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Invited paper

Crystal structure and magnetic properties of the new ternary actinide compounds in An-Pd-Al system (An=U, Np)

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We report the crystal structure and magnetic properties of new ternary actinide compounds. A series of compounds having $AnPd_5Al_2$ composition crystallize in the body-center tetragonal $ZrNi_2Al_5$-type tetragonal structure (*I*4/mmm). Although the magnetic susceptibility of both compounds follows the Curie-Weiss behavior at high temperature, no magnetic phase transition was observed. UPd_5Al_2 has a nonmagnetic ground state where the magnetic susceptibility saturates at low temperature, while NpPd5Al2 superconducts below 4.9 K as reported recently. Another new ternary uranium intermetallic compound $U_{2/3}Pd_2Al_5$ crystallizes in the hexagonal structure ($P6_3/mmc$) with the lattice parameters 4.3278 and c = 16.2870 Å. The composition analysis and the single crystal X-ray diffraction revealed the peculiar disordered structure where 1/3 of uranium atoms are replaced by three aluminum atoms. The similar structure is reported previously for the compound in U-Fe-Si system. Magnetization as well as specific heat measurements revealed a low temperature anomaly corresponding to the magnetic phase transition.

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1. Introduction

Actinide (An) - based intermetallic compounds are known to show a variety of electronic states such as heavy fermions, magnetic and multipole orderings and unconventional superconductivity. Particularly, the An - Pd - Al ternary system is interesting because this system includes the well-known heavy fermion antiferromagnetic superconductor UPd_2Al_3 [1].

Recently we discovered a new compound $NpPd_5Al_2$ with the tetragonal $ZrNi_2Al_5$-type structure, revealing heavy fermion superconductivity at fairly high superconducting transition temperature T_{sc} = 5 K [3]. The upper critical field H_{c2} at 0 K is large and highly anisotropic : H_{c2} = 37 kOe for H || [100] and $H_{c2}(0)$ = 143 kOe for H || [001].

Moreover, H_{c2} is strongly Pauli-limited. The magnetization in the superconducting mixed state shows a step-like increase at H_{c2}, revealing the first-order phase transition. These features are characteristic of the strong paramagnetic effect. This discovery encouraged us to further investigate the actinide intermetallic compounds. The aim of this paper is therefore to report the survey on the ternary An-Pd-Al system and to investigate the crystal structure as well as the magnetic properties.

2. Experimental

The sample preparation of these actinide compounds have been performed at two facilities in Japan. Less radioactive uranium compounds were prepared at a JAEA facility in Tokai, while neptunium compounds were prepared in a glove box at the actinide laboratory in Tohoku university (Oarai).

The crystal structure was analyzed based on either powder or single-crystal X-ray diffraction techniques. Magnetization was measured using a SQUID magnetometer (Quantum Design MPMS). Specific heat was measured by the heat relaxation methods in a ^{3}He cryostat.

3. $AnPd_5Al_2$ compounds

The polycrystals of UPd_5Al_2 were prepared by melting

the stoichiometric amount of constituent elements using an arc furnace under argon atmosphere. The arc-melted ingot consists of two parts: silver platelet crystals and golden polycrystals. The former is the new ternary compound UPd_5Al_2 with the tetragonal structure, while the latter is a mixture of UPd_3 and PdAl. We found that the annealing treatment at rather low temperature 800 ◦C decomposes UPd_5Al_2 into UPd_3 and PdAl. Therefore

UPd_5Al_2 is produced at high temperature and remains as a meta-stable form at room temperature.

On the other hand, the $NpPd_5Al_2$ single crystals were obtained by the Pb-flux method, as described in the previous paper [3]. The similar method was not applicable to grow single crystals of UPd_5Al_2.

The samples were characterized by the electron microprobe analysis (EPMA) for the homogeneity and stoichiometry, using UPd_2Al_3 as a standard material. Both $NpPd_5Al_2$ and UPd_5Al_2 compounds are shown to have a good homogeneity and stoichiometry 1:5:2 within an experimental accuracy of a few %.

For UPd_5Al_2 , we succeeded in obtaining a small single crystal from the arc-melted ingot suitable for the singlecrystal X-ray diffraction. However, it was not possible to obtain such crystals of $NpPd_5Al_2$ with sufficiently small mossaicity. Therefore the crystal structure of $NpPd_5Al_2$ was determined based on the powder X-ray diffraction, as described below.

The crystal structure of UPd_5Al_2 was investigated by the single-crystal X-ray diffraction techniques on a small single crystal with a typical dimension 70 x 70 x 10 μm using an imaging plate (IP) area detector (Rigaku corporation) with Mo K_α radiation at room temperature. Details of the experimental condition are listed in Table 1.

