Site-selective NMR measurements in single crystal PrNb$_2$Al$_{20}$

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Abstract. We report the result and analysis of the nuclear magnetic resonance (NMR) measurements at the magnetic field of 8.57 T and temperature of 80 K using a single crystal PrNb$_2$Al$_{20}$. Combining the field dependence of NMR spectra, numerical simulation, and band calculation, we deconvoluted the NMR signals from the Nb, Al 48f, and Al 96g sites. Unfortunately, the overlapping of NMR lines prevents us to extract the NMR signals from the Al 16c site. However, the obtained nuclear quadrupole resonance (NQR) parameters for the Nb and Al 48f sites are consistent with the previous reports [T. Kubo et al., 2014 JPS Conf. Proc. 3 012031; 2015 J. Phys.: Conf. Ser. 592 012093; 2016 J. Phys. Conf.: Ser. 683 012015] and for the Al 96g site are refined to be $\nu_Q = 0.98$ MHz and $\eta = 0.46$.

1. Introduction

Pr$T_2X_{20}$ system ($T = Ti, V, Nb, Rh, Ir, X = Al, Zn$) which crystallizes in a cubic CeCr$_2$Al$_{20}$-type structure with the space group $Fd\overline{3}m$ has been studied intensively because of their intriguing behaviors at low temperatures such as superconductivity, quadrupole ordering, and non-Fermi liquid (NFL) behaviors [1, 2, 3, 4, 5]. In this system, the $4f$ electronic ground state of Pr$^{3+}$ ion is considered to be the non-Kramers’ $\Gamma_3$ doublet which has no magnetic dipole but has two electric quadrupoles $O_{20}$ and $O_{22}$, and one magnetic octupole $T_{xyz}$. These multipole degrees of freedom are believed to play an important role in exotic ground states in these materials at low temperatures. Among them, PrNb$_2$Al$_{20}$ shows NFL behaviors such as $T$-linear resistivity below 2 K and logarithmic divergent specific heat divided by temperature below 10 K, in which the relationship between these behaviors and quadrupole degrees of freedom has been discussed [1].

To clarify the importance of multipole degrees of freedom, site-selective nuclear magnetic resonance (NMR) measurements are desirable since NMR can obtain the microscopic electronic information from static and dynamical viewpoints based on the local symmetry at the ligand sites of Pr ions. The NMR spectrum of PrNb$_2$Al$_{20}$ becomes complex because of its crystal structure. Thus, it is important to deconvolute the complex NMR lines since the microscopic electronic state at the ligand sites directly reflects the essential information of coupling between conduction electrons and multipoles through the bond symmetry between the Pr and ligand sites [6, 7, 8, 9, 10]. In this paper, we report the results of $^{93}$Nb- and $^{27}$Al-NMR measurements using a single crystal and the analysis of the NMR lines.
Figure 1. NMR lines with the applied magnetic field parallel to one of the (a) ⟨111⟩ and (b) ⟨110⟩ directions at 8.57 T, and at 80 K. Colored dash-dotted, solid, and dashed lines are the results of the simulation for Nb, Al 48f, and Al 96g sites, respectively. As shown in the inset of Fig. 1(b), θ and φ denote the field angle from the crystal c-axis and in the ab-plane, respectively. Both the ideal and actual angles are presented. The details of the simulation are described in the text.

2. Experimental Procedure
The single crystal sample of PrNb2Al20 was prepared by the Al-flux method. Details of the sample preparation method were reported in the previous paper [1]. The field angle dependence of NMR spectra is measured by using a 17 T superconducting magnet and a phase-coherent pulsed spectrometer. The angle between the applied field and crystal axes is controlled by a uniaxial goniometer. 93Nb- (nuclear spin I = 9/2, gyromagnetic ratio γ/2π = 10.421 MHz/T, nuclear quadrupole moment Q = −0.32 × 10−28 m²) and 27Al- (I = 5/2, γ/2π = 11.094 MHz/T, Q = 0.1466 × 10−28 m²) [11, 12] NMR lines are obtained by summing up the fast Fourier transformed spin echo signals obtained with a step of 5 kHz at a fixed magnetic field μ0H ≈ 8.57 T.

