by the hyperfine coupling between the crystalline-electric-field ground state of the 4$f$ electrons and the $^{141}$Pr nuclear spin in Pr ions of the filled skutterudite PrRu$_4$P$_{12}$ [1]. PrRu$_4$P$_{12}$ is one of the Pr-based filled skutterudites Pr$_T$$_4$X$_{12}$, which have received intense interest since they display a variety of exotic strongly-correlated-electron behaviors [2, 3, 4]. The charge ordering appearing below $T_{co} = 63$ K [5] has been found to be of unconventional type in the sense that it involves the internal degrees of freedom of the 4$f$ electrons through the coupling with the conduction electrons. Below $T_{co}$, the crystal structure changes into a simple cubic (Pm$\bar{3}$m, $T_h^1$, #200) that contains two crystallographically-in-equivalent Pr sites [6] (referred to as Pr1 and Pr2 hereafter) as shown in Fig. 1. The CEF level schemes of the two Pr sites show pronounced $T$ dependence and finally the Pr1 and Pr2 ions have a $\Gamma_1$ singlet and a $\Gamma_4^{(2)}$ triplet CEF ground state at $T < T_{co}$, respectively [7, 8].

Each Pr ion has a $^{141}$Pr nucleus (the natural abundance of 100%) with a nuclear spin $I = 5/2$. Well-established Hamiltonian [9, 10, 11] to deal with the Pr1 and Pr2 single ion is

$$\mathcal{H} = \mathcal{H}_{CEF} + A \mathbf{I} \cdot \mathbf{J} - (-g_J \mu_B \mathbf{J} + g_N \mu_N \mathbf{I}) \cdot \mu_0 \mathbf{H}.$$ (1)
Figure 1. Diagram illustrates the formation of the 4f-electron-nuclear hyperfine-coupled composite multiplets in the Pr2 ion of PrRu4P12. The 4f-electron triplet CEF state (pseudo-spin τ = 1) and the nuclear spin (I = 5/2) are coupled by the hyperfine interaction, transforming into 3 composite multiplets (effective total spin F' = 7/2, 5/2 and 3/2). Calculated energy level scheme in applied magnetic fields is after Ref.[1].

For the CEF Hamiltonian $H_{CEF}$ [12], we use the CEF parameters determined at 5 K by inelastic neutron scattering measurements [7]. The second term $A I \cdot J$ represents the hyperfine interaction. The coupling constant $A$ was theoretically calculated to be +0.052 K [13, 14] and this value has been confirmed in metallic compounds PrFe4P12 and PrOs4Sb12 by thermodynamical measurements [15, 16, 17]. The third term represents the Zeeman energy of the magnetic moments due to the 4f-electron $-g_J \mu_B J$ and due to the nuclear spin $g_N \mu_N I$, where $g_J = 4/5$, $\mu_B$, $g_N = +1.72$, and $\mu_N$ are the Landé g-factor, Bohr magneton, the nuclear g-factor, and the nuclear magneton, respectively. Note that there are no fitting parameters in eq. (1).

The term $A I \cdot J$ mixes the 4f-electron and the nuclear-spin states and can form composite multiplets. The formation of such composite multiplets has been revealed in PrRu4P12 by the observation of a distinct Schottky-type peak structure at $T_p = 0.30$ K in specific heat and a remarkable rounding below 1 T in magnetization curve [1]. Note that most Pr-based compounds having a triplet ground state order magnetically at low temperatures, preventing formation of such composite multiplets. In this sense, the formation of the lattice of the composite multiplets without showing any magnetic or quadrupolar orderings in PrRu4P12 at least down to 20 mK [18] is an extremely rare case. To the best of our knowledge, this is the first thermodynamical observation of its kind.

In this paper, we analyze the low-temperature specific heat data and discuss the thermodynamic properties of the composite multiplets. We also confirm that the hyperfine coupling constant $A$ for Pr ion is independent of the type of material.

2. Experimental Details
PrRu4P12 single crystals have been grown by the Sn-flux method using high-purity raw materials of 4N(99.99% pure)-Pr, 4N-Ru, 6N-P and 5N-Sn. The single crystalline nature has been checked by X-ray back-reflection Laue technique. No impurity phases were detected in an X-ray powder diffraction experiment for crystals from the same batch. Observed de Haas-van Alphen oscillations in LaRu4P12 single crystals grown by the same manner [19] attest to high quality of the present samples. Specific heat was measured by a quasi-adiabatic heat pulse method using
a $^3$He-$^4$He dilution refrigerator equipped with an 8 T superconducting magnet.

3. Results and discussion

![Figure 2](image_url)  
**Figure 2.** (a) Specific heat $C(T)$ of PrRu$_4$P$_{12}$ in $\mu_0H = 0$ and 8 T for $H \parallel [100]$ (after Ref. [1]). (b) Entropy for the Pr2 ion in zero field.

