

Multipolar Phase Transition in the $4f^2$ fcc Lattice Compound PrCdNi_4

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Transport and magnetic properties of a $4f^2$ fcc lattice compound, PrCdNi_4 , were studied. The magnetic susceptibility, $\chi(T)$, follows the Curie–Weiss law from 300 K to 20 K, as expected for a free Pr^{3+} ion. As the temperature decreases below 5 K, $\chi(T)$ approaches a constant, indicating van-Vleck paramagnetic behavior. The specific heat, $C(T)$, displays a broad shoulder at around 4 K, which can be reproduced by a doublet-triplet two-level model with an energy gap of 12 K. These results suggest a non-magnetic Γ_3 doublet ground state of the Pr^{3+} ion in the cubic crystalline electric field. $C(T)$ exhibits a peak at $T_O = 1.0$ K and this peak remains robust against magnetic fields up to 5 T. In powder neutron diffraction measurements, no magnetic reflection was observed at $0.32 \text{ K} < T_O$. Two anomalies at $B = 2.1$ and 5.3 T in magnetoresistance $\rho(B)$ at 0.05 K likely originate from switching in the order parameter. These results suggest that the phase transition at T_O is ascribed to an antiferro-type order of the electric quadrupole or magnetic octupole of the Γ_3 doublet in the $4f^2$ fcc lattice.

I. INTRODUCTION

Praseodymium-based cubic compounds with a $4f^2$ configuration have attracted significant interest [1–3]. In these compounds, a strong interaction between their active multipolar degrees of freedom in the (quasi-) degenerated crystalline electric field (CEF) ground states and conduction electrons leads to various phenomena such as metal-insulator transition [5, 6], heavy-fermion superconductivity [7–9], and non-Fermi liquid (NFL) behavior due to the two-channel (quadrupole) Kondo effect [10–12].

When the Pr^{3+} ion site has a cubic point group, the CEF ground state can be a non-Kramers doublet. In this state, the magnetic dipole is quenched, and instead, the electric quadrupole and magnetic octupole become active. As a result, the quadrupole or octupole order may manifest itself [13–16], while the two-channel Kondo effect is expected to occur if the quadrupoles are over-screened by equivalent conduction bands [12, 17–19]. An example is PrPb_3 , which has a non-Kramers Γ_3 doublet ground state, showing an antiferroquadrupole (AFQ) order at $T_Q = 0.4$ K [20–22]. The order parameter is the O_2^0 -type quadrupole [23]. Neutron diffraction measurements in a magnetic field along the [100] direction revealed incommensurate sinusoidal modulation of

the quadrupoles [24]. This modulated structure suggests not only long-range quadrupole interaction mediated by conduction electrons but also the quenching of the quadrupoles due to hybridization with the conduction electrons. On the other hand, no long-range order of quadrupoles has been found in PrAg_2In and PrMg_3 with the Γ_3 doublet ground state. In these compounds, quadrupoles are prevented from ordering by either the quadrupole Kondo effect or atomic disorder inherent in their Heusler-type structures which lowers the site symmetry of Pr^{3+} [25–27].

The discovery of the coexistence of the superconductivity and AFQ order in $\text{PrIr}_2\text{Zn}_{20}$ has drawn significant attention to Pr 1-2-20 systems crystallizing in a cubic $\text{CeCr}_2\text{Al}_{20}$ -type structure [28]. $\text{PrIr}_2\text{Zn}_{20}$ exhibits the AFQ order at $T_Q = 0.11$ K below which the superconducting transition was observed at $T_c = 0.05$ K [29–37]. The coexistence of the superconductivity and quadrupole order was also observed in isostructural $\text{PrRh}_2\text{Zn}_{20}$ [38, 39], $\text{PrTi}_2\text{Al}_{20}$ [40–44], and $\text{PrV}_2\text{Al}_{20}$ [40, 45]. These findings imply that the superconductivity is related to the interaction between conduction electrons and the multipoles in the non-Kramers doublet [46]. Moreover, the NFL behaviors were observed not only in $\text{PrIr}_2\text{Zn}_{20}$ [10] and $\text{PrRh}_2\text{Zn}_{20}$ [39] but also in dilute Pr systems $\text{Y}(\text{Pr})\text{Ir}_2\text{Zn}_{20}$ [11, 47–49] and $\text{Y}(\text{Pr})\text{Co}_2\text{Zn}_{20}$ [50]. These NFL behaviors probably result from the quadrupole Kondo effect to form a composite electronic order involving the local quadrupole and the itinerant

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bands as the ground state [12, 51–54].

