Abstract. In order to clarify unusual superconducting properties, we have carried out \(^{9}\)Be NMR measurements for a single crystal of UBe\(_{13}\) with \(T_c \approx 0.85\) K. The NMR spectra under \(5\) T parallel to [001] crystal axis show no change between \(T_c(H = 5\) T) = 0.41 K and \(T_a(H = 5\) T) = 0.35 K. Below \(T_a\), however, the reduction of the Knight shift was observed. The reduction of the Knight shift of Be(II) is amount to \(0.02\) \%, which is much smaller than spin part of the Knight shift, \(K_0\) \(\approx 0.107\) \% estimated from electronic specific coefficient \(e\gamma_e = 1000\) \(mJ/(K^2\) amol). The origin of reduction of the Knight shift cannot be explained by spin singlet superconductivity.

1. Introduction

Since the discovery of heavy fermion superconductivity in UBe\(_{13}\), extensive experimental and theoretical works have been carried out in order to clarify the nature of the unusual normal and superconducting(SC) states of UBe\(_{13}\). The SC transition occurs at around \(T_c \approx 0.85\) K with large specific heat jump, \(\Delta C/\gamma_e T_c \approx 1\) [1, 2], indicating that the heavy-quasiparticles are responsible for the superconductivity. In the SC state, the power law temperature dependence of the specific heat, the NMR spin-lattice relaxation rate, magnetic field penetration depth, etc., suggest that the SC energy gap vanishes at points and/or lines on the Fermi surface [2, 3, 4, 5]. These features have been interpreted as evidence for an anisotropic pairing state, most likely a \(p\)-wave triplet state in UBe\(_{13}\). Furthermore, the anomalies have been observed at \(B^*\) in several measurements, specific heat, magnetization, surface impedance etc.[6, 7, 8], which have been discussed the change of the SC order parameters like UPr\(_3\)[9], related to second phase transition in U_{1-x}Th_xBe\(_{13}\)(\(x = 0.02 \sim 0.04\)) [10]. However, the reduction of the Knight shift below \(T_c\) have been observed in \(\mu^+\)SR studies and suggests that the spin singlet state is realized in UBe\(_{13}\) [11]. Moreover, recent specific heat measurements suggest multi-band full-gap like symmetry [12]. Therefore, the parity of the superconductivity of UBe\(_{13}\) has been controversial and more information is needed in order to clarify the nature of superconductivity.

In order to gain a further understanding of the unconventional SC state, we have carried out \(^{9}\)Be NMR measurements on a single crystal UBe\(_{13}\) applied field 5 T parallel to [001] crystal axis. In an applied field of 5 T, UBe\(_{13}\) shows the SC transition and anomalous behavior at \(T_c =\)
0.45 K and $T_a = 0.32$ K respectively, which have been obtained by surface impedance studies as shown in Fig.1.

![Figure 1.](image-url)

Figure 1. The $T$-$H$ phase diagram of UBe$_{13}$ obtained from surface impedance measurements. $H_1^*(\text{open square})$ and $H_2^*$ (open triangle) are indicate maximal and minimal point of the surface resistance respectively. Closed circle indicates the $H_{c2}$. $T_c$ and $T_a$ indicate SC transition and appearance of anomaly temperature under applied field of 5 T respectively. NMR measurements were carried out under 5 T, which is shown by the solid line. The inset shows field dependence of the surface resistivity $R_S$ [8].

2. Experimental procedures

Single crystals of UBe$_{13}$ were grown by the Al-flux method. Details of sample preparation techniques for single crystals of UBe$_{13}$ was reported elsewhere [13]. Samples were characterized to be a single phase by a Laue photograph as well as the X-ray diffraction. The SC phase transition was confirmed to occur at $T_c \approx 0.85$ K by DC electrical resistivity and surface impedance measurements [8, 13]. NMR measurements have been carried out using a conventional pulsed NMR spectrometer and a 12 T solenoid superconducting magnet. The sample was fixed on a Bakelite holder and installed a top loading type $^3$He-$^4$He dilution refrigerator down to 0.12 K. The sample temperature was monitored using a calibrated RuO$_2$ resistor at low $T$'s (50 mK - 20 K).

3. Results and Discussion

The temperature dependence of $^9$Be-NMR spectra of UBe$_{13}$ under applied field of 5 T $\parallel$ [001] axis is shown in Fig.2. The NMR spectra show no change between 1 K and 0.37 K, even though
temperature is below $T_c = 0.45$ K. On the other hand, the change of the spectra can be observed below $T_a = 0.35$ K and the change become more clearly with decreasing the temperature. The $T_a$ at which the anomalous spectra change was observed is equivalent to the minimal point in surface impedance as shown in Fig.1 by open square.

