$^{31}$P-NMR, $^{101}$Ru-NQR, $\mu$SR study of filled skutterudite TbRu$_4$P$_{12}$

H. Fukazawa$^{a,b}$, K. Hachitani$^{b,c}$, M. Shimizu$^b$, R. Kobayashi$^{a}$, Y. Kohori$^{a,b}$, I. Watanabe$^c$, K. Akahira$^d$, C. Sekine$^d$, I. Shirotani$^d$

$^a$Department of Physics, Chiba University, Chiba, Japan,  
$^b$Graduate School of Science and Technology, Chiba University, Chiba, Japan,  
$^c$Advanced Meson Science Laboratory, RIKEN, Saitama, Japan,  
$^d$Department of Electrical and Electronic Engineering, Muroran Institute of Technology, Hokkaido, Japan

E-mail: hideto@nmr.s.chiba-u.ac.jp

Abstract. Filled skutterudite TbRu$_4$P$_{12}$ exhibits antiferromagnetic ordering below 20 K. Additional magnetic ordering below 10 K exists under zero field and the origin of this successive magnetic ordering might be related to multipole ordering. In order to reveal the detailed properties of the magnetic transition in TbRu$_4$P$_{12}$, we performed zero-field $^{31}$P nuclear magnetic resonance(NMR), $^{101}$Ru nuclear quadrupole resonance(NQR), muon spin rotation($\mu$SR). The zero-field $^{31}$P-NMR spectra indicate the magnetic transition only at 20 K, while the time spectra of $\mu$SR of TbRu$_4$P$_{12}$ indicate the additional increase of the internal field below 10 K. Moreover, we observed an anomalous temperature dependence of the spin-lattice relaxation rate $T_1^{-1}$ just below 20 K and small anomaly at around 10 K in $^{101}$Ru-NQR.

1. Introduction

Filled skutterudite compounds $RT_4X_{12}$ ($R$: rare earth, actinide; $T$: Fe, Ru, Os; $X$: P, As, Sb) crystallize in a body-centered cubic (bcc) structure [1]. Their space group is $Im\bar{3}$ (No. 204). These compounds have recently attracted much attention as improved thermoelectric materials and for their various fascinating physical properties, such as the superconductivity, the heavy fermion (HF) system, the magnetic order, the multipolar order, the metal-insulator (M-I) transition and the non-Fermi-liquid behavior [2, 3, 4, 5, 6]. Among them, filled skutterudite TbRu$_4$P$_{12}$ exhibits antiferromagnetic ordering below 20 K ($T_N$) [8] with the q-vector $\vec{q} = (1,0,0)$ [9]. Furthermore, it exhibits quite complicated phase diagram at low temperature under external magnetic field [10]. In zero field, additional magnetic ordering below 10 K ($T_s$) exists, which is confirmed by specific heat measurement [10]. Though this lower magnetic anomaly cannot be observed by neutron diffraction measurements [9], the origin of the successive magnetic ordering might be related to multipole ordering which is recently discussed in the related material SmRu$_4$P$_{12}$ [4, 5, 11, 12, 13, 14]. In order to reveal the detailed properties of the magnetic transition in TbRu$_4$P$_{12}$, we performed zero-field $^{31}$P nuclear magnetic resonance(NMR), $^{101}$Ru nuclear quadrupole resonance(NQR), muon spin rotation($\mu$SR).
2. Experiments
The $^{31}$P-NMR and $^{101}$Ru-NQR measurements of TbRu$_4$P$_{12}$ were performed using a phase-coherent pulsed NMR/NQR spectrometer in the resonance frequency range 10-60 MHz. The spin-lattice relaxation time $T_1$ was determined by the saturation recovery method. Polycrystalline samples were synthesized by the high temperature and high pressure method. The crystals were crushed into powders in order to gain the sufficient NMR/NQR signal-intensity.

The $\mu$SR measurements were performed at the GPS continuous beam line in Paul Scherrer Institut of Switzerland. The direction of the initial muon spin is parallel to the beam line where forward and backward counters were located on the upstream and the downstream sides.

