NMR study of heavy fermion compound EuNi$_2$P$_2$

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Abstract. We report the results of $^{31}$P-nuclear magnetic resonance (NMR) measurements on heavy fermion compound EuNi$_2$P$_2$ in order to investigate the magnetic properties at low temperatures from a microscopic viewpoint. The Knight shift has a negative value in an entire temperature range, and the absolute value increases with decreasing temperature but exhibits a broad maximum around 40 K, which is similar to the behavior of the magnetic susceptibility. Also, the nuclear spin-lattice relaxation rate $1/T_1$ is almost constant at high temperatures above 200 K, which is reminiscent of the relaxation mechanism dominated by the interaction of the $^{31}$P nucleus with fluctuating Eu-4$f$ moments. Below 200 K, $1/T_1$ gradually decreases on cooling due to the change of the valence in the Eu ion. At low temperatures, $1/T_1$ does not obey the Korringa relation, in contrast to typical heavy fermion compounds. The nuclear spin-spin relaxation rate $1/T_2$ shows the similar behavior as $1/T_1$ at high temperatures. But, below 50 K, $1/T_2$ increases upon cooling due to the development of the magnetic excitation.

1. Introduction

Some Eu-based intermetallic compounds are known to exhibit valence instability. Among them, EuNi$_2$P$_2$ with the ThCr$_2$Si$_2$-type tetragonal structure is a typical material exhibiting valence fluctuation. From the Mössbauer measurements[1], this compound shows a gradual change of the valence in the Eu ion between 2.25 (at 300 K) and 2.50 (at 1.4 K), thus intermediate valence even at the lowest temperature. The magnetic susceptibility has the Curie-Weiss temperature dependence at high temperatures, but it almost saturates below 40 K and does not diverge as $T \rightarrow 0$ K[1, 2], which is typical of a mixed-valence materials. The specific heat measurements exhibits no phase transitions down to 80 mK, which strongly suggests a non-magnetic ground state[2, 3]. Also, an electronic specific heat coefficient $\gamma$ is estimated to be $\sim$ 100 mJ/(mol K$^2$)[2, 3], thus EuNi$_2$P$_2$ is known as a heavy fermion compound. A recent photoemission spectroscopy experiment reveals the presence of a heavy band[4]. Recently, Hiranaka et al., have reported an intensive shrinkage of the volume below about 100 K in the temperature dependence of thermal expansion and have indicated that the heavy fermion state is clarified to be based on the Kondo effect as in a typical heavy fermion compound CeRu$_2$Si$_2$[2].

In this paper, we focus on the magnetic properties of EuNi$_2$P$_2$ by $^{31}$P-nuclear magnetic resonance (NMR) experiments, and discuss the microscopic electronic states related to a change of the valence in the Eu ion and the heavy fermion state. It is helpful to make use of the NMR method for a study of local electronic properties. We also compare with the previous and recent NMR results[5, 6, 7].
2. Experimental

Single crystalline EuNi$_2$P$_2$ samples were synthesized using the Sn-flux method. Samples were characterized by powder X-ray diffraction at room temperature. Magnetic susceptibility was measured using a SQUID magnetometer in the temperature range of 2–300 K. For the NMR measurements, samples were crushed into powder. NMR measurements were performed in the temperature range of 1.5–300 K using a conventional phase-coherent pulsed spectrometer. NMR spectrum was obtained by sweeping magnetic field. The nuclear spin-lattice relaxation rate $1/T_1$ was measured by the saturation recovery method. The nuclear spin-spin relaxation rate $1/T_2$ was determined with the standard $\pi/2 - \tau - \pi$ pulse sequence with changing the interval $\tau$.

3. Results and Discussion

Figure 1(a) displays the $^{31}$P NMR spectrum of EuNi$_2$P$_2$ at $f = 18.59$ MHz and $T = 4.2$ K. The spectrum is almost symmetric, suggesting that the anisotropy of the Knight shift components is small. Figure 1(b) presents the temperature dependences of the full width at half maximum (FWHM) of the spectrum. FWHM increases with decreasing temperature, but it shows a maximum around 30 K and decreases upon cooling.

