

Magnetic properties of the filled skutterudite-type structure compounds $\text{GdRu}_4\text{P}_{12}$ and $\text{TbRu}_4\text{P}_{12}$ synthesized under high pressure

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We have succeeded in synthesizing filled skutterudite-type structure compounds $\text{GdRu}_4\text{P}_{12}$ and $\text{TbRu}_4\text{P}_{12}$ under high pressure. The magnetic properties of $\text{GdRu}_4\text{P}_{12}$ and $\text{TbRu}_4\text{P}_{12}$ have been studied by means of electrical resistivity, magnetic susceptibility, and magnetization measurements. Magnetic experiments suggest that the Gd and Tb ions in the compounds have trivalent state. The compound $\text{GdRu}_4\text{P}_{12}$ displays features that suggest the occurrence of antiferromagnetic ordering below $T_N = 22$ K. In $\text{TbRu}_4\text{P}_{12}$, thermal variation of magnetic susceptibility indicates the existence of two successive magnetic transitions ($T_N = 20$ K and $T_1 = 10$ K). Magnetization up to 18 T exhibits two-step metamagnetic transitions below T_1 for $\text{TbRu}_4\text{P}_{12}$.

I. INTRODUCTION

Ternary metal pnictides with general formula MT_4X_{12} ($M =$ alkaline earth, rare earth, and actinide; $T =$ Fe, Ru, and Os; $X =$ P, As, and Sb) crystallize with the filled skutterudite-type structure (space group $Im\bar{3}$).¹⁻⁴ The MT_4X_{12} compounds have various and anomalous physical properties at low temperature, such as superconductivity,⁵⁻⁷ small gap semiconductorlike behavior in several Ce compounds,^{6,8} (anti)ferromagnetism,^{5,8} metal-insulator transition,⁹ and heavy fermion or intermediate-valence behavior.^{10,11} Recent work has shown that $\text{CeRu}_4\text{Sb}_{12}$ exhibits non-Fermi liquid behaviors.¹² While most of these anomalous behaviors are not understood, band structure peculiar to the compounds and hybridization effects between localized f electrons and conduction ones seem to play an important role. Recently, band-structure calculations were carried out for several filled skutterudite compounds.^{13,14} In La compounds, the Fermi level is situated at a large peak originating in the T - d band in the compound,¹⁴ which may cause instability of the electronic system. Further, band-structure calculations on $\text{CeFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$ indicate that the Ce is nearly trivalent in both compounds, and these compounds possess a small band gap that arises from strong hybridization of Ce- $4f$ states with both Fe- $3d$ and pnictogen- p states.¹³ The semiconductorlike behavior, which is observed in CeT_4X_{12} , may arise from strong hybridization of $4f$ electrons of the Ce atom with the conduction electrons.

Moreover, the filled skutterudite compounds are important in the viewpoint of application. The compounds have been very actively studied as very efficient thermoelectric materials for either refrigeration or power generation applications.^{15,16} $\text{CeFe}_4\text{Sb}_{12}$ and alloys $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$ have recently attracted much attention for potentially useful thermoelectric materials because of low lattice thermal conductivity.¹⁷

Many various materials with this structure have been synthesized for the applications and basic studies of solid-state physics. However, there have been no reports of successful synthesis of any filled skutterudites containing heavier rare earths, $M =$ Gd-Lu, except Yb, and it was conjectured within the context of the MT_4X_{12} series that the smaller radii of the heavier M^{3+} ions prevent adequate bonding to the lattice. Recently, $\text{YbFe}_4\text{Sb}_{12}$ and $\text{YbOs}_4\text{Sb}_{12}$ have been synthesized.^{18,19} In the Yb compounds, however, Yb ions have divalence or intermediate valence in contrast to the other rare earths in this series that all appear to be trivalent. It is possible that this larger ionic radius stabilizes Yb in the skutterudite structure. $M =$ Eu compounds may be the same case. Thus it was supposed that all other trivalent rare earths in the range $M =$ Gd-Lu are too small to be accommodated in the atomic ‘‘cages’’ that are formed by the transition-metal (T)-pnictogen (X) sublattice. However, we have succeeded in preparing two different filled skutterudite compounds containing heavier trivalent rare earths, $\text{GdRu}_4\text{P}_{12}$ and $\text{TbRu}_4\text{P}_{12}$, using high-pressure synthesis technique. In this paper, we report the results of magnetic and electrical properties for $\text{GdRu}_4\text{P}_{12}$ and $\text{TbRu}_4\text{P}_{12}$.

