^{75}As-NQR study of the hybridization gap semiconductor $CeOs_4As_{12}$

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Abstract. We performed an ^{75}As nuclear quadrupole resonance (NQR) measurement on $CeOs_4As_{12}$. The ^{75}As-NQR spectrum shape demonstrates that the Ce-site filling fraction of our high-pressure synthesized sample is close to unity. A presence of the $c-f$ hybridization gap is confirmed from the temperature dependence of the nuclear spin-lattice relaxation rate $1/T_1$. An increase of $1/T_1$ below $\sim$3 K indicates a development of the spin fluctuations. The $1/T_1$ for $CeOs_4As_{12}$ shows similar behavior as that for $CeOs_4Sb_{12}$ with different magnitude of the $c-f$ hybridization gap. An absence of phase transition in $CeOs_4As_{12}$ may be caused by the increase of the $c-f$ hybridization, which increases the gap magnitude and reduces the residual density of state inside the gap.

1. Introduction

The filled skutterudite compounds with the chemical formula RT_4X_{12} (R = rare earth; T = Fe, Ru or Os; X = P, As or Sb) have unique body-centered cubic structure (space group: $Im\bar{3}$, T_h^5 No.204); a rare-earth ion is surrounded by the cage consists of twelve pnictogen atoms. As a consequence, strong hybridization occurs between conduction and f-electrons which gives rise to various physical phenomena, such as metal-insulator transition, exotic multiband superconductivity, unconventional heavy fermion state, and so on [1, 2, 3].

Most Ce-based filled skutterudite compounds show insulating or semiconducting behavior, on the basis of which they are called hybridization-gap semiconductors or Kondo semiconductors. The magnitude of the $c-f$ hybridization gap is related to a lattice constant of the crystal and collapses for Sb-based compounds [4, 5]. Among them, $CeOs_4Sb_{12}$ is one of unique compound in Ce-base filled skutterudite which indicates an apparent spin fluctuations below $\sim$25 K and antiferromagnetic (AFM) order below $\sim$1 K [6]. The AFM order is suppressed by applying magnetic field $\mu_0 H \approx 1$ T [7]. However, in the magnetic field above $\sim$1 T, another ordered phase with anomalous $H-T$ phase diagram were reported [4, 8, 9].

Recently, Yan *et al.* reported similar band alignments for $CeOs_4Sb_{12}$ and $CeOs_4As_{12}$ from density-functional-theory calculations [10]. From their calculations, $CeOs_4Sb_{12}$ and $CeOs_4As_{12}$ are predicted to become topological Kondo insulators at low temperatures. Macroscopic experiment also observed similar behavior between $CeOs_4Sb_{12}$ and $CeOs_4As_{12}$ [4, 11]. To clarify

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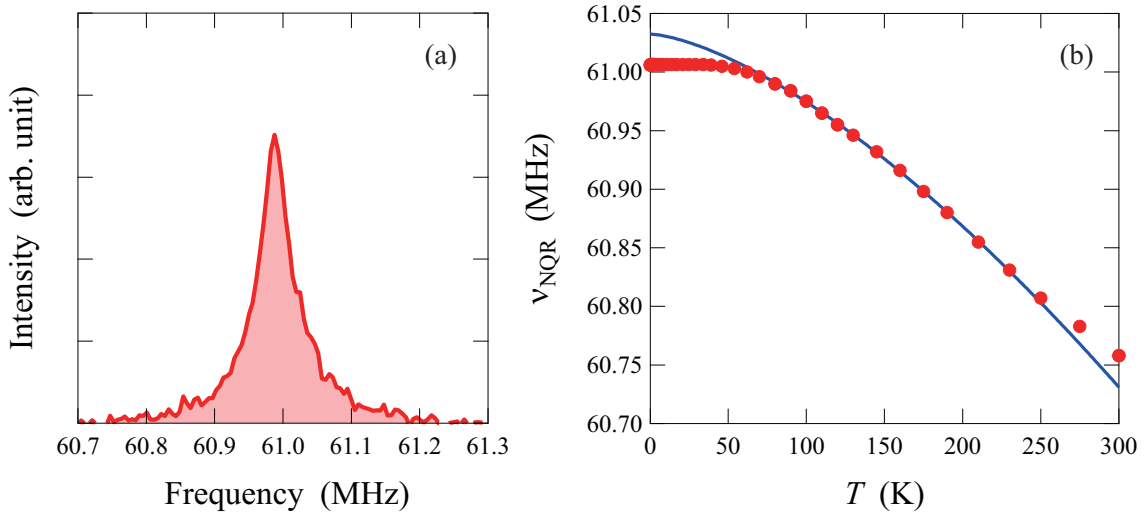


