$f$-Electron-Nuclear Hyperfine-Coupled Multiplets in the Unconventional Charge Order Phase of Filled Skutterudite PrRu$_4$P$_{12}$

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The filled skutterudite PrRu$_4$P$_{12}$ is known to undergo an unconventional charge order phase transition at 63 K, below which two sublattices with distinct $f$-electron crystalline-electric-field ground states are formed. In this paper, we study experimentally and theoretically the properties of the charge order phase at very low temperature, particularly focusing on the nature of the degenerate triplet ground state on one of the sublattices. First, we present experimental results of specific heat and magnetization measured with high quality single crystals. In spite of the absence of any symmetry breaking, the specific heat shows a peak structure at $T_p = 0.30$ K in zero field; it shifts to higher temperatures as the magnetic field is applied. In addition, the magnetization curve has a remarkable rounding below 1 T. Then, we study the origin of these experimental findings by considering the hyperfine interaction between $4f$ electron and nuclear spin. We demonstrate that the puzzling behaviors at low temperatures can be well accounted for by the formation of $4f$-electron-nuclear hyperfine-coupled multiplets, the first thermodynamical observation of its kind.

KEYWORDS: $4f$-electron-nuclear hyperfine-coupled multiplets, PrRu$_4$P$_{12}$, charge ordering, filled skutterudite, crystalline electric field

1. Introduction

Pr-based filled skutterudites PrT$_4$X$_{12}$ have received intense interest since they display a variety of exotic strongly-correlated-electron behaviors.$^{1-7}$ Among them, a charge-ordering transition in PrRu$_4$P$_{12}$ appearing at $T_{co} = 63$ K from a high-$T$ metallic phase to a low-$T$ nonmetallic phase is unique.$^8$ No clear anomaly at $T_{co}$ in the magnetic susceptibility suggests that this ordering has a nonmagnetic origin. Above $T_{co}$, the crystal structure is a body-centered

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cubic (bcc) with the space group \text{Im}^3 (T_h^5, \#204). Below \( T_{\text{co}} \), the unit cell is doubled in size and the resulting simple cubic (sc) lattice (Pm\( \overline{3} \), \( T_1 \), \#200) contains two crystallographically-inequivalent Pr sites (referred to as Pr1 and Pr2 hereafter).\(^9\) Both the unit-cell doubling and the decrease of the carrier density in the ordered state can be accounted for as being due to the Fermi-surface nesting with a wave vector \( \mathbf{q} = (1, 0, 0)(2\pi/a) \) of the conduction band consisting mainly of the \( a_u \) molecular orbital on \( P_{12} \).\(^{10,11}\) However, the charge ordering in \( \text{PrRu}_4\text{P}_{12} \) is unconventional in the sense that the \( 4f \)-electrons of Pr ions play an essential role in the ordering, since such a transition is absent in \( \text{LaRu}_4\text{P}_{12} \).\(^{12}\) This is also supported by a significant \( T \) dependence of the crystalline-electric-field (CEF) level schemes of the two Pr sites,\(^{13–15}\) resulting in a \( \Gamma_1 \) singlet ground state at the Pr1 site and a \( \Gamma_4^{(2)} \) triplet ground state at the Pr2 site for \( T \ll T_{\text{co}} \).

Some theoretical studies have been made to understand the nature of the charge ordering and the metal-non-metal transition. The characteristic behavior of the \( T \) dependent CEF level schemes has been explained as a multipole ordering of \( 4f \) electrons associated with charge ordering of conduction electrons.\(^{16}\) Anomalous \( T \) dependences of the electrical resistivity and Hall coefficient (with a sign change in the latter) below \( T_{\text{co}} \)\(^{17}\) have been explained by taking into account \( 4f \)-orbital fluctuations.\(^{18}\) A recent microscopic derivation of an effective Hamiltonian has shown that the charge order originates simply and exclusively from the \( c-f \) mixing whose magnitude depends strongly on the CEF states.\(^{19}\) Concerning the nature of the triplet ground state in the charge order phase, the effective Hamiltonian predicts that the ratio of the possible magnetic transition temperature to \( T_{\text{co}} \) should be unusually small, that is, of the order of \( 10^{-3} \).\(^{19}\) In fact, no sign of long-range order has been detected so far below \( T_{\text{co}} = 63 \) K in \( \text{PrRu}_4\text{P}_{12} \) (no magnetic ordering down to 20 mK by zero-field \( \mu \text{SR} \)). Thus, one important issue to be clarified is whether and how the degeneracy of the triplet CEF ground state is lifted as \( T \) approaches \( T = 0 \).

