

# A Cu NQR study in a $d$ -electron heavy-fermion system, $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$

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## Abstract

Cu nuclear quadrupole resonance (NQR) studies have been carried out for  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ , which has been suggested to show a heavy-fermion-like behavior although it possess no  $f$  electron. A Lorentzian shape of the Cu NQR line with a narrow width implies that no magnetic ordering appears, at least, down to 5K. The spin-lattice relaxation rate of the Cu nuclei probes a change of the Cu  $3d$  electron nature, resulting in the Fermi liquid state at a low temperature. These facts strongly support that the heavy fermion picture is available in the compound concerned.

*Key words:* NMR, heavy fermion

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## 1 Introduction

One of the attractive topics in strongly correlated electron system is a heavy fermion (HF), where the current carriers act as if they have heavy masses that are of  $10$ - $10^3$  times the free electron mass. The important key in understanding the HF phenomenon is the Kondo effect, which mixes the localized magnetic moment and the conduction electrons by spin singlet formation. A HF phase is usually realized in compounds containing crystallographically ordered allays of lanthanide or actinide atoms, wherein the  $f$  electrons from the lanthanide or actinide atoms participate in the HF formation as localized moments; the

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localized moments are quenched by the Kondo effect and the consequential quasiparticles are inferred to have heavily enhanced masses.

Nuclear magnetic resonance (NMR) has provided valuable information regarding microscopic electron behavior at the NMR nucleus site. On this merit, a lot of NMR studies in HF systems have been widely carried out and have brought us many fruits in understanding the HF state. So far, most of the studies have been subject to the ligand nucleus that has no localized moment, since NMR for lanthanide or actinide nucleus practically accompanies a lot of difficulties. The ligand-site NMR in the HF systems proves the conduction electron nature, helping us trace the HF formation on the conduction electron side. However, we still note that, from the ligand-site NMR, the properties of the localized moments in the HF phase are indirectly evidenced only through the change of the conduction electron nature.

Recently, a few transition metal compounds with containing no  $f$  electron are suggested to show a HF-like behavior. One candidate is an A-site-ordered cubic perovskite system,  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ , which exhibits the moderately enhanced electron specific heat coefficient  $\gamma_e = 28 \text{ mJ}/(\text{Cu mol K}^2)$ , the  $T^2$  dependence of the resistivity  $\rho$ , and the susceptibility of  $\sim 1.4 \times 10^{-3} \text{ emu/Cu mol}$  with showing a maximum around 200 K[1]. Since the ratio between  $\gamma$  and the  $T^2$  coefficient  $A$  of  $\rho$  in the compound is in the framework of the Kadowaki-Woods plot, Kobayashi *et al.* have suggested that the compound is a HF system with the Kondo temperature  $T_K$  of about 200 K, wherein the Cu  $3d$  electrons play a role analogous to the  $f$  electrons role in the conventional HF systems, (i.e., the localized moments constituting the HF state) while the Ru  $4d$  works as the conduction electrons[1]. Recent photoemission study supports the  $3d^9$  configuration for Cu ( $\text{Cu}^{2+}$ ) whose band resides well below the Fermi surface, as well as the highly itinerancy of the Ru- $4d$  electron[2]. Hence, in order to clarify whether the compound is a true HF system or not, we have tried to elucidate the microscopic nature of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  by means of NMR. We also note that, if this system is a true HF, NMR survey of the concerned compound would be attractive since the possible localized moment site (Cu) is distinguishable from the conduction electron sites and is a transition metal, which would allow us to carry out on-site NMR studies directly probing the localized electron nature in the HF state. In the previous report[3], we have presented the field-sweep NMR spectrum of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  and evaluated the Knight shift as well as the quadrupole parameters of the Cu site. In this paper, we report nuclear quadrupole resonance (NQR) studies of the Cu nuclei, which indicate that no (short- nor long-ranged) magnetic ordering appears in this compound and that the spin-lattice relaxation rate  $1/T_1T$  divided by the temperature  $T$  is  $T$ -dependent and shows a Korringa-like behavior below 20 K. These findings strongly suggest the formation of the HF state below the temperature.