Figure 1. (a) ^{75}As-NQR spectrum of $CeOs_4As_{12}$ at $T = 70$ K. (b) Temperature dependence of the resonance frequency ν_{NQR}. Solid curve indicates an empirical relation $\nu_{NQR} = \nu_q(1-\alpha T^{3/2})$ (see text).

its electric state from a microscopic viewpoint, we have carried out ^{75}As-NQR measurement on $CeOs_4As_{12}$.

2. Experimental

Polycrystalline of $CeOs_4As_{12}$ was prepared at high-temperature and high-pressure using a wedge-type cubic anvil high-pressure apparatus [5]. The compound was prepared by reaction of stoichiometric amounts of each metal and arsenic powder at 4 GPa. The reaction temperature and time were 800 °C and 90 min, respectively. The sample was characterized by powder X-ray diffraction using CuKα_1 radiation and silicon as a standard. For the NQR measurement, the crystal was powdered to facilitate applied rf-field penetration. The pulse NQR measurement was performed on ^{75}As nucleus ($I = 3/2$) by a conventional spin-echo method using a conventional phase-coherent spectrometer in the temperature range 0.2-300 K. The NQR spectrum was obtained by a summation of the FFT spectrum as a function of frequency. The nuclear spin-lattice relaxation time T_1 was measured by a saturation-recovery method.

3. Results and Discussion

The NQR Hamiltonian is described as

$$\mathcal{H}_Q = \frac{h\nu_Q}{6}[3I_z^2 - I^2 + \frac{\eta}{2}(I_+^2 + I_-^2)], \tag{1}$$

with $\nu_Q \equiv \frac{3eQV_{zz}}{2I(2I-1)h}$ and $\eta \equiv \frac{V_{xx}-V_{yy}}{V_{zz}}$, where ν_Q is the nuclear quadrupole frequency, and η is the asymmetry parameter. Here, Q is the nuclear quadrupole moment, and $V_{\alpha\alpha} \equiv \partial^2 V/\partial\alpha^2$ ($\alpha = x, y, z$) are three components of the electric field gradient (EFG) tensor, where V is the electrostatic potential at the nuclear position. In the case of $I = 3/2$, one resonance line appears at frequency,

