

Plutonium–Rhodium Pu₅Rh₄*

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Abstract. Pu₅Rh₄, *Pnma*, *Z* = 4, *a* = 7.276 (2), *b* = 14.332 (4), *c* = 7.419 (2) Å, $\rho_c = 13.79 \text{ g cm}^{-3}$. Data were collected on an automatic diffractometer. The structure was solved by direct methods and refined by full-matrix least squares. $R_w = 0.0417$ for 1063 observed reflections. Pu–Pu distances range from 3.316 to 3.945 Å, Pu–Rh distances from 2.714 to 3.214 Å and Rh–Rh distances from 2.749 to 3.826 Å. The structure is similar to those of Sm₅Ge₄ and Gd₅Si₄.

Introduction. The Pu–Rh phase diagram has been given by Kutaitsev, Chebotarev, Lebedev, Andrianov, Konev & Menshikova (1965) who report the binary compounds Pu₂Rh, Pu₃Rh₃, Pu₅Rh₄, PuRh, Pu₃Rh₄, PuRh₂ and PuRh₃. The above authors found that PuRh₂ has the Cu₂Mg structure and that PuRh₃ has the AuCu₃ structure. Beznosikova, Chebotarev, Luk'yanov, Chernyi & Smimova (1974) have reported the structure of Pu₅Rh₃. Pu₅Rh₃ has a tetragonal structure, different from the other Pu₅X₃ compounds which otherwise have either the W₅Si₃ or the Mn₅Si₃ structure. In addition to the above compounds, Cromer & Larson (1977) have reported Pu₃₁Rh₂₀. After the present work on Pu₅Rh₄ was completed the work of Chebotarev & Beznosikova (1976) on Pu₅Rh₄ and Pu₅Ir₄ was published. The authors used film techniques for intensity measurements. Most of their structural parameters are close to those found in the present work but there are significant differences in cell dimensions.

An alloy containing 45 at. % Rh was prepared by arc melting, followed by heat treatment at 950°C for 76 h.

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Table 1. Crystallographic data for Pu₅Rh₄

Space group	Present work	Chebotarev & Beznosikova (1976)
	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> ($\lambda = 0.70930 \text{ \AA}$)	7.276 (2) Å	7.263 Å
<i>b</i>	14.332 (4)	14.48
<i>c</i>	7.419 (2)	7.464
<i>Z</i>	4	4
d_{calc}	13.79 g cm ⁻³	13.59 g cm ⁻³
d_{meas} (of ingot)	13.62	
μ	582 cm ⁻¹	

Single crystals were found among the crushed fragments. Preliminary precession photographs showed the crystals to be orthorhombic with space group *Pnma*, if centrosymmetric. Reflections *Ok**l* were absent unless $k + l = 2n$ and reflections *hk*0 were absent unless $h = 2n$. All other classes were present. The volume of the unit cell was such that four formula units of Pu₅Rh₄ could be reasonably accommodated. Crystallographic data are given in Table 1, and compared with the results of Chebotarev & Beznosikova (1976).

Intensity data were collected on an automated Picker diffractometer and processed in the manner given by Cromer & Larson (1977). Reflections were measured for $h \geq 0$ and all values of *k* and *l* with graphite-monochromated Mo *K* α radiation. The crystal used was so irregular in shape that approximation of the shape by plane faces and subsequent analytical absorption corrections could not be made. Spherical absorption corrections with the mean radius of the irregularly shaped crystal plus empirical absorption corrections (Furnas, 1957; Cromer & Larson, 1972) were therefore made. Information concerning data collection and reduction is given in Table 2.

Table 2. Data collection and reduction

Radiation	Mo <i>K</i> α (graphite-monochromated)
$2\theta_{\text{max}}$	60°
Take-off angle	3°
Step size	0.05°
Step time	2 s
Scan range	2°
T_{min} (threshold parameter)	2.0
Number of reflections	4048
Unique reflections	1180
Unique reflections observed	1063
Reflections measured once	19
Reflections measured twice	296
Reflections measured three times	23
Reflections measured four times	842
Mean radius of crystal	0.0030 cm
$\dagger R_p$ (no corrections)	0.0723
R_p (empirical corrections)	0.0458
Minimum transmission	0.041
Maximum transmission	0.230

$\dagger R_p$ defined in Cromer & Larson (1977).

