Site-selective $^{11}$B NMR studies on YbAlB$_4$

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Abstract. $\beta$-YbAlB$_4$ is a distinctive heavy fermion superconductor that exhibits unconventional quantum criticality without tuning in a strongly intermediate valence state. In this paper, we report the result of $^{11}$B NMR measurements on the single crystals of $\beta$-YbAlB$_4$ and $\alpha$-YbAlB$_4$, the locally isostructural polymorph of $\beta$-YbAlB$_4$. All $^{11}$B NMR lines for both samples were successfully assigned to inequivalent crystallographic sites by comparing the experimental results and the ab-initio calculation of the electric field gradient. In both compounds, the anisotropy of the Knight shift exhibits a characteristic radial pattern, indicating approximate axial symmetry of the hybridization between the Yb-4$f$ electrons and the conduction electrons.

1. Introduction

Heavy fermion systems have been studied over decades with great interest in unconventional superconductivity and non-Fermi liquid behavior in the vicinity of quantum critical points (QCP). $\beta$-YbAlB$_4$ is the first Yb-based heavy fermion superconductor ($T_c = 80$ mK) [1] and exhibits pronounced non-Fermi liquid behavior which can be seen in the temperature dependences of the resistivity ($\rho \sim T^{1.5}$ up to 0.1 K), the susceptibility ($\chi \sim T^{-0.5}$ up to 2 K), and the magnetic part of the specific heat ($C_M/T \sim \ln T$ up to 3 K) in zero magnetic field and ambient pressure [2]. Moreover, the hard X-ray photoemission spectroscopy (HXPES) measurement has revealed an intermediate valence of Yb$^{2.75+}$, providing the first example of quantum criticality in mixed valence systems [3]. On the other hand, $\alpha$-YbAlB$_4$, the locally isostructural polymorph of $\beta$-YbAlB$_4$, shows conventional Fermi liquid behavior in zero magnetic field though $\alpha$-YbAlB$_4$ also has an intermediate valence (Yb$^{2.73+}$ [3]) and similar crystal structure with $\beta$-YbAlB$_4$ [4] (figure 1).

Figure 1 shows the crystal structure of $\alpha$-YbAlB$_4$ and $\beta$-YbAlB$_4$ [4]. Both polymorphs of YbAlB$_4$ have orthorhombic structure but with different space group, $Pbam$ for $\alpha$-YbAlB$_4$ and $Cmmm$ for $\beta$-YbAlB$_4$. In both cases, the Yb and Al atoms reside within the same $ab$-plane which is sandwiched between two B layers. Yb atoms are centered between two heptagonal B-rings, and Al atoms are centered between pentagonal B-rings. The local structure of the two polymorphs are quite similar but distinguished by the packing pattern of the Yb hexagonal rings in the $ab$-plane. In this paper, we report the results of $^{11}$B NMR measurements on the single crystals of both polymorphs.
2. Experiment

Single crystals of $\alpha$-YbAlB$_4$ and $\beta$-YbAlB$_4$ were prepared by Al self flux method reported in [4]. We can distinguish these polymorphs by the typical sizes of the crystal, $1 \times 1 \times 5$ mm$^3$ for $\alpha$-YbAlB$_4$ and $1 \times 1 \times 0.1$ mm$^3$ for $\beta$-YbAlB$_4$ though both materials are synthesized together. The $^{11}$B NMR spectra were obtained by Fourier transforming the spin echo signals at discrete frequencies and summing them up. The measurements for $\alpha$-YbAlB$_4$ ($\beta$-YbAlB$_4$) were performed in a magnetic field of 6.0 T (5.0 T) and at $T = 20$ K (4.2 K).

3. Results

$\alpha$-YbAlB$_4$ ($\beta$-YbAlB$_4$) has four (three) crystallographically inequivalent B sites, B1-B4 (B1-B3) as shown in figure 1. The Wyckoff numbers and site symmetries of these sites are summarized in table 1. Figure 2(a) (2(b)) shows $^{11}$B NMR spectra for $\alpha$($\beta$)-YbAlB$_4$ observed at 3.0 K (4.2 K) under the magnetic field applied along the c-direction. Since $^{11}$B nuclei have spin $I = 3/2$, the electric field gradient (EFG) splits the NMR spectrum into equally spaced three lines due to the first order effect of the nuclear quadrupole interaction (quadrupole splitting). Then the spectrum can be decomposed of 4 (3) sets of resonance lines denoted A-D (E-G). In order to assign these four (three) sets of resonance lines to four (three) B sites, we measured the spectra under the field rotated in the ab-plane.

