

Plutonium–Iridium Pu₅Ir₃*

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Abstract. Pu₅Ir₃, *I4/mcm*, *Z* = 4, *a* = 11.012 (3), *c* = 5.727 (2) Å, $\rho_c = 16.94 \text{ g cm}^{-3}$, for an approximately stoichiometric alloy. For an Ir-rich alloy *a* = 11.015 (3), *c* = 5.621 (2) Å. This structure is of the *D8_m* (W₅Si₃) type. For the Ir-rich alloy it is postulated that some Ir is substituted in the $0, \frac{1}{2}, \frac{1}{4}$ Pu site.

Introduction. Kutaitsev, Chebotarev, Lebedev, Andrianov, Konev & Menshikova (1965) reported three compounds in the Pu–Ir system: PuIr₂ having the Cu₂Mg structure and Pu₅Ir₄ and Pu₅Ir₃ with unknown structures. This note reports the refinement of the structure of Pu₅Ir₃ which is a representative of the W₅Si₃ (*D8_m*) structure type. An approximately stoichiometric crystal and an Ir-rich crystal were both refined. The results for the Ir-rich crystal are close to those reported by Beznosikova, Chebotarev, Luk'yanov, Chernyi & Smirnova (1974) for Pu₅Ir₃.

Alloys containing 37.1 and 40.1 at.% Ir were prepared by arc melting and subsequent heat treatment. Crystals of Pu₅Ir₃ were found in both alloys. Because the *c* axes differ very significantly in the two specimens, complete structure determinations were made in the hope of determining the type of disorder that must be present. Data for the two specimens are given in Table 1. Intensity data were taken and equivalent reflections averaged in the manner described by Cromer & Larson (1977).

Full-matrix least-squares refinements minimizing $\sum w(\Delta F)^2$ were made with the scattering factors of Cromer & Waber (1974) and the anomalous-dispersion terms of Cromer & Liberman (1970). The positional parameters for the two specimens are given in Table 2.†

Discussion. After correction for anomalous dispersion the Pu and Ir scattering factors do not differ greatly.

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† Lists of the final least-squares cycles, 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 32509 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Data concerning two specimens of Pu₅Ir₃

Specimen number	14362	14363A
Gross composition		
Ir	37.1 at.%	40.1 at.%
Pu	62.9	59.9
Heat treatment	73 h, 1100°C	72 h, 900°C
Space group	<i>I4/mcm</i>	<i>I4/mcm</i>
<i>a</i> ($\lambda = 0.70930 \text{ \AA}$)	11.012 (3) Å	11.015 (3) Å
<i>c</i>	5.727 (2)	5.621 (2)
<i>Z</i>	4	4
<i>d</i> _{meas} (of ingot)	16.64 g cm ⁻³	16.99 g cm ⁻³
<i>d</i> _{calc} (stoichiometric)	16.94	17.25
Data collection		
Radiation	Mo K α (graphite monochromated)	
Take-off angle	3°	
Scan range	2.2°	
Step size	0.05°	
Step time	1.8 s	
$2\theta_{\text{max}}$	60°	
<i>T</i> _{min} (threshold parameter)	2.0	
Number of reflections		
measured	1996	1923
Unique reflections	302	293
Unique reflections observed	281	260
Reflections measured twice	14	13
Reflections measured three times	8	10
Reflections measured four times	64	60
Reflections measured six times	19	20
Reflections measured seven times	2	13
Reflections measured eight times	195	177
Absorption corrections	Spherical + empirical*	Analytic† (7 faces)
Crystal volume	0.23 × 10 ⁻³ mm ³	0.57 × 10 ⁻⁴ mm ³
μ	1127 cm ⁻¹	1127 cm ⁻¹
Transmission maximum	0.036	0.237
Transmission minimum	0.005	0.035
<i>R_F</i> (no corrections)	0.0859	0.2152
<i>R_F</i> (abs. corrected)	0.0619	0.0866

* Furnas (1957); Cromer, Larson & Roof (1972).