Face-centered cubic (fcc) compounds $\text{Pr}T\text{Ni}_4$ ($T = \text{Mg}$ and In) are another family of Pr-based intermetallic compounds having the Γ_3 doublet ground state [55–58]. They crystallize in a cubic MgSnCu_4 -type structure [59]. As illustrated in Fig. 1(a), since the Pr sublattice is equivalent to an fcc lattice, we anticipate an unusual ground state due to the geometrical frustration between active multipoles of the nearest neighbor Pr ions. Additionally, anisotropic terms in the quadrupole interactions on the fcc lattice become effective alongside isotropic ones [61, 62]. These potentials are quite distinct from the Pr-based compounds mentioned above in terms of the anisotropic and competitive multipolar interaction. In fact, though PrInNi_4 exhibits ferromagnetic order at $T_C = 0.75$ K due to exchange interaction induced by coupling between the Γ_3 doublet and the first-excited triplet [57, 58], PrMgNi_4 exhibits no phase transition down to 0.1 K [55]. This hindered quadrupole order in PrMgNi_4 was attributed to a symmetry lowering caused by excess Mg atoms substituting for the Pr atoms or strong hybridizations between the $4f^2$ and conduction bands [55]. Otherwise, if the isotropic and anisotropic interactions in the fcc lattice are relatively weak compared to the energy splitting from the Γ_3 doublet to the excited Γ_1 singlet, the quadrupole order may be suppressed [61, 62].

In our current study, we have focused on PrCdNi_4 crystallizing in the cubic MgSnCu_4 -type structure [63]. As shown in Fig. 1(b), Pr is surrounded by Cd atoms at $4c$ site and Ni atoms at $16e$. If the atomic disorder is reduced compared to the sister compound PrMgNi_4 [55], the electric quadrupolar and/or magnetic octupolar order of the non-Kramers doublet may not be hindered. With bearing this in mind, we conducted measurements of the transport and magnetic properties of PrCdNi_4 to determine the CEF ground state and understand the possible involvement of quadrupole and/or octupole in the formation of the ground state. Powder neutron diffraction measurements were performed to judge whether the phase transition results from a magnetic or non-magnetic origin. Recently, physical properties of the series of $R\text{CdNi}_4$ have been reported for $R = \text{Ce}, \text{Nd}, \text{Sm},$ and Gd-Tm [64] except for $R = \text{Pr}$.

II. EXPERIMENTAL PROCEDURE

A. Preparation and characterization of samples

We synthesized samples of PrCdNi_4 using the Cd self-flux method. First, we prepared the binary PrNi_4 alloy by arc melting. Substantially, we sealed the PrNi_4 ingot and Cd shots in double quartz amples in an argon atmosphere. The ampoule was then heated up to 1100°C in an electric furnace and slowly cooled down. At 500°C , the ampoule was quickly removed from the furnace and centrifuged to remove the molten Cd flux. The PrCdNi_4 samples were cubes of typically 3.0 mm^3 and found to

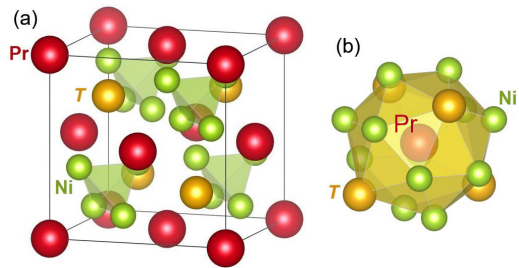


FIG. 1. (a) Cubic MgSnCu_4 -type crystal structure of $\text{Pr}T\text{Ni}_4$ ($T = \text{Mg}, \text{Cd},$ and In) with the space group of $F\bar{4}3m$ [59]. In the structure, large (red) spheres represent Pr atoms, the small (orange) spheres represent T atoms, and the tetrahedra are formed by four Ni atoms shown with the (green) spheres. The Pr sublattice forms an fcc lattice. (b) A Pr-centered atomic cage made of four T atoms at $4c$ and twelve Ni atoms at $16e$. The crystal structure images were drawn using VESTA [60].

consist of grains smaller than 0.3 mm , as characterized by metallographic examination. The grain size was too small to select single crystalline samples for our transport and magnetic measurements.

The samples were analyzed using powder x-ray diffraction and electron-probe microanalysis (EPMA). Back-scattered electron images and x-ray diffraction patterns are shown in Supplementary Material [65]. The atomic compositions were determined by averaging over 10 different regions for each sample with a JEOL JXA-8200 analyzer. Assuming that the sum of the compositions of the Pr and Cd atoms were 2, the atomic ratio of the sample batch for measurements was determined as $\text{Pr}_{1.00(1)}\text{Cd}_{1.00(1)}\text{Ni}_{3.89(4)}$, where the numbers in parentheses are the standard deviations. It is noted that the composition obtained for Pr and Cd closely matches the stoichiometric ratio, which remains consistent across samples within the standard deviations. Small amounts of impurity phases of $\text{PrNi}_2\text{Cd}_{20}$ and PrNi_5 were detected not only in the backscattered electron images but also in the powder x-ray diffraction patterns. The powder x-ray diffraction pattern confirms the cubic MgSnCu_4 -type structure for the main phase. The single-crystal x-ray structural analysis was performed at 293 K with a crystal smaller than 0.2 mm using the $\text{Mo } K\alpha$ radiation with the wavelength of $\lambda = 0.71073 \text{ \AA}$, monochromated by a multilayered confocal mirror using a Rigaku XtaLAB Synergy-DW area-detector diffractometer. Details of the measurement, data collection, and refinement are described in Supplemental Materials [65]. Figure 1(a) shows the cubic MgSnCu_4 -type structure of PrCdNi_4 [63]. In this structure, the Pr atoms occupy the fcc position of the unit cell, and the point group of the Pr site is the cubic T_d . The structural refinement did not show any evidence for the site exchange between Pr and Cd sites. The lattice constant was evaluated as $a = 7.12932(8) \text{ \AA}$ for PrCdNi_4 . This value is 0.15% larger than $7.11832(16) \text{ \AA}$ for PrMgNi_4 , determined by refining the powder x-ray

diffraction pattern at room temperature.

