Transport Properties in Filled Skutterudite
GdRu$_4$P$_{12}$

M. Watanabe$^1$, K. Tanaka$^1$, S. Tatsuoka$^1$, T. Saito$^1$, R. Miyazaki$^1$, K. Takeda$^1$, T. Namiki$^1$, K. Kuwahara$^2$, R. Higashinaka$^1$, Y. Aoki$^1$ and H. Sato$^1$

$^1$ Department of Physics, Tokyo Metropolitan University, Tokyo 192-0397, Japan
$^2$ Institute of Applied Beam Science, Ibaraki University, Ibaraki 310-8512, Japan
E-mail: watanabe-makoto@ed.tmu.ac.jp

Abstract.
We have investigated the Hall effect in GdRu$_4$P$_{12}$ for the first time. From the temperature and magnetic field dependences of the Hall effect along with the magnetoresistance, we evaluated the change in carrier density across the antiferromagnetic (AF) transition accompanied by the Fermi surface reconstruction. About one tenth of carriers remain in the AF phase, in contrast with PrRu$_4$P$_{12}$ where most of the carriers disappear in the ordered phase. The anomalous part of Hall coefficient in GdRu$_4$P$_{12}$ is smaller than those in the PrRu$_4$P$_{12}$ and PrFe$_4$P$_{12}$, which is consistent with the well localized nature of 4f electrons.

1. Introduction
The filled skutterudite compounds with a general formula $RT_4X_{12}$ ($R$ : rare earth, $T$ : Fe,Ru and Os, $X$ : P,As and Sb) have attracted much attention, since they exhibit variety of novel features due to the strongly correlated electrons. Among them, the Fermi surface (FS) nesting with the wave vector $q = (100)$ has been predicted to play a common key role both in $R$Fe$_4$P$_{12}$ and $RRu_4P_{12}$ to realize various types of phase transitions by the band structure calculation [1]. As typical examples, the metal-insulator transition at $T_{MI} = 63$ K in PrRu$_4$P$_{12}$ [2] and the nonmagnetic transition accompanied by huge carrier number reduction at $T_{uo} = 6.5$ K in PrFe$_4$P$_{12}$ [3], both are now thought to be scalar type orders. The absence of such transition in LaRu$_4$P$_{12}$ without 4f electron [4] indicates that some additional factors related with 4f electrons are essential in realizing such transitions. In order to obtain the deeper understanding of these transitions triggered by the FS nesting, we have investigated GdRu$_4$P$_{12}$ that exhibits an antiferromagnetic (AF) ordering below $T_N = 22$ K [5]. Across the AF transition, GdRu$_4$P$_{12}$ shows a sudden increase in the electrical resistivity ($\rho$), suggesting FS reconstruction. K. Matsuhira et al. reported that the sudden increase in $\rho$ is quickly suppressed by magnetic field and disappears in 7 T. [6]. They also reported an increase of $c$-f exchange scattering component $\rho_{cf}(T)$ below $\sim 60$ K, above which it is constant. From the strong field dependence below 60 K, they inferred that the increase in $\rho_{cf}(T)$ is caused by a magnetic fluctuation such as a short range order. In the case of AF ordering accompanied by the FS reconstruction, it is not usually easy to separate the contributions from the decrease in carrier number ($n_c$) and the
increase in scattering probability of conduction electrons. However, it is important to evaluate both components separately to clarify the features of this transition. Recently, we have succeeded in synthesizing polycrystalline GdRu$_4$P$_{12}$ samples with the smaller residual resistivity than that in the previous report [6], possibly due to the longer heat treatment under a higher pressure of 5 GPa. In this paper, we report the first Hall effect measurement along with the magnetoresistance and the magnetization measurements on a same GdRu$_4$P$_{12}$ sample, to clarify the change of $n_c$ across the phase transition.

2. Experimental details

Polycrystalline GdRu$_4$P$_{12}$ was prepared by high-pressure synthesis under ~ 5 GPa. The starting elements, chips of Gd (99.9%-3N) and powders of Ru (4N) and P (6N), placed in a cylindrical BN crucible in the atomic ratio of 1:4:12 were heated up to 1250 °C and kept for 2 hours, then quenched down to room temperature. The lattice constant $a = 8.0372$ Å is close to the reported value $a = 8.0375$ Å [5]. The Hall effect and magnetoresistance were measured with the AC five-probe method using a Quantum Design PPMS down to 2 K and up to 9 T. The magnetization was measured using a Quantum Design MPMS down to 2 K and up to 7 T.