3. Results and Discussion
Figure 1 shows 93Nb- and 27Al-NMR spectra obtained at the fixed magnetic field 8.57 T applied parallel to one of the (a) ⟨111⟩ and (b) ⟨110⟩ axes, and at a temperature of 80 K. Each of the resonance lines are as sharp as about 30 kHz. There are one Nb site and three crystallographically inequivalent Al sites (16c, 48f, and 96g) in PrNb2Al20. Due to the local symmetry at the ligand sites which is lower than cubic as described below, these sites split further under the magnetic field. In order to deconvolute the obtained
lines into the above sites, we carried out the simulation numerically solving the \((2I + 1) \times (2I + 1)\) nuclear spin hamiltonian \(\mathcal{H}\) by an exact diagonalization method. Such a hamiltonian can be written as follows:

\[
\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_Q + \mathcal{H}_{\text{hf}},
\]

\[
\mathcal{H}_Z = -\gamma_n h \mathbf{I} \cdot \mathbf{H}.
\]

\[
\mathcal{H}_Q = \frac{eQ}{6(I+1)} \sum_{i,j} V_{ij} \left[ \frac{3}{2} (I_i I_j + I_j I_i) - \delta_{ij} I(I+1) \right]
\]

\[
= \frac{1}{6} \hbar Q \left[ (3I_x^2 - I(I+1)) + \frac{3}{2} \left( I_y^2 + I_z^2 \right) \right]
\]

\[
\mathcal{H}_{\text{hf}} = -\gamma_n h \mathbf{I} \cdot (\mathbf{D} + \mathbf{K}) \mathbf{H}
\]

where \(h\) is the Planck constant \((h \equiv h/2\pi)\) and \(e\) is the elementary charge. The first term in Eq. (1) is a Zeeman interaction between the nuclear spin \(\mathbf{I}\) and applied field \(\mathbf{H}\), and is expressed in Eq. (2). The second term is a nuclear quadrupole interaction between the nuclear spin and electric field gradient (EFG) created by the surrounding charge distribution at the nuclear site, and is expressed in Eq. (3). EFG is characterized by the second rank EFG tensor \(\mathbf{V}\) \(V_{ij} \equiv \partial^2 V/\partial x_i^2\) \((x_i = x, y, z)\). In the principal coordinate system, \(\mathbf{V}\) is diagonalized and Eq. (3) can be rewritten as Eq. (4), where \(\nu_Q \equiv 3eQ/2h(2I - 1)\) is the nuclear quadrupole frequency, \(\eta \equiv (V_{XX} - V_{YY})/V_{ZZ}\) is the asymmetry parameter, and \(V_{XX}, V_{YY}\), and \(V_{ZZ}\) are the principal values of \(\mathbf{V}\) which satisfy the relation \(|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|\) and \(V_{XX} + V_{YY} + V_{ZZ} = 0\). The third term is a hyperfine interaction between the nuclear spin and electron spins, which is represented by the second rank classical dipole field tensor \(\mathbf{D}\) and Knight shift tensor \(\mathbf{K}\), and is expressed in Eq. (5). \(\mathbf{D}\) describes the classical dipole interaction between the nuclear spin and Pr 4f magnetic dipoles. \(\mathbf{K}\) has the information of c-f hybridization and is decomposed into the isotropic part \(K_{\text{iso}}\) and the anisotropic part \(K_{\text{ani}}\). \(\mathbf{D}\) and \(\mathbf{K}\) are traceless and are designated by their principal values \((D_1, D_2, D_3)\) and \((K_1, K_2, K_3)\) that satisfy the relation of \(|D_3| \geq |D_2| \geq |D_1|\) and \(|K_3| \geq |K_2| \geq |K_1|\).

