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Letter

The crystal structure of $CePd_2Al_3$

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Abstract

The structure of $CePd_2Al_3$ has been studied by single-crystal X-ray diffractometry and was refined to the $R(R_w)$ values 0.035(0.028). The $CePd_2Al_3$ compound crystallizes in hexagonal symmetry belonging to the space group *P6/mmm*; the lattice constants are: $a=5.4764(2)$ Å, $c=4.2187(2)$ Å. It is corroborated that the structure is a $CaCu_5$-type derivative, with Pd and Al atoms, respectively, replacing the Cu atoms on two crystallographically distinct structure sites. An occupational refinement of the atom sites indicated the presence of an appreciable proportion of vacant sites (*ca.* 4%) at the Pd position.

1. Introduction

Ternary intermetallic compounds containing rare earth metals have various crystal structures and frequently manifest several interesting properties which are different from those of binary compounds. Accurate structure analysis of those ternary compounds is, therefore, indispensable for the study of physical properties as well as for the crystal chemistry of the materials. Recently, Geibel and co-workers have discovered new heavy fermion (HF) superconductors, UNi_2Al_3 [1] and UPd_2Al_3 [2], and studied their physical properties, including their superconducting nature. During the search for similar new HF superconductors, Kitazawa *et al.* [3] have found a third antiferromagnetically ordered yet nonsuperconducting HF compound, $CePd_2Al_3$, which was thought, from powder X-ray diffraction data, to have the same structure as UNi_2Al_3 or UPd_2Al_3. In the present work, therefore, we have studied the crystal structure of $CePd_2Al_3$ by means of X-ray diffraction using a single crystal.

2. Experimental procedures

Single crystals of $CePd_2Al_3$ were grown by the Czochralski method using a triarc furnace at Tohoku University. The purities of the starting materials were 99.9%, 99.9% and 99.999% for Ce, Pd and Al respectively. To compensate for the loss of Al, a mixture with the composition $CePd_2Al_{3.03}$ was used as the starting material. The lattice constants were measured with the same single-crystal diffractometer as used for intensity measurements; the wavelength employed was 0.70930 Å for Mo $K\alpha_1$ radiation.

For the intensity measurements, a specimen having an approximate size of 0.1 mm was selected from the crystal fragments which were obtained by cracking relatively larger crystals. Intensity data were measured on an Enraf–Nonius CAD-4 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.71073$ Å). Reflections in a full sphere ($0<2\theta<120°$) were measured. The total number of collected reflections ($|F_o|>5\sigma(|F_o|)$) was 6025, of which 378 were unique. Absorption effects were corrected by the semi-empirical method of North *et al.* [4].

3. Structure analysis and discussion

The atomic scattering factors and the anomalous dispersion correction factors were taken from the *International Tables for X-ray Crystallography* [5]. Calculations for the structure analysis were performed by using the program UNICS-III [6].

Placing the Ce, Pd and Al atoms respectively at the Ca (1a), Cu1 (2c) and Cu2 (3g) sites of the $CaCu_5$ structure [7], the structure of $CePd_2Al_3$ was refined with the aid of a full-matrix least-squares program. Anisotropic temperature factors were applied to all the atoms. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ where the weights w were $1/\sigma^2_F$. An experimental isotropic secondary extinction parameter was also included in the final stage of the refinement. The $R(R_w)$ values obtained were 0.038(0.031). To investigate the possibility of the presence of vacant sites, an occupational refinement was performed, fixing the occupancy of the Ce site at 100%. The $R(R_w)$ values decreased to 0.035(0.028). The occupancies obtained were 100%, 95.7(4)% and 98(1)% for the Ce, Pd and Al sites respectively. The difference synthesis finally calculated was featureless.

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The results of the structure analysis are given in Table 1. The present single-crystal study has demonstrated that $CePd_2Al_3$ crystallizes in the $PrNi_2Al_3$ structure, which is a $CaCu_5$-type derivative and closely related to the $CeCo_3B_2$ type with transition-metal and p-element sites interchanged [8]. The validity of the structure analysis is based on a reasonably low R value, a featureless final difference synthesis, normal values of the thermal parameters for all the atoms, and excellent agreement in the chemical composition between the structure and chemical analyses.

From the occupational refinement it is shown that there is an appreciable proportion of vacant sites (*ca.* 4%) at the Pd position. In contrast, the Al position (occupancy 98(1)%) is practically fully occupied. The agreement between the Pd contents obtained by two different methods, X-ray and chemical analyses, is noteworthy; the occupancies of the Pd position were 95.7(4)% and 95% respectively (Table 1). Therefore, there appears to be no significant mixing of Pd and Al atoms at Pd and Al sites. The lattice constants of the present single crystal are significantly larger than those for the polycrystalline samples ($a = 5.47117(4)$ Å, $c = 4.21593(4)$ Å) published by Kitazawa *et al.* [3]. Since no accurate chemical composition was obtainable from the polycrystalline sample, we could not interpret the difference between the lattice constants in terms of the occupational parameter at the Pd position. It seems reasonable, however, to assume that a variation in chemical composition is responsible for the difference between the lattice constants in the single-crystal and polycrystalline samples. It is reported that the magnetic susceptibility $\chi(T)$ for the polycrystalline sample shows antiferromagnetic ordering at $T_N = 2.8$ K [3]. However, $\chi_{\parallel c}(T)$ and $\chi_{\perp c}(T)$ for the single crystal show no anomaly and increase monotonously down to 1.7 K [9]. This fact also suggests a variation in the concentration of Pd vacant sites (and possibly of Al vacant sites) in the polycrystalline and single-crystal samples. In Table 2, interatomic distances in the $CePd_2Al_3$ single crystal are compared with their respective equivalents in the polycrystalline samples; on the whole, the interatomic distances in the former are longer than those in the latter, reflecting the differences in the lattice constants.

