\( ^{105}\text{Pd} \) NQR Study on NpPd\(_5\)Al\(_2\) and CePd\(_5\)Al\(_2\)

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Abstract. We report the results of \( ^{105}\text{Pd} \) NQR experiments on NpPd\(_5\)Al\(_2\) and CePd\(_5\)Al\(_2\). In the normal state at 6 K, the \( ^{105}\text{Pd} \) NQR spectrum consists of four lines in both systems. These lines can be assigned to two sets of \( \pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2} \) and \( \pm \frac{3}{2} \leftrightarrow \pm \frac{5}{2} \) NQR transitions arising from two crystallographically inequivalent Pd sites. From the analysis of the \( ^{105}\text{Pd} \) NQR spectrum, the nuclear quadrupole frequency \( \nu_Q \), asymmetry parameter \( \eta \), and electric field gradient \( V_{zz} \) have been deduced.

1. Introduction

Recently, the first neptunium-based heavy fermion superconductor NpPd\(_5\)Al\(_2\) with \( T_c = 4.9 \) K was discovered by D. Aoki \etal [1]. The large electronic specific heat \( \gamma = 200 \text{mJ/mol-K}^2 \) at 4.9 K, and the large initial slope of the upper critical field \( H_{c2} \) below \( T_c \) suggest that heavy fermions form Cooper pairs in this system. A step-like increase of magnetization associated with the first-order phase transition at \( H_{c2} \) was also observed for this system. In a previous paper, we have reported the results of \( ^{27}\text{Al} \) NMR studies in NpPd\(_5\)Al\(_2\) [2]. From the temperature dependence of the nuclear spin-lattice relaxation rate and the Knight shift, we show that NpPd\(_5\)Al\(_2\) is a strong coupling \( d \)-wave superconductor with a superconducting gap \( 2\Delta_0/k_B T_c = 6.4 \).

Soon after the discovery of NpPd\(_5\)Al\(_2\), the isostructural compound CePd\(_5\)Al\(_2\) has been synthesized [3]. In CePd\(_5\)Al\(_2\), successive AF orderings at \( T_{N1} = 3.9 \) K and \( T_{N2} = 2.9 \) K have been observed from specific heat, electrical resistivity and magnetic susceptibility measurements. In powder neutron diffraction experiments, magnetic reflections were observed below \( T_{N1} \), whereas no apparent anomaly was observed at \( T_{N2} \) [4]. The magnetic structures of CePd\(_5\)Al\(_2\) below \( T_{N1} \) and \( T_{N2} \) are still unclear. More recently, F. Honda \etal revealed that CePd\(_5\)Al\(_2\) shows superconductivity under a pressure of 10.8 GPa with \( T_c = 0.57 \) K [5].

In this paper, we report the results of the first \( ^{105}\text{Pd} \) NQR studies in NpPd\(_5\)Al\(_2\) and CePd\(_5\)Al\(_2\). In both systems, we have observed four NQR lines arising from two inequivalent Pd sites. From analyses of the NQR spectra, nuclear quadrupole frequencies \( \nu_Q \), asymmetry parameters \( \eta \), and electric field gradients \( V_{zz} \) for each Pd site have been deduced.
2. Experimental Results

In zero field and in finite electric field gradient EFG, NQR resonance frequencies $\nu_{\text{NQR}}$ have been obtained by solving the secular equation of an electric quadrupole Hamiltonian as follows,

$$\mathcal{H}_Q = \frac{h}{6} \nu_Q [3I_z^2 - I(I + 1) + \frac{1}{2} \eta(I_x^2 + I_y^2)].$$

Here $\nu_Q$ and $\eta$ are defined as $\nu_Q = \frac{3}{2I(2I-1)} h e Q V_{zz}$, and $\eta = |V_{xx} - V_{yy}|/V_{zz}$, where $h$ is the Planck constant, $Q$ is the nuclear quadrupole moment, and $V_{\alpha\alpha}(\alpha = x, y, z)$ the electric field gradient at the position of the nucleus[6]. Conventionally, $V_{zz}$ has the largest magnitude, and $V_{xx}$ and $V_{yy}$ are chosen so that $0 \leq \eta \leq 1$. The calculated $\nu_{\text{NQR}}$ for $I=5/2$ nuclei (for $^{105}\text{Pd}$) vs. $\eta$ is shown in Fig. 1(a). For $\eta=0$, the $\nu_{\text{NQR}}$ of the $\pm 1/2 \leftrightarrow \pm 3/2$ transitions are equal to $\nu_Q$ and $2\nu_Q$, respectively. For $\eta \neq 0$, the $\nu_{\text{NQR}}$ of the $\pm 1/2 \leftrightarrow \pm 3/2$ transition increases with increasing $\eta$, while $\nu_{\text{NQR}}$ for the $\pm 3/2 \leftrightarrow \pm 5/2$ transition decreases with increasing $\eta$.

The $R(An)\text{Pd}_5\text{Al}_2$ systems crystallize in the tetragonal $\text{ZrNi}_2\text{Al}_5$-type structure of the space group $I4/mmm$ (Fig. 1(b)) [7]. This structure can be viewed as alternating $R(An)\text{Pd}_3$ and AlPd layers stacked along the $c$ axis. There are two crystallographically inequivalent Pd sites, which are denoted Pd(1) (the 2b site) and Pd(2) (the 8g site), respectively. The Pd(1) site is surrounded by four $R(An)$ atoms in the $c$ plane and has tetragonal symmetry. On the other hand, the Pd(2) site is surrounded by two $R(An)$ and two Al atoms in the $a$ plane and has
orthorhombic symmetry. The directions of $V_{zz}$ at the Pd(1) and Pd(2) sites are parallel to the $c$ and $a$ axes, respectively.

