

## The Crystal Structure of $\text{Pu}_3\text{Pd}_4^*$

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(Received 18 September 1972; accepted 7 November 1972)

Crystals of the intermetallic compound  $\text{Pu}_3\text{Pd}_4$  are rhombohedral, space group  $R\bar{3}$ , with 2 formula units per cell. The unit-cell dimensions for the hexagonal representation are  $a=13.344 \pm 2$ ,  $c=5.744 \pm 2$ . Three-dimensional intensity measurements were made with graphite monochromated  $\text{Mo K}\alpha$  radiation utilizing the  $\theta-2\theta$  scan mode of a Picker four-circle goniometer interfaced with a PDP-8 computer. The structure was solved by the symbolic addition method followed by a full-matrix least-squares refinement. The conventional  $R$  index with anisotropic thermal parameters is 0.045 for 1092 observed reflections. Interatomic distances for Pu-Pu ranged from 3.44 to 3.97 Å, for Pu-Pd from 2.89 to 3.30 Å, and for Pd-Pd from 2.87 to 3.69 Å.

### Introduction

The phase diagram for the plutonium-palladium system has been published by Kutaitsev, Chebotarev, Lebedev, Andrianov, Konev & Menshikova (1967). Four compounds were reported:  $\text{Pu}_5\text{Pd}_4$  and  $\text{PuPd}$ , whose structures are unknown;  $\text{PuPd}_3$  having the cubic  $\text{AuCu}_3$  structure; and  $\text{Pu}_3\text{Pd}_4$  having rhombohedral symmetry, hexagonal lattice constants of  $a=13.304$  and  $c=5.783$  Å, and containing 6 formula units per hexagonal cell. No structure was given for  $\text{Pu}_3\text{Pd}_4$ ; the purpose of this paper is to present the results of our structure determination for this compound.

### Experimental

A 5 g alloy button of composition 41 at. % Pu and 59 at. % Pd was prepared by melting the components seven times in an arc furnace to ensure a homogeneous composition. The button was then heat treated for 10 days at 800°C and rapidly cooled. Preliminary precession photographs showed the crystals to be rhombohedral in space group  $R\bar{3}$ , if centric.

Lattice constants and intensities were measured using graphite monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda=0.70926$  Å) and a Picker four-circle goniometer interfaced with a PDP-8 computer. The orientation, least-squares, and data collection programs were obtained from Busing, Ellinson, Levy, King & Roseberry (1968). The crystallographic data are given in Table 1 and are in reasonable agreement with those reported by Kutaitsev *et al.* (1967). The  $\theta-2\theta$  scan mode was used for making intensity measurements in steps of  $0.05^\circ 2\theta$  over a scan range of  $2.5^\circ$  plus the  $\alpha_1-\alpha_2$  dispersion. Two-sec counts were taken at each step. The background was counted for 20 sec at each extreme and was assumed to vary linearly over the scan range. A total of 3796 reflections with  $2\theta \leq 80^\circ$  were measured

in a hemisphere of reciprocal space. Thus, in general, equivalent reflections were measured in three different orientations. The shape of the crystal fragment was approximated by 13 bounding planes, and absorption corrections were applied with a linear absorption coefficient of  $\mu=546 \text{ cm}^{-1}$ .

Table 1. Crystallographic data for  $\text{Pu}_3\text{Pd}_4$

Space group	$R\bar{3}$
$a$	13.344 (2) Å
$c$	5.744 (2)
$c/a$	0.430 (1)
$Z$	6
$d_{\text{calc}}$	12.85 g cm <sup>-3</sup>
$d_{\text{obs}}$	13.07
$\mu$	546 cm <sup>-1</sup>
$R_F$	0.086
Transmission factor range 0.121 to 0.010	
$\langle E \rangle$	0.82
$\langle E^2 - 1 \rangle$	0.93

The absorption corrections were applied by the Busing & Levy (1957) method using Burnham's (1962) program modified for the present geometry. Equivalent reflections were averaged to give the final unique data set. A disagreement index defined as  $R_F = \sum_n \sum_i |\bar{F}_n - F_{i,n}| / \sum_n \bar{F}_n$  was 0.086, where  $\bar{F}_n = \sum_i w_i F_i / \sum w_i$ , and the summation is over each of the  $i$  measurements of the unique reflection  $F_n$ , provided  $F_i$  is observed according to the criterion

$$(I - B) \geq 3\sigma(I) = 3[I + B + (kI)^2]^{1/2},$$

where  $k=0.015$  and represents the variation of a periodically measured standard reflection. Of the 1233 non-redundant reflections in the sphere of measurement, 1092 were observed.

### Solution and refinement of the structure

The structure was solved by application of the symbolic addition method. After an origin choice was made, a

\* Work performed under the auspices of the U.S. Atomic Energy Commission.

unique solution with 406 signs was reached. An *E* map gave prominent peaks corresponding to 18 Pu and 24 Pd atoms in the unit cell, the number expected for the structure.

