

**27^\text{Al}-NQR study in BaNiSn_3-type CeCuAl_3**

M. Matsumura, Y. Kawamura, M. Yoshina, T. Nishioka and H. Kato

Graduate School of Integrated Arts and Sciences, Kochi University, Kochi 780-8520, Japan

E-mail: matumura@cc.kochi-u.ac.jp

**Abstract.** We have firstly observed 27^\text{Al}-NQR signal in CeCuAl_3, which is assigned to the Al(2) site, one of the two crystallographic sites of Al (Al(1) and Al(2)). The NQR spectrum in the paramagnetic region is composed of two kinds of Al(2) signals associated with the different environments. One comes from Al(2) in the regular atomic configuration and the other is attributed to Al(2) affected by the neighboring site-disorder between Cu and Al(1) sites. NQR measurement were performed on sample containing less than 5% site-disorder which is the best one we obtained. The start of the spectral broadening as well as the critical divergence of the nuclear spin-lattice relaxation rate 1/T_1 indicate that T_N \approx 3.3 K. The broad spectrum suggests an incommensurate modulation in the antiferromagnetic state. 1/T_1 in the paramagnetic state is well explained in terms of the dynamics of Ce 4^f localized moment through RKKY and the cf exchange interactions.

1. Introduction

The BaNiSn_3-type heavy Fermion (HF) compounds recently attract much attention concerning to their superconductivity in the noncentrosymmetric lattice. For example, BaNiSn_3 type CeRhSn_3, CeIrSi_3 and CeCoGe_3 exhibit superconductivity near neighbor to the quantum critical point (QCP) under pressure.[1, 2, 3] It is proposed that the absence of the inversion symmetry violates the parity conservation of the Cooper pairing state and a mixture of singlet and triplet spin state of Cooper pair is stabilized.[4, 5] The experimental determination of the symmetry of the Cooper pairing in the superconductivity near QCP in BaNiSn_3-type HF metal is an intriguing subject in connection with their strong electron correlation.

The present BaNiSn_3-type CeCuAl_3 is one of the candidates of the HF superconductor near QCP. In the ambient pressure, the electrical resistivity, the magnetic susceptibility and the specific heat measurements reveals the Kondo temperature T_K of about 10 K, the antiferromagnetic (AF) ordering temperature T_N of about 3 K and the crystalline electric field (CEF) splitting T_{CEF} of about 10 K.[6, 7] The same order among T_K, T_N, and T_{CEF} is a characteristic property in this compound. Although the superconductivity has not been found at present, the previous NMR measurements for Cu and Al up to 0.5 GPa prospected that QCP would be attained by applying relatively low pressure of about 1 GPa.[8]

In CeCuAl_3, Al atoms occupy two crystallographic sites, so called Al(1) and Al(2) sites. Alternative occupation of Cu and Al(1) atoms along the c-axis raises the absence of the inversion symmetry in this compound. It is known that the macroscopic properties depends on the sample quality, which is probably ascribed to the site-disorder between Al(1) and Cu atoms. Hence the site order/disorder is a crucial issue to be solved beforehand in this compound. The Al(2)-NQR spectrum, which was detected for the first time in the present experiment, is found to be sensitive...
to the site-disorder. We will evaluate the site-disorder from the Al(2)-NQR spectrum for a few samples prepared by the different synthetic conditions. Furthermore, the NQR result in ambient pressure will be reported for the sample with less than 5% site-disorder.

2. Experimental Results and Discussion

The three kind of samples were prepared as followings; (1) the poly crystal annealed at 800 °C for 1 week (Poly Anneal), (2) the single crystal by tri-arc Czocralski method (Single) and (3) the non-stoichiometric CeCu_{0.9}Al_{3.1} poly crystal annealed at 800 °C for 1 week. All the samples were confirmed to be a single phase by XRD. The NQR measurements were carried out using the phase coherent spin-echo spectrometer.