The well-defined Bragg peaks were corrected and successfully indexed as the body-centered tetragonal cell with the lattice parameters a = 4.1693(5) and c = 14.629(2) ˚A. The crystal structure was successfully solved by the direct methods using a software SIR-2002 [4]. Atomic coordinates, anisotropic atomic displacement parameters and secondary extinction parameters were refined by the least-sqare method using SHELX-97 [5], and the obtained results are listed in Table 2. The final result was obtained with a conventional agreement factor $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 5.1$ %, where F_o and F_c are observed and calculated structure factors, respectively. Fig. 1 shows the crystal structure of $AnPd_5Al_2$. The structural parameters refined based on the single crystal X-ray diffraction are shown in Table 2. The structure is similar to the previously reported $ZrNi_2Al_5$-type structure. Lattice parameters and atomic coordinates of $AnPd_5Al2$ are very similar to those in $ZrNi_2Al_5$ (a = 4.023, c = 14.44, $z(Al_2)$ = 0.149 and z(Ni) = 0.238) [7].It should be noted, however, that the existence of rare-earth or actinide-based intermetallic compounds with this structure has not been reported so far.

The uranium atom located in (0, 0, 0) is surrounded by palladium atoms in a similar way to that in the $AuCu_3$-type arrangements. Namely, palladium atoms are located in a face-centered position of a square formed by the uranium atoms.

Such binary compounds $AnPd_3$ with the $AuCu_3$-type structure are actually existent for An = Np and Pu. Nellis *et al.* reported two structures for $NpPd_3$ [8].

Table 1. Crystallographic data for Upd_5Al_2

Composition	UPd_5Al_2
Space group	I4/mmm (No. 123)
Lattice parameters	a = 4.1693(5) ˚A
	c = 14.629(2) ˚A
Cell volume	254.52(7) ˚A 3
Formula units per cell	Z = 2
Formula weight	823.99
Calculated density	10.761 g/cm^3
Crystal size (mm3)	0.07 × 0.07 × 0.01
Radiation	$Mo_{K\alpha}$ (λ = 0.71075 ˚A)
	graphite monochromated
$2\theta_{max}$	60 ˚
Linear absorption coefficient	491.8 cm−1
Number of reflections	Total : 1198
	Unique : 139 (Rint = 0.145)
Goodness-of-fit	1.115
Conventional residual	R_1 = 0.046
Weighted residual	wR_2 = 0.105

One is the hexagonal $P6_3/mmc$ which is stable at room temperature and iso-structural with UPd_3. The other $AuCu_3$-type cubic $NpPd_3$ with the lattice parameter a = 4.053 ˚A can be obtained by quenching the arc-melted ingot. We also note that only cubic phase is reported for $PuPd_3$ [8]. From these view points, it is suggested that the $PuPd_5Al_2$ can also be stabilized. Such a difference in the structural stability of $AnPd_3$ is indicative of a gradual change of 5*f* electron characteristics across the actinide series. It should be noted, however, that detailed experiments such as the low temperature electronic specific heat as well as the de Haasvan Alphen study are needed to clarify the 5f electronic states in these compounds.

It is also well known that a series of $AuCu_3$-type RPd_3 exist. Very recently a cerium analogue $CePd_5Al_2$ has been reported with the possible antiferromagnetic ordering at low temperature.[9]

The crystal structure of the neptunium analogue $NpPd_5Al_2$ was determined by the powder X-ray diffraction measured for about 15 small pieces of single crystals which were put into a quartz capirary mounted on a goniometer. The X-ray beam was exposed for 30 min. with rotating the sample around the ω-axis. The powder diffraction profile was obtained by integrating the Debye-Scherrer ring recorded on the IP detector. A typical diffraction profile is shown in Fig. 2. The powder diffraction profile is well reproduced by the UPd_5Al_2-type structure, as shown by solid line in Fig. 2. We succeeded in refining the atomic coordinates using the Rietveld method using a software RIETAN-2000 [6]. The crystallographic parameters of $NpPd_5Al_2$ are shown in Table 3.