![Figure 2. The temperature dependence of $^{9}$Be NMR spectra at $\mu_0 H = 5$ T parallel to [001]. The dashed line is guide to the eye.](image)

In order to clarify the origin of the change of the spectra below $T_a$, we tried the spectral simulation calculation. The resonance frequencies for each Be sites were calculated by exact diagonalization of the $4 \times 4$ nuclear spin Hamiltonian matrix of $^{9}$Be as follow,

$$
\mathcal{H} = -\gamma_n \hbar I \cdot H_0 - \gamma_n \hbar [I \cdot \hat{K} \cdot H_0] - \gamma_n \hbar I \cdot H_d
+ \frac{1}{6} \hbar \nu_Q [3I_Z^2 - I(I + 1) + \eta (I_+^2 + I_-^2)]
$$

The first term represents to the Zeeman interaction. The second term is due to the hyperfine interaction described by the second rank Knight shift tensor $\hat{K}$. Here, $\hat{K}$ is composed of the isotropic part $K_{iso}$ and the anisotropic part $K_i (i=1, 2, 3)$. The third term is the classical dipolar interaction between nuclear spin and the dipole field arising from the localized U spin moment. The last term corresponds to the nuclear quadrupole interaction. Here, $\hbar$ is Planck constant and $\hbar = \hbar/2\pi$. $\nu_Q = 3e^2qQ/2hI(2I-1)$ denotes the NQR frequency where $eq = V_{ZZ}$ is the maximum principal value of the electric field gradient (EFG) tensor at each sites. $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ exhibits the asymmetry parameter. The notation described here follows the previous report and the detail of the calculation has been reported in ref [13]. These simulation calculations were carried out through a trial and error process.

Fig.3(a) displays the observed spectrum(solid line) and its simulation (dotted line) at $T = 1$ K for $H \parallel [001]$ at 5 T. The simulation calculation using previous NMR/NQR parameters reproduces well the experimental results. The best fit parameters are obtained as $\nu_Q = 0.8 \pm 0.02$
Figure 3. The comparison of the spectra between experimental data (solid line) and simulation (dotted line) at (a) 1K and (b) 0.12K.

kHz, $\eta = 0.21 \pm 0.01$, $K_{\text{iso}} = 0.13 \pm 0.01\%$, $(K^1, K^2, K^3) = (0.04, 0.015, -0.055) \pm 0.01\%$ and line width $\sigma = 9 \pm 1$ kHz at 1 K.

Fig.3(b) shows the spectrum observed at 0.12 K. Apparently, it is difficult to reproduce the whole line profile using the parameters at 1 K. Therefore, we try to determine the parameters which can explain NMR the spectrum at 0.12 K. The calculated spectrum is shown by dotted line in Fig.3(b).

At 0.12 K, the NMR spectrum can be reproduced by changing only the isotropic Knight shift and line width with $K_{\text{iso}} = 0.11 \pm 0.01\%$, and $\sigma = 13 \pm 1$ kHz. The reduction of the $K_{\text{iso}}$ is $\Delta K_{\text{iso}} \sim 0.02\%$, which is 15% of the $K_{\text{iso}}$. At the present stage, the change of $K_{i}$ cannot be determined. Because, the amount of the change of $K_{i}$ is smaller than $\Delta K_{i} = 0.01\%$. Even if we assume the reduction of $K_{i}$ the same ratio ($\sim 15\%$) as $K_{\text{iso}}$, the NMR spectra can be also reproduced in anomaly phase.

The temperature dependence of $K_{\text{iso}}$ are obtained and shown in Fig.4. The temperature dependence of $K_{\text{iso}}$ does not change between 1 K and 0.37 K passing through $T_{c}$, whereas it decreases below 0.37 K and reaches constant value at 0.32 K. The observed reduction of $K_{\text{iso}}$ is very small amount to $\Delta K_{\text{iso}} \sim 0.02\%$, as mentioned before. If we estimate the Knight shift of the quasiparticle spin part from the specific heat coefficient $\gamma_{c}$, $K_{\gamma} \sim 0.107\%$ is obtained assuming the conventional Fermi liquid picture [14]. This estimated value $K_{\gamma}$ is almost comparable to the experimental value $K_{\text{iso}}$ in the normal state. Thus the Knight shift would be almost constituted by spin part $K_{s}$ contribution.

If the reduction of the Knight shift is related with superconductivity, several possibilities are expected. One is that the spin singlet state is realize in UBe$_{13}$, another is existence of degenerated order parameters like UPt$_{3}$ [9]. In the former case which the spin singlet state is realized below $T_{a}$, Knight shift should decrease to $K \sim 0.01\%$ at $T \ll T_{c}$. This expected value is markedly different from observed value $K_{\text{iso}} \sim 0.1\%$. Hence it is difficult that the origin of the reduction of the Knight shift is ascribed to spin singlet superconductivity. Whereas, in the latter case that UBe$_{13}$ has the degenerated order parameters of SC state, the reduction of Knight shift can be explained by the change of the order parameter below $T_{a}$. However, recent several measurements suggest that a short range ordering occurs below $B^{*}(T_{a})$ [15, 16]. If such a short range ordering occurs, the NMR spectra are expected to change. Unfortunately, our data are insufficient to conclude that such a short range ordering occurs. To confirm whether or not such a short range ordering occurs below $T_{a}$, we have to measure NMR spectra in other
4. Summary

We have performed the NMR studies and observed the anomaly in the Knight shift which decrease below \( T_a \). The reduction of the Knight shift is very small \( \sim 0.02\% \). This reduction of the Knight shift cannot be explained by spin singlet state. On the other hand, the degenerated order parameters can be exist in spin triplet SC state, which can cause the change of the Knight shift. Hence the reduction of Knight shift would be related to spin triplet SC state. However, the possibility of short range order have not been excluded. To obtain more information of the anomaly below \( T_a \), the measurements in various field and direction are needed.

Acknowledgments

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