NMR study of magnetic properties in $SmRu_4P_{12}$

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Abstract

^{31}P-NMR spectra and nuclear spin-lattice relaxation time T_1 have been measured in the temperature range between 4.2 and 300 K. NMR spectrum becomes suddenly broad below metal-insulator transition temperature (T_{MI}=16.2K), suggesting that $SmRu_4P_{12}$ shows magnetic phase transition just below T_{MI}. Relaxation rate $1/T_1$ obeys the exponential relation ($\propto$ exp[-ΔE/k$_B T$]) with ΔE/k$_B$ = 47 K below T_N. The NMR results around T_{MI} are discussed.

Key words: $SmRu_4P_{12}$; NMR; Metal-insulator transition; Magnetic ordering

The $LnRu_4P_{12}$ compounds (Ln = Lanthanide element) with the filled skutterudite structure have various physical properties. $PrRu_4P_{12}$ and $SmRu_4P_{12}$ show metal-insulator (MI) transition at 61.5 K [1-3] and 16.2 K [4], respectively. In the powder X-ray diffraction experiment, $PrRu_4P_{12}$ exhibits no distinct change of the pattern, indicating that cubic symmetry hold below T_{MI}. The MI transition has no relation to magnetic phase transition, because magnetic susceptibility shows no anomaly at T_{MI}. Recently, superlattice structure below T_{MI} was found using the electron diffraction technique. [5,6] This structural phase transition provides some scenario of origin of MI transition (e.g.; charge density wave transition or antiferro-quadrupolar ordering) in $PrRu_4P_{12}$.

On the other hand, the electrical resistivity, magnetic susceptibility and specific heat studies reveals that $SmRu_4P_{12}$ shows an antiferromagnetic transition and a metal-insulator transition at the same temperature (16.2 K). [4] Therefore, the mechanism of the MI transition in $SmRu_4P_{12}$ seems to be different from that in $PrRu_4P_{12}$. In this paper, we report NMR studies for ^{31}P nuclei (spin 1/2) in $SmRu_4P_{12}$ around the metal-insulator transition temperature.

The polycrystalline samples, $SmRu_4P_{12}$ and $LaRu_4P_{12}$, were prepared at high temperatures of 1100 °C and high pressures of 4 GPa using a wedge-type cubic-anvil high pressure apparatus. The detail of the preparation is published elsewhere. The sample was crushed into powder for measurements of ^{31}P-NMR. NMR measurement was preformed with a conventional spin-echo method. $LaRu_4P_{12}$ without 4f electrons was used as reference.

^{31}P-NMR spectrum of $SmRu_4P_{12}$ were measured at the frequency of 17.0000 MHz in the temperature range of 4.2-300 K. Figure 1 shows T-dependence of NMR spectrum below 17 K. In the metallic state above T_{MI}, NMR spectrum is very sharp with the full width of half maximum $W_{1/2}\sim$5 Oe. The line shape is symmetric and Knight shift is isotropic, as expected from the cubic symmetry. Below T_{MI}, the spectrum change suddenly into a broad and triangular-like pattern, indicating that $SmRu_4P_{12}$ shows magnetically ordered state below 16.3 K ($\sim T_{MI}$). Since the triangular pattern is different from the rectangular one expected in the normal AF ordered state, the spin structure seems to be complicated, such as the incommensurate ordering.

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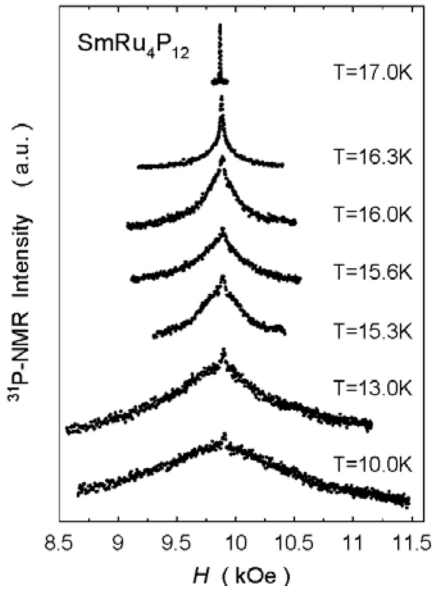

Fig. 1. Temperature dependence of the ^{31}P-NMR spectrum in $SmRu_4P_{12}$ below 17 K.