II. EXPERIMENT

Ternary compounds $\text{GdRu}_4\text{P}_{12}$ and $\text{TbRu}_4\text{P}_{12}$ were prepared at high temperatures and high pressures using a wedge-type cubic-anvil high-pressure apparatus.²⁰ These metal phosphides were prepared by reaction of stoichiometric amounts of metals and red phosphorus powder at around 4 GPa. The reaction temperature and time were 1100 °C and 30 min, respectively. The samples were characterized by powder x-ray diffraction using $\text{CuK}\alpha_1$ radiation and silicon as a standard. We also succeeded in making single crystalline samples of RRu_4P_{12} ($R =$ La, Ce, Pr, Nd, Sm, and Eu) using a Sn flux method.²¹ However, the sample

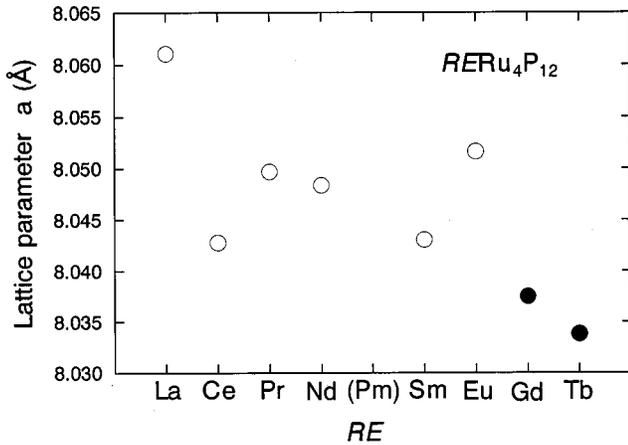


FIG. 1. Cubic lattice parameters in the $RERu_4P_{12}$ series (RE = rare earth). The lattice parameters shown as open symbols are quoted from Refs. 21 and 22.

of $GdRu_4P_{12}$ and $TbRu_4P_{12}$ compounds failed to be synthesized by the same procedure.

Resistivity was measured with a standard dc four-probe method in the range 1.7–300 K. The dc magnetic susceptibility and magnetization up to 5 T were measured in the range 2–300 K with a Quantum Design MPMS superconducting quantum interference device magnetometer. The high-field magnetization measurements up to 18 T were performed by an induction method using pulsed magnetic field at the Institute for Solid State Physics, University of Tokyo.

III. RESULTS AND DISCUSSION

The cubic lattice parameters a of $GdRu_4P_{12}$ and $TbRu_4P_{12}$ were determined from x-ray powder diffractometry to be $a = 8.0375$ and 8.0338 Å, respectively. In Fig. 1 the lattice parameters a of $GdRu_4P_{12}$ and $TbRu_4P_{12}$ are plotted together with those reported earlier for RRu_4P_{12} (R = rare earth).^{21,22} Starting with La, one observes the typical reduction of the lattice parameter due to the contraction of the ionic radii of the rare earths with increasing atomic number except for $CeRu_4P_{12}$ and $EuRu_4P_{12}$. This suggests that Gd and Tb ions are trivalent state in the compounds. The small lattice constant of Ce compound is due to strong c - f hybridization. On the other hand, the large lattice constant of $EuRu_4P_{12}$ is caused by the Eu ion being divalent or mixed-valence state in the compound.²¹