Table 2. Crystallographic parameters for UPd5Al2

Atom	site	x	y	z	U_{11}	U_{22}	U_{33}	B_{eq}
U	2*a*	0	0	0	0.0109(5)	0.0109(5)	0.0170(8)	1.02(4)
Pd_1	2*b*	0	0	½	0.0102(8)	0.0129(15)	0.0129(15)	0.88(5)
Pd_2	8*g*	0	½	0.14309(13)	0.112(6)	0.0106(6)	0.0167(10)	1.01(4)
Al	4*e*	0	0	0.2554(6)	0.013(2)	0.013(2)	0.039(6)	1.70(18)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}$. The equivalent isotropic displacement factor exponent takes the form: $-B_{eq}(\sin\theta/\lambda)^2$

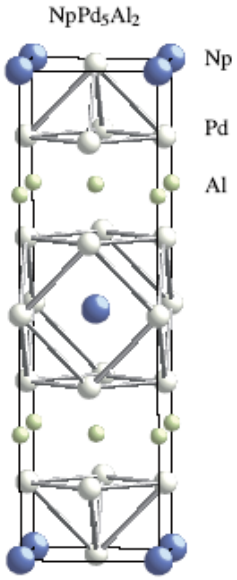

Fig. 1. Crystal structure of UPd_5Al_2.

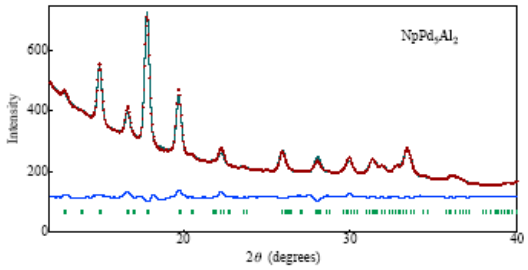

Fig. 2. Powder X-ray diffraction profile obtained for $NpPd_5Al_2$.

As reported in the previous paper for NpPd5Al2, the magnetic susceptibility follows the Curie-Weiss law above 50 K, with an effective magnetic moment of 3.22 μB/Np along the magnetic easy axis, as shown in Fig. 3, which is fairly larger than the one observed in many intermetallic Np compounds ≈ 2.66 corresponding to $5f^4$ configuration. Note that in general Pd atoms in actinide intermetallic compound do not contribute to magnetic moment [10].

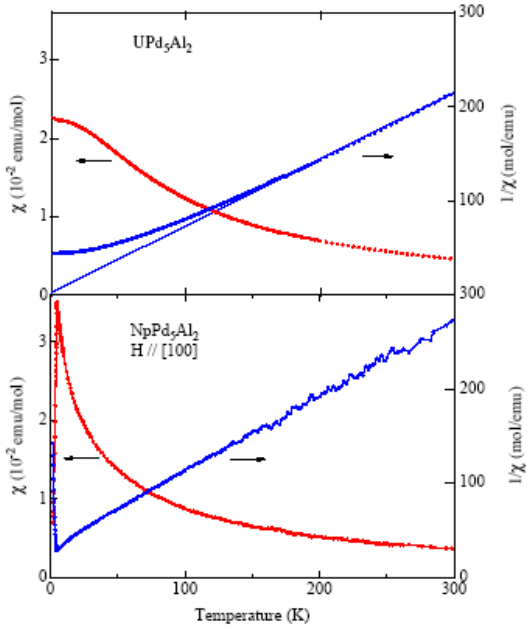

Fig. 3. Temperature dependence of the magnetic susceptibility in UPd_5Al_2 (upper panel) and $NpPd_5Al_2$ (lower panel).

It is therefore suggested that 5f electronic states in $NpPd_5Al_2$ deviate from pure $5f^4$ localized states. With decreasing temperature, it increases monotonically, and a sudden drop of the susceptibility occurs below about 5.0 K, revealing onset of superconductivity.

Table 3. Crystallographic parameters for $NpPd_5Al_2$ Space group : I4/mmm Lattice parameters a = 4.148(2), c = 14.716(5) ˚A

Atom	Site	x	y	Z
Np	2*a*	0	0	0
Pd1	2*b*	0	0	½
Pd2	8*g*	0	½	0.1467(9)
Al	4*e*	0	0	0.255(3)

Moreover, the electrical resistivity follows the *T*-linear dependence. These results suggest that the electronic state in $NpPd_5Al_2$ is close to the quantum critical point where the Neel temperature becomes zero. Note that the paramagnetic Curie temperature θ_p = −42K. Namely, it is

located close to the antiferromagnetic ordering, but $NpPd_5Al_2$ condenses into the superconducting state below about 5 K. In general, most of the neptunium intermetallic compounds with the Curie-Weiss behavior order magnetically, except a few compounds such as $NpGe_3$. $NpPd_5Al_2$ thus demonstrates peculiar magnetic characteristics. We also measured the magnetic susceptibility of UPd_5Al_2 measured at 5 kOe in the temperature range from 2 K to room temperature for the polycrystal, as shown in Fig. 3, together with the data of $NpPd_5Al_2$ [3]. The suceptibility follows the Curie-Weiss law above about 200 K. The effective magnetic moment and the paramagnetic Curie temperature are $\mu_{\rm eff}$ = 3.4 and $\theta_{\rm p}$=13 K, respectively.