B. Physical property measurements

The electrical resistance was measured using a standard four-probe AC method. The measurements were done with a Gifford-McMahon-type refrigerator for 3–300 K and with a commercial Cambridge Magnetic Refrigerator mFridge mF-ADR50 for 0.1–4 K. The magnetic field dependences of $\rho(B)$ were measured up to 17.5 T at temperatures down to 0.05 K by the AC method using a ^3He - ^4He dilution refrigerator equipped with a 20 T magnet at NIMS. Magnetization was measured from 1.8 to 300 K in magnetic fields for $B \leq 5$ T using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS). For $0.3 < T < 4.2$ K in $B \leq 8.5$ T, a capacitive Faraday method was adopted. Thereby, we used a high-resolution capacitive force-sensing device installed in a ^3He single-shot refrigerator (Heliox, Oxford Instruments) [66]. The specific heat was measured using the thermal relaxation method in the temperature range of $0.4 < T < 300$ K for $B \leq 7$ T with a Quantum Design physical property measurement system (PPMS).

In order to observe possible magnetic reflections in an ordered phase, powder neutron diffraction experiments were conducted using the ISSP triple-axis spectrometer GPTAS at JRR-3M in JAEA at Tokai, Japan [67]. Neutron beams with a wavelength of $\lambda = 2.4563$ Å (~ 13.7 meV) were obtained by the 002 reflection of a pyrolytic graphite (PG) monochromator. Horizontal collimation of 40'-Monochromator-40'-Sample-40'-Analyzer-80' for a triple-axis mode was utilized. A ^3He refrigerator achieved the base temperature at 0.32 K. In order to prevent strong neutron absorption of Cd atoms, the powdered sample of 0.35 g was thinly spread (approximately 0.2 mm thick) on a single-crystalline silicon wafer [68, 69]. The scattering plane was tilted by 1 degree away from the [100] direction, which is perpendicular to the surface of the silicon wafer.

III. RESULTS AND DISCUSSION

A. Electrical resistivity

The temperature-dependent electrical resistivity, $\rho(T)$, of PrCdNi_4 is compared with that of PrMgNi_4 [55] in Fig. 2. The residual resistivity ratio (RRR), evaluated as $\rho(300 \text{ K})/\rho(0.1 \text{ K})$, is 6.3 for PrCdNi_4 . This RRR value is more than two times higher than 2.8 for a single crystalline PrMgNi_4 [55]. The higher RRR value for PrCdNi_4 is consistent with the EPMA result. The composition of $\text{Pr}:\text{Cd}:\text{Ni} = 1.00(1):1.00(1):3.89(4)$ is close to the stoichiometric ratio by assuming that the total composition of Pr and Cd is 2. For the PrMgNi_4 sample, on the other hand, the composition was $\text{Pr}:\text{Mg}:\text{Ni}$

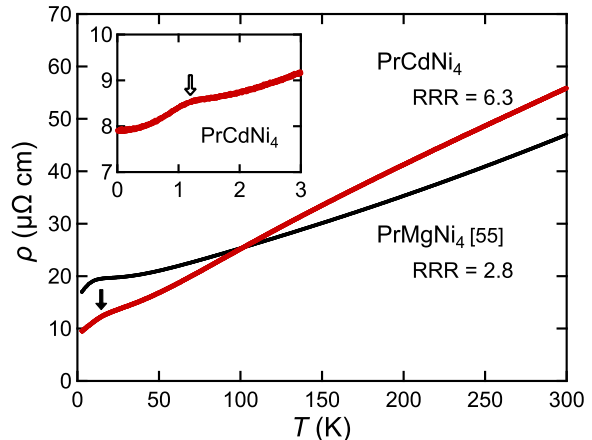


FIG. 2. Temperature dependence of the electrical resistivity $\rho(T)$ of PrCdNi_4 (red) and PrMgNi_4 (black) [55]. The inset displays the $\rho(T)$ data for $T \leq 3$ K. The open arrow indicates a broad shoulder at 1.2 K.

$= 0.94(1):1.06(1):3.86(2)$, where excess Mg atoms substitute for the Pr atoms, leading atomic disorder [55].

As shown with the arrow in the main panel of Fig. 2, $\rho(T)$ for PrCdNi_4 exhibits a shoulder at around 15 K, possibly due to the increase in scattering of conduction electrons by thermal excitations of the $4f^2$ electrons between the CEF levels [70]. This energy scale is consistent with the 12 K energy gap between the ground state Γ_3 doublet and the first excited triplet, as discussed later. Focusing on the lower temperature range in the inset of Fig. 2, there is a broad shoulder centered at around 1.2 K. This shoulder results from a phase transition observed in the specific heat measurements shown later.