$$\nu_{NQR} \equiv \nu_Q\sqrt{1 + \frac{\eta^2}{3}}. \tag{2}$$

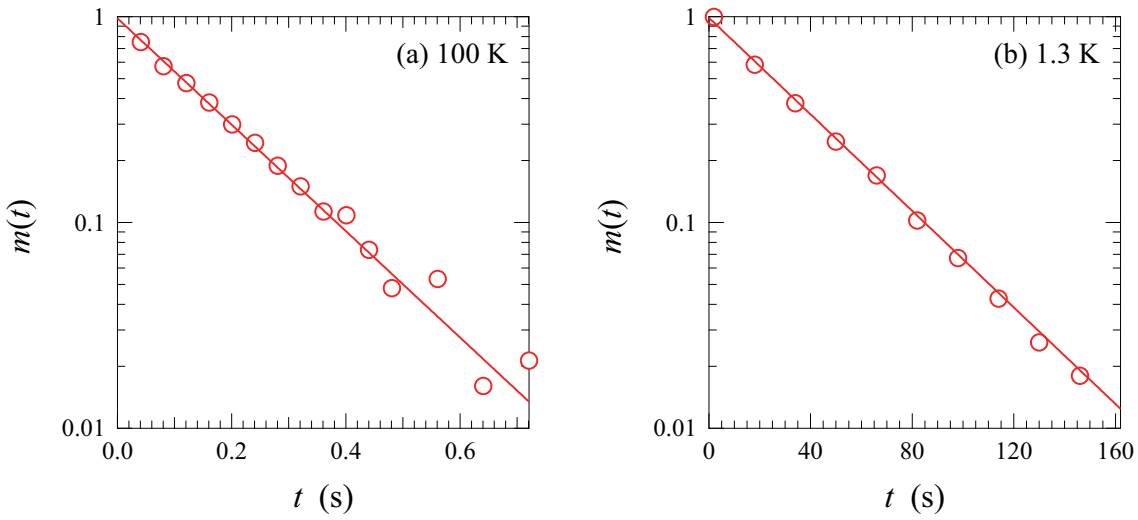


Figure 2. Recovery curves $m(t)$ of the nuclear magnetization $M(t)$ at $T = 100$ and 1.3 K.

Figure 1(a) shows ^{75}As-NQR spectrum at 70 K. The spectrum has almost symmetric shape without additional peaks indicating the filling fraction of Ce atom is close to unity.

The temperature dependence of the NQR frequency $\nu_{\rm NQR}$, which is determined from the peak position of the spectrum, is shown in Fig. 1(b). The $\nu_{\rm NQR}$ increases with decreasing temperature and becomes almost constant below $\sim$ 50 K. Usually, thermal lattice expansion is one of the origin of the temperature dependence of $\nu_{\rm NQR}$ and an empirical relation

$$\nu_{\rm NQR} \equiv \nu_q(1 - \alpha T^{3/2}) \tag{3}$$

was often applied in simple metals such as Cd, In, and Sb [12]. Here, α and ν_q are fitting parameters. This relation can be applied above $\sim$ 80 K as shown in the solid curve in Fig. 1(b). However, a deviation from the fit is observed above 250 K, which might be related to different temperature dependence of ν_Q and η.

The nuclear spin-lattice relaxation time T_1 of ^{75}As-NQR was measured at the peak position of the spectrum. Figure 2 shows the recovery curves of the nuclear magnetization $m(t) \equiv 1 - M(t)/M_0$ as a function of t, where M_0 and $M(t)$ are the respective nuclear magnetizations for the thermal equilibrium condition and at time t after the saturation pulse at 100 and 1.3 K. T_1 was obtained by fitting the recovery data with a theoretical recovery curve for $I = 3/2$, which is expressed in a simple exponential function as

$$m(t) = \exp(-3t/T_1). \tag{4}$$

The solid lines shown in Fig. 2 indicate fits of the recovery data using the fitting function.

Figure 3(a) shows temperature dependence of $1/T_1$ for $CeOs_4As_{12}$. An evident decrease of $1/T_1$ with temperature indicates an existence of the $c - f$ hybridization gap, similar to other Ce-based filled skutterudite compounds. To estimate a value of the gap, Arrhenius plot of $1/T_1$ is displayed in Fig. 3(b). It is apparent that $1/T_1$ does not obey simple exponential behavior as $1/T_1 \propto \exp(-\Delta/k_{\rm B}T)$ in the wide temperature range. This may be caused by the complicated structure of the electric density of states (DOS) and the gap. Indeed, the electrical resistivity was not described by a simple Arrhenius function expected for a semiconductor with a single energy gap [11]. Instead, a phenomenological expression which has three exponential terms with

