Acta Cryst. (1975). B31, 1756

The Structure of Pu_5Ru_3*

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(*Received* 9 *December* 1974; *accepted* 7 *February* 1975)

Abstract. Pu_5Ru_3, $I4/mcm$, $Z=4$, $a=10{\cdot}745$ (3), $c=5{\cdot}719$ (2) Å, $\varrho_c=15{\cdot}07$ g cm^{-3}. This structure is of the $D8_m$, W_5Si_3 type.

Introduction. The Pu–Ru phase diagram given by Ellinger, Land & Gschneidner (1967) shows five intermetallic compounds; $Pu_{19}Ru$, Pu_3Ru, Pu_5Ru_3, PuRu and $PuRu_2$. The structures of the first two compounds are unknown. PuRu has the CsCl structure and $PuRu_2$ the $MgCu_2$ structure. It is the purpose of this note to report the structure of Pu_5Ru_3.

An alloy containing 39 at.% Ru was prepared by arc melting followed by a heat treatment for 10 days at 800°C. The alloy was crushed and many of the fragments were found to be single crystals. Preliminary precession photographs showed the crystals to be tetragonal, space group $I4/mcm$ and probably of the $D8_m$ or W_5Si_3 structure type. Reflections hkl were present only for $h+k+l=2n$ and $0kl$ only for $l=2n$. Lattice constants [$a=10{\cdot}745$ (3), $c=5{\cdot}719$ (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 have been described elsewhere (*e.g.* Cromer & Larson, 1972). Reflections were measured for $h, k>0$, all values of l and for $2\theta\le 60°$. Equivalent general reflections were thus measured eight times. The shape of the irregular crystal fragment was approximated by a six-sided polygon. Absorption corrections ($\mu=500$ cm^{-1}) were applied by the Busing & Levy (1957) method using a modification of Burnham's (1962) program. The crystal volume was $4{\cdot}2\times10^{-4}$ mm^3 and transmission factors varied from 0·039 to 0·183. An index defined as $R_F=\sum_n\sum_i|\bar{F}_n-F_{i,n}|/\sum_n\bar{F}_n$ was 0·087 where $F_n=\sum w_iF_i/\sum w_i$ and the summations are over the i equivalent measurements with weight w_i of the reflection F_n. This rather poor agreement between equivalent reflections is due to the difficulty of defining the shape of a rough, irregular crystal fragment. F_i was considered observed if $(I-B)\ge 2\sigma(I)=2[I+B+(0{\cdot}014I)^2]^{1/2}$. Of the 287 unique reflections measured, 265 were observed.

Because the compound was thought to belong to a known structure type, full-matrix least-squares refinement was begun immediately. Relativistic Hartree–Fock scattering factors computed by Cromer & Waber (1974) were used along with the anomalous dispersion values of Cromer & Liberman (1970). The assumption of the structure type was shown to be correct and the final positional and thermal parameters are given in Table 1. For these parameters, $R=\sum|\Delta F|/\sum F_o=0{\cdot}066$ and $R_w=[\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}=0{\cdot}073$, with unobserved reflections omitted.*

Table 2. *Interatomic distances in* Pu_5Ru_3 (Å)

Pu(1)–2Pu(1)	2·860	Ru(1)–2Ru(1)	2·860
–8Pu(2)	3·453 (1)	–8Pu(2)	2·899 (1)
–4Ru(2)	2·815 (4)		
Pu(2)–2Pu(1)	3·453 (1)	Ru(2)–2Ru(2)	3·966 (7)
–Pu(2)	3·000 (2)	–2Pu(1)	2·815 (4)
–2Pu(2)	3·371 (1)	–2Pu(2)	2·839 (4)
–2Pu(2)	3·532 (2)	–2Pu(2)	2·913 (2)
–2Pu(2)	3·566 (2)	–4Pu(2)	3·247 (1)
–2Ru(1)	2·899 (1)		
–Ru(2)	2·839 (4)		
–Ru(2)	2·913 (2)		
–2Ru(2)	3·247 (1)		

Discussion. The interatomic distances are listed in Table 2 and the unit-cell contents and coordination polyhedra are shown in Fig. 1. If the midpoint between

Table 1. *Final least-squares parameters for* Pu_5Ru_3

The anisotropic temperature factor is $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$. β values are $\times 10^5$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}
Pu(1)	0	$\frac{1}{2}$	$\frac{1}{4}$	255 (16)	β_{11}	3432 (140)	
Pu(2)	0·0831 (1)	0·2195 (1)	0	201 (13)	161 (13)	1189 (44)	12 (15)
Ru(1)	0	0	$\frac{1}{4}$	220 (29)	β_{11}	938 (161)	
Ru(2)	0·1596 (3)	$\frac{1}{2}+x$	0	322 (25)	β_{11}	1902 (144)	82 (58)

