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The crystal structure of the high temperature form of $PuGa_3$.*

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A phase diagram of the plutonium–gallium system was recently reported by Ellinger, Land & Struebing (1964). Among the compounds listed is $PuGa_3$, which exists in both a high temperature and a low temperature form. The low temperature form has the Ni_3Sn structure type, a close packed hexagonal structure with layering *abab*---. The high temperature form (metastable at room temperature) is the subject of the present note.

A specimen was prepared by arc melting and slowly cooling a stoichiometric mixture of Pu and Ga. The high temperature phase (designated μ' by Ellinger *et al.*, 1964) is readily preserved to room temperature, even if the alloy is slowly cooled.

The alloy was crushed and selected fragments were examined with a precession camera and with a single-crystal orienter on a General Electric XRD 5 diffractometer. All fragments were found to be twinned rhombohedral crystals, with each twin making up about half of any fragment. Photomicrographs taken with polarized light showed faint striations typical of twin boundaries. The single-crystal regions were about 5 to 10 microns wide. In a typical fragment of 50 to 100 microns in size there might be 5 to 10 fragments of each twin, thus accounting for the fact that the two orientations were always present in nearly equal amounts. The lattice constants, measured on a carefully aligned single crystal orienter, were found to be $a = 6{\cdot}178 \pm 0{\cdot}001$ and $c = 28{\cdot}031 \pm 0{\cdot}004$ Å (λ, Mo $K\alpha_1 = 0{\cdot}70926$ Å). The primitive rhombohedral cell has constants $a = 10{\cdot}001$ Å and $\alpha = 35° 59'$. The measured density of the ingot was 9·3 g.cm^{-3} at room temperature. The calculated density, with 12 formula units per unit cell, is 9·63 g.cm^{-3}.

Because of the similarity between the unit cells of $PuGa_3$ and $PuAl_3$ (Larson, Cromer & Stambaugh, 1957; $a_{PuGa_3} \simeq a_{PuAl_3}$ and $c_{PuGa_3} \simeq 2c_{PuAl_3}$) it seemed probable

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Table 1. *Final least-squares parameters (hexagonal unit cell)*

Atom	Set	x	z	$B_{11} \times 10^5$	B_{22}	$B_{33} \times 10^6$	$B_{12} \times 10^5$	$B_{13} \times 10^6$	B_{23}
Pu(1)	6(*c*)	0	0·12977 ± 8	990 ± 63	B_{11}	391 ± 45	B_{11}	0	0
Pu(2)	6(*c*)	0	0·28798 ± 9	966 ± 52	B_{11}	197 ± 38	B_{11}	0	0
Ga(1)	18(*h*)	0·4791 ± 3	0·1247 ± 1	1284 ± 113	B_{11}	372 ± 58	1209 ± 248	319 ± 239	$-B_{13}$
Ga(2)	18(*h*)	0·5011 ± 4	0·2915 ± 2	1248 ± 99	B_{11}	432 ± 54	640 ± 222	713 ± 209	$-B_{13}$

$g = 4{\cdot}34 \pm 0{\cdot}17 \times 10^{-8}$

Table 2. *Observed and calculated structure factors for* $PuGa_3$

The column headings are l, $|F_o|/K$ and F_c^*/K (see text). A minus sign preceding $|F_o|/K$ means 'less than'

H= 0 K= 1			H= 0 K= 5			H= 1 K= 3			H= 2 K= 1			H= 3 K= 1			H= 4 K= 2		
2	198	-208	1	157	161	1	102	103	10	160	160	20	143	-166	5	614	-594
5	466	-456	4	-93	-49	4	119	-127	13	149	-154	23	-98	17	8	147	153
8	180	187	7	168	159	7	462	463	16	-81	-19	26	248	-259	11	-106	-100
11	-72	-45	10	154	172	10	-82	17	19	324	-315				14	403	405
14	327	331	13	139	-132	13	104	-84	22	-92	9	H= 3 K= 2			17	430	410
17	204	201	16	-95	-26	16	-90	17	25	-105	92						
20	170	-162	19	153	-160	19	401	-404	28	-103	101	1	-81	-24	H= 4 K= 3		
23	-86	-16				22	-108	83				4	-84	-53			
26	305	-313	H= 1 K= 0			25	-100	53	H= 2 K= 3			7	449	439	1	-112	126
29	-98	-30										10	118	-101	4	-106	-63
32	118	113	1	-74	77	H= 1 K= 5			2	-84	-15	13	-88	24	7	164	179
			4	94	-103				5	346	-350	16	-98	-30			
H= 0 K= 2			7	594	572	2	192	-202	8	116	106	19	411	-397	H= 5 K= 0		
			10	-79	-20	5	248	-248	11	-89	33	22	152	155			
1	358	358	13	-71	-51	8	153	159	14	123	123				2	327	-316
4	341	-350	16	-84	-39	11	-110	-114	17	190	185	H= 3 K= 4			5	-104	-102
7	1120	1133	19	489	-479	14	266	261	20	-104	-107				8	-105	99
10	471	484	22	148	140				23	-100	-54	2	209	-229	11	146	-137
13	292	-293	25	-91	25	H= 2 K= 0						5	149	-133	14	398	379
16	170	159	28	-107	121				H= 2 K= 4			8	-107	100	17	-97	23
19	944	-955	31	316	317	2	691	-709							20	-110	-101
22	190	-205				5	1083	-1075	1	-120	124	H= 4 K= 0					
25	190	188	H= 1 K= 2			8	423	414	4	130	-108				H= 5 K= 1		
28	-96	-4				11	270	-280	7	650	649	1	224	218			
31	626	609	2	372	-370	14	742	718	10	233	234	4	179	-189	1	-114	140
			5	273	-268	17	830	794	13	-116	-107	7	862	856	4	-108	-120
H= 0 K= 4			8	174	177	20	321	-330	16	-100	26	10	363	347	7	307	301
			11	156	-159	23	137	137				13	181	-184	10	-104	91
2	508	-521	14	448	450	26	564	-555	H= 3 K= 1			16	-94	70	13	-110	-120
5	769	-798	17	-94	104	29	412	-410				19	720	-704	16	-103	40
8	246	245	20	156	-161				2	159	-168	22	132	-149			
11	167	-177	23	-98	69	H= 2 K= 1			5	375	-378	25	-116	124			
14	530	550	26	370	-391				8	190	186						
17	550	553	29	-100	6	1	200	199	11	-87	-76	H= 4 K= 2					
20	194	-215				4	95	-104	14	274	263						
23	-102	90				7	368	360	17	204	201	2	362	-365			