Specific heat $C$ shows a Schottky-type peak structure at $T_p = 0.30$ K in zero field as shown in Fig. 2(a) and it shifts to higher temperatures with increasing magnetic field (see Ref. [1] for details). This structure can be accounted for as the thermal excitations in the 4f-electron-nuclear hyperfine-coupled composite multiplets formed in the Pr2 ions. In this temperature range, the observed $C$ includes contributions from the excitations in the Pr1 ions ($C_{Pr_1}$), the Pr2 ions ($C_{Pr_2}$), phonons ($C_{ph}$), conduction electrons ($C_{c.e.}$) and the Ru and P nuclei ($C_n$).

Since the CEF ground state of the Pr1 ions is $\Gamma_1$ singlet and the 1st excited state $\Gamma_4^{(2)}$ (triplet) is well separated with the excitation energy of 94 K [7], $C_{Pr_1}$ has extremely small contribution in the present $T$ range in zero field. Considering the extremely low carrier density in this $T$ range ($T \ll T_{co}$) [20], the conduction-electron contribution $C_{c.e.} = \gamma T$, where $\gamma$ must be two or three orders of magnitude smaller than 44.4 mJ/K$^2$mol-f.u. of LaRu$_4$P$_{12}$, should also be negligibly small. For the other contributions, we use $C_{ph} = \beta T^3$ with $\beta = 0.50$ mJ/K$^4$mol-f.u. determined for LaRu$_4$P$_{12}$ and $C_n = A_N/T^2$ with $A_N = 3.4 \times 10^{-6}$ JK/mol-f.u. estimated by the $^{101}$Ru-NQR resonance frequency $\nu_Q = 12.735$ MHz at $T = 4$ K [21]. Subtracting these contributions from the $C(T)$ data, $C_{Pr_2}(T)$ can accurately be obtained. The entropy $S_{Pr_2}(T)$ calculated using $C_{Pr_2}(T)$ is shown in Fig. 2(b). It is clear that the entropy release from the Pr2 ions below 4 K (where $C_{Pr_2}/T$ vs $T$ has a minimum, i.e., $S_{Pr_2}(T)$ has an inflection point) exceeds $R\ln 3$, which is the maximum value of the entropy release that can be caused by the $\Gamma_4^{(2)}$ triplet CEF ground state of the Pr2 4f electrons. This fact provides unambiguous evidence for the involvement of the nuclear degrees of freedom in the formation of the Schottky-type peak structure along with the

![Figure 3](image_url)  
**Figure 3.** Specific heat $C(T)$ of PrRu$_4$P$_{12}$ measured in $\mu_0H = 8$ T for $H \parallel [100]$ (after Ref. [1]) compared with model calculation $C_{Pr_2}/2 + C_{Pr_1}/2$ for different values of the hyperfine coupling constant $A$. 

Figure 3. Specific heat $C(T)$ of PrRu$_4$P$_{12}$ measured in $\mu_0H = 8$ T for $H \parallel [100]$ (after Ref. [1]) compared with model calculation $C_{Pr_2}/2 + C_{Pr_1}/2$ for different values of the hyperfine coupling constant $A$. 

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Pr2 4f electrons. In this temperature range, there has been observed no magnetic ordering and no lowering of the Pr site-symmetry from cubic, either of which is necessary for the splitting of the T(2) triplet state and 141Pr nuclear spin state. All of these facts are consistent with the formation of 4f-electron-nuclear hyperfine-coupled composite multiplets.

The value of $A$ can be accurately determined using high-field $C(T)$ data. In Fig. 3, $C(T)$ data measured in $\mu_0 H = 8$ T for $H || [100]$ are compared with calculated $C_{Pr2}/2 + C_{Pr1}/2$ (note that one formula unit of PrRu$_4$P$_{12}$ contains 0.5×Pr2-ion and 0.5×Pr1-ion) using different values of $A$. The model calculation is easily performed by diagonalizing the Hamiltonian of eq. (1). Below 1 K, magnetization $M = g_J\langle J \rangle$ is saturated for both Pr1 and Pr2 ions. Therefore, the low-$T$ increase in $C(T)$ is dominated by the Zeeman splitting of the nuclei, which feel the effective hyperfine-enhanced magnetic field of $\mu_0 H - A\langle J \rangle/N_{PrN}$ for each Pr ion. From the fitting to the $C(T)$ data shown in Fig. 3, $A = +0.050(2)$ K is obtained for Pr ions in extremely-low-carrier PrRu$_4$P$_{12}$. This value is remarkably close to those in metallic PrFe$_2$P$_{12}$ [15] and PrOs$_4$Sb$_{12}$ [16, 17]. This fact corroborates that the intra-ion hyperfine coupling of Pr ions is not affected by the background electronic structure in materials.

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