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

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* 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 30917 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

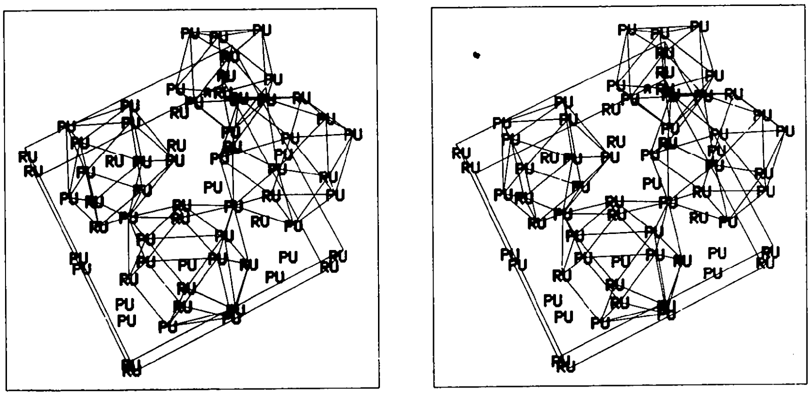

Fig. 1. View of the unit-cell contents of Pu_5Ru_3 and the four polyhedra. The origin is at the upper rear corner where the positive **a**, **b**, and **c** directions are labeled. The upper polyhedron is that of Ru(1). The left polyhedron is Ru(2) at $0{\cdot}6596,0{\cdot}1596,\frac{1}{2}$; the right polyhedron is Pu(1) at $0,\frac{1}{2},\frac{3}{4}$ and the lower polyhedron is Pu(2) at $0{\cdot}5831,0{\cdot}7195,\frac{1}{2}$.

two atoms is closer to these atoms than to any other atoms these atoms are defined as neighbors. The polyhedra shown in Fig. 1 are the convex polyhedra formed by the neighbors of the central atom.

Other Pu intermetallic compounds known to have this structure type are Pu_5Si_3 (Cromer, Larson & Roof, 1964) and the ternary phase $(Pu,Ce)_5Co_3$ (Larson, Roof & Cromer, 1964). This latter compound has an *a* axis of 10·730 Å, virtually the same as that of the present compound, but a rather shorter *c* axis of 5·383 Å. This short *c* axis crowds the large cerium atoms in the $0,\frac{1}{2},\frac{1}{4}$ position and produces some disorder and vacancies. This disorder was manifested by an anomalously high apparent thermal motion along the *c* axis.

Table 3. *Thermal ellipsoids in* Pu_5Ru_3

	B_i	Angles (°) relative to direct cell axes		
		α	β	γ
Pu(1)	1·1 (1) Å^2	0	90	90
	1·1 (1)	90	0	90
	4·9 (2)	90	90	0
Pu(2)	0·9 (1)	6·5	83·5	90
	0·7 (1)	96·5	6·5	90
	1·6 (1)	90	90	0
Ru(1)	1·1 (1)	0	90	90
	1·1 (1)	90	0	90
	1·2 (2)	90	90	0
Ru(2)	1·7 (2)	45	45	90
	1·3 (2)	135	45	90
	2·5 (2)	90	90	0

The major axes of the thermal ellipsoids of Pu_5Ru_3 and their orientations are given in Table 3. For Pu(2) and Ru(2), B_3 is the largest axis. These atoms have no neighbors directly above and below in the **c** direction, but Pu(2) has five neighbors and Ru(2) has four neighbors in the plane normal to **c**. The motion parallel to **c** is therefore less restricted. The motion of Ru(1) is virtually isotropic for its ten neighbors are nearly equidistant. Pu(1) has two close Pu(1) neighbors at 2·859 Å directly above and below along the *c* axis. In spite of this proximity, B_3, parallel to **c**, is much larger than the other axes, and a disorder similar to that found in $(Pu,Ce)_5Co_3$ was suspected.

A further refinement with an occupancy parameter added for Pu(1) suggested that its site was only 92% occupied. R was reduced to 0·0633 and R_w to 0·0679. This result should be accepted with caution and perhaps represents an 'over refinement', because the agreement index is substantially smaller than the index obtained from comparison of equivalent reflections.

All calculations were made with a CDC 7600 computer using the LASL system of crystallographic programs. We are indebted to V. O. Struebing for preparation of the alloy.

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