Figures 3(a) and 3(b) show the angle dependences of $^{11}$B NMR frequencies under the magnetic field in the ab-plane. In general, resonance frequency $\nu_m(\theta)$ should obey the following equation.

$$\nu_m = (1 + K(\theta))\gamma H_0 + (m - 1/2)\nu_Q(\theta)$$

Table 1. The list of the Wyckoff number, the site symmetry and the direction(s) of the principal axis (axes) for each B site.

| Site | $\alpha$-YbAlB$_4$ | $\beta$-YbAlB$_4$ |
|------|-------------------|-------------------|
|      | B1    | B2    | B3    | B4    | B1    | B2    | B3    |
| Wyckoff number | 4h    | 4h    | 4h    | 4h    | 4h    | 8q    | 4j    |
| Site symmetry  | .m    | .m    | .m    | .m    | 2mm   | .m    | m2m   |
| Principal axes | c     | c     | c     | c     | a, b and c | c     | a, b and c |
Figure 2. $^{11}$B NMR spectra for (a)α-YbAlB$_4$ ($H||c; H = 6.0$ T, $T = 3.0$ K), and (b)β-YbAlB$_4$ ($H||c; H = 5.0$ T, $T = 4.2$ K).

Here, $\gamma$ is the nuclear gyromagnetic ratio ($^{11}\gamma = 13.66012$ MHz/T), $\theta$ is the angle between the magnetic field and the $a$-axis, $K(\theta)$ is the Knight shift, $\nu_Q(\theta)$ is the quadrupole splitting, and $m$ specifies the nuclear transitions $I_z = m \leftrightarrow m - 1$. Only the frequencies of quadrupole satellite lines ($m = 3/2$ or $m = -1/2$) are plotted in figures 3(a) and 3(b) since the center lines ($m = 1/2$) from different sites overlap and cannot be well resolved. We also note that, except for B1 and B3 sites for β-YbAlB$_4$, the resonance lines from individual sites split into two sets of lines under the magnetic field in the $ab$-plane (see the discussion below). $K(\theta)$ and $\nu_Q(\theta)$ are determined by the following equations.

$$K(\theta) = (\nu_{3/2} + \nu_{-1/2} - 2\gamma H_0)/2\gamma H_0$$

$$\nu_Q(\theta) = (\nu_{3/2} - \nu_{-1/2})/2$$

The angle dependences of $K(\theta)$ and $\nu_Q(\theta)$ are shown in figures 3(c)-(f), which are well fitted by the following equations.

$$K(\theta) = K_{xx} + (K_{yy} - K_{xx}) \cos^2(\theta - \theta_K)$$

$$\nu_Q(\theta) = \nu_{xx} + (\nu_{\alpha\alpha} - \nu_{xx}) \cos^2(\theta - \theta_Q) \quad (\alpha = y \text{ or } z)$$

The directions of the principal axes (PA), $x$, $y$ and $z$, are defined to satisfy the relations $|K_{xx}| \leq |K_{yy}| \leq |K_{zz}|$ and $|\nu_{xx}| \leq |\nu_{yy}| \leq |\nu_{zz}|$. Here, $\theta_K$ and $\theta_Q$ indicate the $y$-direction of the Knight shift tensor and $\alpha$-direction for EFG tensor respectively. $\alpha$ represents the $y$-axis of the EFG tensor of all B sites except for D and G. For these sites, the $y$-axis of the EFG tensor is the $c$-axis and $\alpha$ becomes the $z$-axis. We summarize the principal values, the directions of the PA, and anisotropic parameters $\eta = (\nu_{yy} - \nu_{xx})/\nu_{zz}$ obtained by the fit in table 2.

In case of β-YbAlB$_4$, $a$- and $b$-axes are the PA of both the Knight shift and the EFG tensors for B1 and B3 sites whereas they are not for the B2 site. Therefore, $K(\theta)$ and $\nu_Q(\theta)$ for B2 site show neither a maximum nor a minimum along the $a$- and $b$-axes. Since the crystal structure has the mirror symmetry with respect to the $a$- and $b$-planes, the angle dependence of the whole spectrum must be symmetric about $a$- and $b$-axes. Therefore, a second set of resonance lines originating from the B2 site must exist to satisfy this requirement, as is indeed observed experimentally (solid and dashed lines in figure 3). Then, the set of lines F is immediately
assigned to B2 but the other B sites (E and G) cannot be assigned by considering only the site symmetry. NMR spectra for all B sites (B1-B4) of $\alpha$-YbAlB$_4$, on the other hand, exhibit qualitatively the same angle dependences with B2 site of $\beta$-YbAlB$_4$ since their site symmetries are the same and the crystal structure has the glide symmetries with respect to the a- and b-planes.

It has been recognized that the state-of-art technique of ab-initio calculation based on the density functional theory provides reliable estimate of the EFG [5, 6]. Table 3 shows the results of ab-initio calculation of the quadrupole splitting parameters $^{11}\nu^{\text{cal}}$, $|\theta_Q^{\text{cal}}|$ and $\eta^{\text{cal}}$. Comparison of the experimental and the calculated results of the EFG parameters immediately allows us to assign all the B sites as shown in the last line of table 2.