In order to calculate NMR lines, we have to know the principal values and the principal axis directions of \(\mathbf{V}, \mathbf{D}, \) and \(\mathbf{K}\). The principal values of \(\mathbf{D}\) are calculated by the lattice sum of the classical dipole field \(\mathbf{H}_D = \sum_i \left[ -\mu_i/r_i^3 + (\mu_i \cdot r_i) r_i/r_i^2 \right]\), where \(\mu_i = g_i \mu_B J_i\) is the 4f electronic magnetic dipole in which \(g_J, \mu_B\), and \(r_i\) are the Landé \(g\)-factor, the Bohr magneton, and the distance between the site considered and \(i\)th Pr site, respectively. The magnitude of magnetic dipole is estimated to be \(\approx 0.2 \mu_B\) at 80 K from the crystalline electric field analysis [10]. \(\nu_Q\) and \(\eta\) for Nb, Al 48f, and Al 96g sites are previously determined [13, 14, 15]. The principal values of \(\mathbf{K}\) are treated as fitting parameters.

Next, we consider the principal axis directions. Generally, these directions do not coincide with the crystal axes or with each other due to the local symmetry at the ligand sites. In such a case, the analysis taking into account of the local symmetry is previously reported [9, 15, 16, 17, 18, 19]. Shown in Fig. 2 is the geometry of neighboring Nb, Al 48f, and Al 96g atoms around a Pr atom. The local symmetry axis directions at these ligand sites are also represented. For the Nb site with local symmetry of \(\bar{3}m\), the maximum principal axis direction coincides with the local threefold rotation axis. As shown in Fig. 2(a) with the crystal axis directions, this axis is parallel to \([111]\) direction for the Nb site at \((1/2, 1/2, 1/2)\). \(\mathbf{V}, \mathbf{D}, \) and \(\mathbf{K}\) are axially symmetric around this axis. The Al 16c site has the local symmetry of \(\bar{3}m\), thus the principal axis directions are same with those for the Nb site. For the Al 48f site at which local symmetry is \(2mm\), there are two mirror planes. For example, the Al 48f site at \((1/8, 1/8, z)\) have the mirror planes \((110)\) and \((1\overline{1}0)\). In this case, the principal axis directions are constrained in these mirror planes but the maximum principal axis direction cannot be determined beforehand. For the Al 96g site at which local symmetry is \(\cdot m\), there are only one mirror plane which is parallel to one of the \((110)\) plane. In this case, one of the three principal axes are perpendicular to the plane and the other two axes are in the plane. Since the principal axis directions in the plane cannot be predetermined, we calculated \(\mathbf{V}\) for each sites by a band calculation in local density approximation for the isostructural LaNb₂Al₃₀. The details of the calculation method are described in the previous paper [20]. As shown in Fig. 2(b) with the crystal axis
Figure 2. (a) Pr and surrounding Nb atoms with crystal axes and local symmetry axis at Nb sites. Red, light green, and blue arrows denote crystal $a$, $b$, and $c$ axes, respectively. Black arrows indicate local threefold rotation axes, which coincide with the maximum principal axis directions of $V$, $K$, and $D$ in this case. (b) Pr and nearest-neighboring Al 48$f$ atoms with the crystal and EFG principal axes. Black and gray arrows indicate the maximum ($V_{ZZ}$) and minimum ($V_{XX}$) principal axis directions of the EFG tensor from the band calculation, respectively. (c) Pr and nearest-neighboring Al 96$g$ atoms with the crystal and EFG principal axes. Black arrows indicate $V_{ZZ}$ directions from the band calculation. These figures were drawn with VESTA 3 [21].