For this purpose, we report in the present paper our results of specific heat and magnetization measurements in the temperature interval \( T = 0.1 \sim 10 \) K on \( \text{PrRu}_4\text{P}_{12} \) single crystals. It is shown in these experiments that a distinct peak structure appears in the specific heat at around \( T_p = 0.30 \) K, which shifts to higher temperatures as the magnetic field is applied. In addition, it is revealed that the magnetization curve displays a remarkable rounding below 1 T. Note again that these anomalies cannot be attributed to any phase transition. Remembering that the Pr ion has a large hyperfine coupling, we consider the effect of the on-site hyperfine interaction between the triplet magnetic moment and the \( ^{141}\text{Pr} \) nuclear spin \( I = 5/2 \). Then we find that the experimental results can be reproduced even quantitatively as a formation of new multiplets due to the hyperfine interaction (hereafter called \( 4f\)-electron-nuclear hyperfine-coupled multiplets).

It is to be noted that although the hyperfine coupling strength is relatively enhanced in
rare-earth ions, its energy scale (e.g., $A = +0.052$ K for Pr ion) is usually still smaller than those of inter-ion exchange interactions of various types (dipolar, quadrupolar, etc.). Therefore, most Pr-based compounds having a triplet ground state order magnetically at low temperatures, preventing such phenomenon. In this sense, the formation of the lattice of $4f$-electron-nuclear hyperfine-coupled multiplets without showing any long-range orderings in PrRu$_4$P$_{12}$ is an extremely rare case. To the best of our knowledge, this is the first thermodynamical observation of its kind.

This paper is organized as follows. After a description of the experimental details in the next section, we present the results of specific heat and magnetization measurements in §3. We compare them with the theoretical results based on the hyperfine interaction in §4, and discuss some remaining problems in §5. The final section (§6) is devoted to the summary of the paper. In the Appendix, we describe in detail the pseudo-spin representation for the ground triplet in a Pr ion to explain the new multiplet formation.

2. Experimental Details

Two single crystals, each used for the specific heat and magnetization measurements, are from the same batch of PrRu$_4$P$_{12}$ 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 LaRu$_4$P$_{12}$ single crystals grown by the same manner) 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. For the measurement of dc magnetization, a capacitive Faraday force magnetometer installed in a dilution refrigerator was used below 2 K and a SQUID magnetometer (MPMS, Quantum Design Co.) above 2 K. In both measurements, the magnetic field was applied along [100], [110], or [111] direction.

3. Results

Figure 1 shows the specific heat $C$ for magnetic fields applied along the three principal directions. The most significant finding is that a Schottky-type peak structure appears in zero field at $T_p = 0.30$ K and it shifts to higher temperatures with increasing field for all the field directions. It is obvious that this peak structure is caused by the thermal excitations in the Pr$_2$ ions from the following reasons. The phonon contribution $C_{ph} = \beta T^3$ with $\beta = 0.50$ mJ/K$^3$mol-f.u. determined for LaRu$_4$P$_{12}$ is negligibly small (see the dashed line in Fig. 1). Considering the extremely low carrier density in this $T$ range ($T \ll T_{co}$), the conduction-electron contribution $C_e = \gamma T$, 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 Pr$_1$ ions, since the
Fig. 1. (Color online) Specific heat $C(T, H)$ of PrRu$_4$P$_{12}$ for (a) $H \parallel [100]$, (b) $H \parallel [110]$, and (c) $H \parallel [111]$. The broken curve depicted in (a) represents the phonon part $C_{ph}$ estimated from the $C(T)$ data of LaRu$_4$P$_{12}$. (d) The field dependence of the peak temperature $T_p$. The dashed lines represent the low-$H$ and high-$H$ asymptotic behaviors.