3. Results and Discussion

Figure 1 shows the temperature ($T$-) dependence of (a) the Hall coefficient ($R_H$) and (b) the electrical resistivity ($\rho$) measured simultaneously on a GdRu$_4$P$_{12}$ sample. In the inset, $R_H$ and $\rho$ in PrFe$_3$P$_{12}$ are shown for comparison [3]. $R_H$ was evaluated below 1.5 T where the Hall resistivity ($\rho_H$) depends almost linearly on $H$ as shown in Fig.2(b). Both $R_H$ and $\rho$ show a sudden increase below $T_N$, indicating the reduction of $n_c$ due to the FS reconstruction. Overall, the $T$-dependence of $\rho$ in Fig.1(b) is not much different from the previous report except the smaller residual resistivity in the present work [6]. The peak in $\rho$ of GdRu$_4$P$_{12}$ below $T_N$ mimics that in PrFe$_3$P$_{12}$ where $\rho$ decreases after showing a peak around 5 K, while $\rho$ in PrRu$_4$P$_{12}$ increases monotonically below $T_{MI}$ up to ~ 40 mΩ-cm at ~ 0.4 K, indicating disappearance of most carriers [3]. From the $T$-dependence of $\rho$, a clear difference between GdRu$_4$P$_{12}$ and PrFe$_3$P$_{12}$ below the transition temperature is only a larger residual resistivity in the former, which may be ascribed to the insufficient crystallinity. However, Figure 1(a) demonstrates a clear difference in the $T$-dependence of $R_H$. At low temperatures below $T_N$, $R_H$ in GdRu$_4$P$_{12}$ exhibits only a shallow peak around 5 K. In contrast, $R_H$ in PrFe$_3$P$_{12}$ exhibits a sharp peak at almost the same temperature of 5 K as in $\rho$. One of the possible reasons is the stronger $c$-$f$ hybridization in PrFe$_3$P$_{12}$ as evidenced in the apparent -log($T$) dependence of $\rho$ and the dominating quasielastic response without any peak associated with crystalline-electric-field excitation in the neutron scattering experiment above $T_{so}$ [7]. The magnetic moment close to the Gd$^{3+}$ free ion’s value as shown in Fig.2(a) and the ordinary magnitude of thermoelectric power above $T_N$ [6] indicate well localized nature of $4f$ electrons in GdRu$_4$P$_{12}$. Most naively, the decrease both in $\tau$ and $n_c$ lead to the enhancement of $\rho$ below the transition temperature. The evaluation of $R_H$ is not so simple in the magnetic materials, since there exist two components: $R_H = R_{H0} + R_{Hm}$. The first term is the normal part of Hall coefficient caused by the cyclotron motion of conduction electrons, and the second term is the anomalous part of Hall coefficient caused by the left-right asymmetry of conduction electrons scattering by magnetic disorders. Note that the anomalous Hall effect associated with the skew scattering is highly enhanced in Kondo and mixed valence systems, while it is not the case in the well localized $f$-electron systems [8]. In fact in PrFe$_3$P$_{12}$, the two components collaborate to increase both $\rho$ and $R_H$ just below $T_{so}$. With further decreasing temperature, the change in $n_c$ tends to saturate, while the conduction electron scattering by critical fluctuation is suppressed, leading to the decrease in both $\rho$ and $R_{Hm}$, which is a common feature of the $f$-electron systems with strong $c$-$f$ hybridization. For GdRu$_4$P$_{12}$ with well localized $4f$ electrons, the anomalous Hall effect produced by the critical fluctuation is expected to be
smaller. In fact, the dominance of the change in $n_c$ can be judged from the only slight decrease in $R_H$ below the shallow peak around 5 K. The carrier concentrations at 2 K and room temperature (RT) can be roughly estimated by the single carrier model to be $n_c \sim 0.40$ per formula unit (/f.u.) and $\sim 2.7$/f.u. respectively. However, it should be noted that $n_c$ exhibits considerable $T$-dependence within the investigated temperature range.