## 2 Experiments

The polycrystalline  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  measured was prepared by a conventional solid state reaction. The starting materials were  $\text{CaCO}_3$ ,  $\text{RuO}_2$ , and  $\text{CuO}$ , and the stoichiometric mixture was calcined at 880 °C. The resulting sample was checked by X-ray diffraction and was confirmed as a single phase of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ . The powder sample with the polycrystalline randomly oriented was packed in a teflon tube of  $\sim 9\phi$ . All NQR measurements in zero magnetic field were performed with a phase-coherent spin echo spectrometer. The spin-lattice relaxation was measured by monitoring the recovery of the spin echo intensity  $M(t)$  following a saturating pulse sequence, where  $t$  is the separation time between the saturating pulse and the echo sequence.

## 3 Results and discussion

In general, a nucleus with the spin moment  $I > 1/2$  in a noncubic environment is affected by quadrupole interactions. The Hamiltonian can be written as,  $H = \frac{\hbar\nu_Q}{6}\{3I_z^2 - I^2 + \frac{1}{2}\eta(I_x^2 - I_y^2)\}$ . Here, the axes  $x, y, z$  are the principal axes of the electrical field gradient (EFG) tensor  $V_{ij}$ , so that  $|V_{zz}| > |V_{yy}| > |V_{xx}|$ ;  $\nu_Q$  is defined as  $3e^2qQ/2I(2I-1)\hbar$ , where  $eq$  is the nuclear quadrupole moment, and  $eQ \equiv V_{zz}$ . The asymmetry parameter  $\eta$  denotes  $(V_{xx} - V_{yy})/V_{zz}$ .  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  has the space group of  $Im\bar{3}$ , wherein Cu is located at one crystallographic site, the  $6b$   $(\frac{1}{2}, \frac{1}{2}, 0)$  with the  $mmm$  local symmetry (no axial symmetry)[4]. Since the two isotopes of Cu ( $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ ) both have  $I$  of  $3/2$ , the asymmetric environment of Cu gives rise to quadrupole interactions, causing one NQR line for each isotope in zero magnetic field. With the diagonalization of  $H$ , the NQR line of Cu appears at the position of

$$\nu_{NQR} = \nu_Q \sqrt{1 + \eta^2/3}. \quad (1)$$

The zero-field Cu NQR spectrum taken at 5 K is shown in Fig. 1. At the frequencies of 19.73 and 18.26 MHz,  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  sharp peaks are well observed. The resonance positions agree well with the  $\nu_{NQR}$  values expected from  $\nu_Q$  and  $\eta$  evaluated in our previous studies[3] ( $^{63}\nu_Q = 18.0$  MHz,  $^{65}\nu_Q = 17.0$  MHz and  $\eta = 0.34$ ). The peak shapes are single-Lorentzian-like, being consistent with the one site of Cu involving no atomic disorder such as antisite to the Ru or Ca sites. The line widths are narrow; the full-widths at half maxima (FWHM) of the peaks are only  $\sim 0.2$  MHz. At higher temperatures (up to 300 K), although the peak positions are slightly shifted to higher frequency, the line shapes and FWHM are almost independent of  $T$ . This indicates that no short- nor long-ranged magnetic ordering appears in this compound, at

least down to 5 K; if any magnetic ordering arises, the hyperfine fields from the ordered moments would affect the nuclear spin energy levels, causing line broadening or considerable  $T$ -dependent shift of the NQR lines. Hence, we find that the gradual decrease seen in the susceptibility below 200 K[1] owes *not* to any ordering including a formation of spin-glass state.

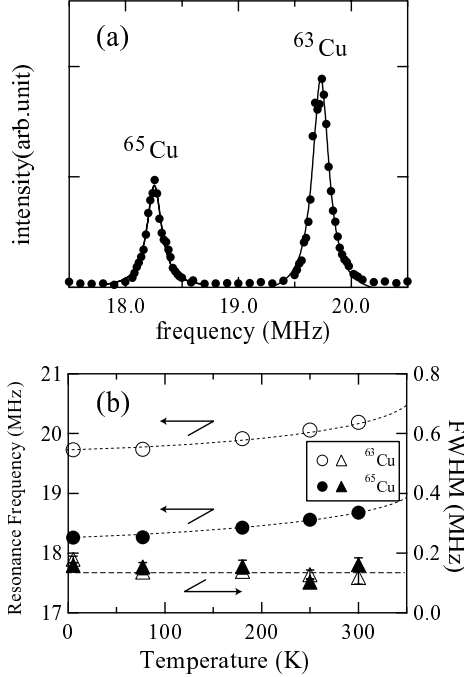


Fig. 1. (a) Cu NQR spectrum of CaCu<sub>3</sub>Ru<sub>4</sub>O<sub>12</sub>. The temperature is 5 K. (b)  $T$ -dependences of the resonance frequencies and the full-widths at half-maxima (FWHM) for the two lines. The broken lines are guide for eyes.