CEF ground state is $\Gamma_1$ singlet and the 1st excited state $\Gamma_4^{(2)}$ (triplet) is well separated with the excitation energy of 94 K, the Pr1-ion contributions are invisibly small in the present $T$ range, except that enhanced nuclear contribution appears as $\sim 1/T^2$ at low temperatures in applied fields (see Fig. 4). As we demonstrate below, the peak structure can be accounted for as the thermal excitations in the 4f-electron-nuclear hyperfine-coupled multiplets of Pr2 ions. The involvement of the Pr2 nuclear degrees of freedom in this peak is evidenced by the fact that the estimated entropy release from the Pr2 ions in the temperature range of 0.13 to 4 K amounts to 9.18 J/Kmol-Pr2-ion, which exceeds already $R \ln 3$ expected from the $\Gamma_4^{(2)}$ triplet.
Fig. 2. (Color online) (a) The temperature dependence of magnetization $M(T)/(\mu_0 H)$ of PrRu$_4$P$_{12}$ measured for $H || [110]$. (b) Isothermal magnetization curves measured at 0.06 K for the three principal directions [100], [110], and [111] (data originally reported in ref. 13). An expanded view for $\mu_0 H < 1$ T is shown in the inset.

The field dependence of the peak temperature $T_p$ plotted in Fig. 1(d) indicates that there is a crossover at $\mu_0 H^* \sim 0.3$ T from a low-$H$ regime with field-insensitive $T_p$ to a high-$H$ regime with field-sensitive $T_p$, as depicted by the two dashed lines. In the latter regime, the slope of the linear behavior is estimated to be $T_p/(\mu_0 H) = 0.76 \pm 0.02$ K/T in $\mu_0 H = 2 \sim 6$ T. As shown in Fig. 1(d), the magnetic anisotropy in the $T_p$ vs $H$ is weak; it is only noticeable in the crossover field region ($H \sim H^*$). In contrast, the anisotropy in the peak height $C(T_p)$ is more pronounced especially in the crossover field region: e.g., $C(T_p, H || [111])/C(T_p, H || [100]) = 1.17$ in 0.2 T.

Figure 2(a) shows the temperature dependence of magnetization measured for several fixed fields along the [110] direction. For $\mu_0 H < 0.2$ T, $M/(\mu_0 H)$ shows a Curie-type divergence at low temperatures as expected for the magnetically degenerate $\Gamma_4^{(2)}$ triplet ground state of Pr2 ions. With increasing $H$ the divergence becomes weaker, and low-$T$ saturation becomes pronounced for $\mu_0 H > 0.2$ T. Isothermal magnetization curves at 0.06 K are shown in Fig. 2(b). Above $\sim 2$ T, $M(H)$ increases almost linearly up to at least $\sim 12.5$ T. In the high-$H$ region, it has been reported that $M(H)$ data agree well with those calculated using the CEF level schemes of Pr1 and Pr2 ions determined by inelastic neutron scattering (INS). In contrast, the CEF model fails to reproduce the $M(H)$ data below 1 T. As shown in the inset, $M(H)$ shows a significant rounding and a downward curvature remains up to $\sim 1$ T. This anomalous rounding, which cannot be explained with the Brillouin function for the $\Gamma_4^{(2)}$ triplet ground state of Pr2 ion, will be discussed below (see Fig. 5). In this field re-
gion, magnetic anisotropy is noticeable with $M(H \parallel [111]) \gtrsim M(H \parallel [110]) > M(H \parallel [100])$. This anisotropy seems to be thermodynamically consistent with the anisotropic peak height $C(T_p, H \parallel [111]) \gtrsim C(T_p, H \parallel [110]) > C(T_p, H \parallel [100])$ (see Fig. 1), i.e., specific heat is relatively insensitive to fields when applied along the hard magnetization axis [100].

4. Model Calculation

Now we study the microscopic origin of the observed low-temperature behaviors of PrRu₄P₁₂. Let us note again that there is no experimental indication of long range ordering within the temperature range explored, though the CEF ground state on one of the sublattice remains triply degenerate. This fact is in accord with the theoretical study showing that the effective magnetic interaction among the triplets in the charge order phase is extremely small.¹⁹) On the other hand, it is known that the hyperfine interaction between nuclear spin and ⁴f electron in Pr ion can influence on the thermodynamic quantities in the temperature region of the order of 0.1 K. Therefore, we analyze here possible consequences of the hyperfine interaction at the single Pr site.