Table 2. The list of the principal values and the angle of the y-axis from a-axis of the Knight shift tensor (upper part). The principal values, the angles of the y-axis (z-axis for D and G) and the anisotropic parameters $\eta$ of the EFG tensor are listed in the middle part. The last line shows crystallographic sites assigned with A-G.

| Site  | A   | B   | C   | D   | E   | F   | G   |
|-------|-----|-----|-----|-----|-----|-----|-----|
| $^{11}K_{xx}$ [%] | 0.006 | −0.022 | −0.026 | −0.025 | 0.014 | −0.013 | −0.018 |
| $^{11}K_{yy}$ [%] | 0.083 | 0.103 | 0.097 | 0.093 | 0.103 | 0.106 | 0.104 |
| $^{11}K_{zz}$ [%] | −0.248 | −0.234 | −0.228 | −0.198 | −0.313 | −0.369 | −0.384 |
| $|\theta_K|$ [deg.] | 37.3 | 71.0 | 34.3 | 36.4 | 90.0 | 20.5 | 90.0 |
| $^{11}\nu_{xx}$ [MHz] | −0.296 | −0.067 | −0.052 | −0.032 | −0.322 | −0.020 | −0.018 |
| $^{11}\nu_{yy}$ [MHz] | −0.396 | −0.464 | −0.440 | −0.378 | −0.397 | −0.487 | −0.329 |
| $^{11}\nu_{zz}$ [MHz] | 0.701 | 0.532 | 0.500 | 0.379 | 0.720 | 0.506 | 0.343 |
| $|\theta_Q|$ [deg.] | 24.6 | 4.5 | 75.4 | 54.4 | 90.0 | 53.9 | 0.0 |
| $\eta$ | 0.143 | 0.747 | 0.775 | 0.913 | 0.105 | 0.922 | 0.907 |

| Site  | B3 | B2 | B4 | B1 | B3 | B2 | B1 |
|-------|----|----|----|----|----|----|----|

Table 3. The results of ab-initio calculation for the quadrupole splitting parameters. $|\theta_Q^{\text{cal}}|$ indicates angles of y-axis from a-axis.

| Site  | A   | B   | B3 | B4 | B1 | B2 | B3 |
|-------|-----|-----|----|----|----|----|----|
| $^{11}\nu^{\text{cal}}_{xx}$ [MHz] | −0.034 | −0.129 | −0.352 | −0.134 | −0.086 | −0.092 | −0.378 |
| $^{11}\nu^{\text{cal}}_{yy}$ [MHz] | −0.446 | −0.542 | −0.484 | −0.488 | −0.361 | −0.563 | −0.507 |
| $^{11}\nu^{\text{cal}}_{zz}$ [MHz] | 0.480 | 0.670 | 0.836 | 0.621 | 0.447 | 0.655 | 0.885 |
| $|\theta_Q^{\text{cal}}|$ [deg.] | 52.8 | 1.5 | 0.2 | 73.5 | 0.0 | 33.9 | 90.0 |
| $\eta^{\text{cal}}$ | 0.858 | 0.616 | 0.159 | 0.570 | 0.615 | 0.719 | 0.146 |
Figure 3. The angle dependences of NMR frequency ((a), (b)), the Knight shift ((c), (d)) and the quadrupole splitting ((e), (f)). (a), (c) and (e) are data for α-YbAlB$_4$, (b), (d) and (f) for β-YbAlB$_4$. Observed data are shown by the solid symbols while open symbols are the mirror reflection around a-axis. NMR frequency, $K$ and $\nu_Q(\theta)$ are fitted by equation (1), (4) and (5), respectively as shown by solid and dashed lines.
4. Discussions

The principal values of the Knight shift satisfy the relation $|K_{cc}| \gg |K_{yy}| \gg |K_{xx}|$ for all B sites. The value of $K_{cc}$ does not depend much on the sites, $K_{cc} = -0.2 \sim -0.25$ % for $\alpha$-YbAlB$_4$ and $K_{xx} = -0.31 \sim -0.38$ % for $\beta$-YbAlB$_4$. This is also the case for $K_{yy}$ (0.08 \sim 0.10 % for $\alpha$-YbAlB$_4$ and 0.09 \sim 0.10 % for $\beta$-YbAlB$_4$). However, the direction of the $y$-axis ($\theta_K$) varies significantly with the sites. In order to visualize the anisotropy of the Knight shift, we show the magnitude of $K_{yy}$ and the direction of the $y$-axis by the red arrows in figure 4. We can see that $y$-axis directs almost radially outward with respect to the heptagonal B ring for both polymorphs. This suggests that hybridization between the Yb-4f states and conduction B states has approximate axial symmetry. Yb-4f orbital has axial symmetry around $c$-axis and directs towards B-ring which surrounds Yb atom and the orbital may hybridize with $s$ or $p$ orbitals of conduction B atoms. This result is expected from the local crystal structure around Yb atoms and considered in the theoretical models [7, 8]. This also suggests that we can expect overall similar electronic structure for both $\alpha$-YbAlB$_4$ and $\beta$-YbAlB$_4$, even though physical properties at low temperatures and low magnetic fields are quite different.

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