The effective moment is close to the free ion value of 3.58 μB/U in the 5*f*2 configuration or 3.62 μB/U in the 5*f*3 configuration. With decreasing temperature, the susceptibility increases monotonically and tends to saturate below 20 K, reminiscent of either the formation of a crystal-field singlet ground state or the heavy fermion state at low temperatures. It is noted that a week increase of the susceptibility below 4 K is most likely due to magnetic impurities. It is thus clear from the present data that UPd_5Al_2 does not order magnetically. Further experiments as for the magnetic susceptibility for a single crystal and specific heat are necessary to clarify the electronic state of this compound.

4. $U_{2/3}Pd_2Al_5$

Single crystals of the new compound was found in the ingot prepared by the Al-self flux method. Starting materials of uranium (99.98 % purity), palladium (99.99 %) and aluminum (99.9999 %) were put into an alumina crucible with the composition U : Pd : Al = 1 : 2 : 20. It was further encapsulated in an evacuated quartz tube. The ampoule was placed in an electrical furnace and heated up to 1050˚C and then slowly cooled down. Single crystals were embedded in the remaining flux and they were extracted by removing the flux by the centrifuge.

The composition of the sample was determined approximately as 1 : 3 : 8, using UPd_2Al_3 as a standard material.

The crystal structure was determined by the single crystal X-ray diffraction using an imaging plate (IP) diffractometer with Mo K_α radiation. The new compound crystallizes in the hexagonal structure (space group P63/mmc) with lattice parameters a = 4.3278 and c = 16.287 ˚A. The integrated intensity was obtained from the Bragg spots recorded on the IP and the absorption correction was made using the empirical method. The first attempt to solve the structure gave only a poor agreement between calculated and observed intensities. Moreover, the number of atoms in the unit cell derived from the conventional structural analysis was not consistent with the composition estimated by EPMA. Then we carefully analyzed the electron density reconstructed from the observed structure factors and found significant disordered structures, as shown in Fig. 1 and Table I. The structural refinement has been performed using the SHELX97 software[5], where the secondary extinction was corrected and the anisotropic atomic displacement factors were applied to all the atoms.

The uranium atom located at 2*c* position has an occupancy factor 0.674(5). In the same layer Al(1) atoms are located at 6*h* positions with the occupancy factor 0.37(2). However, the interatomic distance between U-Al(1) 1.511 ˚A is too small compared to the average distance in other intermetallic compounds which is typically more than 3 ˚A.

Therefore uranium and aluminum cannot exist simultaneously at these positions. Considering the partial occupation mentioned above and the fact that the sum of the occupancy of uranium and aluminum site is close to unity, we came to the conclusion that U(2*c*) is randomly replaced by Al(6*h*).

Table 4. Crystallographic parameters for $U_{2/3}Pd_2Al_5$

Atom	site	x	y	z	occ.	$B_{eq}(A^2)$
Al(1)	6*h*	0.534(18)	0.068(3)	¼	0.37(2)	2.3(4)
Al(2)	4*f*	1/3	2/3	0.0482(3)	1	0.43(8)
Pd	4*f*	1/3	2/3	0.60787(9)	1	0.79(4)
Al(3)	4*e*	0	0	0.1365(3)	1	0.76(4)
U	2*c*	1/3	2/3	1/4	0.674(5)	0.88(4)

Conventional agreement factors was $R_1 = \sum||Fo| - |Fc||/\sum|Fo| = 5.1$ %, where F_o and F_c are observed and calculated structure factors, respectively.

The anisotropic displacement factor exponent takes the form :

$$-2\pi^2[h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}.$$

The equivalent isotropic displacement factor exponent takes the form : $-B_{eq}(\sin\theta/\lambda)^2$

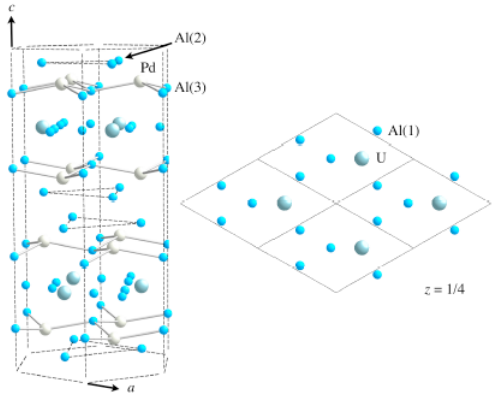

Fig. 4. Crystal structure of $U_{2/3}Pd_2Al_5$.