Table 3. Final positional parameters for Pu₅Rh₄

	Equipoint	x	y	z
Pu(1)	4(c)	0.32245 (14)	$\frac{1}{4}$	0.01077 (9)
Pu(2)	8(d)	0.34236 (10)	0.62196 (4)	0.16361 (6)
Pu(3)	8(d)	0.00148 (10)	0.40796 (4)	0.17796 (6)
Rh(1)	4(c)	0.1898 (3)	$\frac{1}{4}$	0.3529 (2)
Rh(2)	4(c)	0.4602 (3)	$\frac{1}{4}$	0.6114 (2)
Rh(3)	8(d)	0.1845 (2)	0.5391 (1)	0.4609 (1)

With the assumption of the centrosymmetric space group *Pnma* and four formula units of Pu₅Rh₄, direct methods easily found the correct structure. Refinement was by full-matrix least squares with anisotropic thermal parameters. Positional parameters are given in Table 3.* Refinement minimized $\Sigma w(\Delta F)^2$ and used relativistic Hartree–Fock scattering factors (Cromer & Waber, 1974) and the anomalous dispersion terms of Cromer & Liberman (1970). $R = \Sigma |\Delta F| / \Sigma F_o$ and $R_w = [\Sigma w(\Delta F)^2 / \Sigma w F_o^2]^{1/2}$, with unobserved reflections omitted, were 0.0385 and 0.0417 respectively; the goodness of fit was 1.64.

* Lists of the final least-squares cycle, structure factors, anisotropic thermal parameters and interatomic-distance, thermal-ellipsoid and polyhedron calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32508 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. Interatomic distances are given in Table 4. Two atoms are defined as neighbors if the midpoint

Table 4. Interatomic distances (Å) in Pu₅Rh₄

Pu(1)–Pu(2)	3.315 (1)	Pu(3)–2Rh(3)	3.792 (1)
–2Pu(2)	3.382 (1)	–Rh(1)	2.947 (2)
–2Pu(3)	3.491 (1)	–Rh(1)	3.213 (2)
–2Pu(3)	3.486 (1)	–Rh(2)	3.134 (1)
–Rh(1)	2.716 (2)	–Rh(3)	2.896 (2)
–Rh(1)	2.858 (3)	–Rh(3)	3.096 (1)
–Rh(2)	2.787 (2)	–Rh(3)	3.117 (1)
–Rh(2)	3.128 (2)	–Rh(3)	3.149 (2)
–2Rh(3)	3.045 (2)	Rh(1)–Pu(1)	2.716 (2)
Pu(2)–Pu(1)	3.315 (2)	–Pu(1)	2.858 (3)
–Pu(1)	3.382 (1)	–2Pu(2)	2.956 (1)
–Pu(2)	3.670 (2)	–2Pu(3)	2.947 (2)
–2Pu(2)	3.857 (1)	–2Pu(3)	3.213 (2)
–Pu(3)	3.483 (1)	–Rh(2)	2.747 (3)
–Pu(3)	3.587 (1)	–Rh(2)	3.828 (3)
–Pu(3)	3.802 (1)	Rh(2)–Pu(1)	2.787 (2)
–Pu(3)	3.946 (1)	–Pu(1)	3.128 (2)
–Rh(1)	2.956 (1)	–2Pu(2)	2.867 (2)
–Rh(1)	2.956 (1)	–2Pu(2)	2.892 (2)
–Rh(2)	2.867 (2)	–2Pu(3)	3.134 (1)
–Rh(2)	2.892 (2)	Rh(1)	2.747 (3)
–Rh(3)	2.755 (1)	–Rh(1)	3.828 (3)
–Rh(3)	2.763 (1)	Rh(3)–Pu(1)	3.045 (2)
–Rh(3)	2.909 (2)	–Pu(2)	2.755 (1)
Pu(3)–Pu(1)	3.481 (1)	–Pu(2)	2.763 (1)
–Pu(1)	3.486 (1)	–Pu(2)	2.909 (2)
–Pu(2)	3.483 (1)	–Pu(3)	2.896 (2)
–Pu(2)	3.587 (1)	–Pu(3)	3.096 (1)
–Pu(2)	3.802 (1)	–Pu(3)	3.117 (1)
–Pu(2)	3.946 (1)	–Pu(3)	3.149 (2)
–Pu(3)	3.733 (1)	–Rh(3)	2.968 (3)

