Single crystal growth and magnetic properties of pseudo-kagome lattice $R$RhPb ($R = \text{Nd, Sm and Gd}$)

Y Matsumoto$^1$, R Goto$^1$, Y Haga$^2$, Z Fisk$^{2,3}$, and S Ohara$^1$

$^1$Department of Engineering Physics, Electronics and Mechanics, Graduate school of Engineering, Nagoya Institute of Technology, Nagoya, Aichi 466-8555, Japan
$^2$Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
$^3$Department of Physics and Astronomy, University of California, Irvine, California 92697, USA

E-mail: matsumoto.yuji@nitech.ac.jp

Abstract.

We have synthesized single crystals of $R$RhPb ($R = \text{Nd, Sm and Gd}$) with hexagonal ZrNiAl-type structure from Pb-flux. The crystal structures were confirmed by powder X-ray diffraction and the compositions were determined by electron-probe micro-analyzer (EPMA). We have measured their magnetic properties of $R$RhPb. It is found that the $R$RhPb ($R = \text{Nd, Sm and Gd}$) are antiferromagnets with two successive phase transitions with magnetic ordering occurring at $T_{N1} = 3.6$ K and $T_{N2} = 3.4$ K in NdRhPb, $T_{N1} = 11.5$ K and $T_{N2} = 8.3$ K in SmRhPb and $T_{N1} = 17.6$ K and $T_{N2} = 15.3$ K in GdRhPb.

1. Introduction

Rare earth and actinide intermetallic compounds with the hexagonal ZrNiAl-type structure ($RTX : R=\text{rare earth, actinide, } T=\text{transition metal, } X=\text{Al, Ga, In, Sn and Pb}$) are one of the extensively studied systems $[1, 2]$. The $R$-$T$(1) layer and $T$(2)-$X$ layer are stacked along c-axis as shown in Fig. 1. The $R$ ion of the $R$-$T$(1) layer coordinates a pseudo-kagome lattice possessing geometrical frustration. The typical $120^\circ$ array of magnetic moments observed in TbNiIn, DyNiIn, YbAuIn, DyAuIn and ErAuIn arises from this frustration $[3, 4]$.

In heavy fermion systems, interesting magnetic order has been found. CePdAl is a heavy fermion antiferromagnet with antiferromagnetic temperature $T_N = 2.7$ K and specific heat coefficient $\gamma = 250$ mJ/mol K$^2$ $[5]$. The magnetic structure of CePdAl consists of three inequivalent Ce sites. The magnetic ordering vector $q = (1/2, 0, \tau)$ where $\tau \sim 0.35$ weakly depends on temperature. Two-thirds of the Ce ions order while one-third does not order below $T_N$. The magnetic structure is considered to originate from the geometrical frustration $[6]$.

The search for new compounds with ZrNiAl-type structure is motivated by the possible discovery of new physical phenomena due to the geometrical frustration. Until now, there are few studies on $RT$Pb systems $[7, 8, 9, 10]$ and physical properties have been only reported for Ce$T$Pb ($T = \text{Pd, Rh and Pt}$). This prompted the study of single crystal growth and physical properties of $R$RhPb ($R = \text{Nd, Sm and Gd}$) reported here.
2. Experimental

The single crystals of $R$RhPb ($R =$ Nd, Sm and Gd) were grown from Pb-flux. 3N (99.9 %) $R =$ Nd, Sm and Gd, 4N Rh, and 5N Pb were reacted in with starting composition of 1:1:10. These materials were placed in an alumina crucible and sealed in an evacuated quartz tube. The sealed tubes were heated to 1150 °C, soaked for 12 hours, then cooled down to 700 °C in 90 hours. The excess Pb was spun off in a centrifuge.

The single phase of the hexagonal ZrNiAl-type structure was confirmed by powder X-ray diffraction. The powder was obtained from crashed single crystals. Figure 2 shows the powder X-ray diffraction patterns of the $R$RhPb. We mixed in Si powder as a standard. The X-ray diffraction patterns gave $a = 7.706$ Å, $c = 3.951$ Å for NdRhPb, $a = 7.695$ Å $c = 3.876$ Å for SmRhPb, and $a = 7.697$ Å, $c = 3.826$ Å for GdRhPb.

The crystal compositions and homogeneity were determined by using an electron-probe microanalyzer with wavelength dispersive spectrometers (EPMA-WDS; JEOL-8530). We used NdB$_6$, SmB$_6$, Gd$_3$Ga$_5$O$_{12}$, Rh and PbF$_2$ as standard reference materials for EPMA. The chemical compositions were determined to be Nd:Rh:Pb = 1.00:1.02:1.04, Sm:Rh:Pb = 1.00:0.93:0.96 and Gd:Rh:Pb = 1.00:1.05:1.06, which were in good agreement with the ideal 1:1:1 stoichiometry.

The magnetic properties were measured by using a commercial superconducting quantum
interference device magnetometer (Quantum Design).