The magnetic susceptibility χ and the reciprocal magnetic susceptibility χ^{-1} is plotted versus temperature between 2 and 300 K for $GdRu_4P_{12}$ in Fig. 2. An anomaly at $T_N = 22$ K is seen in the $\chi(T)$ curve as indicated by the arrow. This suggests that an antiferromagnetic (AF) ordering occurs below T_N . A Curie-Weiss temperature dependence of the susceptibility is observed at sufficient high temperatures. The linear slope of χ^{-1} vs T from 150 to 300 K yields an effective magnetic moment of $8.04\mu_B/Gd$. This value is in good agreement with $7.94\mu_B/Gd$ calculated for a Hund's-rule ground state of Gd^{3+} . This suggests that the Gd ion is trivalent. The Curie-Weiss temperature θ_p is +23 K. It should be noticed that the value of θ_p is positive, while the compound shows AF ordering.

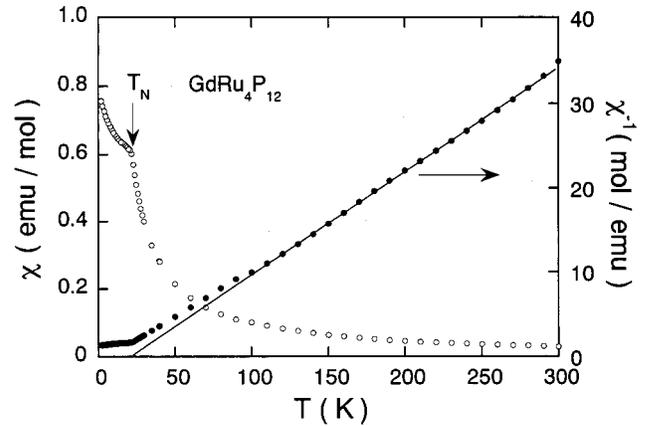


FIG. 2. Magnetic susceptibility $\chi = M/H$ (open circles) at $H = 1$ T and inverse magnetic susceptibility χ^{-1} (filled circles) vs temperature for $GdRu_4P_{12}$. The line shows a fit to a Curie-Weiss law for $150 < T < 300$ K.

Figure 3 shows the temperature dependence of the χ and the χ^{-1} for $TbRu_4P_{12}$. Two anomalies are found in the $\chi(T)$ behavior at $T_N = 20$ K and $T_1 = 10$ K as shown in the inset of Fig. 3. The cusp at T_N may be associated with the paramagnetic to AF transition. The anomaly at T_1 may be associated with change of the magnetic structure. A Curie-Weiss behavior is observed at higher temperatures. The deduced effective magnetic moment for $TbRu_4P_{12}$ is $9.76\mu_B/Tb$, which is very close to $9.72\mu_B/Tb$ calculated for Tb^{3+} . This suggests that the Tb ion is also trivalent. The Weiss temperature θ_p is +8 K for $TbRu_4P_{12}$. It also should be noticed that the value of θ_p is positive.

The observed high-field magnetization curves of $GdRu_4P_{12}$ at various temperatures are given in Fig. 4. In the AF regime below $T_N = 22$ K the magnetization increases linearly with field before leveling off above a critical field ($H_C = 6.1$ T at 4.2 K). The magnetization is saturated above 18 T at 4.2 K. The saturation moment is in good agreement with the Gd^{3+} free-ion value of $7\mu_B/Gd$. The critical field shifts to 5.4 T at 10 K and is not found at 25 K above T_N .