The  $\text{Pu}_3\text{Pd}_4$  structure determined from the *E* map was refined by least-squares methods. The minimized function was

$$\sum w(F_o - kF_c)^2,$$

in which  $k$  = a scale factor, and  $F_c$  is the structure factor calculated in the usual way. Relativistic Hartree-Fock scattering factors were used for Pu and Pd (Cromer & Waber, 1968). Anomalous dispersion corrections  $\Delta f'$  and  $\Delta f''$  were applied (Cromer & Liberman, 1970). The weights,  $w$ , were derived from  $\sigma(I)$ , [equation (H. 13), Stout & Jensen, 1968]. The *R* indices quoted are  $R = \sum |\Delta F| / \sum |F_o|$  and  $R_w = [\sum w(\Delta F)^2 / \sum wF_o^2]^{1/2}$

(Hamilton, 1964), with unobserved reflections excluded. Refinement with anisotropic thermal parameters led to  $R = 0.0451$  and  $R_w = 0.0605$ .

A difference Fourier map computed at this time was quite featureless and showed no significant electron density representing missing atoms in the structure. The final parameters are given in Table 2, and the observed and calculated structure factors are shown in Table 3.

## Discussion

The structure consists of Pd atoms in special-position sets 3(a) and 3(b); and Pu and Pd atoms in the general-position set 18(f) of space group No. 148,  $R\bar{3}$ . We believe this arrangement to be a new structure type.

Fig. 1 is a stereo drawing showing the coordination about the Pd atom in set 3(b) and the Pu atom in one of

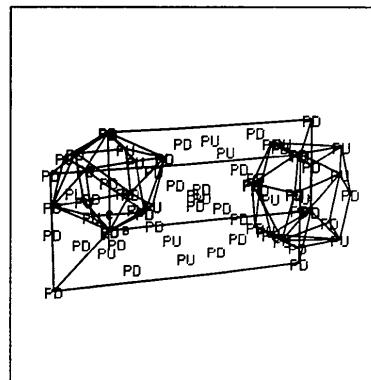
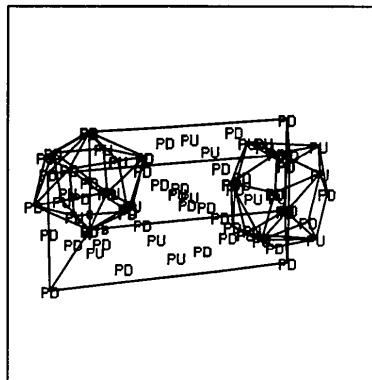


Fig. 1. Stereo drawing of the coordination about a Pu atom in a general position and a Pd atom at  $0,0,\frac{1}{2}$ .

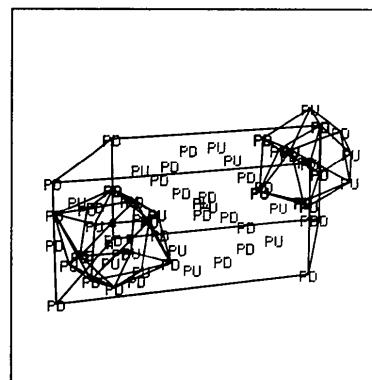
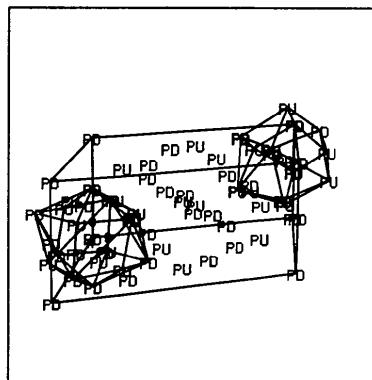


Fig. 2. Stereo drawing of the coordination about a Pd atom in a general position and a Pd atom at  $0,0,0$ .

Table 2. Least-squares parameters for  $\text{Pu}_3\text{Pd}_4$

Position and thermal parameters have been multiplied by  $10^5$ .

The temperature factor is  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$ .

Atom	Set	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Pd(1)	3a	0	0	0	240 (7)	240 (7)	660 (42)	240 (7)	0	0
Pd(2)	3b	0	0	0.5	313 (8)	313 (8)	622 (44)	313 (8)	0	0
Pd(3)	18f	27255 (8)	21762 (8)	27772 (15)	259 (5)	253 (5)	823 (20)	297 (8)	78 (15)	18 (15)
Pu	18f	4448 (3)	21134 (3)	23709 (7)	175 (2)	196 (3)	670 (10)	196 (4)	-33 (6)	-83 (6)

THE CRYSTAL STRUCTURE OF  $\text{Pu}_3\text{Pd}_4$ 

the positions of set 18(f). Fig. 2 is a stereo drawing showing the coordination about the Pd atom in set 3(a) and the Pd atom in one of the positions of set 18(f).

The Pu atom has 16 neighbours consisting of 7 other Pu atoms, 7 Pd atoms in general positions, and one Pd atom in each of the special sets. The Pd atom in a

general position has 12 neighbours consisting of 7 Pu atoms in general positions, 3 Pd atoms in general positions and one Pd in each of the special sets. The Pd atom at  $0,0,\frac{1}{2}$  has 14 neighbours consisting of 6 Pu atoms, 6 Pd atoms, and 2 Pd atoms in set 3(a). The Pd atom at  $0,0,0$  has 14 neighbours consisting of 6 Pu

Table 3. Calculated and observed structure factors for  $\text{Pu}_3\text{Pd}_4$ Column headings are  $I$ ,  $F_o/K$ ,  $F_c$ , and  $10\sigma(F_o/K)$ .