Table 1. (Left) The number of NMR sites and corresponding number of NMR lines for $H \parallel \langle 111 \rangle$ case. (Right) The number of NMR sites and corresponding number of NMR lines for $H \parallel \langle 110 \rangle$ case.

| $H \parallel \langle 111 \rangle$ | NMR sites | NMR lines | $H \parallel \langle 110 \rangle$ | NMR sites | NMR lines |
|-------------------------------|-----------|-----------|-------------------------------|-----------|-----------|
| Nb                            | 2         | 18        | Nb                            | 2         | 18        |
| Al 16$c$                      | 2         | 10        | Al 16$c$                      | 2         | 10        |
| Al 48$f$                      | 2         | 10        | Al 48$f$                      | 3         | 15        |
| Al 96$g$                      | 3         | 15        | Al 96$g$                      | 4         | 20        |

For directions, $V_{ZZ}$ and $V_{XX}$ directions for the Al 48$f$ site at ($x$, 1/8, 1/8) are obtained to be [011] and [100] directions, respectively. Figure 2(c) shows the crystal axis and $V_{ZZ}$ directions for the Al 96$g$ site. For the Al 96$g$ site at ($x$, $x$, $z$), the $V_{ZZ}$ direction is calculated to be parallel to the [100] direction.

Using the principal values and principal axis directions, we can obtain each of the tensor components in the crystal coordinate by an appropriate frame transformation $\tilde{T}_c = R\tilde{T}_p R^{-1}$, where $\tilde{T}_p$ and $\tilde{T}_c$ are the representations of a tensor in its principal and crystal coordinate, respectively, and $R$ is a frame transformation matrix between these coordinates. In addition, tensor components are transformed from one site to another under symmetry operations such as 120° rotation around one of the ⟨111⟩ axes and mirror operation for one of the ⟨110⟩ planes.

Based on the above considerations, we analyzed the NMR lines. In Table 1, we summarized the number of the NMR sites and corresponding number of NMR lines for two magnetic field directions. As shown in Fig. 1, the number of the observed NMR lines is larger than expected number of NMR lines for each of the field directions. This is due to a misalignment of the sample, which causes further splitting of the NMR sites. Such a misalignment is inevitable since we use a uniaxial goniometer in the present measurement. For general field direction, we have four Nb, six Al 48$f$, and twelve Al 96$g$ sites.

First, we determined the exact field angle by calculating the $^{93}$Nb-NMR lines because the principal axis directions of $\bar{V}$, $\bar{D}$, and $\bar{K}$ at Nb sites are uniquely determined as discussed above. We defined the
Table 2. (Upper) The experimental and calculated NQR parameters for each of the ligand sites. (Lower) The calculated dipole field tensor and experimentally determined Knight shift tensor with $D_3$ and $K_3$ directions, respectively. The magnitude of $D_i$’s and $K_i$’s is given as the relative values for the Zeeman frequency $\gamma_B H/2\pi$. As described in the text, NMR signals from the Al 16c site cannot be deconvoluted due to the overlapping of NMR lines.

| Nb            | $v_Q$ (MHz) / $\eta$ (exp.) | $v_Q$ (MHz) / $\eta$ (cal.) | $V_{ZZ}$ (cal.) |
|---------------|-----------------------------|-------------------------------|----------------|
| Al 16c        | - / -                       | 0.715 / 0                    | $\parallel \langle 111 \rangle$ |
| Al 48f        | 2.28 / 0.17                 | 2.427 / 0.191                | $\parallel \langle 110 \rangle$ |
| Al 96g        | 0.98 / 0.46                 | 1.005 / 0.348                | $\parallel \langle 110 \rangle$ |



| Nb            | $(D_1, D_2, D_3)$ (%) (calc.) | $D_3$ | $(K_{iso}, K_1, K_2, K_3)$ (%) (exp.) | $K_3$ |
|---------------|-----------------------------|-------|--------------------------------------|-------|
| Nb            | (0.018, 0.018, −0.036)      | $\parallel \langle 111 \rangle$ | (0.43, −0.08, −0.08, 0.16) | $\parallel \langle 111 \rangle$ |
| Al 16c        | (−0.132, −0.132, 0.264)    | $\parallel \langle 111 \rangle$ | −                     | −     |
| Al 48f        | (0.005, 0.025, −0.030)      | $\parallel \langle 110 \rangle$ | (0.25, 0.03, −0.09, 0.12) | $\parallel \langle 110 \rangle$ |
| Al 96g        | (−0.026, −0.081, 0.107)     | $\perp \langle 110 \rangle$ | −                     | −     |

