Inelastic neutron scattering study of crystalline electric field excitations in a cubic compound PrMgNi$_4$

Y. Kusanose$^1$, T. Onimaru$^1$, Y. Yamane$^{1,*}$, K. Umeo$^2$, T. Takabatake$^1$, T. Guidi$^3$, D. Le$^3$ and D. T. Adroja$^{3,4}$

$^1$Department of Quantum Matter, Graduate School of Advanced Science and Engineering, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8530, Japan
$^2$Integrated Experimental Support/Research Division, N-BARD, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan
$^3$ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, United Kingdom
$^4$Highly Correlated Matter Research Group, Physics Department, University of Johannesburg, Auckland Park 2006, South Africa

E-mail: d206038@hiroshima-u.ac.jp

Abstract. We performed inelastic neutron scattering experiments on PrMgNi$_4$ with the cubic MgSnCu$_4$-type structure. The magnetic excitations were observed at 1.1, 2.5, 5.9, 10.7, and 11.7 meV. Since the energy of the excitations is constant for $|Q| < 5$ Å$^{-1}$, they are ascribed to the crystalline electric field (CEF) excitations of the Pr$^{3+}$ ions. We adopted CEF parameters of $W = -3.3$ K and $x = 0.80$ for the cubic $T_d$ point group to reproduce the strong excitations at 1.1, 10.7, and 11.7 meV. The calculated CEF level scheme reveals the $\Gamma_3$ doublet ground state with the quadrupolar degrees of freedom and the excited states of $\Gamma_4$ triplet (1.16 meV), $\Gamma_1$ singlet (2.78 meV), and $\Gamma_5$ triplet (11.6 meV). This scheme, however, does not explain the observed two excitations at 2.5 and 5.9 meV. These additional excitations may arise from splitting of the doublet by symmetry lowering due to excess Mg atoms occupying the Pr sites. This splitting is probably responsible for the absence of the long-range quadrupole order in PrMgNi$_4$.

1. Introduction
Cubic praseodymium-based intermetallic compounds with nonmagnetic $\Gamma_3$ doublet crystalline electric field (CEF) ground states of $4f^2$ electrons have received much interest. They show a variety of phenomena such as multipole order, heavy fermion superconductivity and non-Fermi liquid state originating from quadrupolar degrees of freedom in the $\Gamma_3$ doublet through strong exchange interaction with conduction electrons ($c$–$f$ hybridization). For example, PrPb$_3$ exhibits an antiferroquadrupole order at $T_Q = 0.4$ K [1], below which the electric quadrupoles are modulated sinusoidally [2]. In contrast, PrAg$_3$In [3] and PrMg$_3$ [4] exhibit no quadrupole order in spite of the $\Gamma_3$ doublet ground states. The absence of the quadrupole order may be ascribed to the Kondo effect due to strong $c$–$f$ hybridization, because the specific heat divided

*Present address: Department of Material Science, Graduate School of Science, University of Hyogo, Kamigori, Hyogo 678-1297, Japan
by temperature, $C/T$, is strongly enhanced on cooling below 1 K. Another possibility is splitting of the $\Gamma_3$ doublet by symmetry lowering of the Pr site due to the atomic disorder inherent in their Heusler-type structures.

Recently, we have proposed that a cubic compound PrMgNi$_4$ possesses the $\Gamma_3$ doublet ground state [5]. PrMgNi$_4$ crystallizes in the cubic MgSnCu$_4$-type structure with the space group of $F\bar{4}3m$ [6]. A single-crystal X-ray structural analysis revealed that the excess Mg atoms occupy 4.5% of the Pr sites [5]. The Schottky-type anomaly in $C(T)$ and van-Vleck paramagnetic behavior of the magnetic susceptibility suggest that the CEF ground state is the $\Gamma_3$ doublet. Though no long-range quadrupole order was observed down to 0.1 K, both $C(T)$ and the electrical resistivity $\rho(T)$ exhibit shoulder-like anomalies at around 0.7 K. Since the shoulder of $C(T)$ becomes more pronounced when the amount of excess Mg atoms is decreased [7], the absence of the long-range quadrupole order may be attributed to symmetry lowering of the Pr site owing to the excess Mg atoms substituting for the Pr atoms. In addition, the shoulders of $C(T)$ and $\rho(T)$ at around 0.7 K are robust against the magnetic field up to 5 T, indicating development of intersite correlation of the quadrupoles in the ground state doublet [8]. In the present work, we performed inelastic neutron scattering experiments to confirm the $\Gamma_3$ doublet ground state by measuring the CEF excitations of a Pr$^{3+}$ ion.

