Acta Cryst. (1973). B29, 564

The Crystal Structure of Pu_3Pd_4*

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(*Received* 18 *September* 1972; *accepted* 7 *November* 1972)

Crystals of the intermetallic compound Pu_3Pd_4 are rhombohedral, space group $R\bar{3}$, with 2 formula units per cell. The unit-cell dimensions for the hexagonal representation are $a=13{\cdot}344\pm2$, $c=5{\cdot}744\pm2$. Three-dimensional intensity measurements were made with graphite monochromated Mo $K\alpha$ radiation utilizing the θ–2θ 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: Pu_5Pd_4 and PuPd, whose structures are unknown; $PuPd_3$ having the cubic $AuCu_3$ structure; and Pu_3Pd_4 having rhombohedral symmetry, hexagonal lattice constants of $a=13{\cdot}304$ and $c=5{\cdot}783$ Å, and containing 6 formula units per hexagonal cell. No structure was given for Pu_3Pd_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 Mo $K\alpha$ radiation ($\lambda=0{\cdot}70926$ 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 θ–2θ scan mode was used for making intensity measurements in steps of $0{\cdot}05°$ 2θ over a scan range of 2·5° plus the α_1–α_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 $2\theta\leq80°$ 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 $\mu=546$ cm^{-1}.

Table 1. *Crystallographic data for* Pu_3Pd_4

Space group	$R\bar{3}$
a	13·344 (2) Å
c	5·744 (2)
c/a	0·430 (1)
Z	6
d_{calc}	12·85 g cm^{-3}
d_{obs}	13·07
μ	546 cm^{-1}
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 $\bar{F}_n=\sum w_iF_i/\sum w_i$, and the sumation is over each of the i measurements of the unique reflection F_n, provided F_i is observed according to the criterion

$$(I-B)\geq3\sigma(I)=3[I+B+(kI)^2]^{1/2},$$

where $k=0{\cdot}015$ 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 Pu_3Pd_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 $R_w = [\sum w(\Delta F)^2/\sum wF_0^2]^{1/2}$ (Hamilton, 1964), with unobserved reflections excluded. Refinement with anisotropic thermal parameters led to $R = 0{\cdot}0451$ and $R_w = 0{\cdot}0605$.

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

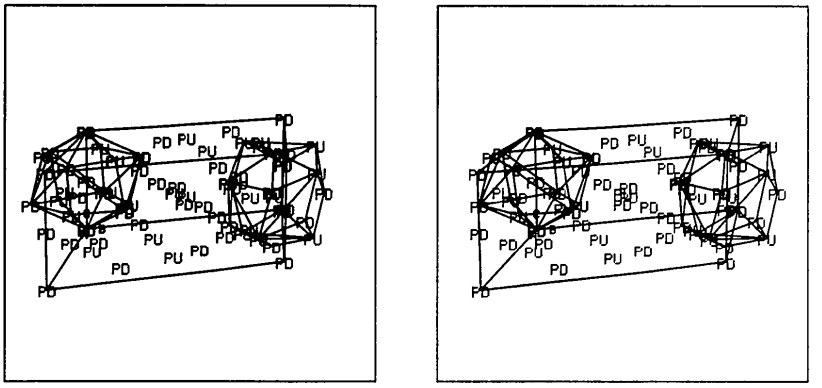


Fig. 1. Stereo drawing of the coordination about a Pu atom in a general position and a Pd atom at $0,0,\frac{1}{2}$.

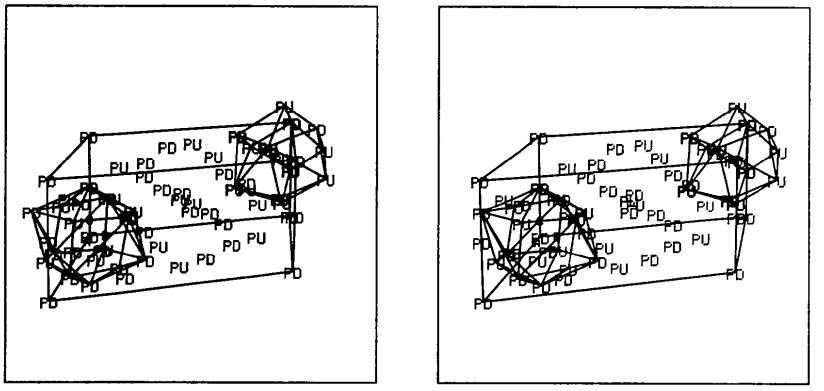


Fig. 2. Stereo drawing of the coordination about a Pd atom in a general position and a Pd atom at 0,0,0.