B. Magnetic susceptibility and isothermal magnetization

Figure 3 shows the temperature dependence of the magnetic susceptibility $\chi(T)$ and the inverse $\chi^{-1}(T)$ of PrCdNi_4 measured in the magnetic field of $B = 1$ T. $\chi^{-1}(T)$ follows a modified Curie–Weiss equation: $\chi(T) = C/(T - \theta_p) + \chi_0$, where C , θ_p , and χ_0 represent the Curie constant, paramagnetic Curie temperature, and temperature independent susceptibility, respectively. The (red) solid curve represents the fit to the $\chi(T)$ data between 20 and 300 K using the above equation with $\theta_p = -8.3(4)$ K and $\chi_0 = 5.7(2) \times 10^{-4}$ emu/mol. The negative value of θ_p indicates antiferromagnetic intersite interaction between the Pr moments. The effective magnetic moment was evaluated to be $\mu_{\text{eff}} = 3.70(1) \mu_B/\text{f.u.}$, which is moderately close to the value of $3.58 \mu_B$ for a free trivalent Pr ion. On cooling below 4 K, $\chi(T)$ does not diverge but approaches a constant, as shown in the inset. This is a van-Vleck paramagnetic behavior of a nonmagnetic CEF ground state of the Pr ion. As shown

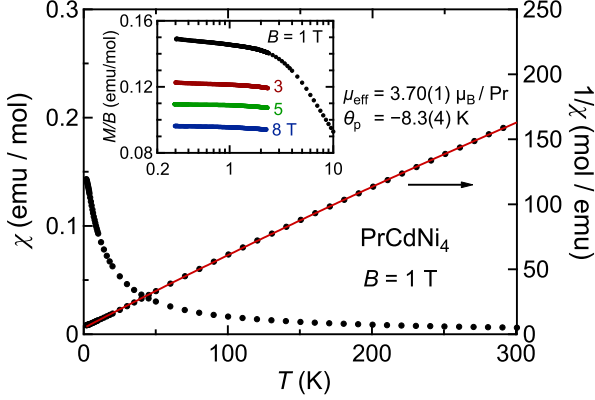


FIG. 3. Temperature dependence of the magnetic susceptibility, $\chi(T)$, and the inverse $\chi^{-1}(T)$ of PrCdNi_4 measured in a magnetic field of $B = 1$ T. The χ^{-1} data can be fitted with a modified Curie-Weiss equation. See text in detail. The inset shows the magnetization divided by the magnetic field, $M(T)/B$, at magnetic fields of $B = 1, 3, 5,$ and 8 T, without any offset.

in the inset of Fig. 3, the $M(T)/B$ data at $B = 1, 3, 5,$ and 8 T do not exhibit a clear anomaly for $T < 2$ K.

The isothermal magnetization $M(B)$ data of PrCdNi_4 at temperatures of $0.3, 0.8, 1.5, 4.2,$ and 10 K are shown in Fig. 4. The data for temperatures below 4.2 K were obtained by the capacitive Faraday method, while the data at 10 K were measured by the SQUID magnetometer. The $M(B)$ data for $T \leq 4.2$ K are vertically offset for clarity. All $M(B)$ data show a monotonous increase with increasing magnetic field up to 8.5 T. These magnetization curves are reproduced reasonably well using a CEF

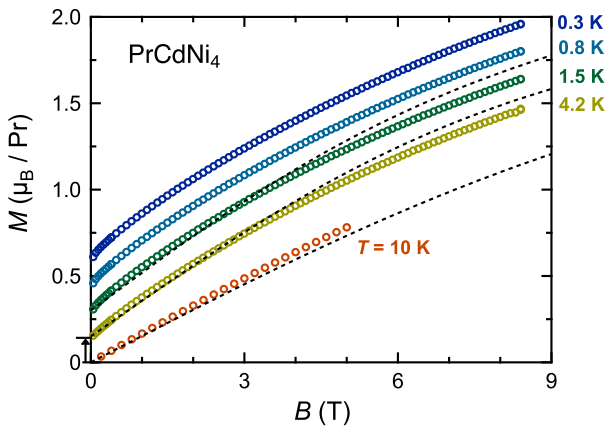


FIG. 4. Isothermal magnetization $M(B)$ of PrCdNi_4 at $T = 0.3, 0.8, 1.5, 4.2,$ and 10 K. The data at $T \leq 4.2$ K are vertically offset for clarity. The dashed curves are calculations with the CEF parameters of $W = -3.3$ K and $x = 0.8$ and antiferromagnetic exchange interaction of $K_1 = -0.6$ K between the Pr moments. See text in detail.

level scheme and antiferromagnetic exchange interaction, which will be discussed later.

C. Specific heat and magnetic entropy

The specific heat $C(T)$ data of PrCdNi_4 for $T \leq 15$ K are shown in Fig. 5(a). Since a nonmagnetic counterpart LaCdNi_4 could not be synthesized, the phonon contribution $C_{\text{ph}}(T)$ was evaluated using the Debye model with $\theta_D = 270.7(6)$ K as described in the Supplemental Materials [65, 71]. By subtracting $C_{\text{ph}}(T)$ from the total $C(T)$ data, we estimated the magnetic contribution $C_{\text{mag}}(T)$. C_{mag} exhibits a shoulder at around 4 K, which is attributable to the Schottky specific heat due to thermal excitations from the CEF ground state to excited levels.

