Thermal Expansion of Filled Skutterudite Compound GdRu$_4$P$_{12}$

C. Sekine$^1$, K. Akahira$^1$, K. Takeda$^1$, Y. Ohishi$^2$ and P. Haen$^3$

$^1$Department of Electrical and Electronic Engineering, Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan
$^2$Japan Synchrotron Radiation Research Institute, Sayo, Hyogo, 679-5198, Japan
$^3$CRTBT, CNRS, BP 166, 38042 Grenoble Cedex 9, France
E-mail: sekine@mmm.muroran-it.ac.jp

Abstract. We have performed X-ray diffraction and thermal expansion measurements at low temperatures of the filled skutterudite compound GdRu$_4$P$_{12}$ in order to investigate structural changes related to the antiferromagnetic phase transition at $T_N=22$K. No significant change in the X-ray powder diffraction pattern of GdRu$_4$P$_{12}$ was detected down to 10K. The variation of thermal expansion is continuous at $T_N$. Therefore, the transition is not accompanied with any crystallographic transformation. The temperature dependence of the linear thermal expansion coefficient shows large jump ($1.2 \times 10^{-6}$ K$^{-1}$) at $T_N$. This value is comparable to that of isostructural compound SmRu$_4$P$_{12}$ at the metal-insulator transition temperature $T_{MI}=16$K.

1. Introduction

The compounds $MT_4X_{12}$ ($M =$ rare earth and actinide; $T=$ Fe, Ru Os and Pt; $X=$ P, As, Sb and Ge) crystallized in the cubic filled skutterudite-type structure with space group Im$ar{3}$ ($T^5_h$, No.204) [1] have attracted much interest because they exhibit various interesting properties on the components $M$, $T$, and $X$ such as metal-insulator (M-I) transition [2, 3], multipole ordering [4] or unconventional superconductivity [5]. The filled skutterudite compound GdRu$_4$P$_{12}$ shows an antiferromagnetic (AFM) ordering below $T_N=22$K [6]. There is no direct information about the magnetic ordered structure in this compound so far. The electrical resistivity indicates a metallic behavior below room temperature and shows a sharp upturn at $T_N$, where the thermoelastic power $S(T)$ also shows a dramatic increase, indicating a sudden change of carrier number across the AFM transition [7]. The band structure calculation reveals that RERu$_4$P$_{12}$ ($RE =$ rare earth) system has an instability of the main Fermi surface with the nesting vector $q = (1, 0, 0)$ [8]. Therefore, it is concluded that the dramatic change in the main Fermi surface is caused by the AFM ordering. This is consistent with the results of optical conductivity measurements, which suggests the formation of a pseudo-gap induced by the AFM ordering [9]. Though the phase diagram of GdRu$_4$P$_{12}$ is simple [7, 10], it has recently been found that the $^{101}$Ru NQR (nuclear quadrupole resonance) frequency $\nu_Q$ exhibits temperature dependence below $T_N$ [11]. $\nu_Q$ probes the local charge distributions surrounding nuclei through the electric-field gradient and nuclear spin couples with magnetic internal field. If the low-temperature phase below $T_N$ is a simple AFM ordering structure suggested by the band calculation, then the magnetic internal field at the Ru-site is cancelled out, since the Ru atoms are located at the middle between two Gd-sites. Therefore, this anomalous behavior suggests that the existence of
any crystallographic transformation below $T_N$ or the effect of quadrupoles or higher multipoles in addition to the dipole moment. In order to uncover the origin of the low-temperature phase, first of all, we need to obtain information about lattice anomalies accompanied with the AFM ordering in this compound. In this paper, we report the results of X-ray diffraction and thermal expansion measurements at low temperatures of GdRu$_4$P$_{12}$.

2. Experiment

Single-phase polycrystalline GdRu$_4$P$_{12}$ was prepared at high temperature and high pressure using a wedge-type cubic-anvil high pressure apparatus. The compound was prepared by reaction of stoichiometric amounts of each metal and red phosphorus powder at 4GPa. The reaction temperature and time were 1100°C and 30 min, respectively. For thermal expansion measurements, the sample was shaped into a cylindrical shape with 3.4mm diameter and 3.9mm length (L). The coefficient of linear thermal expansion $\alpha=(1/L)(dL/dT)$ in the magnetic field up to 6 T was measured using a sensitive three-terminal capacitance cell, with a detection limit $\Delta L/L \sim 10^{-8}$. Powder X-ray diffraction experiment at low temperature was performed by an angle-dispersive method with a flat imaging plate detector using synchrotron radiation sources in SPring-8, BL10XU. The wavelength of the incident beam was 0.4956(1)Å.

