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Plutonium – Palladium Pu_3Pd_5*

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Abstract. Pu_3Pd_5, *Cmcm*, $Z=4$, $a=9{\cdot}201$ (5), $b=7{\cdot}159$ (5), $c=9{\cdot}771$ (7) Å, $\varrho_c=12{\cdot}89$ g cm^{-3}. This is a previously unreported phase and is a new structure type, possibly isostructural with Ga_5Zr_3.

Introduction. The Pu–Pd phase diagram given by Kutaitsev, Chebotarev, Lebedev, Andrianov, Konev & Menshikova (1965) shows four compounds: Pu_5Pd_4, PuPd, Pu_3Pd_4 and $PuPd_3$. The structure of Pu_3Pd_4 has been determined by Cromer, Larson & Roof (1973) and of PuPd by Cromer (1975). $PuPd_3$ has the $AuCu_3$ structure (Kutaitsev *et al.*, 1965). We have so far been unable to prepare Pu_5Pd_4 although we have prepared the possibly isostructural compound Pu_5Rh_4 and will report its structure later.

In a study of an alloy containing 67 at. % Pd which had been arc melted and heat treated at 950°C for 7 days, a crystal fragment was found which gave an X-ray pattern different from any known phase. This crystal was found to be Pu_3Pd_5, a compound not previously found in this system. This phase was also found in a 65 at. % Pd alloy similarly prepared.

Precession photographs showed that the crystal belonged to space group *Cmcm*, if centrosymmetric. Reflections $h0l$ were present only if $l=2n$ and reflections hkl were present only if $h+k=2n$. Lattice constants [Mo $K\alpha_1=0{\cdot}70930$ Å] and intensities were measured with graphite-monochromated Mo $K\alpha_1$ radiation on a Picker automatic diffractometer. The details of data collection were as described by Cromer & Larson (1972). A complete sphere of intensities was measured for $2\theta\le 50°$. Empirical absorption corrections were applied (Furnas, 1957) as well as a spherical correction using a mean value of $\mu r=1{\cdot}32$ ($\mu=441$ cm^{-1}) for the irregularly shaped crystal fragment.

The agreement between equivalent reflections was assessed by the index R_F defined as:

$$R_F=\sum_n \sum_{i=1}^{j_n} |\bar{F}_n-F_{i,n}|/\sum_n j_n\bar{F}_n=0{\cdot}098\ ,$$

where the summations are over the n unique reflections each having been observed j_n times ($j_n>1$) and

$$\bar{F}_n=\sum_{i=1}^{j_n} w_{i,n}F_{i,n}/\sum_{i=1}^{j_n} w_{i,n}.$$

* Work performed under the auspices of the U. S. ERDA.

The w_i's of the individual reflections were calculated from $\sigma(I)$ according to the expressions given by Stout & Jensen (1968). A reflection was considered observed if $I\ge 2\sigma(I)=2[I+B+(0{\cdot}02I)^2]^{1/2}$, where I is the net count and B is the background. The agreement between equivalent reflections, for some unknown reason, is larger than we usually achieve by the empirical method of absorption correction. Possibly the shape was too irregular for any absorption correction method to be very useful. Of the 323 unique reflections measured, 230 were observed.

Consideration of atomic volumes, deduced from structures of known Pu–Pd compounds, suggested that

Table 1. *Parameters from least-squares refinement of* Pu_3Pd_5

	x	y	z	B
Pu(1)	0	0·6251 (5)	$\frac{1}{4}$	0·75 (8) Å²
Pu(2)	0·2018 (3)	0	0	0·62 (6)
Pd(1)	0	0·0254 (11)	$\frac{1}{4}$	0·89 (15)
Pd(2)	0	0·3147 (8)	0·4510 (7)	0·89 (11)
Pd(3)	0·2219 (7)	0·2863 (7)	0	1·01 (12)

