NMR studies on polyphosphide Ce$_6$Ni$_6$P$_{17}$

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Abstract. We report the result of $^{31}$P nuclear magnetic resonance (NMR) studies on Ce$_6$Ni$_6$P$_{17}$. The observed NMR spectra show a Lorentzian-type and an asymmetric shapes, reflecting the local symmetry around each P site in the cubic unit cell. We have identified the observed NMR lines corresponding to three inequivalent P sites and deduced the temperature dependence of the Knight shift for each site. The Knight shifts increase with decreasing temperature down to 1.5 K, indicating a localized spin system of Ce$_6$Ni$_6$P$_{17}$. Antiferromagnetic correlation between 4f spins is suggested from the negative sign of the Weiss-temperature.

1. Introduction

Rare-earth polyphosphides Ln$_6$Ni$_6$P$_{17}$ (Ln=La, Ce, Pr) crystallize in the cubic structure (space group $I43m$, No. 217) with 58 atoms per unit cell [1]. A subject of interest in this structure is the coordination of Ln atoms which occupy a crystallographically single site (12e) and form an octahedral cage at the corner and the body-centered position in the cubic unit cell as shown in Fig. 1. The nearest-neighbor (NN) bond of Ln-Ln is the edge of octahedron and the next-nearest-neighbor (NNN) is Ln-Ln dumbbell along the cubic edge. When Ln is a magnetic ion and satisfies some particular conditions, unusual magnetic properties possibly emerge. In the case that the NN interaction is antiferromagnetic and much stronger than the NNN one, typical 3D frustration in the octahedron would be expected. On the other hand, if the NNN interaction exceed the NN one, dimerization between the NN pairs takes place [2]. For Ce-based polyphosphide Ce$_6$Ni$_6$P$_{17}$, the distances between NN Ce atoms (4.139 Å) and NNN (4.262 Å) are so close that the competition between frustration and dimerization is expected.

Magnetic susceptibility $\chi(T)$ of Ce$_6$Ni$_6$P$_{17}$ increases monotonically with decreasing temperature in the measured temperature range of 2 - 350 K [3]. The low temperature specific heat exhibits broad peak at around 1.4 K followed by two sharp peaks at 0.5 and 0.9 K. These two peaks were considered to associate with magnetic transitions [3]. The magnetic entropy is evaluated to be about a half of Rhn2 implying a frustrated system of Ce$_6$Ni$_6$P$_{17}$ [3]. In order to investigate the magnetic properties microscopically, we performed $^{31}$P nuclear magnetic resonance (NMR) measurement on Ce$_6$Ni$_6$P$_{17}$.

2. Experimental method

Single crystals of Ce$_6$Ni$_6$P$_{17}$ were grown by molten Sn-flux method. The obtained single crystals were less than 500µm. The x-ray diffraction pattern shows that the sample contains a small
amount of paramagnet NiP$_3$ as an impurity phase [3]. For the NMR measurement, powered single crystals were immersed into daphne oil 7373 to avoid partial orientation of particles in a magnetic field. The NMR measurement was carried out using a phase-coherent spin-echo spectrometer. Field-swept NMR spectra were obtained by recording the integrated spin-echo intensity at a constant frequency.

3. results and discussion

Figure 2 shows the temperature dependence of the $^{31}$P NMR spectra (gyromagnetic ratio $^{31}\gamma=17.235$ MHz/T, nuclear spin $I=1/2$) at 190 MHz. P atoms occupy crystallographically three different sites 2$a$, 8$c$, and 24$g$, as shown in Fig. 1. Generally, in the absence of a nuclear quadrupole moment, the powder pattern of a NMR spectrum reflects the anisotropy of Knight shift. Its components are written as $K_x$, $K_y$, and $K_z$ for the external field parallel to the local $x$, $y$, and $z$ axes, respectively. When a nucleus is located in an environment of cubic symmetry, these values satisfy the relation of $K_x = K_y = K_z$ resulting in the Lorentzian-type NMR line shape. When the nuclei are in a noncubic environment, these components are $K_x = K_y \neq K_z$ ($K_x \neq K_y \neq K_z$) for axial symmetry (lower than axial). In these cases, the resonance is not symmetrical any more [4].

By considering the local symmetry around each P site, we assigned corresponding sites by following procedure. Since 2$a$ site has cubic symmetry, the Lorentzian shape of the resonance line painted in blue as shown in Fig. 2 can be assigned to 2$a$. Next, the spectrum painted in green can be considered to be consisting of 8$c$ and 24$g$ sites. Taking the intensity ratio and $T_2$ correction into account, this spectrum can be reproduced by the superposition of two powder-pattern signals with axial and lower than axial symmetries as shown in Fig. 3. Here $T_2$ is the spin-echo decay time. The deduced components of the Knight shift at 150 K are listed in Table 1. The resonance lines painted by blue and green shift to lower field with decreasing temperature. On the other hand, we observed the temperature-independent line indicated by the arrow in Fig. 2. This line is probably the signal of the paramagnetic impurity of NiP$_3$.