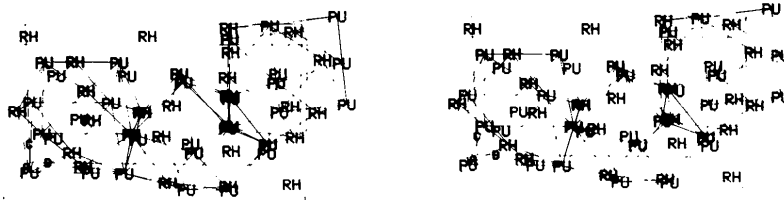


Fig. 1. Unit-cell contents of Pu₅Rh₄ with the three Pu polyhedra outlined. The origin is at the lower, left rear and the view is approximately along *x*. Pu(1) at 0.882 $\frac{1}{4}$, 0.489 is on the left. Pu(2) at 0.842, 0.622, 0.336 is in the middle and Pu(3) at 0.999, 0.908, 0.822 is on the right.

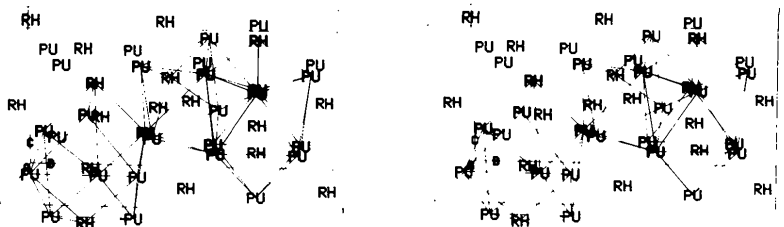


Fig. 2. Unit-cell contents of Pu₅Rh₄ with the three Rh polyhedra outlined. The origin and view direction are as in Fig. 1. Rh(1) at 0.690 $\frac{1}{4}$, 0.147 is on the left. Rh(3) at 0.185, 0.539, 0.461 is in the middle and Rh(2) at 0.540 $\frac{1}{4}$, 0.389 is on the right.

between the atoms is closer to these two atoms than to any other atom. The convex polyhedra formed by these neighbors are shown in Figs. 1 and 2. All distances are normal and the thermal parameters do not suggest any disorder.

Pu₃Rh₄ has a structure similar to that of Sm₅Ge₄ (Smith, Johnson & Tharp, 1967) and Gd₅Si₄ (Iglesias & Steinfink, 1972); these authors have discussed important features of the structure. The space group, axial ratios and equipoints occupied are the same for the three compounds but positional parameters are significantly different. Indeed, Iglesias & Steinfink (1972) state that they could not refine the structure of Gd₅Si₄ when they started with the Sm₅Ge₄ parameters. The parameters for Pu₃Rh₄ found by Chebotarev & Beznosikova (1976) and those of Sm₅Ge₄ and Gd₅Si₄ are reproduced in Table 5. Equivalent atoms have been chosen and reordered so that they can be compared with each other and with those in Table 3. The parameters from the two determinations of the Pu₃Rh₄ structure are virtually the same, except for those of Rh(3).

The main differences among these three M₅X₄ compounds are in the values of the *x* parameters, the

Table 5. Comparison of parameters of M₅X₄ structures

	Sm ₅ Ge ₄ ⁽¹⁾	Gd ₅ Si ₄ ⁽²⁾	Pu ₃ Rh ₄ ⁽³⁾
M(1) <i>x</i>	0.2880 (8)	0.3560 (1)	0.322
<i>z</i>	-0.0024 (8)	0.0113 (1)	0.011
M(2) <i>x</i>	0.3795 (5)	0.3164 (1)	0.342
<i>y</i>	0.6157 (3)	0.6223 (0)	0.622
<i>z</i>	0.1612 (5)	0.1795 (1)	0.162
M(3) <i>x</i>	-0.0253 (5)	0.0289 (1)	0.001
<i>y</i>	0.3996 (3)	0.4028 (0)	0.410
<i>z</i>	0.1781 (5)	0.1827 (1)	0.180
X(1) <i>x</i>	0.1761 (15)	0.2411 (10)	0.190
<i>z</i>	0.3667 (15)	0.3746 (10)	0.356
X(2) <i>x</i>	0.4132 (16)	0.4787 (10)	0.459
<i>z</i>	0.6115 (15)	0.5986 (10)	0.607
X(3) <i>x</i>	0.2206 (11)	0.1435 (6)	0.194
<i>y</i>	0.5449 (6)	0.5395 (3)	0.534
<i>z</i>	0.4688 (11)	0.4716 (7)	0.451