In a Pr ion, ¹⁴¹Pr nucleus (the natural abundance of 100%) has a nuclear spin $I = 5/2$ so that we start from the following simple and well-established Hamiltonian²⁵–²⁷) to deal with each Pr ion (Pr₁ and Pr₂):

$$
\mathcal{H} = \mathcal{H}_{CEF} + A \mathbf{I} \cdot \mathbf{J} - (-g_J \mu_B \mathbf{J} + g_N \mu_N \mathbf{I}) \cdot \mu_0 \mathbf{H}.
$$

(1)

The first term corresponds to the CEF Hamiltonian for the cubic $T_h$ site symmetry,

$$
\mathcal{H}_{CEF} = A_4 (O_4^0 + 5O_4^4) + A_6^0 (O_6^0 - 21O_6^4) + A_6^2 (O_6^2 - O_6^6),
$$

(2)

where $O_n^m$’s are Stevens’ operator equivalents.²⁸) For the CEF parameters $A_4, A_6^0, A_6^2$, we use the set of values determined at 5 K by INS.¹³) The second term in eq. (1) represents the hyperfine interaction of a Pr ion and we use the coupling constant $A = +0.052$ K, given by theoretical calculations²¹,²²) and confirmed later by thermodynamical measurements for PrFe₄P₁₂ and PrOs₄Sb₁₂.⁶,²⁹,³⁰) We have neglected the quadrupolar hyperfine interaction, whose energy scale is calculated to be less than $|PI(2I - 1)/3| \sim 5 \times 10^{-4}$ K (see ref. 22 for the quadrupole coupling constant $P$). The third term in eq. (1) represents the Zeeman energy of the magnetic moments due to the $4f$-electron $-g_J \mu_B \mathbf{J}$ and due to the nuclear spin $g_N \mu_N \mathbf{I}$, 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 energy level scheme in applied fields is obtained by diagonalizing the Hamiltonian. Figure 3 shows the low-energy region for Pr₂ ion. At zero field the $\Gamma_4^{(2)}$ triplet of Pr₂ ion is reconstructed into three multiplets through the hyperfine coupling with the nuclear spin. This feature is well understood by using the pseudo-spin representation of the interaction as
Fig. 3. Calculated energy level scheme of the 4f-electron-nuclear hyperfine-coupled multiplets for the Pr2 $\Gamma_4^{(2)}$ triplet as a function of applied magnetic field. No visible field direction dependence appears in the low $H$ region.

described in the Appendix. In contrast, the Pr1 ion has the energetically well-separated $\Gamma_1$ singlet ground state so that a sextet nuclear state (corresponding to $I_z = +5/2 \sim -5/2$) is left in the low-energy region. In applied fields, the Van-Vleck magnetism of 4f-electrons leads to the enhanced nuclear magnetism on Pr1 ion through the hyperfine coupling. Note that, in $\mu_0 H < 1$ T (as shown in Fig. 3), the field direction dependence of the energy level scheme is hardly noticeable.

The $T$ and $H$ dependences of the specific heat are calculated separately for Pr2-ion ($C(\text{Pr2})$) and Pr1-ion ($C(\text{Pr1})$) (see Fig. 4). The experimental data of $C$ should be compared with $C(\text{Pr2})/2+C(\text{Pr1})/2$ since one formula unit of PrRu$_4$P$_{12}$ contains $0.5 \times \text{Pr2-ion}$ and $0.5 \times \text{Pr1-ion}$. At zero field, the Pr1 contribution $C(\text{Pr1})/2$ is almost zero (slight increase visible around 10 K is due to the $\Gamma_1 - \Gamma_4^{(2)}$ excitation). At 8 T it is still small enough compared to $C(\text{Pr2})/2$, although the hyperfine-enhanced nuclear contribution shows up as $C(\text{Pr1}) \propto (\text{AM}(\text{Pr1})/T)^2$ below $\sim 0.5$ K.

It is evident that the observed peak structure for $H = 0$ is reasonably well reproduced by $C(\text{Pr2})/2$. From the energy level scheme shown in Fig. 3, it is clear that the peak structure originates from the thermal excitations among the three multiplets. Note that if the value of $A$ were zero then the three-multiplet structure would collapse and the $C(T)$ peak structure would disappear. Since the three multiplets have fixed ratios of the energy separation ($-7/2 : -1 : +5/2$) and the degeneracy ($4 : 6 : 8$) as shown in the Appendix, the peak height $C(T_p) = 3.43$ J/Kmol-f.u. is a universal $A$-independent constant. The observed value 3.03 J/Kmol-f.u. is close to this theoretical expectation. The increase in $C(\text{Pr2})/2$ above $\sim 5$ K is
Fig. 4. (Color online) Model calculation of the specific heat $C(T, H)$ for PrRu$_4$P$_{12}$. Contributions from Pr2 ion ($C(\text{Pr2})/2$) and from Pr1 ion ($C(\text{Pr1})/2$) are shown separately. No noticeable magnetic anisotropy is present in the $T$ and $H$ regions shown here. $C(\text{Pr1})/2$ (shown by thin lines for $\mu_0H = 0$ and 8 T) has a very small contribution. Contributions from Ru and P nuclei are negligibly small.$^{31}$