3. Results and discussion

We have performed powder X-ray diffraction experiment of GdRu$_4$P$_{12}$ between 300 and 10K. No superlattice structure was found and no significant change in the X-ray powder diffraction pattern of GdRu$_4$P$_{12}$ was detected down to 10K. Figure 1 shows the temperature dependence of lattice constant of GdRu$_4$P$_{12}$. The lattice constant contracts continuously with decreasing temperature. We could not any anomaly around $T_N$ in experimental resolution. Thus, the AFM transition is not accompanied with any crystallographic transformation.

![Figure 1. Temperature dependence of lattice constant of GdRu$_4$P$_{12}$.](image)

Then we have performed high resolution thermal expansion experiments in order to investigate thermal anomaly at $T_N$ in detail. Figure 2 shows the relative change of thermal expansion $\Delta L/L$ in GdRu$_4$P$_{12}$ as a function of temperature at various fields. Experimental values are normalized to 28K. With decreasing temperature, the crystal contracts more steeply below $T_N$ than above $T_N$ caused by magnetostriction due to the onset of AFM ordering. The variation of thermal expansion is continuous at $T_N$. Below $T_N$, the sample length contracts, $\Delta L/L \sim 1.8 \times 10^{-5}$, with decreasing temperature down to 5K at zero field. The length change at $T_N$ becomes small with increasing field and the inflection point shifts to low temperature. Finally, the anomaly almost disappears in 6T.

Figure 3 shows temperature dependence of the linear thermal expansion coefficient $\alpha=(1/L)(dL/dT)$ of GdRu$_4$P$_{12}$ at various fields. Temperature dependence of the linear thermal expansion coefficient shows large jump $\Delta \alpha (1.2 \times 10^{-6} \text{ K}^{-1})$ at $T_N$. No hysteresis was observed
in the T-sweep. The anomaly of \( \alpha = (1/L)(dL/dT) \) at \( T_N \) shifts to lower temperature side and becomes small with increasing field. At 6T, a small upturn due to the AFM transition is still visible around 6K. This result is consistent with the magnetic phase diagram reported previously [7, 10].

We estimate the contribution to NQR frequency \( \nu_Q \) from the contraction due to the magnetostriction below \( T_N \). The contribution to \( \nu_Q \) from ionic charges on the lattice sites is roughly in inverse proportion to the unit-cell volume. The observed shift of \( \nu_Q \) below \( T_N \) is several times larger than expected from the thermal expansion data. The result suggests that the temperature variation of \( \nu_Q \) below \( T_N \) may not be attributed to a simple thermal contraction but to an additional origin, such as a local charge redistribution at the Gd-site.

Next we compare the thermal properties of GdRu\(_4\)P\(_{12}\) with those of isostructural compounds PrRu\(_4\)P\(_{12}\) and SmRu\(_4\)P\(_{12}\). It is considered that these compounds show multipole orderings [4]. Table I shows some physical parameters of \( RERu_4P_{12} \) (\( RE = Pr, Sm \) and Gd). The value of \( \Delta \alpha \) at \( T_N \) for GdRu\(_4\)P\(_{12}\) is comparable to that of SmRu\(_4\)P\(_{12}\) at the metal-insulator transition temperature \( T_{MI}=16K \) [12] and is larger than PrRu\(_4\)P\(_{12}\) [13]. Then, we evaluated Grüneisen parameter, which is given by \( \Gamma = \alpha V B_0 V_m/C_V \) where \( \alpha V (=3\alpha) \) is the thermal expansion coefficient, \( B_0 \) is bulk modulus, \( V_m \) is molar volume and \( C_V \) is specific heat. The value of \( \Gamma \) for GdRu\(_4\)P\(_{12}\) is 4.4, which is larger than those of Sm and Pr compounds. Grüneisen parameter can be also estimated from elastic constant [14]. For SmRu\(_4\)P\(_{12}\), it is reported that there is a large discrepancy between \( \Gamma \)’s obtained by two method [14]. We have to check whether similar tendency is observed for GdRu\(_4\)P\(_{12}\) or not. This may be a key to understand the origin of the ordered state in this system.