PAGE 1				PAGE 2			
PU-3 PD-4				PU-3 PD-4			
H 6 X 17				H 7 X 10			
1 42 33 29				2 101 95 17			
H 7 195 201				3 101 95 17			
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atoms, 6 Pd atoms and 2 Pd atoms in the set 3(b). Interatomic distances in  $\text{Pu}_3\text{Pd}_4$  are given in Table 4.

Table 4. Interatomic distances in  $\text{Pu}_3\text{Pd}_4$

Standard deviations are all approximately 0.001 Å.			
Pu—Pd(1)	2.913 Å	$2[\text{Pd}(2)-\text{Pd}(1)]$	2.872 Å
Pu—Pd(2)	2.986	$6[\text{Pd}(2)-\text{Pu}]$	2.986
Pu—Pd(3)	2.888	$6[\text{Pd}(3)-\text{Pd}(3)]$	3.568
Pu—Pd(3)	2.893		
Pu—Pd(3)	3.011	Pd(3)—Pd(1)	3.693
Pu—Pd(3)	3.052	Pd(3)—Pd(2)	3.568
Pu—Pd(3)	3.190	Pd(3)—Pd(3)	2.883
Pu—Pd(3)	3.302	$2[\text{Pd}(3)-\text{Pd}(3)]$	3.006
Pu—Pu	3.441	Pd(3)—Pu	2.888
2(Pu—Pu)	3.748	Pd(3)—Pu	2.893
2(Pu—Pu)	3.946	Pd(3)—Pu	3.011
2(Pu—Pu)	3.970	Pd(3)—Pu	3.052
Pd(1)—2Pd(2)	2.872	Pd(3)—Pu	3.056
6[Pd(1)—Pu]	2.913	Pd(3)—Pu	3.190
6[Pd(1)—Pd(3)]	3.693	Pd(3)—Pu	3.302

We are indebted to V. O. Struebing for the preparation of the alloy specimens.

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*Acta Cryst.* (1973). **B29**, 567

## Structure Cristalline de $\alpha$ - $\text{Hg}_2\text{V}_2\text{O}_7$

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(Reçu le 19 juillet 1972, accepté le 10 novembre 1972)

The lattice parameters of the low-temperature phase  $\alpha$ - $\text{Hg}_2\text{V}_2\text{O}_7$  are  $a=7.16_5$ ,  $b=3.63_8$ ,  $c=21.5_2$  Å;  $Z=4$  and the space group is *Pnma*. The structure contains  $[\text{VO}_3]_\infty$  chains parallel to **b**. The mercury atoms link two such chains by essentially ionic bonds, forming  $[\text{Hg}(\text{VO}_3)_2]_\infty$  units between which neutral  $[\text{HgO}]_\infty$  chains are inserted.

### Préparation-description

Par réaction dans l'état solide entre les oxydes  $\text{V}_2\text{O}_5$  et  $\text{HgO}$  quatre phases ont été mises en évidence (Angenault, 1969). Il s'agit des composés  $\text{HgV}_2\text{O}_6$ ,  $\text{Hg}_2\text{V}_2\text{O}_7$ ,  $\text{Hg}_4\text{V}_2\text{O}_9$  et  $\text{Hg}_6\text{V}_2\text{O}_{11}$ , tous dimorphes. La structure de  $\text{HgV}_2\text{O}_6\beta$  a été déterminée précédemment (Angenault & Rimsky, 1968 *a, b*). Le présent travail concerne l'étude structurale de  $\text{Hg}_2\text{V}_2\text{O}_7$ .

Des monocristaux ont pu être obtenus à partir d'un mélange 2  $\text{HgO}/\text{V}_2\text{O}_5$  dans les conditions suivantes:

le mélange est porté à 450°C, 12 h, puis amené à fusion vers 520°C. On refroidit à raison de 1°C h<sup>-1</sup> jusqu'à 380°C. Le produit est maintenu 15 jours à cette température.

Les monocristaux se présentent sous la forme d'ai-

guilles très fines, allongées suivant l'axe **b**, de couleur jaune-citron. Leur longueur peut atteindre 80μ.

Une étude du faciès, effectuée au microscope et au goniomètre 'NEDINSKO' ne permet pas de préciser le système cristallin. En effet, les cristaux obtenus, toujours très petits, ont des faces mal formées, de forme arrondie.

### Etude expérimentale

#### 1. Paramètres de la maille

La radiation  $K\alpha$  du cuivre est utilisée pour l'obtention des clichés de cristal oscillant, de Weissenberg et de précession; ces derniers permettent de déterminer le système cristallin, orthorhombique. Les valeurs des paramètres de la maille élémentaire sont précisées grâce à un diagramme de poudre effectué sur un dif-