due to the thermal excitations to the 1st excited $\Gamma_1$ lying at 36 K.$^{13}$ In high fields, the peak shifts to higher temperatures and the height approaches 2.65($=5.30/2$) J/Kmol-f.u., which is the expected value for a triplet with an equal energy separation.

Concerning the magnetization, as shown in Fig. 5, the Pr2 contribution $M(\text{Pr2})/2$ dominates over the Pr1 contribution $M(\text{Pr1})/2$. $M(T)/\mu_0H$ for $\mu_0H \leq 1$ T shown in Fig. 5(a) agree quite well with the observed data shown in Fig. 2. A fictitious case corresponding to no hyperfine coupling ($A = 0$) is also drawn for $M(\text{Pr2})/2$ at 0.05 T. Comparing the two curves, we find that a partial suppression in the low-$T$ Curie-type divergence is caused by the hyperfine coupling. Our model calculation of magnetization curves at 0.06 K shown in Fig. 5(b) also reproduces well the measured data shown in Fig. 2(b). At high fields, the small magnetic anisotropy with $M(H \parallel [111]) \gtrsim M(H \parallel [110]) > M(H \parallel [100])$ in the calculated $M$ agrees with that in the measured data, confirming the reported CEF parameters of the Pr ions.$^{13}$ Below 2 T, the observed anomalous rounding in the $M(H)$ curves is nicely reproduced by the calculation. Comparing with the calculation for $A = 0$, we conclude that this rounding is due to the hyperfine coupling.

5. Discussions

We have shown that the overall behaviors of the observed low-temperature anomalies, i.e., the peak structure in $C(T)$ and the rounding in the low-field $M(H)$ curves, provide an evidence for the formation of the 4$f$-electron-nuclear hyperfine-coupled multiplets on Pr2 ions.
Fig. 5. (Color online) Model calculation of the magnetization $M(T, H)$ for PrRu$_4$P$_{12}$. $M(\text{Pr1})/2$ and $M(\text{Pr2})/2$ represent the contributions from Pr1 and Pr2 ions, respectively. (a) The $T$ dependences of $M$ for several fields. $M(\text{Pr2})/2$ at 0.05 T for a fictitious case with $A = 0$ is drawn with thin broken lines. (b) Isothermal magnetization curves at 0.06 K for [100], [110], and [111]. At high fields, the small magnetic anisotropy with $M(H \parallel [111]) \gtrsim M(H \parallel [110]) > M(H \parallel [100])$ is due to $M(\text{Pr2})/2$ ($M(\text{Pr1})/2$ has the opposite anisotropy with a smaller magnitude). The calculation for $A = 0$ is shown with thin broken lines below 2 T.

Let us note that the hyperfine-coupled multiplet formation has been observed on the periodic Pr lattice. The $\Gamma^{(2)}_4$ triplet of Pr ion has active magnetic dipole and electric quadrupole moments. Usually, inter-ion interactions of those moments in compounds tend to drive them into ordering at low temperatures. Actually, in PrB$_6$, PrOs$_4$As$_{12}$, and PrCu$_4$Au, all of which have a triplet ground state, antiferromagnetic orderings set in at 7, 2.3, and 2.5 K, respectively. In this respect the charge-ordered phase in PrRu$_4$P$_{12}$ is a rare system, where the hyperfine-coupled multiplet lattice of the triplet Pr ions is observed without showing any phase transition down to 60 mK. This remarkable feature is produced by the charge ordering below $T_{co}$, giving rise to the large Pr2-Pr2 distance (equal to the cubic lattice constant $a=8.0420(9)$ Å$^{35}$) and the disappearance of a large amount of conducting electron carriers, both of which weaken inter-Pr-ion RKKY-type exchange interactions. Furthermore, by the characteristic electronic structure, where the interactions among the 4f-electrons of Pr ions are mediated by mixing with the $a_u$ molecular orbital on P$_{12}$, magnetic interactions are suppressed as demonstrated by a microscopic calculation.$^{19}$

Although the present model successfully accounted for the overall behaviors of the observed low-temperature anomalies, there still remain following discrepancies between the measurements and the calculations: (i) the observed $T_p = 0.30$ K is higher than the calculated value
of 0.17 K and (ii) the anomalous magnetic anisotropies appear in $C$ and $M$ in the crossover field region of $H \sim H^*$.