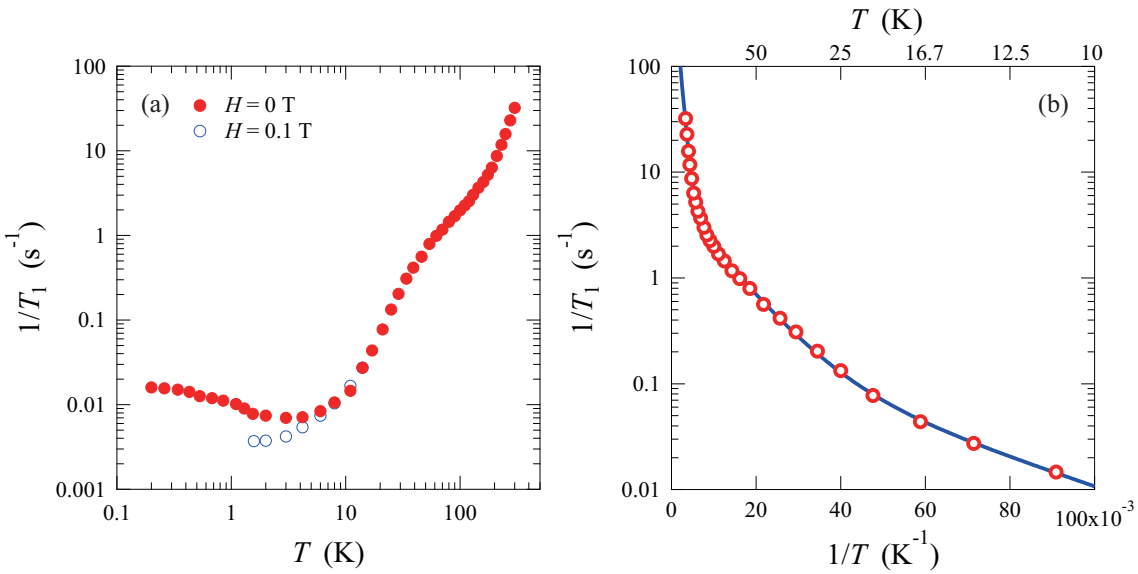


Figure 3. (a) Temperature dependence of $1/T_1$ at $\mu_0 H = 0$ T (closed circles) and 0.1 T (open circles), respectively. (b) Arrhenius plot of $1/T_1$ at $\mu_0 H = 0$ T. Solid curve is a fit using the phenomenological expression. (see text)

Table 1. Evaluated values of the hybridization gap for $CeOs_4Pn_{12}$ (Pn = P, As and Sb). The gap for $CeOs_4P_{12}$ is cited from Ref. 13. The lattice constants are also listed for comparison.

material	Δ_1/k_B (K)	Δ_2/k_B (K)	Δ_3/k_B (K)	lattice constant (Å)
$CeOs_4P_{12}$	-	500	-	8.0626 [14]
$CeOs_4As_{12}$	1059	114	31	8.5296 [5]
$CeOs_4Sb_{12}$	283	32	8	9.3011 [15]

different gap were introduced to explain its temperature dependence. Hence, we try to fit $1/T_1$ using the similar phenomenological expression as follows:

$$\frac{1}{T_1} = \sum_{i=1}^{3} A_i \exp(-\Delta_i/k_B T). \quad (5)$$

Solid curve in Fig. 3(b) shows a fit of the data above 10 K using the expression. Estimated values of the gap are listed in Table 1. As for $CeOs_4Sb_{12}$, an evident spin fluctuations below ∼25 K is suppressed by applying high magnetic field ∼15 T [8]. Therefore, we applied the same procedure for the $1/T_1$ of $CeOs_4Sb_{12}$ at $\mu_0 H = 15$ T and estimated the gap values. In addition, Magishi *et al.* have reported that the $1/T_1$ of $CeOs_4P_{12}$ shows activated-type temperature dependence above 160 K as $1/T_1 \propto \exp(-\Delta/k_B T)$ with $\Delta/k_B \sim 500$ K [13]. These gap values and the lattice constants are summarized in Table 1. This result reveals that the gap magnitude becomes smaller with increasing lattice constant, although the multi-gap analysis was not applied in $CeOs_4P_{12}$.

Next we focus on low temperature region of $1/T_1$. If we consider a simple semiconductor or insulator, $1/T_1$ decreases exponentially with decreasing temperature. On the other hand, several Kondo semiconductors or insulators show $T_1 T =$ const. behavior at low temperature due to an existence of the residual density of states inside the $c - f$ hybridization gap [16, 17]. In comparison with these compounds, $CeOs_4As_{12}$ shows different behavior at low temperature; the

$1/T_1$ starts to increase below $\sim$ 3 K which reveals a development of spin fluctuations similar to $CeOs_4Sb_{12}$. In $CeOs_4Sb_{12}$, the spin fluctuations are suppressed by applying magnetic field. Therefore, to investigate a similarity for both compounds, we have measured $1/T_1$ under small magnetic field $\mu_0 H = 0.1$ T. $1/T_1$ shows magnetic field dependence below $\sim$8 K as shown in Fig. 3(a). Such magnetic field sensitive behavior was also observed in the electrical resistivity [11]. To clarify the electric state of $CeOs_4As_{12}$ more properly, it is necessary to measure $1/T_1$ under various magnetic fields.

