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Single Crystal Growth and Magnetic Anisotropy of Hexagonal $PuGa_3$

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Single crystals of $PuGa_3$ have been prepared by the gallium flux method. X-ray diffraction as well as magnetization measurements show that the hexagonal phase was selectively grown among two allotropes of trigonal and hexagonal ones. Magnetization shows highly anisotropic behavior with a magnetic easy axis along the *c*-direction. The present behavior is discussed in comparison with other actinide-gallium systems.

KEYWORDS: $PuGa_3$, antiferromagnet

1. Introduction

f-electron systems in actinide and rare-earth intermetallics have attracted considerable attention because of the emergence of unconventional superconductivity as well as exotic *f*-electron phase transitions. Among them, a series of superconductors with the tetragonal $HoCoGa_5$ structure, including $PuCoGa_5$ and $CeCoIn_5$, and related compounds are extensively studied [1]. In the case of $CeCoIn_5$, the crystal structure was described as a combination of cubic $CeIn_3$ and Co-In layers. In actinides, however, the situation is slightly different. While in $UCoGa_5$ it can be regarded as the combination of existing cubic UGa_3 and Co-Ga layers, the 'cubic' $PuGa_3$ as a building block of $PuCoGa_5$ does not exist [2]. Previous studies report trigonal and hexagonal allotropes existing for $PuGa_3$, instead of the cubic phase [3, 4]. Trigonal and hexagonal $PuGa_3$ order magnetically at 24 K and 20 K, respectively. While the trigonal phase shows ferromagnetic ordering with a spontaneous magnetic moment, hexagonal phase is considered to be an antiferromagnet.

In the present study we try to grow a single crystal of $PuGa_3$ to investigate magnetic anisotropy.

2. Sample preparation and characterization

Single crystal of $PuGa_3$ was prepared with a gallium-flux method in a purified argon circulated glove box to handle plutonium metal. An isotopically pure ^{239}Pu metal and Ga metal were used as a starting material. They were put into an alumina crucible in a composition Pu:Ga = 1:20. The crucible was then heated up to 1200 °C and slowly cooled down under an argon gas atmosphere. Single crystals were picked up from the melt of gallium flux at room temperature. Powder X-ray diffraction suggested the formation of hexagonal phase of $PuGa_3$. This result is consistent with the

previous report where the hexagonal phase is stabilized by annealing polycrystal at relatively low temperature 800 °C [5].

The single crystal was encapsulated in a polyimide tube to avoid radioactive contamination. The magnetization measurements were performed at Institute for Materials Research, Tohoku University using a Quantum Design MPMS magnetometer. Magnetic anisotropy was measured using a home-made sample rotation mechanism. We found a pronounced uniaxial magnetic anisotropy in the paramagnetic state. Although the crystal orientation determination using X-ray technique was not available, we conclude that magnetic easy axis should be the c-axis, based on the hexagonal symmetry of physical properties.

3. Magnetic Properties

Figure 1 shows the temperature dependence of magnetic susceptibility $\chi(T)$. 55 kOe of magnetic field was applied along the magnetic easy axis, namely the c-axis, and the basal plane. Magnetic susceptibility for the c-axis shows Curie-Weiss behavior between room temperature and about 80 K. The inverse susceptibility in Fig. 1 can be fitted using effective magnetic moment $\mu_{\rm eff}$ = 0.75 $\mu_{\rm B}$/Pu, paramagnetic Curie temperature θ_p = 23 K and temperature independent weak susceptibility $\chi_0 = 1.0 \times 10^{-4}$ emu/mol for the field along the easy direction, as shown by the solid curve. These parameters are roughly consistent with the averaged values reported for polycrystalline samples, $\mu_{\rm eff}$ = 0.79 $\mu_{\rm B}$/Pu, θ_p = 11.3 K and $\chi_0 = 4.42 \times 10^{-4}$ emu/mol [5].

$\mu_{\rm eff}$ = 0.75 $\mu_{\rm B}$/Pu is consistent with that expected for a free Pu^{3+} ion with $5f^5$ configuration. θ_p = 23 K is indicative of a ferromagnetic interaction between Pu moments. The origin of the temperature independent term is not clear but can be attributed to a van Vleck-type contribution from the excited states. $\chi(T)$ under 55 kOe shows a sharp cusp at 22 K and decreases with decreasing temperature down to 13 K. This behavior is reminiscent of that for a typical anisotropic antiferromagnet. It is interesting to note that the antiferromagnetic behavior looks incompatible with the ferromagnetic interaction suggested from the paramagnetic Curie temperature. However, the behavior can be qualitatively explained if one assumes a ferromagnetic interaction dominant between nearest neighbors and a weak antiferromagnetic coupling between second nearest neighbors. A field-induced ferromagnetism is expected under magnetic field strong enough to overcome the weak antiferromagnetic interaction. At lower temperature 4.5 K, $\chi(T)$ shows a second anomaly. Ferromagnetism at higher field is suggested below this temperature in the previous study [5].

$\chi(T)$ for the field perpendicular to the c-axis has smaller value and weaker temperature dependence than for c-axis data, corresponding to a uniaxial magnetic anisotropy. A small cusp at $T_{\rm N}$ is most likely due to the misalignment of the crystal with respect to the magnetic field. The similar Curie-Weiss analyses can be applicable also for the field along the hard axis, as shown by the solid line in Fig. 1. The obtained parameters $\mu_{\rm eff}$ = 0.89 $\mu_{\rm B}$/Pu and $\chi_0 = 0.9 \times 10^{-4}$ are almost the same as those obtained for the easy axis. On the other hand, θ_p = -63 K for the hard axis.