3. Results and discussion

Figure 3 shows the reciprocal magnetic susceptibility $1/\chi(T)$ of NdRhPb as a function of temperature at 0.1 T. Above 70 K, $1/\chi(T)$ can be fit by a Curie-Weiss law. We estimated that the effective moment $\mu_{\text{eff}}$ and Weiss temperature $\theta_p$ are 3.78 $\mu_B$ and -1 K for $H \parallel a$, and 3.83 $\mu_B$ and -55 K for $H \parallel c$ respectively, indicating that the effective moment is close to the value expected for Nd$^{+3}$ configuration ($\mu_{\text{eff}} = 3.62 \mu_B$). $\chi(T)$ has a broad kink around $T_{M1} = 3.6$ K and a maximum at $T_{M2} = 3.4$ K for $H \parallel a$. On the other hand, $\chi(T)$ has a maximum $T_{M1} = 3.6$ K but anomaly not observed at $T_{M2} = 3.4$ K for $H \parallel c$. The decreasing of $\chi(T)$ below $T_{M1}$ for $H \parallel c$ is about 5 times larger than that for $H \parallel a$, indicating that the NdRhPb is an antiferromagnet with two successive transition and an Ising-like magnetic structure.

![Figure 3](image-url)

Figure 3. The temperature dependence of reciprocal magnetic susceptibility of NdRhPb at 0.1 T for $H \parallel c$ and $a$. The inset shows the expanded view of the magnetic susceptibility for $H \parallel c$ (circles, left axis), and for $H \parallel a$ (squares, right axis). The dashed lines indicate the $T_{M1}$ and $T_{M2}$.

Figure 4 shows the reciprocal magnetic susceptibility of SmRhPb as a function of temperature at 1 T. $\chi(T)$ can not be fit with the susceptibility using a modified Curie-Weiss law $\chi = \chi_0 + C/(T - \theta_p)$ because the parameters were not fixed. We need to estimate the energy level splitting and the valence of Sm-ion in SmRhPb. The $\chi(T)$ has a maximum at $T_{M1} = 11.5$ K and a kink at $T_{M2} = 8.3$ K for $H \parallel c$. For $H \parallel a$, $\chi(T)$ has two anomaly at $T_{M1}$ and $T_{M2}$ and $\chi(T)$ is almost independent to the temperature below $T_{M2}$, indicating that the magnetic hard axis would be around $c$-axis.

Figure 5 shows $1/\chi(T)$ of GdRhPb measured in 0.1 T. Above 50 K, $1/\chi(T)$ can be fit with a Curie-Weiss law. We estimated that the $\mu_{\text{eff}}$ and $\theta_p$ are 8.04 $\mu_B$ and 9 K for $H \parallel c$, and 8.06 $\mu_B$ and 10 K for $H \parallel a$, respectively, indicating that the magnetic anisotropy is weak. The effective moment is close to the value expected for Gd$^{+3}$ ($\mu_{\text{eff}} = 7.94 \mu_B$). A peak at $T_{M1} = 17.6$ K and a weak drop at $T_{M2} = 15.3$ K for $H \parallel c$ and $a$ are observed.

We have measured the magnetic properties of RRhPb ($R$=Nd, Sm and Gd). We summarized the results in table 1. It is found that the RRhPb ($R$ = Nd, Sm and Gd) are antiferromagnets with two successive phase transitions. The successive transitions with ZrNiAl-type structure have been observed in PrNiAl, NdPdAl, NdNiAl, YbAgGe, and so on [11, 12, 13, 14]. These double transitions appear to be a common phenomena in ZrNiAl-type structure.

This structure has the geometrical frustration. Therefore the suppression of $T_M$ is expected, especially strong for SmRhPb because of its magnetic structure. The $T_M$ of RRhPb ($R$=Nd, Sm and Gd) roughly follows the de-Gennes scaling ($T_M$ vs. $(gJ-1)^2J(J+1)$, where $g_J$ is the
Figure 4. The temperature dependence of the reciprocal magnetic susceptibility of SmRhPb at 1 T for $H \parallel c$ and $a$. The inset shows the expanded view of the magnetic susceptibility.

Figure 5. The temperature dependence of reciprocal magnetic susceptibility of GdRhPb at 0.1 T for $H \parallel c$ and $a$. The inset shows the expanded view of the magnetic susceptibility.

| Sample    | $T_{M1}$ | $T_{M2}$ | de-Gennes factor | $|\theta_p|/T_{M1}$            |
|-----------|----------|----------|-----------------|-------------------------------|
| NdRhPb    | 3.6 K    | 3.4 K    | 1.84            | 0.28 ($H \parallel c$), 16.18 ($H \parallel a$) |
| SmRhPb    | 11.5 K   | 8.3 K    | 4.46            | -                             |
| GdRhPb    | 17.6 K   | 15.3 K   | 17.6            | 0.51 ($H \parallel c$), 0.57 ($H \parallel a$) |

4. Conclusion
We have succeeded in growing the single crystals of $R$RhPb ($R=$Nd, Sm and Gd) using Pb-flux. We have confirmed the crystal structures of $R$RhPb ($R=$Nd, Sm and Gd) using powder X-ray
diffraction. The \( RRhPb \) (\( R = \text{Nd}, \text{Sm} \) and \( \text{Gd} \)) are antiferromagnets with two successive phase transitions. The magnetic transitions occur at \( T_{N1} = 3.6 \) K and \( T_{N2} = 3.4 \) K in \( \text{NdRhPb} \) and appear Ising-like. The magnetic transitions take place at \( T_{N1} = 11.5 \) K and \( T_{N2} = 8.3 \) K in \( \text{SmRhPb} \) with magnetic hard axis \( c \). \( \text{GdRhPb} \) exhibits magnetic transitions at \( T_{N1} = 17.6 \) K and \( T_{N2} = 15.3 \) K. The effect of geometrical frustration in \( RRhPb \) (\( R = \text{Nd}, \text{Sm} \) and \( \text{Gd} \)) appears to be negligible.

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