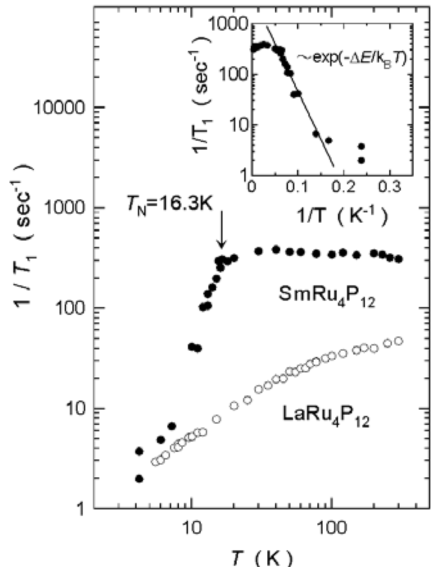

Fig. 2. Temperature dependence of $1/T_1$ in $SmRu_4P_{12}$. An Insert shows $1/T_1$ as a function of inverse temperature. The solid line is best fitted to the function of exp[-ΔE/k$_B$ T].

The Knight shift, K was measured for ^{31}P nuclei in the metallic state. K is expressed by the linear function (K=$A_{hf}\chi$) of the observed magnetic susceptibility, χ, where A_{hf} is a hyperfine coupling constant. $A_{hf} = 2.41$ kOe/μ_B is calculated from the slope of K-χ plot. It is noted that A_{hf} of $SmRu_4P_{12}$ is about nine times as large as that (0.28 kOe/μ_B) of $PrRu_4P_{12}$. [7]

Nuclear spin-lattice relaxation rate $1/T_1$ of $SmRu_4P_{12}$ was measured at the main peak in the T-range of 4.2-300 K. Figure 2 shows T-dependence of $1/T_1$ of $SmRu_4P_{12}$ and $LaRu_4P_{12}$, respectively. In the metallic state, $1/T_1$ of $SmRu_4P_{12}$ is almost independent of temperature and the magnitude of $1/T_1$ is ten times as large as that of $LaRu_4P_{12}$ without 4f-electron spins. Therefore 4f-spin fluctuation contributes to the nuclear relaxation drastically. Taking account for the magnetic susceptibility of the Van Vleck Frank Sm^{3+} above 20 K, 4f-spins are localized at the Sm ions. [4]

On the other hand, below T_{MI} (T_N), $1/T_1$ decreases rapidly without the enhancement around T_N due to the critical slowing down of 4f-moments. As seen in an insert,$1/T_1$ varys approximately exponentially with inverse temperature: $1/T_1 \propto$ exp[-ΔE/k$_B$ T]. Here ΔE is the activation energy and k$_B$ is the Boltzmann's constant. The ΔE/k$_B$ is estimated to be 47 K by the least square fit (solid line in the insert). This energy is considered to correspond to some magnon gap energy.

In conclusion, in $SmRu_4P_{12}$, magnetically long-range order below T_{MI} (T_N) was confirmed from the NMR experiment under the magnetic field of about10 kOe. The relaxation behavior shows that $SmRu_4P_{12}$ has localized 4f-character. The activated behavior of $1/T_1$ was observed below T_N and the energy gap of spin excitation was estimated to be 47 K. The change of 4f-electron state below T_{MI} could not be found due to the remarkable increase of the NMR line-width.

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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] C. Sekine, T. Uchiumi, I. Shirotani and T. Yagi, Phys. Rev. Lett. **79** (1997) 3218.

[4] C. Sekine, T. Uchiumi, I. Shirotani and T. Yagi, AIRAPT-17 (2000) 826-829.

[5] C.H.Lee, H. Matsuhata, A. Yamamoto, T. Ohta, H. Takazawa, K. Ueno, C. Sekine, I. Shirotani, T. Hirayama and Y. Ikuhara, J. Phys.: Condens. Matter **13** (2001) L45.

[6] H. Sugawara Y. Abe, H. Sato, M. hedo, R. Settai, Y. Onuki and H. Harima, J. Phys. Soc. Jpn. **69** (2000) 2938.

[7] K. Fujiwara, K. Ishihara, J. Takeuchi, C. Sekine and I. Shirotani, unpublished.