Growth and NMR evaluation of a single crystal CePd$_2$Ga

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Abstract. We have measured the electrical resistivity and the powder x-ray diffraction (XRD) for ascast, 700 °C, and 800 °C annealed samples of the Ce-based antiferromagnetic compound CePd$_2$Ga. From the XRD measurement, the unit-cell volume of 700 °C and 800 °C annealed sample is smaller by 0.52% and 0.87% than ascast sample. In order to check microscopically, we are carried out Ga-Nuclear Magnetic Resonance (NMR) and Nuclear Quadrupole Resonance (NQR).

1. Introduction
Numerous ternary lanthanoids/actinides-based intermetallic compounds have been studied and attracted, because, in Ce, U based heavy-fermion (HF) compounds, unconventional superconductivity or non-Fermi-liquid behaviors emerge frequently near quantum critical point (QCP) by tuning physical (chemical) pressure and/or magnetic field. Such anomalous ground states are caused by a hybridization between conduction electrons and $f$-electrons. It is known that $LnT_2X$ ($Ln =$ lanthanoid, $T =$ transitionmetal) series possesses three kinds of different structures, i.e., MnCu$_2$Al type (cubic Space group $Fm3m$)[1], ZrPt$_2$Al type (hexagonal, Space group $P6_3/mmc$)[2] and YPd$_2$Si type (Orthohombic, Space group $Pnma$)[3]. CePd$_2$X ($X =$ Al, Ga) crystallizes YPd$_2$Si type structure. Ce ion (local symmetry : .m.) forms zigzag-chain along the $a$-axis which is similar to $\varepsilon$-TiNiSi type structure, e.g., the ferromagnetic superconductor UCoGe[4], Kondo semiconductor CeNiSn[5].

Porycrystalline samples of CePd$_2$Al and Ce$_{(1-x)}$Y$_x$Pd$_2$Ga have been reported by Das et al.[6, 7]. CePd$_2$Al exhibits an antiferromagnetic (AFM) order at $T_N = 3.3$ K. An electronic specific-heat coefficient is as large as $\gamma_e = 110$ mJ/mol K$^2$, and a minimum of the electrical resistivity is observed at $T \sim 14$ K. These results suggest that CePd$_2$Al is Kondo-lattice-system. No ordering was observed in electrical resistivity in Ce$_{(1-x)}$Y$_x$Pd$_2$Ga for $x > 0.2$. Meanwhile the AFM order clearly appears for $x < 0.2$. Macroscopic measurements, such as electric resistivity, magnetic susceptibility and heat capacity have been performed for the single-crystalline CePd$_2$Ga [9]. An AFM order was observed at around 3 K from each measurements, which value is close to CePd$_2$Al. The electronic specific-heat coefficient was $\gamma_e = 63$ mJ/mol K$^2$ in the AFM state. The level scheme of the crystal electric field was estimated to the first and the second excited states lie at 66 K and about 280 K, respectively. The estimated Kondo temperature $T_K = 2-4$ K is comparable with AFM ordering temperature, suggesting the competition between the Kondo effect and RKKY interaction.
2. Experimental

Single-crystalline samples of CePd$_2$Ga were grown by Czochralski method in a tetra-arc furnace. Starting materials of Ce (3N), Pd (4N) and Ga (6N) were taken in the ratio 1 : 2 : 1. The pulling speed was 10 mm/hr. An ingot was 2-3 mm in diameter and 40 mm in length. In order to investigate annealing effect, single crystals were cut from this ingot and were wrapped in tantalum foil and annealed for two days at different annealing conditions 700, 800 and 900 °C in evacuated quartz tubes. The powder x-ray diffraction (XRD) measurements were carried out using a Cu-\( K_{\alpha} \) radiation. The electrical resistivity was measured down to about 1.5 K with a standard four probe method. The ascast sample was crushed for rf field penetration in NMR/NQR measurements. NMR/NQR spectra were obtained by sweeping a magnetic field/Fourier step-sum methods.

3. Experimental result and discussion

3.1. Powder X-ray diffraction

The powder XRD result is shown in Fig.1 with previous report [8]. No impurity phase was detected. We have succeeded in synthesizing single phase of CePd$_2$Ga. Figure 2 shows the powder XRD pattern of ascast (black), 700 °C annealed (red), and 800 °C annealed (blue) sample in the angle range of 2\(^\theta\) from 10° to 90°. The sample annealed at 900 °C was melted. The peak positions of the annealed samples shifted to higher angle, and the peak position of 800 °C annealed sample is higher than that of 700 °C annealed sample slightly. The unit-cell volume is reduced by 0.52% for 700 °C annealing (0.87% for 800 °C annealing) from that of the ascast sample.

3.2. Electrical resistivity

The effect of annealing for the electrical resistivity \( \rho \) is shown in Fig.3, where a current was applied to ab-plane. Although annealing conditions are different, the temperature dependence of \( \rho \) exhibits a similar behavior. A broad shoulder was observed at around 50 K, which is roughly corresponding to the crystal electrical field splitting between the ground and the first
exited state [9]. A clear kink was observed at around 3 K for all annealing conditions and is
ascribed to AFM ordering, which is consistent with the previous report [9]. The present results
indicate that Néel temperature \(T_N\) is independent of an annealing condition, suggesting that
the reduction of the unit-cell volume by 0.87% does not effect a magnetic transition.