For $TbRu_4P_{12}$, two-step metamagnetic transitions are ob-

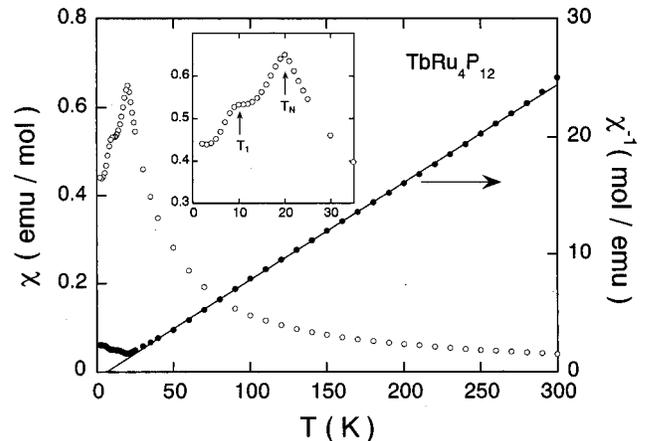


FIG. 3. Magnetic susceptibility χ (open circles) at $H = 1$ T and inverse magnetic susceptibility χ^{-1} (filled circles) vs temperature for $TbRu_4P_{12}$. The line shows a fit to a Curie-Weiss law for $150 < T < 300$ K. Inset: an enlarged view of χ below 20 K.

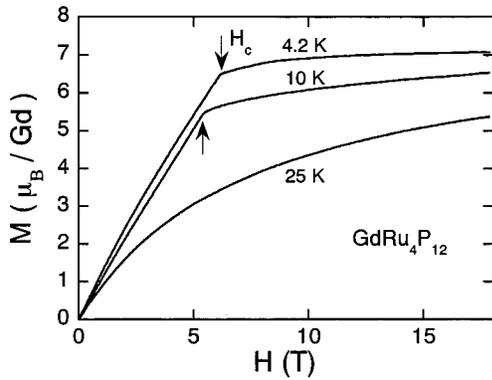


FIG. 4. Magnetization curves $M(H)$ for $\text{GdRu}_4\text{P}_{12}$ at several temperatures.

served below T_1 as shown in Fig. 5. The magnetization increases two steps at critical fields of $H_{C1}=0.8\text{ T}$ and $H_{C2}=2.5\text{ T}$ at 4.2 K , which is associated with the two successive AF phase transitions (inset of Fig. 5). In fact, one step at $H_{C2}=2.2\text{ T}$ is seen at 15 K between T_1 and T_N . Above T_N the magnetization increases monotonically. The induced magnetization increases up to $8.1\mu_B/\text{Tb}$ at 18 T and 4.2 K , which is by 10% smaller than the full moment of Tb^{3+} ion ($9\mu_B/\text{Tb}$).

The electrical resistivity $\rho(T)$ normalized to room-temperature vs temperature for $\text{GdRu}_4\text{P}_{12}$ is displayed in Fig. 6. $\rho(T)$ reveals a positive temperature dependence like typical metals below room temperature. Then, it shows a broad minimum at around 30 K and increases gradually as the temperature is lowered. Furthermore, $\rho(T)$ increases rapidly below $T_N=22\text{ K}$ (inset of Fig. 6), which is the AF ordering temperature determined from magnetic susceptibility, and shows maximum at around 13 K , then decreases.

In the Tb compound, $\rho(T)$ also shows a typical metallic behavior and a broad minimum at around 33 K (Fig. 7). A rapid increase of $\rho(T)$ is also observed below $T_N=20\text{ K}$ (inset of Fig. 7). However, no anomaly was found around T_1

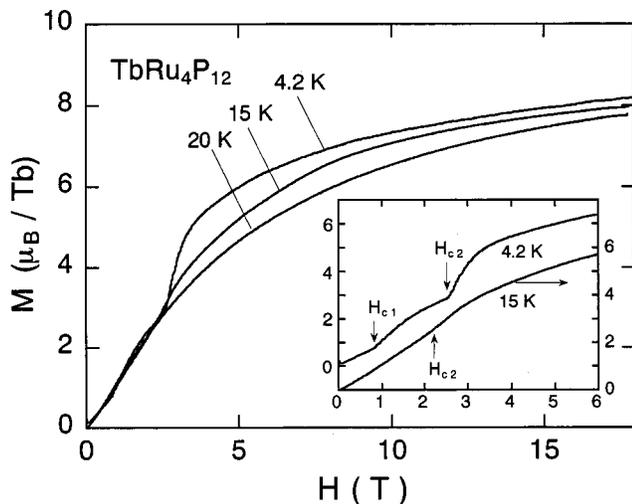


FIG. 5. Magnetization curves $M(H)$ for $\text{TbRu}_4\text{P}_{12}$ at several temperatures. Inset: magnetization curves at 4.2 K and 15 K below 6 T .