(1) Smith *et al.* (1967). (2) Iglesias & Steinfink (1972). (3) Chebotarev & Beznosikova (1976).

Table 6. Number of neighbors in M₅X₄ structures

	Pu ₃ Rh ₄	Sm ₅ Ge ₄	Gd ₅ Si ₄
M(1)	8M	8M	8M
	6X	6X	6X
M(2)	9M	8M	10M
	6X	6X	6X
M(3)	9M	8M	10M
	7X	7X	7X
X(1)	8M	8M	8M
	2X	4X	4X
X(2)	8M	8M	8M
	2X	4X	2X
X(3)	8M	8M	8M
	1X	2X	1X

extremes occurring for *M* = Sm and Gd, with *M* = Pu intermediate. Using the same, objective definition of neighbor we can examine the differences in the resulting polyhedra. The number of neighbors for each atom in the three compounds is shown in Table 6. *M*(1) has the same polyhedron in all three compounds, an approximately cubic array of eight *M* atoms with 6 *X* atoms out from each cube face. *M*(2) for *M* = Sm has the same number and kind of neighbors as *M*(1) but, because of the shifts in the *M*(2) position, Pu(2) has one more Pu(3) neighbor and Gd(2) has two extra Gd(3) neighbors. Sm(3) has eight *M* and seven *X* neighbors and again because of the changing *M*(2) position Pu(3) has one extra Pu(2) neighbor and Gd(3) has two extra Gd(2) neighbors. All of the *M*(2) and *M*(3) polyhedra are so irregular as to defy simple description.

X(1) and *X*(2) have basically the same polyhedra for the closest nine neighbors, namely a trigonal prism of *M* atoms with two *M* and one *X* out from the rectangular prism faces. However, Rh(1), Rh(2) and Si(2) have an additional *X* neighbor and Si(1), Ge(1) and Ge(2) have three additional *X* neighbors more distant. The *X*(3) neighbors are eight *M* atoms in a crude antiprism. Additionally Si(3) and Rh(3) have one *X* atom at one end of the antiprism and Ge(3) has *X* atoms at each end of the antiprism.

All calculations were performed on a CDC-7600 computer with the *LASL* crystal codes developed by A. C. Larson. Thanks are due to V. O. Struebing for preparing the alloy.

References

- BEZDOSIKOVA, A. V., CHEBOTAREV, N. T., LUK'YANOV, A., CHERNYI, A. V. & SMIRNOVA, E. A. (1974). *At. Energ. (USSR)*, **37**, 144–148.
- CHEBOTAREV, N. T. & BEZDOSIKOVA, A. V. (1976). *Plutonium 1975 and Other Actinides*, edited by H. BLANK & R. LINDNER, pp. 115–119. New York: American Elsevier.
- CROMER, D. T. & LARSON, A. C. (1972). *Acta Cryst.* **B28**, 1016–1022.
- CROMER, D. T. & LARSON, A. C. (1977). *Acta Cryst.* **B33**. In the press.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.
- FURNAS, T. C. (1957). *Single-Crystal Orienter Instruction Manual*. Milwaukee: General Electric Company.
- IGLESIAS, J. E. & STEINFINK, H. (1972). *J. Less-Common Met.* **26**, 45–52.
- KUTAITSSEV, V. I., CHEBOTAREV, N. T., LEBEDEV, I. G., ANDRIANOV, M. A., KONEV, V. N. & MENSHIKOVA, T. S. (1965). *Plutonium 1965*, edited by A. E. KAY & M. B. WALDRON, pp. 420–449. London: Chapman & Hall.
- SMITH, G. S., JOHNSON, Q. & THARP, A. G. (1967). *Acta Cryst.* **22**, 269–272.