In the LS coupling scheme, the state of Gd\(^{3+} \) (4f\(^7\)) is uniquely specified by \( J=S=7/2 \) and \( L=0 \). Thus, quadrupole does not seem to appear. However, a recent microscopic theory developed by Hotta for multipole-related phenomena on the basis of a j-j coupling scheme points that quadrupole moments appear even for Gd compound [15]. The anomalous behavior for NQR frequency \( \nu_Q \) of GdRu\(_4\)P\(_{12}\) may be interpreted as the effect of quadrupole due to the deviation from the LS coupling.
Table 1. Transition temperatures to the ordered state ($T_{MI}$: metal-insulator transition, $T_N$: antiferromagnetic transition), jump of thermal expansion coefficient $\Delta \alpha$ and Gruneisen parameter $\Gamma$ of $RE\text{Ru}_4\text{P}_{12}$ ($RE=\text{Pr, Sm and Gd}$).

| Compound    | $T_{MI}$ (K) | $T_N$ (K) | $\Delta \alpha \times 10^{-6}$ (K$^{-1}$) | $\Gamma$ | ref.     |
|-------------|--------------|-----------|-----------------------------------------|--------|--------|
| PrRu$_4$P$_{12}$ | 63           | 0.5       | 2.8                                     | [14]  |
| SmRu$_4$P$_{12}$ | 16           | 1.5       | 3.6                                     | [15]  |
| GdRu$_4$P$_{12}$ | 22           | 1.2       | 4.4                                     | this work |

4. Summary
We have studied the temperature dependence of lattice constant and the thermal expansion of filled skutterudite antiferromagnet GdRu$_4$P$_{12}$. The AFM transition of GdRu$_4$P$_{12}$ is not accompanied with any crystallographic transformation. The observed shift of $\nu_Q$ below $T_N$ is not explained by the thermal expansion. The results suggests that the temperature variation of $\nu_Q$ below $T_N$ may not be attributed to a simple thermal contraction. However, because of the observed results using a polycrystalline sample, we can not exclude a kind of subtle distortion. In order to detect such a subtle crystallographic transformation, we need to carry out the experiment with use of a single crystalline sample.

Acknowledgments
The authors thank Y. Kohori for providing them with the NQR data prior to publication. This work was supported by a Grand-in-Aid for Scientific Research in Priority Area ”Skutterudite” (No. 18027002) of the Ministry of Education, Culture, Sports, Science and Technology, Japan, and a Grant-in-Aid for Scientific Research (C) (No. 17540309) of the Japan Society for the Promotion of Science.

References
[1] Jeitchko W and Braun D 1977 Acta Crystallogr. Sect B 33 3401
[2] Sekine C, Uchiumi T, Shirotani I and Yagi T 1997 Phys. Rev. Lett. 79 3218
[3] Sekine C, Uchiumi T, Shirotani I and Yagi T 2000 Science and Technology of High Pressure, ed. M H Manghnani, W J Nellis and M F Nicol (Hyderabad: Universities Press) p 826
[4] Yoshizawa M, Nakanishi Y, Oikawa M, Sekine C, Shirotani I, Saha S R, Sugawara H and Sato H 2005 J. Phys. Soc. Jpn. 74 2141
[5] Aoki Y, Tayama T, Sakakibara T, Kuwahara K, Iwasa K, Kohgi M, Higemoto W, MacLaughlin D E, Sugawara H and Sato H 2007 J. Phys. Soc. Jpn. 76 051006
[6] Sekine C, Uchiumi T, Shirotani I, Matsuhiro K, Sakakibara T, Goto T and Yagi T 2000 Phys. Rev. B 62 11581
[7] Matsuhira K, Sekine C, Kihou K, Shirotani I, Wakeshima M, Hinatsu Y, Sei Y, Nakamura A and Takagi S 2006 Physica B, Condensed Matter 378-380 235
[8] Harima H, Takegahara K 2002 Physica B 312-313 843.
[9] Matsunami M, Takimoto M, Okamura H, Namba T, Sekine C and Shirotani I 2005 Physica B 359-361 844
[10] Sekine C, Ando H, Sugiuichi Y, Shirotani I, Matsuhira K and Wakeshima M 2008 J. Phys. Soc. Jpn. 77 Suppl. A 135
[11] Kohori Y private communication
[12] Sekine C, Shimaya Y, Shirotani I and P. Haen 2005 J. Phys. Soc. Jpn. 74 3395
[13] Matsuhira K, Takikawa T, Sakakibara T, Sekine C and Shirotani I 2000 Physica B 281-282 298
[14] Yoshizawa M, Nakanishi Y, Tanizawa T, Sugihara A, Oikawa M, Sun P, Sugawara H, Saha S R, Kikuchi D and Sato H 2006 Physica B 378-380 222
[15] Hotta T 2007 J. Phys. Soc. Jpn. 76 083705