Figure 2(a) indicates the temperature dependence of the Knight shift of the $^{31}$P nuclei, $^{31}K$. The Knight shift was determined at the resonance peak. The Knight shift has a negative value in an entire temperature range. The absolute value of the Knight shift increases with decreasing temperature and shows the maximum around 40 K, which is similar to the previous recent reports[5, 7]. Inset shows the temperature dependence of the magnetic susceptibility $\chi$ for the magnetic field $H$ along the [100] direction. $\chi$ shows the Curie-Weiss (CW) behavior above 100 K with the effective magnetic moment $\mu_{\text{eff}} = 7.0 \mu_B$/Eu and the Weiss temperature $\theta_W = -100$ K. The value of $\mu_{\text{eff}}$ is slightly smaller than $\mu_{\text{eff}} = 7.94 \mu_B$/Eu in Eu$^{2+}$. Below 100 K, $\chi$ deviates from the CW law and shows a broad peak around 40 K. Such a broad peak in $\chi$ is one of the characteristic features of intermediate valence compounds. The behavior of $\chi$ is similar to that of the previous report[2]. Also, the behavior of $\chi$ is similar to that of the Knight shift. Figure 2(b) shows the $K - \chi$ plot with the temperature as an implicit parameter. Above 50 K, $^{31}K$ has a linear relation with $\chi$ and the hyperfine field on $^{31}$P nuclei is estimated as $A_{\text{hf}} = -6.0$ kOe/$\mu_B$, which is similar to the previous and recent reports[5, 7]. This negative hyperfine field originates from the core polarization by P-2$p$ states. Below 50 K, the deviation from the linear relationship in $K - \chi$ plot was observed, which is similar to some heavy fermion systems.
Figure 2. (a) Temperature dependence of the Knight shift of the $^{31}\text{P}$ nuclei, $^{31}\text{K}$. Inset shows the temperature dependence of the magnetic susceptibility $\chi$ for the magnetic field $H$ along the [100] direction. (b) $K - \chi$ plot with the temperature as an implicit parameter.

Figure 3 shows the recovery curves of the nuclear magnetization of $^{31}\text{P}$ in EuNi$_2$P$_2$ at (a) 1.5 K and (b) 20 K. The nuclear spin-lattice relaxation rate $1/T_1$ was measured at the resonance peak. The recovery of the nuclear magnetization above 10 K is single component for the spin $I = 1/2$ of $^{31}\text{P}$ nuclei as follows:

$$M(t) = M_0[1 - \exp(-t/T_1)]$$

where $M_0$ and $M(t)$ are the nuclear magnetization in the thermal equilibrium and at a time $t$ after the saturating pulse, respectively. On the other hand, below 10 K, the recovery is not single component, thus we tentatively estimate $1/T_1$ by fitting the recovery data to the two exponential function,

$$M(t) = M_S(t) + M_L(t) = M_0[a(1 - \exp(-t/T_{1S})) + (1 - a)(1 - \exp(-t/T_{1L}))].$$

The coefficient $a$, the short and long relaxation time constants, $T_{1S}$ and $T_{1L}$, are treated as unknown parameters. The obtained volume fraction of the short component is $a \approx 0.4 \pm 0.1$ and is almost temperature-independent within error. The long component $T_{1L}$ leads as $T_{1L}/T_{1S} \sim 10$ at low temperatures.

Figure 3(c) shows the temperature dependence of $1/T_1$ for the external magnetic field of 0.4 and 1.1 T. At high temperatures above 200 K, $1/T_1$ is seen to be nearly independent of temperature, which is reminiscent of the relaxation mechanism dominated by the interaction of the $^{31}\text{P}$ nucleus with fluctuating Eu-$4f$ moments.

When the nuclear magnetic relaxation is dominated by fluctuations of the hyperfine field coming from exchanged-coupled local spins, using the well-known theory by Moriya[8], the relaxation rate is given by

$$1/T_1 = \sqrt{2\pi (g\gamma_N A_{hf})^2 S(S + 1)}/3\omega_{ex}$$

where $\omega_{ex}$ is a fluctuation frequency parameter defined by $(h\omega_{ex})^2 = 6(k_B \theta_W)^2/[zS(S + 1)]$ with $z(= 8)$ nearest neighbouring spins. Thus, with $\theta_W = -100$ K from $\chi(T)$ and $A_{hf} = -6.0$ kOe/$\mu_B$ from $K - \chi$ plot, we obtain $1/T_1 \sim 7 \times 10^4$ s$^{-1}$ in case of $S = 7/2$ for Eu$^{2+}$, which is about one order larger than the experimental value. We suppose that the Eu valence fluctuations, reported from the Mössbauer measurements[1], are one reason for this reduction of $1/T_1$. 