Within the model (1), in order to account for the observed $T_p = 0.30$ K at zero field, a larger value of $A = +0.091$ K would be needed. However, this leads to an inconsistency. The value of $A$ can be accurately estimated with the $C(T)$ data at $\mu_0 H = 8$ T. Below 1 K, $M(\text{Pr2}) = g_J \langle J \rangle_{\text{Pr2}}$ as well as $M(\text{Pr1}) = g_J \langle J \rangle_{\text{Pr1}}$ is saturated and 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 $\mu_0 H - A \langle J \rangle / g_N \mu_N$ for each Pr ion. From the fitting to the $C(T)$ data shown in Fig. 1, we obtain $A = +0.050(2)$ K for PrRu$_4$P$_{12}$. The values for $A$ in metallic PrFe$_4$P$_{12}$ and PrOs$_4$Sb$_{12}$ and extremely-low-carrier PrRu$_4$P$_{12}$ are remarkably close to each other. This means that the intra-ion 4f-electron-nuclear hyperfine coupling is not affected by the background electronic band structure in materials.

There might be other interactions missing in eq. (1) that possibly yields additional energy splittings in the multiplets, whereby resulting in the higher value of $T_p$. The magnetic dipole and electrical quadrupole moments of the $\Gamma_4^{(2)}$ triplet can play a role in such interactions. However, it is difficult to explore this scenario further since no observations have been reported to date on time-reversal symmetry breaking and Pr2-site local symmetry lowering.

As another possible explanation, the discrepancies may be caused by a many body effect associated with the $c$-$f$ hybridizations. The 4f-electron-nuclear hyperfine-coupled multiplets have composite multipole moments and these internal degrees of freedom can be coupled to the slightly remaining conduction electrons in the charge-ordered state. The anomalously $T$- and $H$-dependent transport properties observed below $\sim 10$ K might be reflecting this effect. This interesting possibility should be investigated in future studies.

Finally we note that the antiferromagnetic hyperfine coupling between the nuclear spin $I = 5/2$ and $\Gamma_4^{(2)}$ triplet leaves the effective total spin of $F' = 3/2$ at low temperatures ($T \ll A$). Needless to say, this finite degree of freedom should be lifted at very low temperatures via inter-ion interactions.

6. Summary

Specific heat and magnetization measurements have been carried out to investigate the low-temperature properties of the Pr2-ion CEF triplet ground state of the charge order phase in PrRu$_4$P$_{12}$. It has been revealed that the specific heat shows a Schottky-type broad peak structure at $T_p = 0.30$ K at zero field and the magnetization curve at 0.06 K shows a remarkable rounding below 1 T. We have demonstrated that these anomalous behaviors can be well explained by taking into account the hyperfine coupling of Pr2 ions, thus showing that the 4f-electron-nuclear hyperfine-coupled multiplets are formed in PrRu$_4$P$_{12}$. A comparison with the model calculation shows that there still remain some discrepancies to be understood, i.e., the higher value of $T_p$ in zero field and the small low-$H$ magnetic anisotropies as demon-
strated in the $C(T)$ and $M(H)$ data. Since 4$f$-electron-nuclear hyperfine-coupled multiplets have high degeneracies, the associated multipolar degrees of freedom might be relevant to the appearance of the discrepancy, possibly by a many body effect through the $c$-$f$ hybridizations.

**Acknowledgments**

We thank H. Harima, H. Ishii, K. Iwasa, T. Mito, and C. Sekine for valuable discussions. This work was supported by the Grant-in-Aid for Scientific Research on Priority Area "Skutterudite" (15072206) and "Ubiquitous" (20045015), and on Innovative Areas "Heavy Electrons" (20102007, 21102520) of MEXT and (C: 20540359, 21540368) and (B: 20340094) of JSPS, Japan.