A two-level Schottky model provides the expression of $C(T)$ with the equation as

$$C = \frac{nm\Delta^2}{k_B T^2} \frac{e^{-\Delta/k_B T}}{(n + me^{-\Delta/k_B T})^2}, \quad (1)$$

where n and m represent the degeneracy of the ground and excited multiplets, respectively, and Δ is the energy gap between the two levels. Considering the van-Vleck paramagnetic behavior shown in the inset of Fig. 3, the CEF ground state of the Pr ion for the cubic T_d point group can be either the nonmagnetic Γ_1 singlet or Γ_3 doublet. Calculations with a singlet-triplet (Γ_1) two-

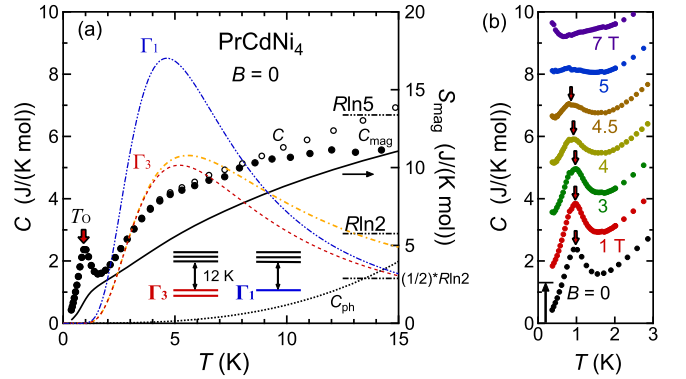


FIG. 5. (a) Temperature variations of the specific heat $C(T)$ (open circles) and the magnetic contribution C_{mag} (close circles), as well as the magnetic entropy S_{mag} (right-hand scale) of PrCdNi_4 . C_{ph} is the phonon contribution evaluated using a Debye model as explained in Supplemental Materials [65]. The (red) dashed and (blue) dotted curves represent the Schottky specific heat calculated by a two-level model of doublet-triplet (Γ_3) and singlet-triplet (Γ_1) with an energy gap of 12 K. The (orange) dot-dashed line represents the calculation with $W = -3.3$ K and $x = 0.8$ determined for PrMgNi_4 [56]. (b) The specific heat $C(T)$ at magnetic fields of $B \leq 7$ T. The data for $B \geq 1$ T are offset for clarity. The arrows indicate the peak temperature, which remains robust against magnetic fields up to 4.5 T.

level model and a doublet-triplet (Γ_3) one, with an energy split of 12 K, are shown with the (red) dashed and (blue) dotted curves, respectively. It is assumed that the first excited state is a triplet, either the Γ_4 or Γ_5 triplet [72]. The respective two-level schemes are depicted in the lower part of Fig. 5(a). The Γ_3 model better reproduces the shoulder of $C_{\text{mag}}(T)$ at around 4 K than the Γ_1 model. Therefore, the CEF scheme likely consists of the Γ_3 doublet ground state and the first excited triplet. Note that the absolute value of C_{mag} at around 4 K is smaller than that expected by the Γ_3 model. This discrepancy may be ascribed to a relatively small fraction of the pristine PrCdNi_4 in the measured sample, which could contain some impurities of PrNi_5 and $\text{PrNi}_2\text{Cd}_{20}$. On the other hand, the larger value of C_{mag} observed above 7 K may result from the contribution of the CEF levels at higher energy. Otherwise, it is attributable to an underestimation of C_{ph} .

In order to verify this CEF scheme, we calculated the isothermal magnetization. The cubic CEF Hamiltonian is described by the equation as

$$\mathcal{H}_{\text{CEF}} = W \left[\frac{x}{60} (O_4^0 + 5O_4^4) + \frac{1-|x|}{1260} (O_6^0 - 21O_6^4) \right],$$

where W and x represent the CEF parameters, and O_n^m 's stand for the Stevens operators [72]. The energy gap of 12 K between the Γ_3 doublet and the first excited triplet is nearly the same as that observed in PrMgNi_4 [55], although it is anticipated that the energy splitting would be smaller in PrCdNi_4 due to its larger lattice parameter. Therefore, we use the parameters of $W = -3.3$ K and $x = 0.8$ for PrMgNi_4 as determined by the inelastic neutron scattering experiments; $\Gamma_3(0)$ – $\Gamma_4(13.2$ K)– $\Gamma_1(31.7$ K)– $\Gamma_5(134.6$ K) [56]. The isothermal magnetization is calculated with the above CEF parameters and an intersite magnetic interaction using the following Hamiltonian.

$$\mathcal{H} = \mathcal{H}_{\text{CEF}} + g_J \mu_B \mathbf{J} \mathbf{B} - K_1 \langle \mathbf{J} \rangle \mathbf{J},$$

where $g_J = 4/5$ is the Landé g -factor for a Pr^{3+} ion, \mathbf{J} a total angular momentum, and K_1 a coefficient of the magnetic inter-site interaction between the Pr ions. The isothermal magnetization calculated for $\mathbf{B} \parallel [111]$ with antiferromagnetic interaction of $K_1 = -0.6$ K is shown with the dashed lines in Fig. 4. The $M(B)$ calculations at $T = 1.5$, 4.2, and 10 K match the data of the polycrystalline sample. It is noted that the specific heat calculated using the above CEF parameters moderately reproduces the shoulder of C_{mag} around 4 K, as depicted by the (orange) dot-dashed line in Fig. 5. These results give further support that the CEF ground state is the Γ_3 doublet carrying the electric quadrupole and magnetic octupole.

