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The Structure of PuPd*

BY DON T. CROMER

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544, *U.S.A.*

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Abstract. PuPd, *Pnma*, $Z=4$, $a=7{\cdot}036$ (4), $b=4{\cdot}550$ (2), $c=5{\cdot}663$ (2) Å, $\varrho_c=12{\cdot}65$ g cm^{-3}. This structure is of the *B*27, FeB type.

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 since been determined by Cromer, Larson & Roof (1973). $PuPd_3$ has the cubic $AuCu_3$ structure and the structures of the other two compounds are not known. It is the purpose of this note to report the structure of PuPd.

The Pu–Pd system is much more complex than Kutaitsev *et al.* (1965) have reported. The compound Pu_3Pd_5 has been found (Cromer, 1975), and also a compound near 67 at.% palladium. We have not yet confirmed the existence of Pu_5Pd_4.

An alloy containing 44·44 at.% Pd was prepared by arc melting followed by a heat treatment at 950°C for 7 days. We had hoped to find the compound Pu_5Pd_4 in this specimen but only found crystals of PuPd. Crystals of PuPd from this alloy were used in the present work. An alloy containing 50 at.% Pd was similarly prepared, heat treated at 1050° for 7 days, and then water quenched. Only very poor quality PuPd crystals were found in this specimen and none were used.

Preliminary precession photographs showed PuPd to be orthorhombic, space group *Pnma* and probably of the FeB or *B*27 structure type. All *hkl* reflections were present; 0*kl* reflections were present only for $k+l=2n$ and *hk*0 reflections were present only for $h=2n$.

Lattice constants [$a=7{\cdot}036$ (4), $b=4{\cdot}550$ (2), $c=5{\cdot}663$ (2) Å, Mo $K\alpha_1=0{\cdot}70926$ Å] and intensities were measured with graphite-monochromated Mo $K\alpha$ 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 $2\theta\leq 70°$. Empirical absorption corrections were applied (Furnas, 1957). In addition, a spherical absorption correction was applied using a mean value of $\mu r=1{\cdot}52$ ($\mu=475$ cm^{-1}) for the irregularly shaped crystal fragment. An index, defined as $R_F=\sum_n\sum_i|\bar{F}_n-F_{i,n}|/\sum_n\bar{F}_n$, was 0·0387 where $\bar{F}_n=\sum w_iF_i/\sum w_i$, and the summations are over the i equivalent measurements, with weight w_i of the reflection F_n. F_i was considered observed if $(I-B)\geq 2\sigma(I)=2[I+B+(0{\cdot}02I)^2]^{1/2}$. Of the 446 unique reflections measured, 417 were observed. For uncorrected data, $R_F=0{\cdot}0583$. An attempt was made to measure the crystal and approximate its shape by six non-reentrant planes. Using this shape and the analytic absorption correction method of De Meulenaer & Tompa (1965) gave $R_F=0{\cdot}0781$. The program for this calculation was obtained from Dr L. Templeton. This exact method of making absorption corrections is clearly limited if one cannot adequately define the shape of an irregular crystal fragment.

Full-matrix least-squares refinement was begun immediately using the parameters of FeB as starting values. Relativistic Hartree–Fock scattering factors (Cromer & Waber, 1974) were used along with the anomalous dispersion values of Cromer & Liberman (1970). The assumption of the FeB structure type was proved to be correct. The final positional and thermal parameters are given in Table 1. For these parameters $R=\sum|\Delta F|/\sum F_o=0{\cdot}0495$ and $R_w=[\sum w(\Delta F)^2/\sum wF_0^2]^{1/2}=0{\cdot}0842$, with unobserved reflections omitted.*

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

* A listing of the final least-squares cycle, including observed and calculated structure factors, followed by the interatomic distance and thermal-ellipsoid calculations has been deposited with the British Library Lending division as Supplementary Publication No. SUP 30919 (18 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final least-squares parameters for* PuPd

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

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{13}
Pu	0·1795 (1)	¼	0·1413 (1)	459 (17)	1072 (41)	664 (26)	82 (19)
Pd	0·0447 (3)	¼	0·6510 (3)	835 (34)	949 (70)	863 (49)	−260 (49)

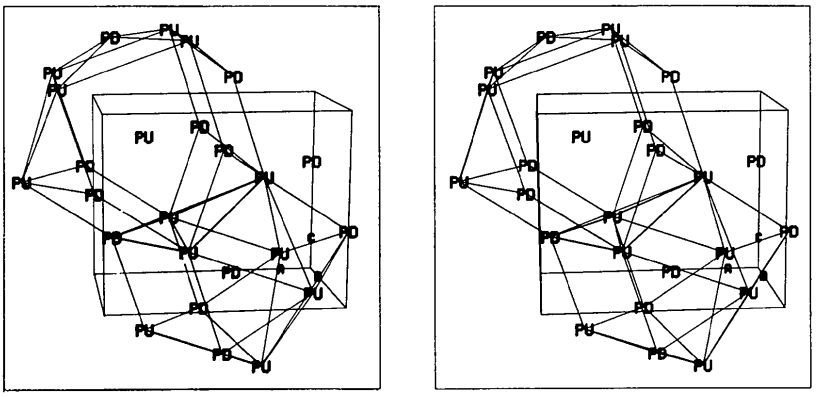

Fig. 1. View of the unit-cell contents of PuPd and the two polyhedra. The origin is at the lower right rear where the positive **a**, **b** and **c** directions are labeled. The Pu polyhedron on the left is centered at 0·8205, ¾, 0·8587. The Pd polyhedron is at 0·4553, ¾, 0·1510.

Discussion. This is a well known structure type which needs little comment. The interatomic distances are listed in Table 2. The Pu atom has 15 neighbors. The unit-cell contents and coordination polyhedra are shown in Fig. 1. The thermal motion of the Pu atom is nearly isotropic. The motion of the Pd atom is somewhat larger in a direction approximately along **a**. The neighbors in this direction are relatively distant as can be seen in Fig. 1.

Table 2. *Interatomic distances in* PuPd (Å)

Pu–Pd	2·934 (2)	Pd–2Pd	2·915 (2)
–2Pd	2·991 (1)	–2Pd	3·692 (1)
–2Pd	3·008 (1)	–Pu	2·934 (2)
–Pd	3·038 (2)	–2Pu	2·991 (1)
–Pd	3·056 (2)	–2Pu	3·008 (1)
–2Pu	3·727 (1)	–Pu	3·038 (2)
–2Pu	3·757 (1)	–Pu	3·056 (2)
–4Pu	3·765 (1)		

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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