The spin-lattice relaxation was measured for the <sup>63</sup>Cu and <sup>65</sup>Cu lines. The recovery curves for the both lines show a single-exponential behavior in the whole temperature range;  $1/T_1$  for the NQR ( $|\pm 3/2\rangle \rightleftharpoons |\pm 1/2\rangle$ ) transitions can be determined with the equation of,

$$M(t) = M(\infty)[1 - \exp(-3t/T_1)]. \quad (2)$$

The evaluated  $1/T_1$  ratio between the both lines,  ${}^{63}(1/T_1)/{}^{65}(1/T_1)$ , is  $\sim 0.86$ , which is similar to the square of the nuclear gyromagnetic ratio between the isotopes,  $({}^{63}\gamma/{}^{65}\gamma)^2 = 0.87$ , rather than the square of the  $Q$  ratio,  $({}^{63}Q/{}^{65}Q)^2 = 1.17$ . This indicates that the relaxation of the Cu nucleus is mainly due to a magnetic origin.

Figure 2 shows the  $T$  dependence of  $1/T_1$  measured for the <sup>63</sup>Cu line. At lower temperature than 20 K,  $1/T_1$  shows a  $T$ -linear dependence, so-called the Korringa-like behavior ( $1/T_1 T = \text{const.}$ ), which is characteristic to a metal system showing a  $T$ -independent susceptibility wherein the low energy magnetic fluctuation on the Fermi surface dominates the relaxation. Now, the

temperature below which the Korringa-like behavior appears is defined as  $T_F$ . The constant behavior of  $1/T_1T$  clearly indicates an appearance of the Fermi liquid state below  $T_F$ .

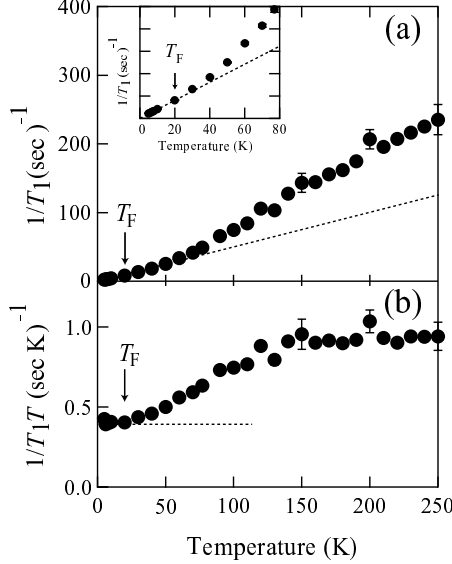


Fig. 2.  $T$ -dependences of the spin-lattice relaxation rate  $1/T_1$  (a) and  $1/T_1T$  (b) for the  $^{63}\text{Cu}$  line. The temperature below which  $1/T_1$  follows  $\propto T$  (a Korringa-like behavior) is denoted as  $T_F$ .

In a dense Kondo scenario which is acceptable for conventional  $f$ -electron HF materials, coherence effects of the Kondo interactions lead the electrons to a crossover from the quasiparticles well described in a Fermi-liquid picture (at a low  $T$ ), to the magnetic state involving the localized moments (well above  $T_K$ ). Based on the constant behavior of  $1/T_1T$  in this compound, we strongly suggest an emergence of the HF-like quasiparticles below  $T_F$ ; this is also consistent with the lack of magnetic ordering at any temperatures. Although  $1/T_1T$  at high  $T$  is expected to show a change reflecting the crossover to the localized moments limits realized well above  $T_K$ , we must note that our measurements, at present, does not cover such the high temperature region; Kobayashi *et al.*[1] have suggested  $T_K$  for this system as an order of about 200 K according to the maximum of the uniform susceptibility. Further measurements at temperatures rather higher than room temperature would be needed to confirm the crossover of the  $d$  electron nature.