**Appendix: Pseudo-spin Description of Hyperfine Interaction**

In eq. (1), the CEF Hamiltonian $H_{CEF}$ leaves the triple degeneracy at the Pr2 site. Here we study how this degeneracy is affected by the hyperfine interaction $A I \cdot J$ using the pseudo-spin representation. The triplet $\Gamma^{(2)}_4$ at the Pr2 site is given as follows

$$|\Gamma^{(2)}_4(j)\rangle = \sqrt{1 - d^2} |\Gamma_5(j)\rangle + d |\Gamma_4(j)\rangle,$$

where $j$ is an index to specify each triplet ($j = +, 0, -$). $|\Gamma_5(j)\rangle$ and $|\Gamma_4(j)\rangle$ are two sets of triplet wave functions for the $O_h$ group:

$$|\Gamma_5(\pm)\rangle = \pm \sqrt{\frac{7}{8}} (|\pm 1\rangle \mp |\mp 3\rangle),$$

$$|\Gamma_5(0)\rangle = \sqrt{\frac{1}{2}} (|2\rangle - |-2\rangle),$$

$$|\Gamma_4(\pm)\rangle = \mp \sqrt{\frac{1}{8}} (|\pm 3\rangle \mp |\pm 1\rangle),$$

$$|\Gamma_4(0)\rangle = \sqrt{\frac{1}{2}} (|4\rangle - |-4\rangle).$$

The coefficient $d$ in eq. (A.1) is a parameter of mixing due to $T_h$, which is known to be small in PrRu$_4$P$_{12}$.

We introduce the $S = 1$ pseudo-spin operator $\tau$ and regard the $\Gamma^{(2)}_4$ triplet with $j = \pm, 0$ as the pseudo-spin states corresponding to $\tau_z = \pm 1, 0$. Then, the original dipole operator is represented as $J = c\tau$ with $c = 5/2 - 2d^2$. Therefore, the hyperfine interaction $A I \cdot J$ can be replaced by $\lambda I \cdot \tau$ with an effective coupling constant $\lambda = cA$. Then, it is clear that the degenerate 18($= 3 \times 6$) states $|\tau_z, I_z\rangle$ are split into three multiplets. Introducing an effective total spin $F' = \tau + I$, the three multiplets can be labeled as $F' = 3/2, 5/2$, and 7/2. It is interesting to note that the half-integer spin multiplets are formed from the integer-spin 4$f$-electron states of non-Kramers Pr ion through the hyperfine coupling with the half-integer-spin $^{141}$Pr nucleus. The characteristic features of each multiplet are listed in Table A.1.

The magnetic moment of each multiplet can be expressed as $-g^* \mu_B F'$, where the effec-
Table A-1. Characteristic features of the three multiplets formed by the hyperfine coupling on Pr2 ion. The effective total spin $F'$, the energy $E_i$, the effective $g$-factor $g^*$, and the magnetic moment $-g^*\mu_B F'$ are listed.

| $F'$ (degeneracy) | energy $E_i$ | $E_i - E_0$ (K) | $g^*$ | $-g^*F'$ (µB) |
|------------------|-------------|-----------------|-------|--------------|
| 7/2 (8)          | $E_2 = +5/2\lambda$ | +0.74 | +0.541 | -1.894 |
| 5/2 (6)          | $E_1 = -\lambda$ | +0.31 | +0.216 | -0.540 |
| 3/2 (4)          | $E_0 = -7/2\lambda$ | 0    | -0.760 | +1.140 |

tive $g$-factor $g^*$ has a specific value for each multiplet as listed in Table A-1. When a weak magnetic field is applied, each multiplet shows the Zeeman splitting (see Fig. 3) with the $g^*$ value, independent on the field direction. With further increasing the field, the Zeeman energy becomes dominant over the hyperfine coupling energy and the 18 states are asymptotically separated into three sextets, i.e., $|+1, I_z\rangle$, $|0, I_z\rangle$, and $|-1, I_z\rangle$ with $I_z = +5/2 \sim -5/2$ in high fields (so called the Paschen-Back effect). For $|\pm 1, I_z\rangle$, since the 4f-electron polarization $\langle J \rangle$ provides strong effective field $-A\langle J \rangle/g_N\mu_N$ on the Pr nucleus, both sextet splits into six equally-spaced lines, in contrast to the degenerate sextet for $|0, I_z\rangle$. The crossover field between the two field regimes appears to be $\sim 0.3$ T, which is consistent with $\mu_0H^* \sim 0.3$ T in Fig. 1(d).
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