3. Results and Discussion
We obtained zero-external-field $^{31}$P-NMR spectra below about 18 K. Two peaks are observed. This is attributable to the antiferromagnetic ordering below $T_N$. Considering the facts that the magnetically ordered state is described with the $\vec{q} = (1, 0, 0)$ and that the observed peaks are only two, we may deduce that the ordered moment directs along [1,1,1] direction. In Fig. 1, we show the temperature $T$ dependence of the internal magnetic fields estimated from $^{31}$P-NMR spectra. We used the higher frequency peak for the estimation of the internal field. We also confirmed that the internal field estimated from the lower peak has the same $T$ dependence of that from the higher peak and that it coincides with the higher-peak internal field by multiplying the appropriate rate. The internal field has a tendency to converge toward 0 T at about $T_N$. Furthermore, it is obvious that no anomaly appears at around $T_N$. This indicates that the only one magnetic ordering occurs from the view point of $^{31}$P-NMR.

Figure 1. Temperature dependence of the internal magnetic fields estimated from $^{31}$P-NMR spectra.

Figure 2. Temperature dependence of the internal magnetic fields estimated from the rotation component of the muon time spectra.

In zero-field $\mu$SR spectra, clear rotation component was observed below 20 K. This corresponds to the antiferromagnetic ordered state below $T_N$. The time spectra of $\mu$SR of TbRu$_4$P$_{12}$ indicate the additional increase of the internal field below 10 K ($= T_\ast$). In Fig. 2, we show the internal magnetic fields estimated from the rotation component of the muon time spectra. It is important to note that the internal field below 10 K was estimated not from the
sum of the two rotation component but from only single component. This suggests that the magnetic anomaly at 10 K is an intrinsic property of TbRu$_4$P$_{12}$ from the view point of zero-field $\mu$SR and that it is not due to antiferromagnetic impurity TbP ($T_N = 10$ K) [15].

In Fig. 3, we show the $T$ dependence of the spin-lattice relaxation rate $1/T_1$ of $^{101}\text{Ru}$ obtained in NQR. The $1/T_1$ above $T_N$ is nearly constant, which indicates that $4f$ electrons of Tb ions are nearly localized above this temperature. The most striking feature of the data is the rapid increase of $1/T_1$ just below $T_N$. This behavior is completely opposite to that of the conventional antiferromagnet. We cannot explain the origin of this increase of $1/T_1$ at present stage. However, this might be related to the freedom of multiple order of the $4f$ electrons of Tb ions. Note that this anomaly itself is ascribable to the antiferromagnetic order at $T_N$. In addition to the anomaly at $T_N$, slight change of the slope of $1/T_1$ at around 10 K exists. This implies the existence of magnetic anomaly at around $T_*$ from the view point of $^{101}\text{Ru}$-NQR. The $1/T_1$ is nearly proportional to $T$ below about 4 K, which indicates that the relaxation of the $^{101}\text{Ru}$ nuclear spins via conduction electrons are dominant compared to that via $4f$ electrons below this temperature.

The present results clearly evidence that the antiferromagnetic order at $T_N$ really exists in TbRu$_4$P$_{12}$. However, the experimental results at around 10 K were controversial. This cannot be well explained, yet. It might be related to the difference of the time window between NMR/NQR and $\mu$SR.

4. Summary
In order to reveal the properties of the magnetic transition in TbRu$_4$P$_{12}$, we performed zero-field $^{31}\text{P}$ nuclear magnetic resonance(NMR), $^{101}\text{Ru}$ nuclear quadrupole resonance(NQR), muon spin rotation($\mu$SR). The experimental results from all the three methods clearly indicates the existence of the antiferromagnetic order at 20 K. However, the experimental results at around 10 K were controversial. Further study is needed to clarify the intrinsic property of the anomaly around 10 K and the role of the degrees of freedom of multipole order in this compound.

Acknowledgments
The authors thank A. Amato and H. Luetkens for their kind help in $\mu$SR measurements at PSI. This work is supported by a Grant-in-Aid for Scientific Research from the MEXT and the KEK-MSL Inter-University Program for Oversea Muon Facilities. The $\mu$SR work was supported by the Toray Science Foundation and the Joint Project of Japan Society for the Promotion of
Science. The work at Muroran Institute of Technology was supported by a Grant-in-Aid for Scientific Research in Priority Area "Skutterudite" (no. 15072201) of the MEXT.

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