Lastly, we mention to the  $1/T_1T$  behavior just above  $T_F$ . With increasing the temperature above  $T_F$ ,  $1/T_1$  *upward* deviates from the Korringa line;  $1/T_1T$  increases from the constant value above  $T_F$ . This behavior seems contrast with those of some typical  $f$ -electron HF materials including  $\text{CeCu}_6$ [5] and  $\text{CeRu}_2\text{Si}_2$ [6], wherein the ligand-site NMR indicates  $1/T_1T$  showing a constant behavior at a low temperature and then monotonically decreasing above the temperature. However, it has been pointed out that the referred two com-

pounds involve strong antiferromagnetic fluctuation as well as Kondo screening effects of the local moments[7]; in this case,  $1/T_1T$  would probe both of the two effects. Here, we refer to another HF material, YbCu<sub>5</sub>[8], showing that the spin-lattice relaxation rate  $(1/T_1T)_f$  owing to the  $f$  electron fluctuations, which was evaluated throughout fine analyses from the ligand site NMR, indicates the behavior similar to  $1/T_1T$  of Cu in CaCu<sub>3</sub>Ru<sub>4</sub>O<sub>12</sub>. In the YbCu<sub>5</sub> case, the temperature dependence of  $(1/T_1T)_f$  is well ascribed to weakly-correlated and screened local-moment fluctuation effects being scaled by a single characteristic temperature  $T_0$ , which relates to the Kondo temperature[8,9]. It was shown that the scaling behavior on  $T_0$  holds for many mixed-valence and HF materials[8–11]. We infer that the similar phenomenon occurs in CaCu<sub>3</sub>Ru<sub>4</sub>O<sub>12</sub>, wherein the  $d$  electrons weakly correlated to each other might play a role as the local moments in constituting the HF state. Of course, at present, this is rather speculative; to evaluate the  $d$  electron fluctuation nature in this compounds, further analyses and experiments (e.g. temperature evolution of the Knight shift and coupling constants determination) would be needed.

## 4 Conclusion

Our NQR measurements regarding the spectrum and spin-lattice relaxation of the Cu nucleus in CaCu<sub>3</sub>Ru<sub>4</sub>O<sub>12</sub> have indicated no magnetic ordering as well as formation of the Fermi-liquid state at a low temperature. These strongly suggests that the compounds concerned can be regarded as a HF system, although it contains no  $f$  electron.

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## References

- [1] W. Kobayashi, I. Terasaki, J. Takeya, I. Tsukada, and Y. Ando, *J. Phys. Soc. Jpn.* 73 (2004) 2373-2376
- [2] T.T. Tran, K. Takubo, T. Mizokawa, W. Kobayashi, and I. Terasaki, *Phys. Rev. B* 73 (2006) 193105
- [3] H. Kato, T. Tsuruta, T. Nishioka, M. Matsumura, H. Sakai, and S. Kambe, *J. Magn. Magn. Mat.* in press
- [4] S.G. Ebbinghaus, A. Weidenkaff, and R.J. Cava, *J. Solid State Chem.* 167 (2002) 126-136

- [5] Y. Kitaoka, K. Fujiwara, Y. Kohori, K. Asayama, Y. Ōnuki, and T. Komatsubara, *J. Phys. Soc. Jpn.* 54 (1985) 3686-3689
- [6] K.Ueda, Y. Kitaoka, H. Yamada, Y. Kohori, T. Kohara, K. Asayama, *J. Phys. Soc. Jpn.* 56 (1985) 867-870
- [7] J. Rossat-Mignod, L.P. Regnault, and J.L. Jacoud *J. Magn. Magn. Mat.* 76-77 (1988) 376-684
- [8] N. Tsujii, K. Yoshimura, and K. Kosuge, *Phys. Rev. B* 59 (1999) 11813-11817
- [9] D.L. Cox, N.E. Bickers, and W. Wilkins, *J. Appl. Phys.* 57 (1985) 3166
- [10] K. Ishida, et al., *Phys. Rev. B* 71 (2005) 024424
- [11] N.J. Curro, J.L. Sarrao, J.D. Thompson, P.G. Pagliuso, S. Kos, Ar. Abanov, and D. Pines, *Phys. Rev. Lett.* 90 (2003) 227202