Figure 1 shows the NQR spectra at 4.2 K for respective samples. The two sharp peaks at 1.66, and 1.35 MHz clearly seen in "Poly Anneal" are assigned to the Al(2) site. The quadrupole frequency \( \nu_Q(=3e^2qQ/2I(2I−1)) \) and the asymmetry parameter \( \eta \) of EFG are estimated as \( \nu_Q=0.91 \) MHz and \( \eta=0.785 \), here \( I \) is the nuclear spin of \(^{27}\text{Al}(I=5/2)\), \( q \) and \( Q \) the maximal component of EFG tensor and the quadrupole moment of the nucleus, respectively. The magnitude of \( \nu_Q \) and the value of \( \eta \) are comparable with those in CeAuAl\(_3\) (\( \nu_Q=1.17 \) MHz and \( \eta=0.88 \)).[9] This assignment of the NQR lines to Al(2) is consistent with the previous NMR results performed on the oriented powder along the a-axis.[10] The singular positions in the NMR spectrum are well reproduced using the present quadrupole parameters if the maximal principal axis (Z-axis) of EFG is along to the crystal a-axis. The Z-axis of EFG lying on the a-axis is the same as the Al(2) site in the isostructural LaAuAl\(_3\), but not as that in CeAuAl\(_3\), suggesting that the Z-axis is sensitive to a slight difference of the charge distribution in the compound.[9]

![Figure 1](image_url)  
**Figure 1.** NQR spectra for three kind of samples at 4.2 K.

Beside the main peaks, the satellite peaks around 1.85 and 1.60 MHz appear in "Single" and CeCu\(_{0.9}\)Al\(_{3.1}\). The tentative decomposition is shown by the dotted lines. Since the volume fraction of the satellite peak becomes large in the non-stoichiometric CeCu\(_{0.9}\)Al\(_{3.1}\), the satellite peaks probably come from Al(2) sites located near neighbor to the disordered sites between Cu
and Al(1). The NQR spectrum was found to be useful probe to evaluate the site-disorder. It is noted that, even in "Single" crystal, about 30% of Al(2) is affected by the site disorder of the neighboring atoms. We have carried out NQR measurements for "Poly Anneal", the best sample at present with the slight site-disorder less than 5% as shown in Fig. 1.

Figure 2 shows the T-dependence of \( \nu_Q \) and \( \eta \) in the paramagnetic state. The almost constant \( \eta \) and monotonous decrease of \( \nu_Q \) with rising temperature indicate no structural transition occurring in this compound other than a simple thermal expansion.

Figure 3 exhibits the NQR spectrum in the AF state. The spectral broadening is seen below 3.5 K, indicating AF ordering. In a narrow range from 3.5 K to 3.0 K, the narrow spectra at the paramagnetic NQR position coexists as shown in Fig. 3 by the dotted line, suggesting a spatially inhomogeneous AF ordering. A small internal field at Al site generally causes a symmetric splitting for the NQR spectrum. Thus the almost symmetric broad spectrum at 1.5 K indicates a continuous distribution of the internal field at Al sites, implying an incommensurate modulation of the AF ordering as like a multi-sinusoidal or the spiral in the c-plane proposed in CeAuAl\(_3\).[9] The half width of the half amplitude \( \sim 0.6 \) MHz correspond to the internal field at Al(2) site of 0.5 kOe in average, moreover, the tail of the spectrum corresponds to the maximum internal field of 2 kOe. If the same contribution of four n.n Ce atoms to the internal field are assumed, the Ce moments are estimated to be about 0.04 \( \mu_B \) in average and 0.16 \( \mu_B \) in maximum referring to the hyperfine coupling constant \( A_{hf} \sim 3.2 \) kOe/\( \mu_B \)Ce obtained in the previous Knight shift measurement.[10] Both values for Ce moments are fairly small compared with the effective moment 2.1 \( \mu_B \) in the paramagnetic static susceptibility. Taking into account the results of 1/\( T_1 \), this might be attributed to a cancellation of the respective internal fields from n.n. Ce moments rather than a Kondo shielding.