2. Experiments
The inelastic neutron scattering experiments were performed using the time-of-flight neutron spectrometer MARI installed at ISIS facility in Rutherford Appleton Laboratory. The temperature was changed from 5 to 120 K using a closed cycle refrigerator. The incident neutron energy was selected at 11.8 and 30.0 meV. Powdered samples of PrMgNi$_4$ of 4.60 g and the nonmagnetic reference compound LaMgNi$_4$ of 1.54 g each were obtained by crushing single-crystalline samples grown by the Mg self-flux method [5].

![Inelastic neutron scattering spectra of PrMgNi$_4$ for 5 ≤ T ≤ 120 K with incident neutron energy of (a) $E_i = 11.8$ and (b) 30.0 meV. Magnetic excitations were observed at 1.1 meV labeled (1), and (2) 2.5, (3) 5.9, (4) 10.7 and (5) 11.7 meV. Black circles are the data for the nonmagnetic counterpart LaMgNi$_4$ measured at 5 K. The inset of (b) shows the data for 8 ≤ $E$ ≤ 16 meV.](image.png)
3. Results and Discussion

Figure 1 shows the inelastic neutron scattering spectra of PrMgNi$_4$ from 5 to 120 K with the incident neutron energy of (a) $E_i = 11.8$ and (b) 30.0 meV. The spectra are evaluated by integrating the neutron scattering intensity of $I(Q, E)$ data for $|Q| < 5 \text{ Å}^{-1}$, where $Q$ is the wave-vector transfer and $E$ the energy transfer. As a reference for the phonon contribution, the spectra of the nonmagnetic counterpart LaMgNi$_4$ are shown with the black circles. In the spectra with $E_i = 11.8$ meV shown in Fig. 1(a), magnetic excitations were observed at $E = 1.1$ and 2.5 meV. In Fig. 1(b), a shoulder appears at around 5.9 meV and excitations at 10.7 and 11.7 meV overlap. Since the energy of these excitations is nearly constant for $|Q| < 5 \text{ Å}^{-1}$, they are ascribed to the CEF excitations of the Pr ions.

Focusing on the temperature variations of the CEF excitations, the intensity of the excitation peak at 1.1 meV becomes half with increasing temperatures from 5 to 20 K, indicating a transition from a low-lying state to an excited state. On the other hand, the intensity of the excitation peak at 2.5 meV increases from 5 to 20 K but decreases above 50 K. The temperature variation of the shoulder at 5.9 meV is small. The two peaks at 10.7 and 11.7 meV merge with increasing temperatures to 20 K. The shift of the peaks to the lower energy is probably ascribed to additional phonon contributions.

With the CEF effect of the cubic $T_d$ point group, the nine-fold multiplet for the Pr$^{3+}$ ion with $J = 4$ is split into the $\Gamma_1$ singlet, $\Gamma_3$ doublet, and $\Gamma_4$ and $\Gamma_5$ triplets. The scattering intensity due to the CEF excitations is estimated from the matrix elements of $|\langle \Gamma_i | J_z | \Gamma_j \rangle |^2$ [9]. Non-zero values of the matrix elements indicate the excitations between the CEF multiplets. The matrix elements of $|\langle \Gamma_i | J_z | \Gamma_j \rangle |^2$ are estimated as follows; 6.67 for $\Gamma_1$ and $\Gamma_4$, 9.33 for $\Gamma_3$ and $\Gamma_4$, 4.0 for $\Gamma_3$ and $\Gamma_5$, and 3.50 for $\Gamma_4$ and $\Gamma_5$. Thereby, the magnetic excitations between the CEF levels are rigidly restricted as shown with the arrows in the inset of Fig. 2(a). A cubic Hamiltonian matrix is diagonalized to give the expectation values of the CEF energy as a function of two CEF parameters of $x$ and $W$ [10]. Here, $x$ is the ratio of fourth- to sixth-order terms and $W$ the...
overall energy scale. Referring to the CEF parameters of \( W = -2.0 \) K and \( x = 0.77 \) proposed to reproduce the temperature variation of the magnetic susceptibility and the Schottky specific heat [5], we adopt modified parameters of \( W = -3.3 \) K and \( x = 0.80 \) to reproduce the inelastic neutron scattering spectra. The calculations are shown with the (red) solid lines in Figs. 2(a) and (b). The excitation peaks at 1.1, 10.7, and 11.7 meV are reproduced. The above CEF parameters give the CEF level scheme as the \( \Gamma_3 \) doublet ground state and excited states of \( \Gamma_4 \) triplet (1.16 meV), \( \Gamma_1 \) singlet (2.78 meV), and \( \Gamma_5 \) triplet (11.6 meV) as shown in the inset.