Figure 3. Temperature dependences of the electric resistivity of ascast (black), 700 °C-annealed
(red) and 800 °C-annealed (blue) sample. A residual resistivity ratio \(300 \text{K}/0 \text{K}\) is
6:4, 6:9, and 7:1 for ascast, 700 °C-annealed and 800 °C-annealed sample respectively. The
AFM ordering temperature is independent of the annealing condition.

3.3. NMR/NQR measurements

\(^{69}\text{Ga-NMR}\) (nuclear spin: \(I = 3/2\), gyromagnetic ratio: \(\gamma_0/2\pi = 10.21885 \text{MHz/T}\))
measurement of the single-crystalline powder sample was performed at 150 K. The nuclear
spin Hamiltonian \((I > 1/2)\) under an external magnetic field \(H\) is given by

\[
\mathcal{H} = \mathcal{H}_z + \mathcal{H}_Q = -\mu_0 \gamma_0 h I \cdot H_{\text{eff}} + \frac{\hbar \nu_Q}{6} \left( 3I_Z^2 - I (I + 1) + \frac{\eta}{2} (I_+^2 + I_-^2) \right)
\]

where \(H_{\text{eff}}\) is the effective field at the Ga nuclei and is written by \((1 + K) \cdot H\). \(K\) is the Knight shift.
The nuclear quadrupole resonance frequency \(\nu_Q\) and the asymmetric parameter \(\eta\) are defined as
\(\nu_Q \equiv \frac{3e^2 q_Q}{2(1-1/\eta)}\) and \(\eta \equiv \frac{|V_{XY}| - |V_{XX}|}{|V_{ZZ}|}\) \((|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|)\).
\(V_{\alpha\beta} = \frac{\partial^2 V}{\partial \eta^2} (\alpha = X, Y, Z)\) is the electric field gradient (EFG) for principle axes at the Ga nucleus position.
Figure 4 shows the \(^{69}\text{Ga-NMR}\) spectrum corresponding to \(|-1/2\rangle \leftrightarrow |+1/2\rangle\) transition at a fixed frequency \(f_0 = 69.050 \text{MHz}\) with the simulation result (solid line). The central peak was spread due
to the second order perturbation effect of the nuclear quadrupole interaction. The result of
the simulation gives a rough estimate of NQR parameters: NQR frequency \(^{69}\nu_Q \sim 13.608\)
MHz and asymmetric parameter \(\eta \sim 0.25\). These parameters allow us to determine the
resonance frequency \(^{71}\nu_{\text{NQR}} = 13.749 \text{MHz}\). Moreover, the nuclear quadrupole moment ratio
\(\left(^{69}Q/^{71}Q = 1.598\right)\) is equal to the ratio of the NQR frequency \((^{69}\nu_Q/^{71}\nu_Q)\). This relationship
gives \(^{71}\nu_{\text{NQR}} = 8.652 \text{MHz}\). Figure 5 displays the \(^{69,71}\text{Ga-NQR}\) spectra (corresponding to
\(|\pm3/2\rangle \leftrightarrow |\pm1/2\rangle\) transition) at 10 K. \(^{69}\text{Ga}\) and \(^{71}\text{Ga-NQR}\) signals are observed at \(f \sim 13.769\)
MHz and 8.668 MHz, respectively. The experimental result is well consistent with those obtained from $^{69}$Ga-NMR.

![Figure 4.](image1.png)

**Figure 4.** The powder pattern of $^{69}$Ga-NMR central line (black) and the simulated spectrum is convoluted with Gaussian function of width of 0.02 T (red). Here, we assumed that a knight shift is 0.5%. The spectrum is spread due to a quadrupole interaction of the second-order perturbation.

![Figure 5.](image2.png)

**Figure 5.** $^{69,71}$Ga-NQR signals in CePd$_2$Ga at 10 K. The dash lines represent the simulations for $^{69}$P$_{NQR}$ and $^{71}$P$_{NQR}$ (details are shown in the text). The narrow full width at half maximum for $^{69,71}$Ga (~200, 150 kHz) indicates that the sample quality is high.

4. Summary

We have measured the electric resistivity and the powder XRD pattern for ascast, 700 °C annealed and 800 °C annealed CePd$_2$Ga. Furthermore, we have succeeded in observing Ga-NMR/NQR signals for the first time. The unit-cell volume was reduced about 0.52% and 0.87% by annealing of 700 °C and 800 °C, respectively. An absolute value of the electrical resistivity was depended on the anneal temperature, whereas, the behavior does not associate with that. The quadrupole parameters in CePd$_2$Ga are determined as $^{69}$$\nu_Q$ ~ 13.608 and $\eta$ ~ 0.25 from the simulation of the $^{69}$Ga-NMR central line. Additionally, we have observed $^{69}$Ga and $^{71}$Ga-NQR spectra at $f$ ~ 13.769 MHz and 8.668 MHz, respectively. In order to investigate microscopic properties of CePd$_2$Ga, the temperature dependence of NMR/NQR spectra and a nuclear spin-lattice relaxation rate should be measured in future studies.

Acknowledgments

This work has been supported by a Grant-in-Aid for Scientific Research on Innovative Areas “J-Physics” (No. 15H05885) and Grants-in-Aid for Scientific Research (Nos. 26400359, 15H05745, and 15H03689) of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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