Table 2. *Interatomic distances in* Pu_3Pd_5

Pu(1)– Pd(1)	2·866 (9) Å	Pd(1)–2Pd(2)	2·854 (9) Å
–2Pd(2)	2·954 (7)	–2Pd(2)	3·803 (8)
–2Pd(2)	2·965 (7)	–2Pd(3)	2·767 (8)
–2Pd(3)	2·807 (6)	–2Pd(3)	3·078 (8)
–2Pd(3)	3·171 (6)	– Pu(1)	2·866 (9)
–4Pd(2)	3·781 (2)	–4Pu(2)	3·074 (2)
–4Pu(2)	4·077 (3)		
		Pd(2)– Pd(1)	2·854 (8)
Pu(2)–2Pd(1)	3·074 (2)	– Pd(1)	3·803 (8)
–2Pd(2)	2·959 (5)	– Pd(2)	2·821 (11)
–2Pd(2)	3·085 (4)	– Pd(2)	3·927 (14)
–2Pd(3)	2·966 (3)	–2Pd(3)	2·840 (7)
–2Pd(3)	3·194 (3)	–2Pd(3)	3·950 (7)
–2Pu(1)	3·781 (2)	– Pu(1)	2·954 (7)
–2Pu(1)	4·077 (3)	– Pu(1)	2·965 (7)
–2Pu(2)	3·688 (1)	–2Pu(2)	2·959 (5)
– Pu(2)	3·714 (6)	–2Pu(2)	3·085 (4)
		Pd(3)– Pd(1)	2·767 (8)
		– Pd(1)	3·078 (8)
		–2Pd(2)	2·840 (7)
		–2Pd(2)	3·951 (7)
		–2Pd(3)	3·617 (2)
		– Pu(1)	2·807 (6)
		– Pu(1)	3·171 (6)
		–2Pu(2)	2·966 (3)
		–2Pu(2)	3·194 (3)

the cell contained $4Pu_3Pd_5$. With this stoichiometry assumed, application of direct methods easily led to the solution of the structure. The position sets used in *Cmcm* are

Pu(1)	4(*c*)	$0y\frac{1}{4}$	$y\simeq\frac{5}{8}$
Pu(2)	8(*e*)	$x00$	$x\simeq 0{\cdot}2$
Pd(1)	4(*c*)	$0y\frac{1}{4}$	$y\simeq 0$
Pd(2)	8(*f*)	$0yz$	$y\simeq 0{\cdot}31,\ z\simeq 0{\cdot}45$
Pd(3)	8(*g*)	$xy\frac{1}{4}$	$x\simeq 0{\cdot}22,\ y\simeq 0{\cdot}28.$

Full-matrix least-squares refinement with isotropic thermal parameters led to the parameters given in Table 1. For these parameters, $R=\sum|\Delta F|/\sum F_o=0{\cdot}0622$ and $R_w=[\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}=0{\cdot}0656$ with unobserved values omitted.* Relativistic Hartree–Fock scattering factors (Cromer & Waber, 1974) were used along with anomalous dispersion values of Cromer & Liberman (1970). Subsequent refinement with anisotropic thermal parameters led to $R_w=0{\cdot}0645$. Hamilton's (1965) test rejects the hypothesis that the atoms vibrate anisotropically. The thermal parameters give no suggestion of disorder in this structure.

* A listing of the final least-squares cycle, including observed and calculated structure factors, followed by the interatomic distance calculations, has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31700 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. This is a new structure type but may have the same structure as Ga_5Zr_3, a phase reported by Potzschke & Schubert (1962). They, however, did not attempt to solve the structure. In their text they give the unit cell in the orientation which makes the space group *Cmcm* and the axial ratios are similar to those of Pu_3Pd_5. In their Table 4, *a* and *b* are interchanged and this incorrect orientation for *Cmcm* has been quoted by Pearson (1967).