4. Summary

In summary, we have carried out ^{75}As-NQR measurement on $CeOs_4As_{12}$. The ^{75}As-NQR spectrum indicates that the Ce-site filling fraction is close to unity for our high-pressure synthesized sample. The temperature dependence of $1/T_1$ shows an evident decrease with decreasing temperature at high temperature region. An increase of $1/T_1$ below $\sim$ 3 K indicates a development of spin fluctuations. The temperature dependence of $1/T_1$ for $CeOs_4As_{12}$ shows similar behavior as that for $CeOs_4Sb_{12}$ with different magnitude of the $c-f$ hybridization gap. This result is consistent with the same band alignments predicted by theoretical calculations. An absence of phase transition in $CeOs_4As_{12}$ may be caused by an increase of the $c-f$ hybridization, which increases the gap magnitude and reduces the residual density of state inside the gap. More detailed NMR experiment under various magnetic fields at low temperatures are required to clarify the electric state of $CeOs_4As_{12}$.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas "Heavy Electrons" (Nos. 20102004 and 20102007) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan.

References

[1] Sekine C, Uchiumi T, Shirotani I and Yagi T 1997 *Phys. Rev. Lett.* **79** 3218
[2] Yogi M, Nagai T, Imamura Y, Mukuda H, Kitaoka Y, Kikuchi D, Sugawara H, Aoki Y, Sato H and Harima H 2006 *J. Phys. Soc. Jpn.* **75** 124702
[3] Sanada S, Aoki Y, Aoki H, Tsuchiya A, Kikuchi D, Sugawara H and Sato H 2005 *J. Phys. Soc. Jpn.* **74** 246
[4] Sugawara H, Osaki S, Kobayashi M, Namiki T, Saha S R, Aoki Y and Sato H 2005 *Phys. Rev.* B **71** 125127
[5] Sekine C, Abe R, Takeda K, Matsuhira K and Wakeshima M 2008 *Physica* B **403** 856-858
[6] Yogi M, Kotegawa H, Zheng G-q, Kitaoka Y, Ohsaki S, Sugawara H and Sato H 2005 *J. Phys. Soc. Jpn.* **74** 1950
[7] Iwasa K, Itobe S, Yang C, Murakami Y, Kohgi M, Kuwahara K, Sugawara H, Sato H, Aso N, Tayama T and Sakakibara T 2008 *J. Phys. Soc. Jpn.* Suppl. A **77** 318-320
[8] Yogi M, Niki H, Yashima M, Mukuda H, Kitaoka Y, Sugawara H and Sato H 2009 *J. Phys. Soc. Jpn.* **78** 053703
[9] Tayama T, Ohmachi W, Wansawa M, Yutani D, Sakakibara T, Sugawara H and Sato H 2015 *J. Phys. Soc. Jpn.* **84** 104701
[10] Yan B, Müchler L, Qi X-l, Zhang S-c and Felser C 2012 *Phys. Rev.* B **85** 165125
[11] Baumbach R E, Ho P C, Sayles T A, Maple M B, Wawryk R, Cichorek T, Pietraszko A and Henkie Z 2008 *Proc Natl Acad Sci USA* **105** 17307-17311
[12] Christiansen J, Heubes P, Keitel R, Klinger W, Lowffler W, Sandner W and Witthuhn W 1976 *Z. Physik* B **24** 177
[13] Magishi K, Sugawara H, Saito T and Koyama K 2012 *J. Phys.: Conf. Ser.* **391** 012039
[14] Jeitschko W and Braun D 1977 *Acta Cryst.* B **33** 3401
[15] Braun D J and Jeitschko W 1980 *J. Less-Common Met.* **72** 147
[16] Nakamura K, Kitaoka Y, Asayama K, Takabatake T, Tanaka H and Fujii H 1994 *J. Phys. Soc. Jpn.* **63** 433-436
[17] Yogi M, Niki H, Kawata T and Sekine C 2014 *JPS Conf. Proc.* **3** 011046