With decreasing temperature below 2 K, $C_{\text{mag}}(T)$ exhibits a peak at $T_O = 1.0$ K. This peak is the manifestation of a phase transition of the Γ_3 doublet. It is crucial to exclude the contribution of the impurity phases; neither

PrNi_5 nor $\text{PrNi}_2\text{Cd}_{20}$ exhibit any phase transition near 1 K [73–76]. The magnetic entropy S_{mag} , estimated by integrating the C_{mag}/T data with respect to temperature, is plotted on the right-hand axis of Fig. 5(a). Here, we assumed that the C_{mag}/T would approach zero linearly as T decreases from 0.4 K to 0 K. Then, we estimated the magnetic entropy S_{mag} at 0.4 K to be 0.21 J/K, which was added to $S_{\text{mag}}(T)$ for $T > 0.4$ K. At T_O , S_{mag} is only 40% of $R \ln 2$, and at around 6 K it reaches $R \ln 2$ expected for the full order of the doublet. This suggests that the phase transition is due to the multipolar degrees of freedom in the Γ_3 doublet, such as Γ_3 -type electric quadrupoles or Γ_2 -type magnetic octupole. S_{mag} reaches $R \ln 5$ at 18 K, which is consistent with the aforementioned CEF level scheme with the triplet state separated by 12 K from the Γ_3 doublet ground state.

Figure 5(b) shows the $C(T)$ data in magnetic fields of $B \leq 7$ T. The peak temperature T_O remains unchanged until the magnetic field is increased up to 4.5 T. The robustness of T_O to the magnetic field is reasonable when the phase transition does not arise from the magnetic dipole but from the quadrupole or the octupole in the Γ_3 doublet ground state. With further increase in the magnetic field above 5 T, the peak is suppressed and becomes vague.

D. Electrical resistivity in magnetic fields

Figure 6(a) shows the electrical resistivity $\rho(T)$ in magnetic fields of $B = 0, 1, 3, 5,$ and 6 T. Here, the direction of the magnetic field is parallel to that of the electrical current. In the inset of Fig. 6(a), the derivative of the electrical resistivity, $d\rho(T)/dT$, is shown. At $B = 0$, a broad maximum is observed at 0.88 K, which is comparable to T_O , the peak of $C_{\text{mag}}(T)$. This maximum shifts slightly to lower temperatures with increasing magnetic fields, reaching 0.86 K at $B = 6$ T. The magnetic-field variation of the maximum is consistent with that of T_O in $C(T)$ shown in Fig. 5(b).

Figure 6(b) shows the magnetic-field dependence of the normalized magnetoresistance $\{\rho - \rho_0\}/\rho_0$ at various constant temperatures. The data were obtained in magnetic fields up to 17.5 T at temperatures of 0.05, 0.2, 0.75, and 1.2 K. At 0.05 K, there are a shallow minimum at $B_1 = 2.8$ T and a hump at $B_2 = 4.7$ T. At $B > 5$ T, the magnetoresistance decreases and then remains constant for $B \geq 10$ T. The anomalies at B_1 and B_2 exist at 0.2 and 0.75 K. However, at 1.2 K above T_O , the minimum at B_1 disappears, and the hump changes to a broad maximum. These anomalies are probably attributed to the switching of the order parameter in the ordered state, as discussed later.