In order to further evaluate the contribution from $n_c$, the magnetic field ($H$-) dependence of $\rho$ and $\rho_H$ has been investigated. Figure 2 shows the $H$-dependence of (a) the magnetization ($M$), (b) the Hall resistivity ($\rho_H$) and (c) the transverse magnetoresistivity ($\rho_T$) at three selected temperatures. Both $\rho$ and $\rho_H$ exhibit a clear kink at a critical field $H_c$ ($\sim 6.3$ T for 2 K and $\sim 5.9$ T for 10 K), which is consistent with the reported phase diagrams [6, 9]. At 25 K and in the field induced paramagnetic phase at 10 K, $\rho$ monotonically decreases up to 9 T, reflecting the reduction of conduction electron scattering by magnetic fluctuation. At 10 K, additional resistivity contribution seems to be superposed below $H_c$ upon the monotonic increase from the highest field of 9 T. At 2 K, almost $H$-independent behavior of $\rho$ above $H_c$ within the experimental accuracy suggests negligible contribution from conduction electron scattering. Therefore, $R_{H0}$ can be estimated from the slope of the $\rho_H$ vs $H$ plot above $H_c$. In fact, the line through the data points go through the origin at 2 K as shown in Fig.2(b), giving $R_{H0} \sim 4.0 \times 10^{-10}$ m$^3$/C and $n_c \sim 4.0$/f.u.. In other words, just one-tenth of the carriers in paramagnetic state are left in AF phase. It usually gives right order of magnitude for $n_c$, however, it should be
Table 1. The comparison of $R_H$ and $\rho$ among GdRu$_4$P$_{12}$, PrFe$_4$P$_{12}$ and PrRu$_4$P$_{12}$ at selected temperatures. ($RT$: Room temperature. $T_{\text{peak}}$: Temperature where $R_H$ and $\rho$ shows a maximum. $T_o$: The lowest investigated temperature in the ordered phase.)

| Compound   | $RT$ (mK) | $T_{\text{peak}}$ (mK) | $T_o$ (mK) | $RT$ (mK) | $T_{\text{peak}}$ (mK) | $T_o$ (mK) |
|------------|-----------|------------------------|-----------|-----------|------------------------|-----------|
| GdRu$_4$P$_{12}$ | 0.6       | 5                      | 4         | 500       | 320                    | 180       |
| PrFe$_4$P$_{12}$ | 1.3       | 1000                   | 30        | 300       | 1000                   | 30        |
| PrRu$_4$P$_{12}$ | 0.4       | -3500                  | -2500     | 90        | 40000                  | 40000     |

noted that $R_H$ in low field condition cannot always be a direct proof of $n_c$ due to the aspherical FS in real metals.

Table I compares $R_H$ and $\rho$ for GdRu$_4$P$_{12}$, PrFe$_4$P$_{12}$ and PrRu$_4$P$_{12}$ [3, 10] at selected temperatures ($RT$, the peak temperature and the ordered state). The remaining carrier density in the ordered phase decreases in the sequence of GdRu$_4$P$_{12}$ $\rightarrow$ PrFe$_4$P$_{12}$ $\rightarrow$ PrRu$_4$P$_{12}$. As clues to understand the sequence, one can discuss the difference in the nesting condition and/or the superzone gap. The band structure calculation predicts that the FS for PrRu$_4$P$_{12}$ has better nesting condition than that for PrFe$_4$P$_{12}$; the former has a single multiply-connected FS with a good nesting condition, while the latter has an extra spherical FS besides the multiply-connected FS. An evident different feature of GdRu$_4$P$_{12}$ from the other two compounds is the weak $c$-$f$ hybridization strength, which is also reflected in the smallest anomalous Hall effect. The weaker $c$-$f$ hybridization naturally creates the smaller periodic potential with $q = (100)$ for conduction electrons, resulting in the smaller superzone gap. As a result, the less area on the original FS can be washed away in GdRu$_4$P$_{12}$. In order to check the scenario, the more intense studies on single crystal samples are planned.

To summarize, we have evaluated the change in carrier density across the AF ordering in GdRu$_4$P$_{12}$ by the $T$- and $H$-dependences of the Hall effect and the magnetoresistance. The results were compared with the reported results on PrFe$_4$P$_{12}$ and PrRu$_4$P$_{12}$, and discussed from the viewpoints of the FS nesting condition and the $c$-$f$ hybridization strength.

This work was supported by a Grant-in-Aid for Scientific Research (B) (No.20340094) from the Japan Society for the Promotion of Science, and a Grant-in-Aid for Scientific Research on Priority Area "Skutterudite" (No.15072206), "Ubiquitous" (No.20045015), and on Innovative Areas "Heavy Electrons" (No.20102007) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. M.W. was also supported by the "Support Program for Improving Graduate School Education" of MEXT.

References
[1] Harima H and Takegahara K 2002 Physica B 312-313 843
[2] Sekine C et al. 1997 Phys. Rev. Lett. 79 3218
[3] Sato H et al. 2006 Physica B 378-380 46
[4] Shirotani I et al. 1996 J. Phys. Chem. Solid 57 211
[5] Sekine C et al. 2000 Phys. Rev. B 62 11581
[6] Matsuhira K et al. 2006 Physica B 378-380 235
[7] Iwasa K et al. 2003 Acta Physica Polonica B 34 1117
[8] Onuki Y et al. 1989 J. Phys. Soc. Jpn. 58 2126
[9] Sekine C et al. 2008 J. Phys. Soc. Jpn. 77 Suppl. A 135
[10] Saha S R et al. 2004 J. Magn. Magn. Mater. 272-276 e317