Interatomic distances are given in Table 2. The unit-cell contents and coordination polyhedra are shown in Figs. 1 and 2. Pu(1) and Pu(2) each have 17 neighbors, nine of which are Pd for Pu(1) and 10 of which are Pd for Pu(2). Pd(1) has 13 neighbors, eight Pd and five Pu. Pd(2) and Pd(3) each have eight Pd and

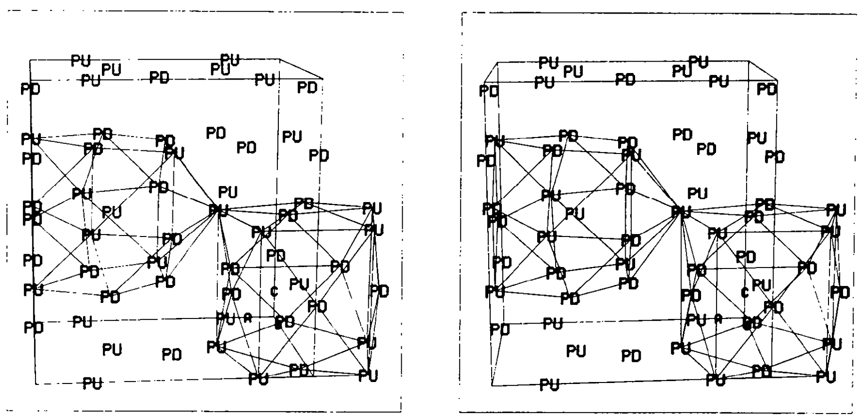

Fig. 1. Stereo view of the unit cell of Pu_3Pd_5 showing the Pu polyhedra. The view is approximately along **b**. The origin is at the lower, right rear. Pu(1) is on the right at $0,0{\cdot}625,\frac{1}{4}$. Pu(2) is on the left at $0{\cdot}702,\frac{1}{2},\frac{1}{2}$.

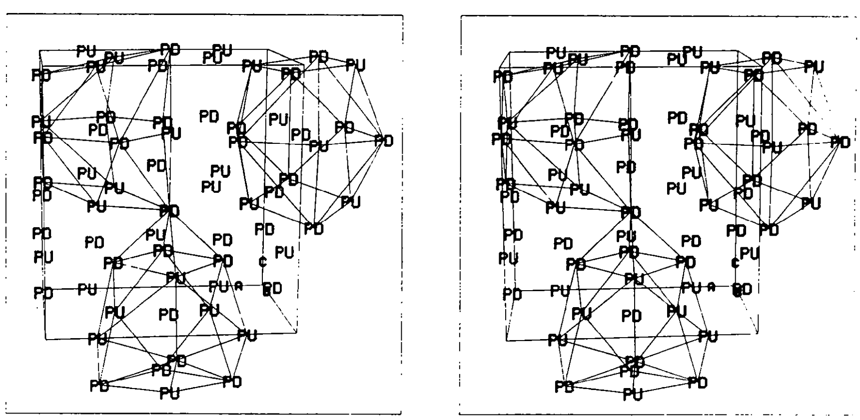

Fig. 2. Stereo view of the unit cell of Pu_3Pd_5 showing the Pd polyhedra. View direction and origin as in Fig. 1. The Pd(1) polyhedron is on the right at $0,0{\cdot}975,\frac{3}{4}$. The Pd(2) polyhedron is in the middle at $\frac{1}{2},0{\cdot}815,0{\cdot}049$. Pd(3) is on the left at $0{\cdot}778,0{\cdot}714,\frac{3}{4}$.

six Pu neighbors for a total of 14. No distances are unusually short and all atoms are fairly uniformly surrounded, a structural feature which is reflected in the nearly isotropic thermal motion.

All calculations were performed on a CDC-7600 computer using the LASL crystal structure codes developed by A. C. Larson. Thanks are due to V. O. Struebing for preparation of the alloys.

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p-Nitrophenyl-β-D-xylopyranoside

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Abstract. $C_{11}H_{13}O_7N$, $M=271{\cdot}2$; orthorhombic, $P2_12_12_1$; $a=5{\cdot}502$ (1), $b=9{\cdot}110$ (1), $c=22{\cdot}859$ (5) Å; $Z=4$, $D_m=1{\cdot}568$ (flotation), $D_c=1{\cdot}573$ g cm^{-3}. $R=0{\cdot}042$ for 915 reflexions. The xylopyranoside is in the C_1 chair conformation. The valence angle of the oxygen atom linking with the *p*-nitrophenyl group is 118·5°. The anomeric C–O bond is twisted by 23·6° against the benzene plane.

