**31P NMR Study of Filled Skutterudite CeOs₄P₁₂**

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Abstract. We report the results of the electrical resistivity \( \rho(T) \) and the \(^{31}\text{P-NMR} \) measurements on filled skutterudite CeOs₄P₁₂ in order to investigate the magnetic properties at low temperatures from a microscopic point of view. For the polycrystalline sample synthesized under high pressure (HP), \( \rho(T) \) increases with decreasing temperature. On the other hand, for the single crystal (SC), \( \rho(T) \) reveals a positive temperature dependence between room temperature and 200 K, and increases with decreasing temperature below 200 K. Also, \( 1/T_1 \) obeys the activated temperature dependence \( 1/T_1 \propto \exp(-\Delta/k_B T) \) above 160 K with an energy gap \( \Delta/k_B \sim 500 \text{ K} \) and 540 K for the HP and the SC samples, which are slightly larger than that of a previous report.

1. Introduction
The family of filled skutterudites with the general formula \( RM_4X_{12} \) (\( R = \text{rare earth, } M = \text{Fe, Ru, Os, } X = \text{P, As, Sb} \) has attracted a great deal of interest. This is not only due to their promising thermoelectric properties, but also because these compounds show a wide variety of transport and magnetic properties at low temperatures. Among them, while most filled skutterudite compounds show metallic behavior, a series of CeM₄P₁₂ (\( M = \text{Fe, Ru, Os} \)) compounds shows semiconducting one with a hybridization gap of 400−1500 K[1, 2, 3], and there is a tendency that the magnitude of the gap decreases with increasing cell volume[4]. Also, CeM₄P₁₂ exhibit an anomalously small lattice constant than that expected from trivalent lanthanides contraction[5]. The reduced lattice constants of CeM₄P₁₂ is qualitatively understood by the change of hybridization between the Ce 4f and the conduction electrons depending on the cell volume.

CeOs₄P₁₂ synthesized under high pressure shows a semiconducting transport property, and its temperature dependence obeys an activation conduction form \( \rho(T) = \rho_0 \exp(-\Delta/k_B T) \) with \( \Delta/k_B \sim 400 \text{ K}[3] \), which is smaller than those for CeFe₄P₁₂[1] and CeRu₄P₁₂[2]. Recently, we have succeeded in synthesizing single crystalline sample of CeOs₄P₁₂ by the Sn-flux method.

In this paper, we focus on the magnetic properties of filled skutterudite CeOs₄P₁₂ at low temperatures via the microscopic probes of \(^{31}\text{P-NMR} \). In order to understand various properties of CeOs₄P₁₂ with 4f electrons, it is important to clarify the characteristic electronic structure of LaOs₄P₁₂ without 4f electrons as a reference compound. LaOs₄P₁₂ is known to as a superconductor with \( T_C = 1.8 \text{ K}[2] \).
2. Experimental

For the NMR measurements, we use two samples, which were crushed into powder. Polycrystalline samples were prepared at high temperature and high pressure using a wedge-type cubic-anvil high pressure apparatus (HP)[6]. Single crystals (SC) were synthesized using the Sn-flux method. Samples were characterized by powder X-ray diffraction at room temperature. Electrical resistivity was measured using a standard four-probe DC method in a temperature range of 0.4−300 K using a 3He refrigerator. Magnetic susceptibility was measured using a SQUID magnetometer in a temperature range of 2−300 K. NMR measurements were performed in a temperature range of 1.5−300 K using a conventional phase-coherent pulsed spectrometer. NMR spectrum was obtained by Fast-Fourier-Transformation (FFT) of the FID signal. The nuclear spin-lattice relaxation time \( T_1 \) was measured by the saturation recovery method.

3. Results and Discussion

Figure 1 shows the temperature dependencies of the electrical resistivity \( \rho(T) \) for CeOs\(_4\)P\(_{12}\) normalized at 280 K. For the HP sample, \( \rho(T) \) increases with decreasing temperature. The temperature dependence of \( \rho(T) \) can be fit over the temperature range from 160 to 300 K to an activation conduction form \( \rho(T) = \rho_0 \exp(-\Delta/k_B T) \), where \( \Delta \) is the activation energy and \( k_B \) is Boltzmann’s constant. The value of \( \Delta/k_B \) is about 500 K for CeOs\(_4\)P\(_{12}\), which is slightly larger than the results for the previous results[3]. On the other hand, for the SC sample, \( \rho(T) \) reveals a positive temperature dependence like metal between room temperature and 200 K, and shows a minimum around 200 K. Then, it increases with decreasing temperature. As shown in the inset, the value of the activation energy \( \Delta/k_B \) is estimated about 220 K over the limited temperature range 50 K \( \leq T \leq 100 \) K, which is quite different from the value for the HP sample.

Figure 2 displays the evolution of the \(^{31}\)P-NMR spectra for the HP sample of CeOs\(_4\)P\(_{12}\). Inset shows the spectrum for the SC sample at 4.2 K. The asymmetrically distributed spectrum, that is, the uniaxially symmetric powder pattern is seen, which may arise from the anisotropic Knight shift. The line width of the spectrum was estimated to be \( \sim 10 \) kHz. The spectrum is very narrow and is almost independent of temperature, except for below 10 K, where it is slightly broadened by the effect of the paramagnetic impurity. Inset shows the spectrum for the SC sample at 4.2 K. The spectrum is sharp compared with that for the HP sample, indicating that the quality of the SC sample is high.
Figure 3. Temperature dependencies of the $^{31}$P Knight shift for the HP samples of CeOs$_4$P$_{12}$ (•) and LaOs$_4$P$_{12}$ (○).