Figure 4 shows the temperature dependence of the Knight shift $K_{2a}$, $K_{8c}$, and $K_{24g}$ for 2$a$, 8$c$, and 24$g$, respectively. $K_{2a}$ is defined at the peak position of the Lorentzian-type of spectra and corresponds to an isotropic component of the Knight shift $K_{iso}$. Moreover, $K_{8c}$, and $K_{24g}$ are defined at the peak positions of the asymmetric spectra and roughly correspond to $K_y$. We could not obtain reliable shift values of $K_{8c}$, and $K_{24g}$ below 40 K. This is because the overlapping of the signals of intrinsic and impurity phases, and the broadening of the spectra make the peak positions ambiguous. In rare-earth compounds, the temperature dependence of
Knight shift $K(T)$ of ligand nuclei is related to the spin susceptibility $\chi_s$ of rare-earth ions with a transferred hyperfine field $H_{hf}$ as

$$K(T) = K_0 + \frac{H_{hf}}{N_A\mu_B}\chi_s(T), \quad (1)$$

where $K_0$ is an on-site contribution consisting of a conduction electron and a field-induced Van Vleck orbital terms, $N_A$ is Avogadros number, and $\mu_B$ is the Bohr magneton. As shown in Fig. 4, $K_{2a}$, $K_{8c}$, and $K_{24g}$ show similar temperature dependence: increase with decreasing temperature. It is apparent that $K_{2a}$ shows a larger temperature dependence than $K_{8c}$ and $K_{24g}$. This is attributed to large $H_{hf}$ at $2a$ site. $H_{hf}$ originates from the transferred hyperfine couplings with 4f spin of neighboring Ce ions. P at $2a$ site is surrounded octahedrally by six Ce atoms, while the number of NN Ce atom of $8c$ and $24g$ are two and three, respectively. Moreover, $2a$ site is closer to the NN Ce atoms than the others. These explain the larger temperature dependence of $K_{2a}$. Since P at $2a$ site is the most sensitive to the magnetism of Ce-4f electron, we focus on the temperature variation of $K_{2a}$.

In most of rare-earth compounds, it is often observed that magnetization data at low

**Table 1.** Deduced $^{31}$P Knight shift parameters of each crystallographic site at 150 K. The local axes of $x$ and $y$ are tentatively defined as the direction of $K_x > K_y$. $K_{iso}$ is defined as $K_{iso} \equiv (K_x + K_y + K_z)/3$.

| Position | Site Symmetry | $K_x$ (%) | $K_y$ (%) | $K_z$ (%) | $K_{iso}$ (%) |
|---------|---------------|-----------|-----------|-----------|---------------|
| 2a      | 43m           | 0.67      | 0.67      | 0.67      | 0.67          |
| 8c      | .3m           | 0.12      | 0.12      | 0.24      | 0.16          |
| 24g     | ...m          | 0.3       | 0.27      | 0.13      | 0.23          |
temperatures show the departure from straight-line against magnetic field. Then we employed data above 90 K and estimated $H_{\text{id}}$ from a slope in the $K_{2a}$ versus $\chi$ plot. The obtained value is roughly $H_{\text{id}} \simeq 0.78 \text{T}/\mu_B$. In order to deduce the Weiss-temperature, $K_{2a}$ was analyzed using the equation of $K(T) = K_0 + C/(T - \theta)$, where $C$ and $\theta$ are fitting parameters. We found that $K_0$ is negligible regardless of the temperature range above 90 K. Then we plotted the inverse of $K_{2a}$ as shown in the inset of Fig. 4 and estimated the value of $\theta$. The obtained varies from -15 K to -10 K depending on the fitting temperature range. The negative sign indicates an antiferromagnetic correlation between 4f spins. NMR measurement at low magnetic field and low temperatures is in progress to clarify the ground state of Ce$_6$Ni$_6$P$_{17}$.

4. Conclusion
$^{31}$P NMR measurement has been performed on Ce$_6$Ni$_6$P$_{17}$. NMR spectra show the Lorentzian-type and an asymmetric shapes. Taking the local symmetry around each site into account, we could assign three inequivalent P sites (2$a$, 8$c$, and 24$g$) and obtained each Knight shift. The large temperature dependence of $K_{2a}$ could be understood by considering the close NN distance and the octahedral coordination of Ce atoms around 2$a$ site. The temperature dependence of this $K_{2a}$ indicates a well-localized 4f electron state and antiferromagnetic correlation between local moments in Ce$_6$Ni$_6$P$_{17}$.

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