Figure 1(c) shows the $^{105}$Pd NQR spectrum observed in NpPd$_5$Al$_2$ at 6K. This NQR measurement was performed with a single crystal of dimensions $(1\times1\times0.5\ \text{mm}^3)$. The spectrum consists of four narrow resonance lines, which can be assigned to two sets of $\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$ NQR lines as shown by arrows in Fig. 1(c). The $^{105}$Pd NQR lines at 35.34 and 79.91 MHz are characterized by $\nu_Q=35.34$ MHz and $\eta=0$. The deduced value $\eta=0$ indicates that these lines arise from $^{105}$Pd(1) with tetragonal symmetry. The value of $V_{zz}$ at the Pd(1) site is estimated to be 12.17 ($\times 10^{17}\text{Vcm}^2$). On the other hand, the $^{105}$Pd NQR lines at 12.72 and 23.83 MHz are characterized by $\nu_Q=12.04$ MHz and $\eta=0.23$. This result indicates that these lines arise from $^{105}$Pd(2) with orthorhombic symmetry. The values of $V_{zz}$ at the Pd(2) site is estimated to be 4.146 ($\times 10^{17}\text{Vcm}^2$).

Figure 1(d) shows the $^{105}$Pd NQR spectrum observed in CePd$_5$Al$_2$ at 6K. Since the $^{105}$Pd NQR spectrum in CePd$_5$Al$_2$ is analogous to that in NpPd$_5$Al$_2$, the four lines in Fig. 1(d) can be assigned in the same way as discussed in the previous paragraph. The lines observed at 39.96 and 79.91 MHz arise from $^{105}$Pd(1), while the lines observed at 11.80 and 22.44 MHz arise from $^{105}$Pd(2).

For the signals arising from $^{105}$Pd(1) the line width of the $\pm 1/2 \leftrightarrow \pm 3/2$ transition is smaller than that of $\pm 3/2 \leftrightarrow \pm 5/2$ transition, indicating that the line width is due to the distribution of $\nu_Q$. On the other hand, for the signals from $^{105}$Pd(2) the line width of the $\pm 1/2 \leftrightarrow \pm 3/2$ transition is larger than that of the $\pm 3/2 \leftrightarrow \pm 5/2$ transition. The reason for this may be that the line width for $^{105}$Pd(2) is due to a distribution of $\eta$ values, since the absolute value of $\left[\frac{\partial \nu_{\text{NQR}}}{\partial \eta}\right]_{\eta\neq 0}$ for $\pm 1/2 \leftrightarrow \pm 3/2$ transition is larger than that for the $\pm 3/2 \leftrightarrow \pm 5/2$ transition.

| Compounds        | site     | $\nu_Q$ (MHz) | $\eta$ | $V_{zz}$ ($10^{17}\text{cm}^2$) |
|------------------|----------|---------------|--------|-------------------------------|
| **Experiment**   |          |               |        |                               |
| NpPd$_5$Al$_2$   | Pd(1)    | 35.34         | 0      | 12.17                         |
|                  | Pd(2)    | 12.04         | 0.23   | 4.146                         |
| CePd$_5$Al$_2$   | Pd(1)    | 39.96         | 0      | 13.76                         |
|                  | Pd(2)    | 11.31         | 0.20   | 3.895                         |
| **Band calculation** | |    |        |                               |
| NpPd$_5$Al$_2$   | Pd(1)    | 22.7          | 0      |                               |
|                  | Pd(2)    | 7.49          | 0.1614 |                               |
| CePd$_5$Al$_2$   | Pd(1)    | 21.5          | 0      |                               |
|                  | Pd(2)    | 8.51          | 0.5610 |                               |

The quadrupole parameters deduced from the present NQR study and from a band calculation are summarized in Table 1 [8]. The band calculations for NpPd$_5$Al$_2$ and CePd$_5$Al$_2$ were performed using the full potential linear-augmented-plane-wave (FLAPW) method with a local-density approximation (LDA). In both systems, the NQR results show that the values of $V_{zz}$ at the respective sites are comparable, and the values of $V_{zz}$ at the Pd(1) sites are larger than at the Pd(2) sites. These features are supported by the band calculation. From the results of the band calculation, the values of $\eta$ at the Pd(2) sites are considerably different between NpPd$_5$Al$_2$ and CePd$_5$Al$_2$, suggesting that the difference of $\eta$ at the Pd(2) sites for these two systems arise from a difference between Np-5$f$ and Ce-4$f$ character. On the other hand, the NQR results show that the values of $\eta$ at the Pd(2) sites in both systems are comparable. This fact may suggest that
the values of $\eta$ at the Pd(2) sites are rather insensitive to the $f$-electron character, although the experimental coincidence could be accidental. Since the band calculation for NpPd$_5$Al$_2$ could not reproduce the $f$-electron Fermi surface character, the real $f$-electron state may be considerably modified due to correlation effects as compared with the band calculation results. From this point of view, the EFG may reflect peculiar $f$-electronic states in NpPd$_5$Al$_2$ and CePd$_5$Al$_2$.

3. Summary
The first $^{105}$Pd NQR measurements have been performed on NpPd$_5$Al$_2$ and CePd$_5$Al$_2$. In both systems, the spectrum consists of four lines. These four lines are assigned to two sets of $\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$ NQR lines arising from two inequivalent Pd sites, Pd(1) and Pd(2). From the analysis of the $^{105}$Pd NQR spectrum, the $\nu_Q$, $\eta$, and $V_{zz}$ for each Pd sites have been deduced.

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