Figure 4. Temperature dependencies of the nuclear spin-lattice relaxation rates $1/T_1$. Inset shows the Ahrrenius plot of $1/T_1$ vs $1/T$.

Figure 3 shows the temperature dependencies of the $^{31}$P Knight shifts for the HP sample of CeOs$_4$P$_{12}$ (•), together with that of LaOs$_4$P$_{12}$ (○). The Knight shift was derived from the peak maximum of the NMR spectrum. For both compounds, Knight shifts are very small ($\sim 0.04\%$) and are almost independent of temperature. Results for the SC samples are quite similar (not shown), and seems to be intrinsic and different from the Curie-like upturn at low temperatures in $\chi(T)$ possibly originating from the paramagnetic impurity, as seen in the inset of Fig.3.

Figure 4 indicates the temperature dependencies of the nuclear spin-lattice relaxation rates $1/T_1$ for $^{31}$P nuclei in CeOs$_4$P$_{12}$, together with the results for LaOs$_4$P$_{12}$[7]. In case for both the HP and the SC samples of LaOs$_4$P$_{12}$, $1/T_1$ is almost proportional to the temperature between 1.5 K and 300 K, that is, $1/T_1$ obeys the Korringa relation $T_1T = \text{constant}$ as expected in the metallic state, indicated by the dotted line in the figure.

On the other hand, for the HP sample of CeOs$_4$P$_{12}$, $1/T_1$ decreases about one order of magnitude, and follows the activated-type temperature dependence above 160 K as $1/T_1 \propto \exp(-\Delta/k_B T)$ with $\Delta/k_B \sim 500$ K, as indicated by the solid line in the figure. It is thought to originate from the existence of the gap of the magnetic excitation due to the hybridization. The magnitude of the energy gap is slightly larger than the results for the previous results[3] and is smaller than those for CeFe$_4$P$_{12}$[8] and CeRu$_4$P$_{12}$[8, 9]. It indicates that the degree of the hybridization between the Ce 4f and the conduction electrons is reduced in CeOs$_4$P$_{12}$ compared with the cases of CeFe$_4$P$_{12}$ and CeRu$_4$P$_{12}$. For the SC sample, $1/T_1$ shows the similar behavior as $1/T_1 \propto \exp(-\Delta/k_B T)$ with $\Delta/k_B \sim 540$ K, where the value of $\Delta/k_B$ is slightly larger than that of the HP sample, as seen in the inset. Also, the value is larger than that estimated from the electrical resistivity measurements.

Below 160 K, $1/T_1$ deviates from the activated behavior, and is almost independent of the temperature, which suggests that other relaxation effect takes place at low temperatures. It may be attributed to the relaxation by the paramagnetic local moments. Furthermore, at low temperatures below 50 K, $1/T_1$ distributes and increases gradually upon cooling. It has a maximum around 10 K and show a rapid decrease below 10 K, which is a similar behavior in CeFe$_4$P$_{12}$[8] and CeRu$_4$P$_{12}$[8, 9]. At this stage, we have no idea to explain these behaviors at
low temperatures. But the relaxation rate for the SC sample is smaller than that for the HP sample, which indicates that the effect by impurity is small and the quality of the sample is high, consistent with a sharp spectrum.

4. Summary
We have carried out the electrical resistivity and the \( ^{31}\text{P}-\text{NMR} \) experiments in CeOs\(_4\)P\(_{12}\) in order to understand the magnetic properties from the microscopic viewpoints. While \( \rho(T) \) for the HP sample increases with decreasing temperature, \( \rho(T) \) for the SC sample reveals a positive temperature dependence like metal between room temperature and 200 K, and increases with decreasing temperature below 200 K. \( 1/T_1 \) obeys the activated temperature dependence \( 1/T_1 \propto \exp(-\Delta/k_B T) \) above 160 K with an energy gap \( \Delta/k_B \sim 500 \) K and 540 K for the HP and the SC samples, which are slightly larger than that of a previous report. Also, the value of the energy gap is smaller than those for CeFe\(_4\)P\(_{12}\) and CeRu\(_4\)P\(_{12}\), indicating that the degree of the hybridization between the Ce 4\( f \) and the conduction electrons is reduced in CeOs\(_4\)P\(_{12}\).

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References
[1] G.P. Meisner, M.S. Torikachvili, K.N. Yang, M.B. Maple and R.P. Guertin: J. Appl. Phys 57 (1985) 3073.
[2] I. Shirotani, T. Adachi, K. Tachi, S. Todo, K. Nozawa, T. Yagi and M. Kinoshita: J. Phys. Chem. Solids 57 (1996) 211.
[3] I. Shirotani, T. Uchiumi, C. Sekine, M. Hori, S. Kimura and M. Hamaya: J. Solid State Chem. 142 (1999) 146.
[4] H. Sugawara, S. Osaki, M. Kobayashi, T. Namiki, S.R. Saha, Y. Aoki and H. Sato: Phys. Rev. B 71 (2005) 125127.
[5] C.B.H. Evers, W. Jeitschko, L. Boonk, D.J. Braun, T. Ebel and U.D. Scholz: J. Alloys Comp. 224 (1995) 184.
[6] D. Kikuchi et al., unpublished.
[7] K. Magishi, Y. Iwahashi, H. Sugawara, T. Saito, K. Koyama, K. Tanaka, D. Kikuchi and H. Sato: J. Phys. Soc. Jpn. 77 (2008) SA22.
[8] K. Magishi, H. Sugawara, T. Saito, K. Koyama and H. Sato: Physica B 378-380 (2006) 175.
[9] K. Fujiwara, C. Sekine and I. Shirotani: Physica B 281&282 (2000) 296.