that the $PuGa_3$ structure consisted of close-packed layers in a 12-layer stacking sequence. There is only one 12-layer rhombohedral sequence: *abacbcbacacb*.

Intensities were measured with a single-crystal orienter and an XRD 5 diffractometer with Mo $K\alpha$ radiation and balanced filters. The entire hemisphere of the obverse orientation was investigated for $2\theta < 50°$. Approximate absorption corrections, based on the variation of intensity with φ at $\chi = 90°$ and on the mean radius of the fragment, and LP corrections were applied using the program described by Larson, Cromer & Roof (1964). Equivalent reflections were averaged. The R index formed by comparing average values with individual values of equivalent reflections was 4·4% based on F and 6·8% based on F^2.

Both twin orientations contribute to reflections with $l = 3n$. Reflections with $l \neq 3n$ are from the obverse twin only and subsequent refinement was made using only this class of reflections. In this class there were 104 non-equivalent reflections observed out of a possible 157.

The 12-layer rhombohedral close-packed structure belongs to space group $R\bar{3}m$. A trial structure based on this model was refined by least squares; the quantity minimized was $\Sigma w(F_o - F_c^*)^2$, where $w = w_E/(|F_o| + 0{\cdot}02F_o^2)$, w_E is the weight based on counting statistics as described by Evans (1961), and

$$F_c^* = KF_c \Big/ \left\{1 + g\mathrm{LP}\left[\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right]F_c^2\right\}^{\frac{1}{2}}$$

where K = scale factor, g = extinction parameter (Zachariasen, 1963), LP = Lorentz-polarization factor and F_c is the ordinary calculated structure factor. Anisotropic temperature factors in the form

$$\exp\left[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})\right]$$

were used. At the end of the refinement, $\Delta\xi_i/\sigma(\xi_i)$ was $< 5 \times 10^{-4}$ for all parameters ξ except g, for which it was 0·015. The final value of $R = \Sigma w|F_o - F_c^*|/\Sigma wF_o$ was 3·0% for the 104 non-zero reflections with $l \neq 3n$. The scattering factors used were those given by Cromer & Waber (1965), modified by the real anomalous dispersion terms calculated by Cromer (1965).

Table 3. *Interatomic distances in* $PuGa_3$

Pu(1)–3 Ga(1)	2·987 ± 4 Å
–6 Ga(1)	3·101 ± 1
–3 Ga(2)	3·037 ± 5
Pu(2)–3 Ga(1)	2·996 ± 4
–3 Ga(2)	3·033 ± 4
–6 Ga(2)	3·092 ± 1
Ga(1)–Pu(1)	2·987 ± 4
–2 Pu(1)	3·101 ± 1
–Pu(2)	2·996 ± 4
–2 Ga(1)	2·703 ± 6
–2 Ga(1)	2·825 ± 6
–2 Ga(1)	3·477 ± 6
–2 Ga(2)	2·874 ± 5
Ga(2)–Pu(1)	3·037 ± 5
–Pu(2)	3·033 ± 4
–2 Pu(2)	3·092 ± 1
–2 Ga(1)	2·874 ± 5
–2 Ga(2)	2·938 ± 7
–2 Ga(2)	3·069 ± 7
–2 Ga(2)	3·111 ± 7

Table 4. *Thermal vibration ellipsoids in* $PuGa_3$

Atom	Axis i	r.m.s. Amplitude	Angles relative to the crystallographic axes α	β	γ
Pu(1)	1	0·120 ± 5 Å	0	120	90
	2	0·120 ± 5	90	30	90
	3	0·125 ± 7	90	90	0
Pu(2)	1	0·118 ± 8	0	120	90
	2	0·118 ± 8	90	30	90
	3	0·088 ± 9	90	90	0
Ga(1)	1	0·144 ± 7	37 ± 8	143 ± 8	68 ± 14
	2	0·135 ± 8	60	60	90
	3	0·118 ± 10	109 ± 12	71 ± 12	22 ± 14
Ga(2)	1	0·171 ± 6	38 ± 4	142 ± 4	66 ± 6
	2	0·123 ± 8	60	60	90
	3	0·122 ± 9	111 ± 5	69 ± 5	24 ± 6

The final parameters are given in Table 1 and the corresponding values of F_o/K and F_c^*/K are given in Table 2. Interatomic distances are listed in Table 3. The vibrational tensors were diagonalized, with the results as shown in Table 4. The standard deviations in Tables 3 and 4 were computed using the entire variance–covariance matrix. Lattice parameter errors were also included in the standard deviations of Table 3.

All calculations were performed on an IBM 7094 computer with codes written by the authors.

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