† de Meulenaer & Tompa (1965).

Consequently, one cannot easily determine site occupancies by inspection of thermal parameters or by introducing occupancy parameters. The site at $0, \frac{1}{2}, \frac{1}{4}$ is the place to look for disorder. In (Pu,Ce)₅Co₃ (Larson, Roof & Cromer, 1964) both positional and substitution-

Table 2. *Positional parameters for Pu₅Ir₃*

Specimen 14362 ($R = 0.0417, R_w = 0.0585$)				
	Equipoint	x	y	z
Pu(1)	4(b)	0	$\frac{1}{2}$	$\frac{1}{4}$
Pu(2)	16(k)	0.0845 (1)	0.2184 (1)	0
Ir(1)	4(a)	0	0	$\frac{1}{4}$
Ir(2)	8(h)	0.1583 (1)	$\frac{1}{2} + x$	0
Specimen 14363A ($R = 0.0536, R_w = 0.0540$)				
Pu(1)	4(b)	0	$\frac{1}{2}$	$\frac{1}{4}$
Pu(2)	16(k)	0.0845 (1)	0.2204 (1)	0
Ir(1)	4(a)	0	0	$\frac{1}{4}$
Ir(2)	8(h)	0.1590 (1)	$\frac{1}{2} + x$	0

Table 3. *Interatomic distances in Pu₅Ir₃ (Å)*

The first distance given is from specimen 14362 and the second from specimen 14363A.

Pu(1)–2 Pu(1)	2.864 (1)	2.810 (1)
–8 Pu(2)	3.540 (1)	3.511 (1)
–4 Ir(2)	2.851 (2)	2.848 (2)
Pu(2)–2 Pu(1)	3.540 (1)	3.511 (1)
–Pu(2)	3.069 (2)	3.040 (2)
–2 Pu(2)	3.415 (1)	3.370 (1)
–2 Pu(2)	3.542 (1)	3.519 (1)
–2 Pu(2)	3.647 (2)	3.676 (2)
–2 Ir(1)	2.950 (1)	2.955 (1)
–Ir(2)	2.909 (2)	2.905 (2)
–Ir(2)	2.999 (1)	2.993 (1)
–2 Ir(2)	3.272 (1)	3.215 (1)
Ir(1)–2 Ir(1)	2.864 (1)	2.810 (1)
–8 Pu(2)	2.950 (1)	2.995 (1)
Ir(2)–2 Ir(2)	4.045 (2)	3.991 (2)
–2 Pu(1)	2.851 (2)	2.848 (2)
–2 Pu(2)	2.909 (2)	2.905 (2)
–2 Pu(2)	2.999 (1)	2.993 (1)
–4 Pu(2)	3.272 (1)	3.215 (1)

al disorder were apparent in this site. In Pu₅Ru₃ (Cromer, Larson & Roof, 1975) there were indications that this site was only 92% occupied by Pu.

In the present two specimens one cannot directly compare thermal parameters because of the uncertainty in absorption corrections. In particular, an error in the estimation of the crystal volume would have a systematic effect on the thermal parameters. However, we can compare the thermal parameters of Pu(1) and

Pu(2) in each of the two specimens. In specimen 14362, which should be nearly stoichiometric, Pu(1) and Pu(2) have nearly identical thermal parameters. In specimen 14363A, with excess Ir, Pu(1) has a larger and more anisotropic motion than Pu(2). One can postulate that in this alloy the 4(b) site has some Ir in it. This substitution would account for the larger thermal parameter and for its being more anisotropic, since the smaller Ir atoms could move farther along the *c* axis. Also, the mean interatomic distance would be smaller, and hence the smaller *c* axis. The increased Ir composition is probably not accompanied by Pu vacancies as the measured density is higher in the high-Ir alloy.

Interatomic distances are given in Table 3. Stereo drawings of the polyhedra in this structure type have been given in the note on Pu₅Ru₃ (Cromer, Larson & Roof, 1975).

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