It is of interest to note that there is a significant difference between the axial ratio c/a of the RET_2Al_3 compounds (RE = rare earth, T = transition metal) of the $PrNi_2Al_3$ structure ($4.064/5.293 = 0.768$) and that of the RET_3B_2 compounds of the $CeCo_3B_2$ structure ($3.036/5.057 = 0.600$) [8]. Since the atomic size of Al is almost the same as that of Co, the axial ratio difference is ascribable to the difference between the atomic sizes of Ni and B. In Fig. 1, the structure of the $CePd_2Al_3$ crystal ($c/a = 4.2187/5.4764 = 0.770$) is presented. Although the a axis length of the present crystal is almost the same as that of $CeRh_3B_2$ ($c/a = 3.087/5.484 = 0.563$) [10], there is a great difference between the c axes of the two crystals. Both the Pd atom in $CePd_2Al_3$ and the B atom in $CeRh_3B_2$ are located at the center of the Al_6 and the Rh_6 trigonal prisms respectively, and the basal plane of one prism has almost the same size as the other, owing to the similar atomic size of Al and Rh ($r(\text{Al}) = 1.39$ Å; $r(\text{Rh}) = 1.31$ Å) [11]. Therefore, the Al_6 prism in $CePd_2Al_3$ necessarily elongates in the c axis direction in comparison with the Rh_6 prism as a result of the larger size of the Pd atom ($r(\text{Pd}) = 1.34$ Å; $r(\text{B}) = 0.68$–0.88 Å) [11].

In the $CeRh_3B_2$ crystal, the thermal vibration of the Ce atom in the c axis direction was less prominent than in the plane perpendicular to the c axis ($U_{11} = 103(4) \times 10^{-4}$, $U_{22} = U_{11}$, $U_{33} = 51(3) \times 10^{-4}$) [10], reflecting the unusually short Ce–Ce bond length along

TABLE 1. Structure data for $CePd_2Al_3$

	Ce	Pd	Al
Position	1(a)	2(c)	3(g)
x	0	1/3	1/2
y	0	2/3	0
z	0	0	1/2
B_{eq} (Å^2)	0.55(1)	0.72(1)	0.70(4)
Occupancy (%)	100	95.7(4)	98(1)
	(99)[a]	(95)[a]	(100)[a]
Anisotropic temperature factors[b]			
U_{11}	64(1)	99(1)	98(6)
U_{22}	U_{11}	U_{11}	63(7)
U_{33}	81(2)	75(2)	92(6)
U_{12}	$1/2 \cdot U_{11}$	$1/2 \cdot U_{11}$	$1/2 \cdot U_{22}$
U_{13}	0	0	0
U_{23}	0	0	0

[a] The occupancy estimated from the result of chemical analysis.

[b] The expression is $\exp\{-10^{-4} \times 2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$.

TABLE 2. Interatomic distances (Å) in $CePd_2Al_3$ single-crystal and polycrystalline samples (<3.5 Å)

Ce–Al_{12}[a]	3.4565(1)	Pd–Ce_3[a]	3.1618(1)	Al–Ce_4[a]	3.4565(1)
Ce–Al_{12}[b]	3.45354(2)	Pd–Ce_3[b]	3.15878(2)	Al–Ce_4[b]	3.45354(2)
Ce–Pd_6[a]	3.1618(1)	Pd–Al_6[a]	2.63603(9)	Al–Pd_4[a]	2.63603(9)
Ce–Pd_6[b]	3.15878(2)	Pd–Al_6[b]	2.63402(2)	Al–Pd_4[b]	2.63402(2)
		Pd–Pd_3[a]	3.1618(1)	Al–Al_4[a]	2.7382(1)
		Pd–Pd_3[b]	3.15878(2)	Al–Al_4[b]	2.73558(1)

[a]Single-crystal sample.
[b]Polycrystalline sample.

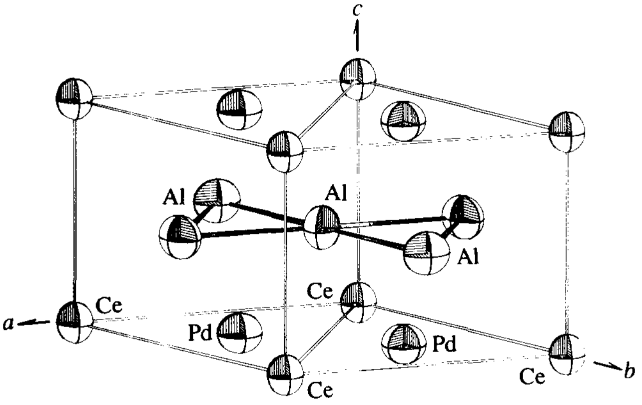

Fig. 1. Perspective view of the structure of $CePd_2Al_3$. Thermal ellipsoids are drawn at the 99.95% probability level.

this direction which corresponds to the *c* axis length. In the present crystal, in contrast, none of the atoms, including Ce, show any significant anisotropy in thermal vibrations (Table 1 and Fig. 1).

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