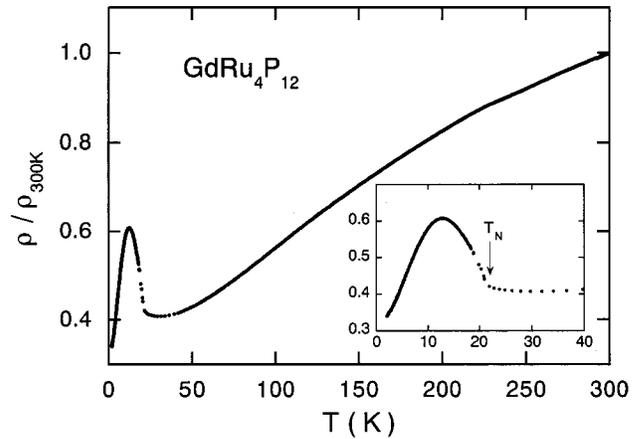


FIG. 6. Normalized electrical resistivity $\rho/\rho_{300\text{ K}}$ vs temperature for $\text{GdRu}_4\text{P}_{12}$. The inset shows an enlarged view below 40 K .

$=10\text{ K}$. T_N and T_1 are magnetic phase transition temperatures determined from magnetic susceptibility, as shown in the inset of Fig. 3. The sharp increases of resistivity below T_N for both Gd and Tb compounds may be due to nesting of the Fermi surface. Since band-structure calculations indicate that the Fermi level is situated at a large peak of the density of states in La compounds,¹⁴ the electronic system may be stabilized by the nesting. Similar behavior was observed below AF magnetic transition temperature 6.4 K in $\text{PrFe}_4\text{P}_{12}$.⁵ While the broad minimums near 30 K for $\text{GdRu}_4\text{P}_{12}$ and 33 K for $\text{TbRu}_4\text{P}_{12}$ are not well understood, similar behavior was observed near 33 K in $\text{NdFe}_4\text{P}_{12}$.⁵

In summary, we have synthesized the filled skutterudite compounds $\text{GdRu}_4\text{P}_{12}$ and $\text{TbRu}_4\text{P}_{12}$. The measurements of lattice parameter and magnetic experiments reveal that the valence of both Gd and Tb ions is near trivalent in the compounds. The measurements reported in this paper indicate an antiferromagnetic transition at $T_N=22\text{ K}$ for $\text{GdRu}_4\text{P}_{12}$ and two successive antiferromagnetic transitions at $T_N=20\text{ K}$ and $T_1=10\text{ K}$ for $\text{TbRu}_4\text{P}_{12}$. Further experiments are needed to determine the field-temperature magnetic phase diagram and fully characterize the magnetic properties in the compounds. Measurements of the magnetoresistance and the pressure dependence of the magnetic properties are in

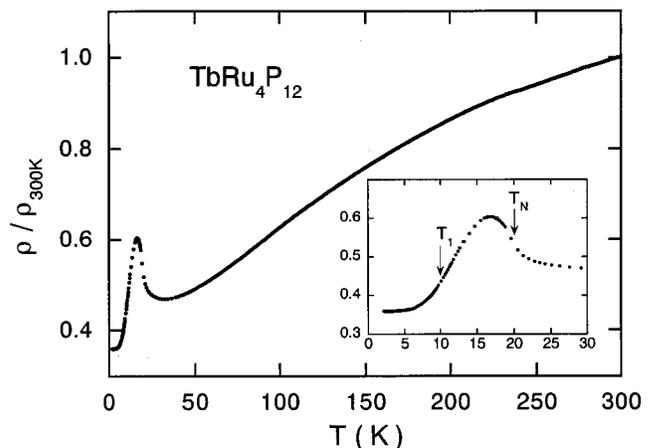


FIG. 7. Normalized electrical resistivity $\rho/\rho_{300\text{ K}}$ vs temperature for $\text{TbRu}_4\text{P}_{12}$. The inset shows an enlarged view below 30 K .

progress. These compounds as well as many other members of the filled skutterudites are highly attractive. However, most of these compounds are difficult or impossible to synthesize under atmospheric pressure in pure form. We would like to emphasize that high-pressure synthesis is one of most efficient techniques to overcome the difficulty in preparation.