Introduction. The needle-like crystals were obtained from an ethanol solution. The space group $P2_12_12_1$ was deduced from systematic absences of $h=2n+1$ for $h00$, $k=2n+1$ for $0k0$, and $l=2n+1$ for $00l$. Intensity data were collected on a Rigaku automatic four-circle diffractometer with a specimen $0{\cdot}2\times0{\cdot}2\times0{\cdot}2$ mm, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0{\cdot}70926$ Å) and the 2θ–ω scanning mode.

Table 1. *Final atomic parameters* ($\times 10^4$) *for the non-hydrogen atoms*

The temperature factor expression used is $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$. Values in parentheses are estimated standard deviations.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	5478 (10)	2769 (5)	6602 (2)	238 (19)	47 (5)	11 (1)	−13 (18)	4 (8)	3 (4)
C(2)	7555 (9)	2854 (5)	7037 (2)	157 (17)	56 (5)	12 (1)	−4 (18)	1 (7)	−6 (4)
C(3)	7906 (9)	4440 (5)	7236 (2)	170 (18)	56 (5)	14 (1)	7 (18)	−1 (8)	−1 (4)
C(4)	7958 (9)	5520 (5)	6726 (2)	187 (19)	53 (6)	16 (1)	11 (17)	−17 (8)	−12 (4)
C(5)	5983 (11)	5174 (6)	6276 (2)	292 (24)	74 (7)	16 (1)	−46 (21)	34 (9)	−11 (5)
O(1)	5322 (7)	1306 (3)	6425 (2)	237 (14)	54 (4)	16 (1)	−7 (14)	17 (6)	9 (3)
O(2)	6993 (6)	2014 (4)	7547 (2)	189 (13)	48 (4)	15 (1)	39 (13)	−16 (6)	−8 (3)
O(3)	117 (7)	4563 (4)	7542 (2)	242 (13)	66 (4)	19 (1)	−62 (13)	58 (6)	−21 (3)
O(4)	7665 (7)	6989 (4)	6940 (2)	223 (15)	43 (4)	19 (1)	8 (14)	−2 (7)	0 (3)
O(5)	6062 (7)	3660 (4)	6114 (1)	316 (16)	68 (4)	12 (1)	−39 (14)	3 (6)	3 (3)
C(6)	3290 (9)	861 (5)	6121 (2)	200 (17)	65 (6)	10 (1)	−25 (17)	−3 (8)	6 (4)
C(7)	2843 (10)	−637 (5)	6136 (2)	314 (22)	58 (6)	13 (1)	16 (20)	−8 (9)	1 (4)
C(8)	897 (10)	−1209 (5)	5842 (2)	301 (22)	51 (6)	16 (1)	−33 (19)	6 (9)	−1 (5)
C(9)	−523 (10)	−276 (5)	5516 (2)	256 (19)	77 (7)	12 (1)	−25 (19)	−10 (8)	10 (4)
C(10)	−117 (10)	1223 (5)	5487 (2)	255 (20)	70 (6)	15 (1)	13 (21)	10 (9)	−10 (5)
C(11)	1827 (10)	1789 (5)	5804 (2)	269 (21)	50 (5)	16 (1)	−17 (18)	13 (9)	1 (4)
O(6)	−3271 (7)	−2124 (4)	5320 (2)	335 (16)	80 (4)	20 (1)	−126 (16)	−6 (6)	8 (3)
O(7)	−3494 (8)	−165 (4)	4797 (2)	457 (19)	127 (6)	24 (1)	−143 (20)	101 (8)	−26 (4)
N	−2575 (8)	−893 (4)	5186 (2)	229 (17)	91 (6)	15 (1)	−46 (17)	−6 (7)	14 (4)