We note that the present results can account for the previous results obtained for polycrystalline samples.

The magnetic transition temperature was further investigated by measuring magnetization at various fields as shown in Fig. 2. In accordance with the previous report, a higher (lower) transition temperature is labelled as $T_{\rm N}$ ($T_{\rm C}$). $T_{\rm N}$ = 24.3 K at 1 kOe. With increasing magnetic field $T_{\rm N}$ gradually decreases. On the other hand, $T_{\rm C}$ is only visible at 55 kOe. At 50 kOe, no anomaly was observed down to 1.9 K.

These results are summarized in the magnetic phase diagram shown in Fig. 3. For the field perpendicular to the c-axis, there is no significant change in the transition temperature (not shown), consistent with the strong uniaxial magnetic anisotropy.

The present magnetic anisotropy is most likely derived from the ligand field effects around the plutonium atom. Taking into account the similarity in atomic arrangements between hexagonal $PuGa_3$

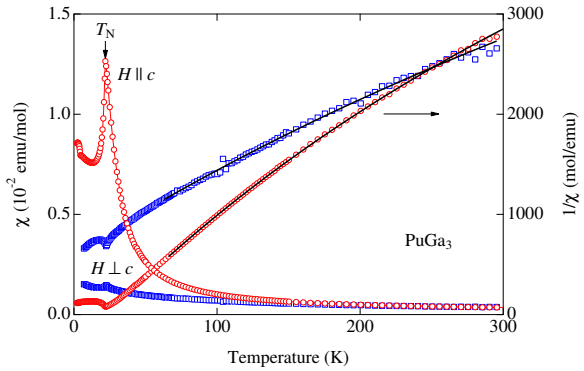

Fig. 1. Temperature dependence of magnetic susceptibility of $PuGa_3$. Black curves correspond to the Curie-Weiss fit described in the text.

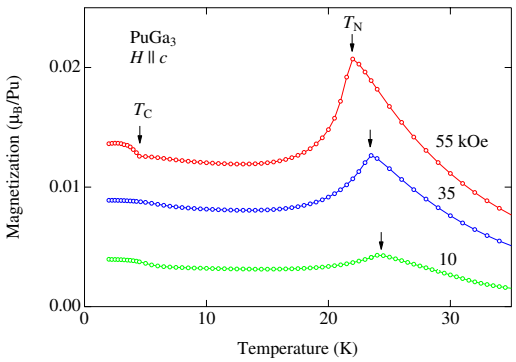

Fig. 2. Temperature dependence of magnetization of hexagonal $PuGa_3$ under magnetic fields parallel to c-axis.

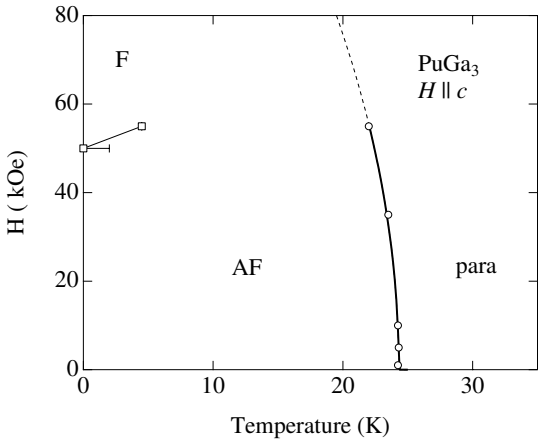

Fig. 3. Magnetic phase diagram of hexagonal $PuGa_3$ under magnetic field parallel to c-axis.

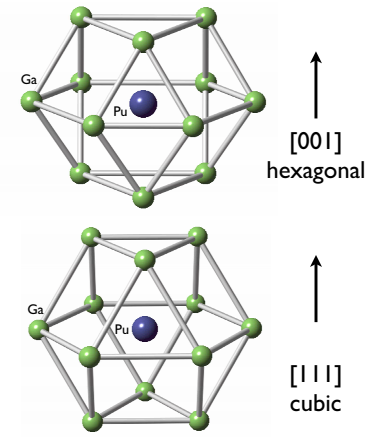

Fig. 4. Atomic arrangements around plutonium of hexagonal $PuGa_3$ and and hypothetical cubic $PuGa_3$. Crystallographic parameters were taken from [5].

and cubic $AuCu_3$-type hypothetical $PuGa_3$, one can imagine that the latter would have an easy axis along the [111] direction, as shown in Fig. 4. The similar situation occurs in cubic $NpGa_3$ and trigonal $NpGa_3$ [6]. In the 115-type heavy fermion superconductors, magnetic fluctuation plays a important role in the pairing interaction. The present magnetic anisotropy observed in hexagonal $PuGa_3$ might also be related to the occurrence of superconductivity in $PuCoGa_5$ and $PuRhGa_5$.

4. Summary

Single crystals of hexagonal $PuGa_3$ have been successfully grown by the gallium flux technique. A significant uniaxial magnetic anisotropy was found from the magnetic susceptibility measurements.

Antifferomagnetic-like transition at 24.3 K as well as the ferromagnetic-like second anomaly at 4.5 K under magnetic field of 55 kOe were observed, in agreement with the previous work. The paramagnetic effective moment is close to the expected value for Pu^{3+} configuration.

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