The \( T \)-dependence of the nuclear spin-lattice relaxation rate 1/\( T_1 \) is shown in Fig. 4. The \( f \)-electron component (1/\( T_1 \))\(_f\) is estimated by subtracting the value of 1/\( T_1 \) in isostructural LaCuAl\(_3\) with no \( f \) electrons ((1/\( T_1 \))\(_{LaCuAl3}\)=0.032 (1/secK) ). At higher temperatures than about 100 K, (1/\( T_1 \))\(_f\) \( \propto 1/T \). At lower temperatures than this, it is nearly constant down to 7 K, and decreases rapidly below \( T_N \) after a critical divergence at \( T_N \sim 3.3 \) K.
In the paramagnetic state, the behavior of $1/T_1$ is well interpreted by the individual dynamics of the Ce localized moment. In a fast fluctuation regime of localized moment model, $(1/T_1)_f$ is roughly written as, $(1/T_1)_f \sim z(A_{hf}/\hbar)^2 \tau$, where $z$ is the number of n.n. Ce atoms, $\tau$ the correlation time of Ce moment. The correlation frequency $1/\tau$ is determined by the following two processes as, $1/\tau = 1/\tau_{\parallel} + 1/\tau_{\perp}$. The first term, $1/\tau_{\parallel}$ is the exchange frequency due to the RKKY exchange interaction between Ce moments and is roughly written as $1/\tau_{\parallel} \sim J_{ex}/\hbar$ using exchange coupling constant $J_{ex}$. The second one, $1/\tau_{\perp}$, is due to the Korringa like relaxation of Ce spin moment through $\epsilon$ exchange interaction, and is written as $1/\tau_{\perp} \sim 1/\hbar \cdot J_{\epsilon \epsilon}^2 \cdot \rho(\epsilon_F)^2 \cdot k_B T$ using $\epsilon$ exchange coupling constant $J_{\epsilon \epsilon}$ and the density of state of conduction electrons at the Fermi energy $\rho(\epsilon_F)$. Combining these relationships, the $T$-dependence of $(1/T_1)_f$ is expected to follow the formula $(1/T_1)_f = a/(1 + bT)$ with fitting constants $a$ and $b$. The dotted line in Fig. 4 represents a fit to this formula, showing a good qualitative agreement. Furthermore, if the parameters are chosen tentatively as; $A_{hf}$ described before, $J_{ex} \sim 100$ K, $\rho(\epsilon_F) J_{\epsilon \epsilon} \sim 0.5$ and $z=4$, the right order of $(1/T_1)_f$ is given quantitatively, for example $160 \text{ (1/sec)}$ at 100 K.

In summary, $^{27}$Al-NQR spectrum at Al(2) site has been firstly measured for the sample “Poly Anneal” with the site-disorder less than about 5%. The broadening of the NQR spectrum without fine structure and the divergence of $1/T_1$ indicate an AF order below $T_N \sim 3.3$ K to be an incommensurate modulated type. The dynamics of the Ce moment is well described based upon a localized moment model, consisting with the low $T_K$ ($\sim 10$ K). The present results provide a base for the future measurements to survey the superconductivity near QCP under pressure.

Figure 4. $T$-dependence of $1/T_1$.

References
[1] Kimura N, Ito K, Saitoh K, Umrda Y, Aoki H and Terashina T 2005 Phys. Rev. Lett. 95 247004
[2] Sugitani I et al 2006 J. Phys. Soc. Jpn. 75 043703
[3] Settai R et al 2007 J. Magn. Magn. Mater. 310 844
[4] Gor’kov L P, Rashba E I 2001 Phys. Rev. Lett. 87 037004
[5] Frigeri P A, Agterberg D F, Koga A and Sigrist M 2004 Phys. Rev. Lett. 92 097001
[6] Kontani M, Ido H, Ando H, Nishioka T and Yamaguchi Y 1994 J. Phys. Soc. Jpn. 63 1652
[7] Mock S, Pfeiffer C and Lounes H v 1999 J. Low. Temp. Phys. 115 Nos. 1/2
[8] Kontani M, Sugihara N, Murase K and Mori N 1996 Czech. J. Phys. 46 Supplement 4, 2067
[9] Vonlanthen P, Gavilano J L, Ambrosio B and Ott H R 1999 Eur. Phys. J. B 7 9
[10] Aoyama S, Ido H, Nishioka T and Kontani M 1996 Czech. J. Phys. 46 Supplement 4, 2069