Table 2. *Least-squares parameters for* Pu_3Pd_4

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

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

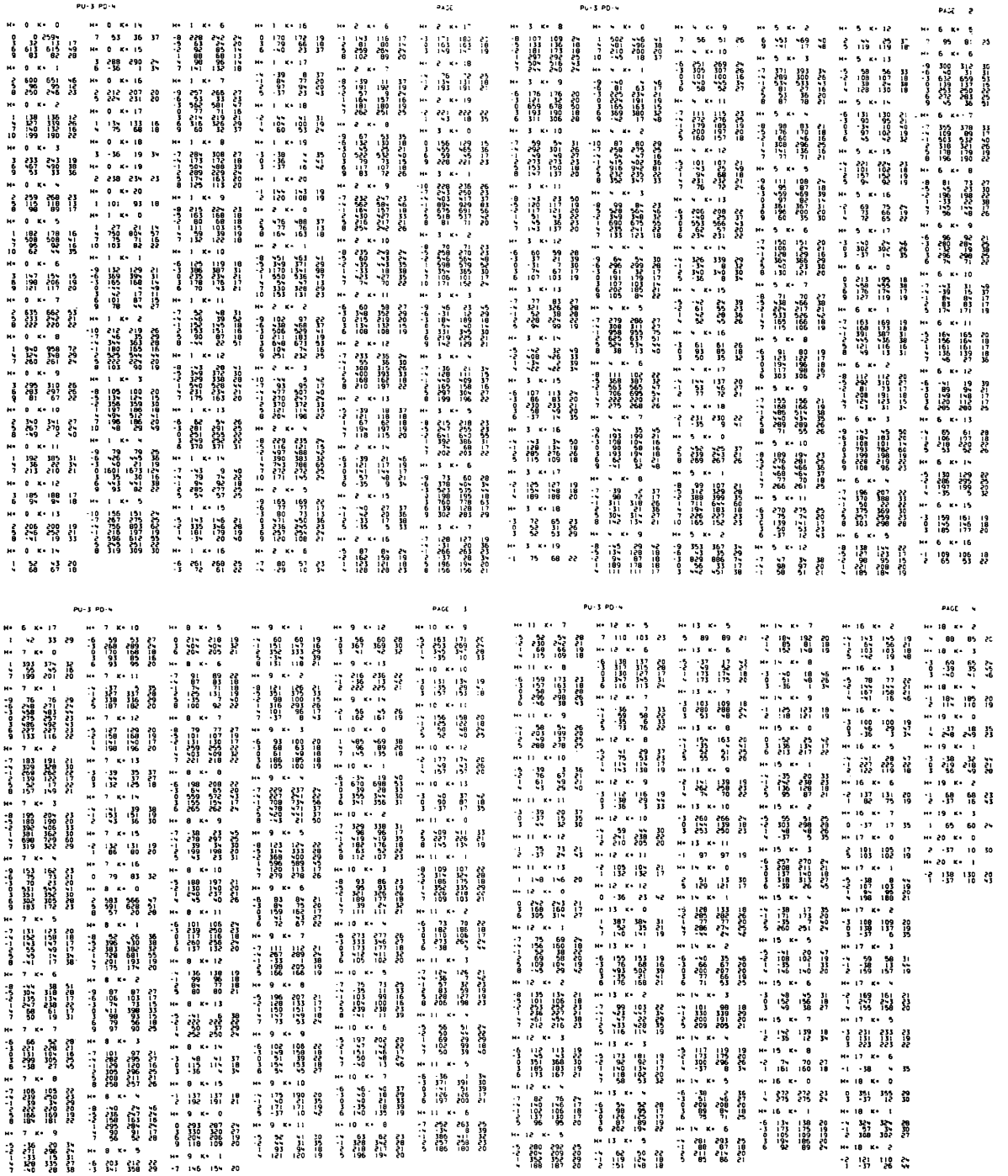
Atom	Set	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd(1)	3*a*	0	0	0	240 (7)	240 (7)	660 (42)	240 (7)	0	0
Pd(2)	3*b*	0	0	0·5	313 (8)	313 (8)	622 (44)	313 (8)	0	0
Pd(3)	18*f*	27255 (8)	21762 (8)	27772 (15)	259 (5)	253 (5)	823 (20)	297 (8)	78 (15)	18 (15)
Pu	18*f*	4448 (3)	21134 (3)	23709 (7)	175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

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 in each of the special sets. The Pd atom in a general position has 12 neighbors 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 neighbors 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 neighbors consisting of 6 Pu

Table 3. *Calculated and observed structure factors for* Pu_3Pd_4

Column headings are *l*, F_o/K, F_c, and $10\sigma(F_o/K)$.



atoms, 6 Pd atoms and 2 Pd atoms in the set 3(*b*). Interatomic distances in Pu_3Pd_4 are given in Table 4.

Table 4. *Interatomic distances in* Pu_3Pd_4

Standard deviations are all approximately 0·001 Å.

Pu——Pd(1)	2·913 Å	2[Pd(2)–Pd(1)]	2·872 Å
Pu——Pd(2)	2·986	6[Pd(2)–Pu]	2·986
Pu——Pd(3)	2·888	6[Pd(3)–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[Pd(3)–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). B**29**, 567

Structure Cristalline de α-$Hg_2V_2O_7$

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

The lattice parameters of the low-temperature phase α-$Hg_2V_2O_7$ are $a=7{\cdot}16_5$, $b=3{\cdot}63_8$, $c=21{\cdot}5_2$ Å; $Z=4$ and the space group is *Pnma*. The structure contains $[VO_3]_\infty$ chains parallel to **b**. The mercury atoms link two such chains by essentially ionic bonds, forming $[Hg(VO_3)_2]_\infty$ units between which neutral $[HgO]_\infty$ chains are inserted.

Préparation-description

Par réaction dans l'état solide entre les oxydes V_2O_5 et HgO quatre phases ont été mises en évidence (Angenault, 1969). Il s'agit des composés HgV_2O_6, $Hg_2V_2O_7$, $Hg_4V_2O_9$ et $Hg_6V_2O_{11}$, tous dimorphes. La structure de $HgV_2O_6\beta$ a été déterminée précédemment (Angenault & Rimsky, 1968 *a*, *b*). Le présent travail concerne l'étude structurale de $Hg_2V_2O_7$.

Des monocristaux ont pu être obtenus à partir d'un mélange 2 HgO/V_2O_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^{-1} jusqu'à 380 °C. Le produit est maintenu 15 jours à cette température.

Les monocristaux se présentent sous la forme d'aiguilles 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 'NEDINSCO' 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-