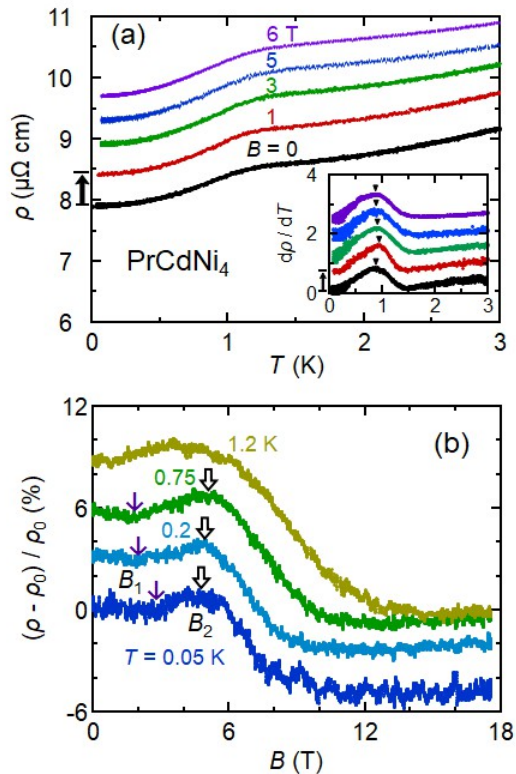


FIG. 6. (a) Temperature dependence of the electrical resistivity $\rho(T)$ of PrCdNi_4 for $T < 3$ K in various constant magnetic fields B up to 6 T. The inset shows the derivative $d\rho/dT$, where the arrows indicate the peak temperatures. The data in B are offset for clarity; for example, the bold arrow outside the vertical left-axis indicates the offset for the data at $B = 1$ T. (b) Normalized magnetoresistance at various constant temperatures 0.05, 0.2, 0.75, and 1.2 K in B up to 17.5 T. The arrows highlight a shallow minimum at 2.8 T and a hump at 4.7 T.

E. Powder neutron diffraction

Neutron diffraction patterns of the powdered sample of PrCdNi_4 at $T = 2.0$ K (red) $> T_O$ and 0.32 K (blue) $< T_O$ are represented in Fig. 7. Most of the observed peaks are identified as nuclear peaks of PrCdNi_4 and aluminum from the sample container. A peak at $2\theta = 33.2^\circ$, indicated by a star, is ascribed to a small amount of impurity PrNi_5 . In the differential pattern (green), no peak appears. Therefore, it is concluded that the phase transition at T_O does not result from a magnetic origin. This finding is consistent with the manifestation of the multipole order in the Γ_3 doublet ground state, as will be discussed with the B - T phase diagram.

The Rietveld profile fitting was conducted to determine the structural parameters of PrCdNi_4 . The fits are shown with the (black) solid lines in Fig. 7. The lattice parameter of $a = 7.1112(3)$ Å at 0.32 K was estimated by RIETAN-FP [77]. Details are provided in the Supplemental Materials [65].

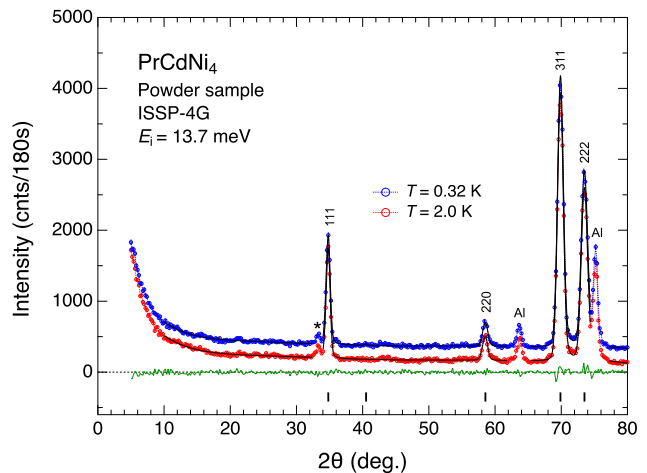


FIG. 7. Powder neutron diffraction patterns of PrCdNi_4 at $T = 2.0$ K (red) and 0.32 K (blue), measured above and below $T_O = 1.0$ K, respectively. The (green) line shows the difference between the data at 2.0 K and 0.32 K. The black lines represent the fits with the Rietveld analysis. The bars indicate the scattering angles for the nuclear Bragg peaks of PrCdNi_4 . A peak indicated by a star signifies an impurity phase of PrNi_5 .

F. Magnetic field vs temperature phase diagram

Figure 8 shows the magnetic-field vs temperature (B - T) phase diagram of PrCdNi_4 . The phase transition temperature T_O is determined from the $C(T)$ and $\rho(T)$ data. T_O remains almost unchanged up to $B = 6.5$ T. The robustness of T_O to the magnetic field is a characteristic of the multipole order, such as the electric quadrupole or magnetic octupole order in the Γ_3 doublet ground state. This behavior is consistent with the absence of magnetic reflection at 0.32 K. Moreover, the anomalies found in the $\rho(B)$ data are plotted in the B - T phase diagram. Two horizontal lines at 2 T and 5 T look like phase boundaries within the ordered phase. Since $M(B)$ shows no anomaly at 0.3 K, as shown in Fig. 4, these boundaries must relate to the multipolar order parameter rather than the realignment of magnetic dipoles in a conventional antiferromagnetic order. Thereby, these boundaries are likely attributed to the switching of the order parameters as observed in the AFQ order in the Pr-based compounds with the Γ_3 doublet ground state [24, 30, 36]. When ferroquadrupole (FQ) order arises from isotropic quadrupole interactions, its uniform order parameter remains unchanged in a magnetic field. Therefore, these results suggest that an antiferro-type multipole order manifests itself below T_O .