On the other hand, the observed excitations at 2.5 and 5.9 meV are not assigned by the simulation with the above CEF parameters. These additional excitations are probably attributed to the symmetry lowering of the Pr sites due to the excess Mg atoms substituting for the Pr atoms as proposed by the single-crystal X-ray structural analysis [5]. To reproduce the additional excitations, it is necessary to include other CEF parameters, e.g., for a trigonal point group. Thereby, the absence of the long-range quadrupole order in PrMgNi\(_4\) is attributed to the splitting of the \( \Gamma_3 \) doublet by the symmetry lowering of the Pr atom.

4. Summary
To determine the CEF level scheme of the Pr\(^{3+}\) ions in the cubic compound PrMgNi\(_4\), inelastic neutron scattering experiments were performed. We observed CEF excitations at \( E = 1.1, 2.5, 5.9, 10.7, \) and 11.7 meV. The CEF parameters of \( W = -3.3 \) K and \( x = 0.80 \) for the cubic \( T_d \) point group were chosen to reproduce the excitations at 1.1, 10.7, and 11.7 meV, indicating that the CEF ground state is the \( \Gamma_3 \) doublet. The obtained CEF level scheme, however, does not explain the excitations at 2.5 and 5.9 meV. The additional peaks are probably attributed to symmetry lowering of the Pr sites due to excess Mg atoms substituted for the Pr atoms. Thereby, symmetry lowering of the Pr sites due to the atomic disorder splits the \( \Gamma_3 \) doublet. This splitting of the \( \Gamma_3 \) doublet is responsible for the absence of the long-range quadrupole order in PrMgNi\(_4\).

Acknowledgments
We acknowledge support from the Center for Emergent Condensed-Matter Physics (ECMP), Hiroshima University. This work was financially supported by Grants in Aid from MEXT/JSPS of Japan, Grants Nos. JP15H05886 (J-Physics) and JP18H01182.

References
[1] Morin P, Schmitt D and du Tremolet de Lacheisserie E 1982 J. Magn. Magn. Mater. 30 257
[2] Onimaru T, Sakakibara T, Aso N, Yoshizawa H, Suzuki H S and Takeuchi T 2005 Phys. Rev. Lett. 94 197201
[3] Yatskar A, Beyermann W P, Movshovich R and Canfield P C 1996 Phys. Rev. Lett. 77 3637
[4] Tanida H, Suzuki H S, Takagi S, Onodera H and Tanigaki K 2006 J. Phys. Soc. Jpn. 75 073705
[5] Kusanose Y, Onimaru T, Park G B, Yamane Y, Umeo K, Takabatake T, Kawata N and Mizuta T 2019 J. Phys. Soc. Jpn. 88 083703
[6] Kadir K, Noréus D and Yamashita I 2002 J. Alloys Compd. 345 140
[7] Kusanose Y and Onimaru T 2021 private communication
[8] Kusanose Y, Onimaru T, Park G B, Yamane Y, Umeo K, Takabatake T, Kawata N and Mizuta T 2020 JPS Conf. Proc. 30 011160
[9] Birgeneau R J 1972 J. Phys. Chem. Solids 33 59
[10] Lea K R, Leask M J M and Wolf W P 1962 J. Phys. Chem. Solids 23 1381