The absence of the superstructure peaks indicates that there is no ordered structure. Using this model and occupancy factors determined from the conventional intensity analysis, the chemical composition is refined as $U_{0.674}Pd_2Al_{5.08}$, in good agreement with the EPMA analysis. Hereafter we approximate the chemical composition as $U_{2/3}Pd_2Al_5$. This structure is very similar to the one reported previously for the U-Fe-Si compound and related ones [11,12]. It was also reported recently that R-Pt-Al (R: rare earth) system also has the compounds with the same structure [14,13,15].

Fig. 5 shows the temperature dependence of the magnetic susceptibility $\chi(T)$ of $U_{2/3}Pd_2Al_5$ for magnetic field (H) parallel to a and c axes. The magnetic susceptibility follows roughly as the Curie-Weiss law above 200 K, showing the paramagnetic effective moment 3.19 ($H \parallel c$) and 3.33 μB/U ($H \parallel a$), corresponding to the free uranium ion value. $\chi(T)$ is anisotropic with the magnetic easy axis along the c axis. For $H \parallel c$, $\chi(T)$ shows a peak at 12 K and decreases with decreasing temperature. On the other hand, $\chi(T)$ along the a axis monotonically increases with decreasing temperature through 12 K down to 2 K. Such behavior is reminiscent of the antiferromagnetic transition. Correspondingly, the specific heat ($C(T)$) also shows an anomaly around this transition, as shown in Fig. 6. However, the

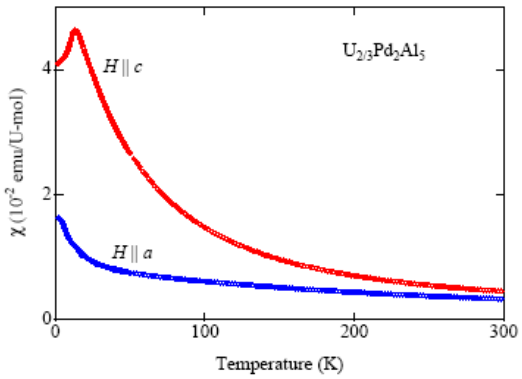

Fig. 5. Temperature dependence of the magnetic susceptibility for $U_{2/3}Pd_2Al_5$.

entropy associated with this transition is very small, implying an imperfect transition. Furthermore, the low temperature C/T value is relatively high, 220 mJ/K2U-mol. Considering the disordered structure mentioned above, the magnetic interaction between uranium 5f electrons might be randomly modified. The large C/T might be due to, for example, spin glass like behavior rather than the heavy fermion formation. Concerning this point, further experimental study is in progress.

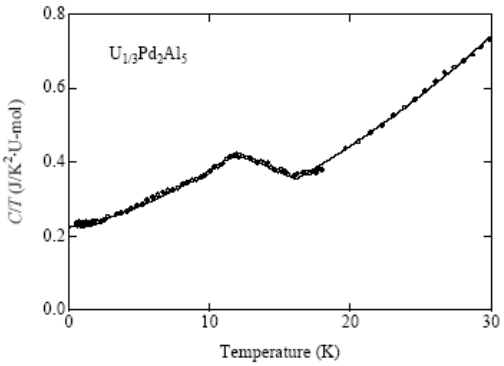

Fig. 6. Temperature dependence of the specific heat for $U_{2/3}Pd_2Al_5$.

5. Summary

We have found three actinide-palladium-aluminum intermetallic compounds $AnPd_5Al_2$ (An = U, Np) and clarified that they crystallize in the ZrNi2Al5-type tetragonal structure. The magnetic susceptibility measurements show the Curie-Weiss behavior at high temperature for both compounds. The paramagnetic effective moments estimated from the Curie-Weiss term correspond to $5f^2$ or $5f^3$ configuration for UPd^5Al^2, while that of $NpPd_5Al_2$ significantly deviates from the value expected from $5f^4$ configuration. Despite the Curie-Weiss behavior at hightemperatures, there is no magnetic ordering for both compounds.

We also found another new ternary comound$U_{2/3}Pd_2Al_5$ with the hexagonal structure. A significant randomness is concluded from EPMA and single-crystal X-ray diffraction analyses. Uranium 5f electrons have an paramagnetic effective moment corresponding to free uranium ion above 200 K. An anomaly observed in the magnetization and specific heat is most likely due to antiferromagnetic transition.

This transition is, however, an inhomogeneous one inferred from the small magnetic entropy associated with the transition as well as the broad transition width, reflecting the disordered structure.

Acknowledgments

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