103Rh-NMR studies in the superconductor Rh$_{17}$S$_{15}$

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Abstract. 103Rh nuclear magnetic resonance (NMR) measurements have been performed in the superconductor Rh$_{17}$S$_{15}$ with the transition temperature $T_C$=5.4 K. The observed 103Rh-NMR spectrum shows an asymmetric shape with several peaks, reflecting the local symmetry around each Rh site. We have identified the observed NMR lines corresponding to four different Rh sites and obtained the temperature ($T$) dependence of the Knight shift of 24$m$ site. The isotropic part of the Knight shift $K_{iso}$ decreases with decreasing $T$, indicating the existence of the electron correlation in Rh$_{17}$S$_{15}$. In the superconducting state, the resonance lines shift to higher frequencies owing to a decrease of the spin part of the Knight shift with negative hyperfine coupling.

1. Introduction

Although most of the rhodium-sulfides are diamagnetic semiconductors, Rh$_{17}$S$_{15}$ is known to be a metallic compound and shows superconductivity below $T_C$=5.4 K [1]. Recently, Naren et al. recognized that the strongly correlated electrons at the narrow d bands are responsible for the superconductivity of this compound [2]. The large electronic specific heat coefficient and the enhanced magnetic susceptibility suggest the presence of the electron correlation. Furthermore the large specific heat jump at $T_C$ implies the superconductivity in a strong coupling regime. Interestingly, the estimated value of upper critical filed $H_{C2}$ ≈ 23.5 T is larger than the Pauli paramagnetic limiting field [2, 3].

Rh$_{17}$S$_{15}$ forms the cubic structure belonging to the space group $Pm3m$. Rh atoms occupy crystallographically four different positions ($24m$, $6e$, $3d$, $1b$) as shown in Fig. 1(a). Among them $1b$ site is located at the body centered position surrounded by $24m$ site which forms the cage with the triangular and quadrangular faces, while $3d$ site is in the middle of $6e$ site on the edge of the cubic cell. The shorter Rh-Rh distance between $3d$ and $6e$ sites is thought to develop considerable d-orbital overlapping and result in narrow d band [1, 2, 3].

2. Experimental

Polycrystalline Rh$_{17}$S$_{15}$ was prepared by the conventional solid-state reaction method as described in ref [2, 3]. The critical field of the present sample agrees well with the literature [2, 3]

For the nuclear magnetic resonance (NMR) experiments, the sample was crushed into powder. NMR measurements were performed using a conventional phase-coherent pulsed spectrometer at the temperature ($T$) -range of 1.5 -240 K and a constant magnetic field of $H$=7.094 T. The
Figure 1. (a) Crystal structure of Rh$_{17}$S$_{15}$. The large circles represent Rh atom and the small circles represent S atoms. The unit cell has 4 types of Rh sites, 24$m$, 6$e$, 3$d$ and 1$b$, and three types of S sites, 12$i$, 12$j$ and 6$f$. (b) An example of the $^{103}$Rh NMR spectrum at 110 K and 7.094 T. The solid curve along experimental points indicates the best-fit line shape after the Gaussian convolution to the powder pattern for 24$m$ site (below 9.55 MHz). On other hand, the solid curve for spectrum at higher frequency (above 9.55 MHz) indicates the simulated overlap of three spectra drown by thin lines. The Knight shift parameters obtained from those spectra are shown in Table 1. The inset shows the $^{103}$Rh NMR spectrum at 210 K. The thin line represents the bare powder pattern. Here, the local axes of $x$ and $y$ are tentatively defined as the direction with $K_x > K_y$ at 240 K.

spectra were measured using standard spin-echo detection ($\pi/2-\tau_D-\pi, \pi/2$ pulse length=70$\mu$s, $\tau_D = 500\mu$s). $T_C$ at 7.094 T is determined as 3.8 K by the sudden change of the self-inductance of an NMR coil.

3. Results and discussion

Figure 1(b) shows a typical powder pattern for the $^{103}$Rh NMR spectra ($\gamma_n/2\pi=0.134$ kHz/Oe, $I=1/2$) at 110 K obtained by sweeping frequency. The asymmetrically broadened line-shape arises from the anisotropy of the Knight shift. Generally the total Knight shift $K$ is a function of $\theta$ and $\phi$, and written as

$$K(\theta, \phi) = K_{\text{iso}} + \frac{K_1}{2}(3 \cos^2 \theta - 1) - \frac{K_2}{2} \sin^2 \theta \cos 2\phi$$

$$K_{\text{iso}} = \frac{1}{3}(K_x + K_y + K_z)$$

$$K_1 = K_z - K_{\text{iso}} = -\frac{1}{3}K_x - \frac{1}{3}K_y + \frac{2}{3}K_z$$

$$K_2 = K_y - K_x,$$

where $K_{\text{iso}}$ is an isotropic shift parameter, $\theta$ is the zenithal angle between the local symmetry axis and the applied field $H$. $\phi$ is the azimuthal angle. $K_x, K_y$ and $K_z$ are the shift parameters for $H$ parallel to the local $x, y, z$ axes, respectively; $K(\pi/2,0) = K_x, K(\pi/2, \pi/2) = K_y, K(0,0) = K_z$. When a nucleus is in an environment of axial symmetry, $K_x = K_y$ results in $K_2=0$ and $K_1 = K_x = K_y$ is generally called an anisotropic shift [4]. Note that we tentatively define the local axes of $x$ and $y$ as the direction with $K_x > K_y$ at 240 K.
Figure 2. (a) $T$-dependence of the $^{103}$Rh Knight shifts in Rh$_{17}$S$_{15}$. $K_x$, $K_y$ and $K_z$ of 24m site were extracted as shown in Fig. 1. $K_{x,y}$ of 6e site was determined at the peak around 9.58 MHz. (b) $T$-dependence of the $^{103}$Rh isotropic Knight shift $K_{iso}$ of 24m site in Rh$_{17}$S$_{15}$. The inset shows $K_{iso}$ at low $T$.