4. Summary
We measured the field-angle dependence of $^{93}$Nb- and $^{27}$Al-NMR signals for single crystal PrNb$_2$Al$_{20}$. Together with previously reported NQR parameters and band calculation, we succeeded to deconvolute...
the NMR signals from the Nb, Al 48f, and one of Al 96g sites. The experimental results are well reproduced by using the numerically obtained EFG tensors, thus confirms the availability of the band calculation. Unfortunately, the strong overlapping of the NMR lines prevents us to obtain the precise NMR and NQR parameters for Al 16c site in the present stage. Nevertheless, these results help us to investigate the importance of multipole degrees of freedom for the anomalous properties of PrNb$_2$Al$_{20}$.

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References
[1] Higashinaka R, Nakama A, Ando M, Watanabe M, Aoki Y and Sato H 2011 J. Phys. Soc. Jpn. 80 SA048
[2] Sakai A and Nakatsuji S, 2011 J. Phys. Soc. Jpn. 80 063701
[3] Onimaru T, Matsumoto K T, Inoue Y F, Umeo K, Sakakibara T, Karaki Y, Kubota M and Takabatake T 2011 Phys. Rev. Lett. 106 177001
[4] Sakai A, Kuga K and Nakatsuji S 2012 J. Phys. Soc. Jpn. 81 083702
[5] Tsujimoto M, Matsumoto Y, Tomita T, Sakai A and Nakatsuji S 2014 Phys. Rev. Lett. 113 267001
[6] Sakai O, Shiina R, Shiba H and Thalmeier P 1997 J. Phys. Soc. Jpn. 66 3005
[7] Tanida H, Takagi S, Suzuki H S, Satoh I and Komatsubara T 2006 J. Phys. Soc. Jpn. 75 074721
[8] Kiss A and Kuramoto Y 2006 J. Phys. Soc. Jpn. 75 103704
[9] Kikuchi J, Takigawa M, Sugawara H and Sato H 2007 J. Phys. Soc. Jpn. 76 043705
[10] Kubo T, Kotegawa H, Tou H, Higashinaka R, Nakama A, Aoki Y and Sato H 2015 J. Phys. Soc. Jpn. 84 074701
[11] Harris R K, Becker E D, Cabral De Menezes S M, Granger P, Hoffman R E and Zilm K W 2008 Mag. Res. Chem 46 582
[12] Pyykko P 2008 Mol Phys 106 1965
[13] Kubo T, Kotegawa H, Tou H, Higashinaka R, Nakama A, Aoki Y and Sato H 2014 JPS Conf. Proc. 3 012031
[14] Kubo T, Kotegawa H, Tou H, Higashinaka R, Nakama A, Aoki Y and Sato H 2015 J. Phys.: Conf. Ser. 592 012093
[15] Kubo T, Kotegawa H, Tou H, Higashinaka R, Nakama A, Aoki Y and Sato H 2016 J. Phys.: Conf. Ser. 683 012015
[16] Tou H, Doi M, Sera M, Yogi M, Kitaoka Y, Kotegawa H, Zheng G-q, Harima H, Sugawara H and Sato H 2005 Physica B 359 892
[17] Tou H, Tsugawa N, Sera M, Harima H, Haga Y and Ônuki Y 2007 J. Phys. Soc. Jpn. 76 024705; 2007 J. Phys. Soc. Jpn. 76 058001
[18] Tokunaga Y, Sakai H, Kambe S, Sakai A, Nakatsuji S and Harima H 2013 Phys. Rev. B 88 085124
[19] Taniguchi T, Yoshida M, Takeda H, Takigawa M, Tsujimoto M, Sakai A, Matsumoto Y and Nakatsuji S 2016 J. Phys.: Conf. Ser. 683 012016
[20] Harima H 2006 Physica B 378–380 246
[21] Momma K and Izumi F 2011 J. Appl. Cryst. 44 1272