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- ¹W. Jeitschko and D. Braun, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **33**, 3401 (1977).
 - ²D. J. Braun and W. Jeitschko, *J. Less-Common Met.* **72**, 147 (1980).
 - ³D. J. Braun and W. Jeitschko, *J. Solid State Chem.* **32**, 357 (1980).
 - ⁴M. E. Danebrock, C. B. H. Evers, and W. Jeitschko, *J. Phys. Chem. Solids* **57**, 381 (1996).
 - ⁵M. S. Torikachvili, J. W. Chen, Y. Dalichaouch, R. P. Guertin, M. W. McElfresh, C. Rossel, M. B. Maple, and G. P. Meisner, *Phys. Rev. B* **36**, 8660 (1987).
 - ⁶I. Shirovani, T. Adachi, K. Tachi, S. Todo, K. Nozawa, T. Yagi, and M. Kinoshita, *J. Phys. Chem. Solids* **57**, 211 (1996).
 - ⁷I. Shirovani, T. Uchiumi, K. Ohno, C. Sekine, Y. Nakazawa, K. Kanoda, S. Todo, and T. Yagi, *Phys. Rev. B* **56**, 7866 (1997).
 - ⁸G. P. Meisner, M. S. Torikachvili, K. N. Yang, M. B. Maple, and R. P. Guertin, *J. Appl. Phys.* **57**, 3073 (1985).
 - ⁹C. Sekine, T. Uchiumi, I. Shirovani, and T. Yagi, *Phys. Rev. Lett.* **79**, 3218 (1997).
 - ¹⁰D. T. Morelli and G. P. Meisner, *J. Appl. Phys.* **77**, 3777 (1995).
 - ¹¹N. R. Dilley, E. J. Freeman, E. D. Bauer, and M. B. Maple, *Phys. Rev. B* **58**, 6287 (1998).
 - ¹²N. Takeda and M. Ishikawa, *Physica B* **259–261**, 92 (1999).
 - ¹³L. Nordström and D. J. Singh, *Phys. Rev. B* **53**, 1103 (1996).
 - ¹⁴H. Harima, *Prog. Theor. Phys. Suppl.* (to be published).
 - ¹⁵D. T. Morelli and G. P. Meisner, *J. Appl. Phys.* **77**, 3777 (1995).
 - ¹⁶B. C. Chen, J. H. Xu, C. Uher, D. T. Morelli, G. P. Meisner, J. P. Fleurial, T. Caillat, and A. Borshchevsky, *Phys. Rev. B* **55**, 1476 (1997).
 - ¹⁷B. C. Sales, D. Mandrus, B. C. Chakoumakos, V. Keppens, and J. R. Thompson, *Phys. Rev. B* **56**, 15 081 (1997).
 - ¹⁸N. R. Dilley, E. J. Freeman, E. D. Bauer, and M. B. Maple, *Phys. Rev. B* **58**, 6287 (1998).
 - ¹⁹J. W. Kaiser and W. Jeitschko, *J. Alloys Compd.* **291**, 66 (1999).
 - ²⁰I. Shirovani, E. Takahashi, N. Mukai, K. Nozawa, M. Kinoshita, T. Yagi, K. Suzuki, T. Enoki, and S. Hino, *Jpn. J. Appl. Phys., Part 1* **32**, Suppl. 32-2, 294 (1993).
 - ²¹C. Sekine, M. Inoue, T. Inaba, and I. Shirovani, *Physica B* **281–282**, 308 (2000).
 - ²²C. Sekine, H. Saito, T. Uchiumi, A. Sakai, and I. Shirovani, *Solid State Commun.* **106**, 441 (1998).