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Below 200 K, on the other hand, $1/T_1$ gradually decreases upon cooling due to the change of the valence in the Eu ion. Inset shows the the plot of $1/T_1$ vs average valence estimated from the Mössbauer measurements[1], with the temperature as an implicit parameter. We find the behavior that $1/T_1$ is scaled to average valence above 50 K. But, it deviates from the linear relation below 50 K, which suggests the quenching the magnetic moments of the localized 4f electrons by the Kondo effect. At low temperatures below 10 K, $1/T_1$ distributions and gradually increases upon cooling, which is quite different from the Korringa relation as expected for typical heavy fermion compounds[9, 10]. Also, $1/T_1$ depends on the external magnetic field, which suggests the existence of the magnetic fluctuations. Recently, Yogi et al., report the magnetic field dependence of $1/T_1$ in the high magnetic field range up to 7 T[7], and they indicate that $1/T_1$ is suppressed by the magnetic field at low temperatures and is proportional to the temperature at the magnetic field of 7 T, such as typical heavy fermion compounds.

Figure 4(a) indicates the spin-echo decay curves of 1.5 K and 50 K. The spin-echo intensity $M(2\tau)$ shows single exponential decay and $1/T_2$ is obtained by fitting the following formula $M(2\tau) = M_0 \exp(-2\tau/T_2)$ in an entire temperature range. Figure 4(b) illustrates the temperature dependence of $1/T_2$. At high temperatures, $1/T_2$ shows the similar behavior as $1/T_1$, that is, $1/T_2$ is almost constant above 200 K and gradually decreases with decreasing temperature down to 50 K due to the change of the valence in the Eu ion. Inset show the plot of $1/T_2$ against $1/T_1$ above 10 K with the temperature as an implicit parameter. $1/T_2$ is scaled to $1/T_1$ above 50 K as $a + b \times 1/T_1$ with $a = 3.0 \times 10^3$ s$^{-1}$ and $b = 1.2$. The first term $a$ is considered to originate from the nuclear dipole interaction and the second term is considered to be the contribution from the electron spins. Below 50 K, on the other hand, in contrast to the behavior of $1/T_1$, $1/T_2$ increases with decreasing temperature. In general, $1/T_2$ probes longitudinal fluctuations around zero frequency and the Redfield contribution proportional to $1/T_1$, while $1/T_1$ probes the transverse fluctuations at the nuclear frequency. The contrasting behavior of $1/T_2$ and $1/T_1$ may be due to the dominance of longitudinal fluctuations, but also to a strong variation of the spectral density as a function of frequency.
4. Summary
We have carried out $^{31}$P-NMR experiments on EuNi$_2$P$_2$ in order to clarify the magnetic properties at low temperatures from a microscopic viewpoint. The NMR spectrum is almost symmetric, indicating the Knight shift component is nearly isotropic. The value of the Knight shift is negative in an entire temperature range. Similar to the behavior of the magnetic susceptibility, the absolute value of the Knight shift increases upon cooling and exhibits a broad maximum around 40 K, as similar to the previous results. $1/T_1$ is nearly constant at high temperatures above 200 K, reminiscent of the relaxation mechanism dominated by the interaction of the $^{31}$P nucleus with fluctuating Eu-4$f$ moments. But, below 200 K, $1/T_1$ gradually decreases with decreasing temperature due to the change of the valence in the Eu ion. Furthermore, below 50 K, $1/T_1$ decreases more than the change of the valence which suggests the quenching the Eu-4$f$ moments by the Kondo effect. In contrast to the results of typical heavy fermion compounds, $1/T_1$ is not proportional to the temperature at low temperatures due to the existence of the magnetic fluctuations. Also, $1/T_2$ shows the similar behavior as $1/T_1$ at low temperatures. But, below 50 K, $1/T_2$ increases upon cooling due to the development of the magnetic fluctuations.

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