Rh$_{17}$S$_{15}$ has crystallographically four inequivalent Rh sites in a unit cell. Taking into account the intensity ratio and the local symmetry around each site, we successfully assigned corresponding sites by following procedure. Since the point symmetry of Rh 24m site is lower than axial one, the spectra arising from that site has three shift parameters, $K_x$, $K_y$ and $K_z$. Typical power pattern spectrum reflecting anisotropic shift effects can be seen in the inset of Fig. 1(b). The line shape around 9.54 MHz can be assigned to the Rh 24m site and reproduced satisfactorily by convoluting the Gaussian function to lower symmetry pattern. The direction of the $x$, $y$ and $z$ of each Rh atom position in the crystal could not be determined in the present study using polycrystalline sample. NMR experiment on single crystal is desirable. An example of calculated line shape is shown with experimental points in Fig. 1(b). On the other hand, spectrum at higher frequency side (9.56-9.59 MHz) has a rather complicated shape. This shape can be considered to be consisting of three different Rh sites and to be reproduced by a sum of three powder patterns of 6e and 3d sites with the axial symmetry and 1b with cubic. The estimated shift parameters at 110 K are given in Table 1.

Table 1. The estimated $^{103}$Rh Knight shift parameters of each crystallographic position (site) at 110 K.

| Position | $K_{iso}$ (%) | $K_1$ (%) | $K_2$ (%) |
|----------|---------------|-----------|-----------|
| 24m      | 0.38          | -0.10     | 0.02      |
| 6e       | 0.76          | -0.09     | —         |
| 3d       | 0.62          | 0.06      | —         |
| 1b       | 0.63          | —         | —         |

Figure 2 shows the $T$-dependence of the Knight shift. $K_x$, $K_y$ and $K_z$ are derived from the parameter-fitting described above. For the spectra at higher frequency side, only $K_1(=K_x=K_y)$ of 6e site is shown. Due to overlap of the signals from three different Rh sites which take close Knight shift values, it is difficult to determine other Knight shifts of them, 6e, 3d and 1b...
sites. The observed Knight shifts are positive and decrease with decreasing $T$ except for $K_y$, which shows the nearly $T$-independent behavior. We have measured the nuclear spin-lattice relaxation rate ($1/T_1$) at 24$m$, 6$e$ and 3$d$ sites. $1/(T_1T)$ of each site increases with decreasing $T$. The value of $1/(T_1T)$ of 24$m$ site is four (ten) times larger than that of 6$e$ (3$d$) site (not shown here). This result indicates that 4$d$ electrons at Rh 24$m$ site play an important role in the electron correlation and superconductivity. Therefore, in order to discuss the $T$ variation of the Knight shift of Rh$_{17}$S$_{15}$, we plot the isotropic shift $K_{iso}$ of Rh 24$m$ site in Fig. 2 calculated with equation (2).

The Knight shift is, generally, comprised of the $T$-independent orbital contribution $K_{orb}$ and the $T$-dependent spin contribution $K_s$, as $K(T) = K_{orb} + K_s(T)$. Here, $K_s(T) = A_s \chi_s(T)$, where $A_s$ is the hyperfine coupling constant and $\chi_s$ is the uniform spin susceptibility. Note that $K_s$ is responsible for the $T$ dependence of the shift. Above $T_C$, in contrast to the increase of $\chi$ with decreasing $T$, $K_{iso}$ decreases with decreasing $T$ [2]. This suggests the negative $A_s$, which is dominated by the Rh 4$d$ inner core-polarization. In order to decompose the $K_{orb}$ and $K_s$ in the measured $K$, a plot of $K(T)$ vs the bulk susceptibility $\chi$ is generally used. However, we did not obtain reliable $\chi$ of our samples because of the strong sample dependence of $\chi$. Although we fail to estimate $K_{orb}$ quantitatively in the present stage, $|K_s|$ increases with the decrease of $T$ indicating the increase of $\chi_s$.

As shown in the inset of Fig. 2(b), we observed the increase of $K_{iso}$ below $T_C$ in contrast with the usual superconducting behaviors. Similar behavior has already been reported in the LaFeAsO$_{0.7}$ [5]. In this case the change of $K_{iso}$ below $T_C$ is fully expected to be smaller than the $T$-variation of $K_{iso}$ in the normal state. Because the change of $K_{iso}$ below $T_C$ is sometimes associated with those of $K_s$ and the superconducting diamagnetic shift $K_{dia}$ due to the screening current. So the decrease of $K_s$ is observed in the increase of $K_{iso}$ owing to the negative hyperfine coupling constant $A_s$, followed by the change of $K_{iso}$ which is reduced by the change of $K_{dia}$. Thus the measured result suggests the formation of the spin-singlet Cooper pairs in Rh$_{17}$S$_{15}$. Applied magnetic field dependence of $K_{iso}$ is highly desirable for the $T$-variation of $K_s$ in the superconducting state.

4. Conclusion

The $^{103}$Rh NMR spectra were obtained both in the superconducting and the normal states of Rh$_{17}$S$_{15}$. Taking into account the number of atoms and local symmetry of each site, we could assign four Rh sites (24$m$, 6$e$, 3$d$, 1$b$) into NMR spectra. The existence of magnetic correlation in Rh$_{17}$S$_{15}$ could be inferred from the $T$-dependent behavior of the Knight shift. The spin-singlet superconductor is evident from the sudden increase of $K_{iso}$ reflecting of the decrease of $|K_s|$.

5. References

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