Let us discuss why the multipolar transition manifests itself in PrCdNi_4 even though the long-range order of the Γ_3 doublet is hindered in the isostructural PrMgNi_4 [55]. One possible reason is that the composition of $\text{Pr}_{1.00(1)}\text{Cd}_{1.00(1)}\text{Ni}_{3.89(4)}$ is close to the stoichiometric ratio, while excess Mg atoms substitute for the Pr atoms in the sample of $\text{Pr}_{0.94(1)}\text{Mg}_{1.06(1)}\text{Ni}_{3.86(2)}$ [55]. With-

out the atomic disorder in PrCdNi₄, the non-Kramers Γ_3 doublet's degeneracy could be conserved to give rise to the phase transition due to intersite exchange interactions. It has been noted that the AFQ order easily collapses due to a small amount of atomic exchange [78, 79]. This may also apply to the absence of quadrupole order in PrMgNi₄, which further supports the AFQ order in PrCdNi₄.

On the other hand, the competitive isotropic J and anisotropic K nearest-neighbor interactions in the fcc lattice may affect quadrupolar order, combined with the CEF effect, as theoretically investigated using a four-site mean-field approximation [61]. According to this calculation, the order parameter is strongly dependent on the values of J and K scaled by the excitation energy from the Γ_3 doublet to the excited Γ_1 singlet, denoted as E_1 . Regarding the finite temperature properties of the quadrupole orders, there appear not only the FQ phase, as well as O_2^0 - and O_2^2 -type AFQ phases, but also triple- q order with partially ordered sites. Moreover, the transition temperature is significantly suppressed over a wide range of small values of J and K [61]. In PrCdNi₄, E_1 is estimated as 31.7 K for $W = -3.3$ K and $x = 0.8$, leading to $T_O/E_1 = 0.03$. This value is roughly comparable to that obtained where the absolute values of K/E_1 and J/E_1 are less than 0.01 in the J - K phase diagram. Furthermore, since the phase transition is of second order and no successive transition was observed, the ground state is likely characterized by the O_2^2 -type AFQ order.

To reveal the impact of the competitive anisotropic and isotropic interactions between the multipoles inherent in the fcc lattice, it is essential to observe the anisotropic dependence of physical properties with respect to the crystal axes and external field axes using single-crystalline samples.

IV. SUMMARY

We have conducted various measurements on a cubic compound PrCdNi₄, including magnetic susceptibility χ , isothermal magnetization M , specific heat C , electrical resistivity ρ , magnetoresistance, and powder neutron diffraction. $\chi(T)$ approaches a constant value on cooling below 10 K. This van-Vleck paramagnetic behavior is consistent with the expected non-magnetic CEF ground state for Pr³⁺. The magnetic specific heat C_{mag} exhibits a shoulder at around 4 K, ascribed to CEF excitations from the Γ_3 doublet ground state to an excited triplet. Furthermore, $C(T)$ shows a peak at $T_O = 1.0$ K, which temperature does not change significantly in magnetic fields up to 4.5 T. This peak is likely attributed to multipolar degrees of freedom in the Γ_3 doublet. No magnetic reflections were observed below T_O in the powder neutron diffraction pattern. It is noted that S_{mag} reaches only 40% of $R\ln 2$ at T_O . This reduction in the entropy is probably attributed to competitive anisotropic multipole interactions inherent in the $4f^2$ fcc lattice [61].

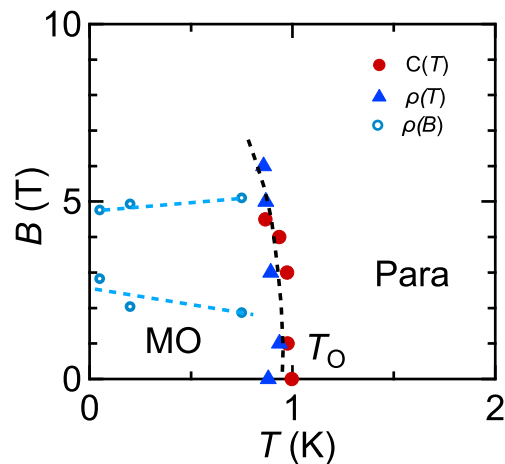


FIG. 8. Magnetic field (B) vs temperature (T) phase diagram of PrCdNi₄ determined by the measurements of the specific heat $C(T)$, electrical resistivity $\rho(T)$, and magnetoresistance $\rho(B)$. “MO” represents a multipole order, T_O is the ordering temperature, and “Para” indicates the state where long-range multipole order is absent.

Moreover, the magnetoresistance $\rho(B)$ at $T = 0.05$ K ($< T_O$) showed two anomalies at $B = 2.8$ and 4.7 T which are attributable to switching in the order parameter. If this is the case, the phase transition at T_O results from an antiferro-type multipole order in the Γ_3 doublet on the $4f^2$ fcc lattice. To further understand the order parameter, it is necessary to measure the anisotropy of the magnetic and transport properties using single-crystalline samples of PrCdNi₄. In addition, neutron diffraction and nuclear magnetic/quadrupole resonance measurements should be conducted in different orientations of magnetic fields. Resonant x-ray diffraction and ultrasonic measurements are promising methods for directly detecting quadrupoles and/or octupoles in a zero magnetic field.

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ing a Rigaku XtaLAB Synergy-DW area-detector diffractometer at N-BARD, Hiroshima University. MANA is supported by World Premier International Research Center Initiative (WPI), MEXT, Japan. This work was carried out by the JRR-3 general user program managed by the Institute for Solid State Physics, the University of

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