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The crystal structures of $PuGa_4$ and $PuGa_6$*.

By F. H. Ellinger and W. H. Zachariasen†, *University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.*

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In a recent paper (Ellinger, Land & Struebing, 1964) $PuGa_3$ was reported to be the most gallium-rich intermediate phase in the plutonium–gallium system. However, further work in this laboratory has shown the existence of both $PuGa_4$ and $PuGa_6$. Their presence was first indicated in thermal analysis experiments carried out by Land, Ellinger & Johnson (1965).

This paper reports the crystal structures of the two compounds as deduced from powder X-ray diffraction patterns.

The experimental work has been described by Ellinger, Land & Struebing (1964). The unit-cell dimensions were calculated from the lines with $\sin^2\theta$ greater than 0·9 and are based upon the chromium radiation wave lengths: $K\alpha_1$ 2·28962 and $K\alpha_2$ 2·29351 Å. The reliabilities are expressed as double the uncertainties indicated by the agreement of the observed and calculated $\sin^2\theta$ values greater than 0·9. The atomic parameters were determined by the trial and error method and the limits of error were estimated.

$PuGa_4$

$PuGa_4$ has the $D1_b$ structure (UAl_4 type) with
$a=4{\cdot}380\pm0{\cdot}001$, $b=6{\cdot}290\pm0{\cdot}001$, $c=13{\cdot}673\pm0{\cdot}004$ Å.

Table 1. *Diffraction data for* $PuGa_4$ (Cr $K\alpha$)

	$10^4 \sin^2\theta$		Intensity	
hkl	calc.	obs.	obs.	calc.
002	280			0·0
011	401	410	*vw*	3·2
101	753	767	*w*	4·8
013	962	980	*w*+	6·8
004	1122	1141	*w*−	4·5
112	1294	1316	*mw*	17·5
103	1314			3·6
020	1325			1·2
022	1605	1631	*vw*	2·0
121	2078	2102	*ms*	54·1
015	2083			1·6
114	2136			0·0
105	2435	2464	*s*	50·3
024	2447			32·6
006	2524			0·1
123	2639	2662	*mw*	14·5
200	2733	2759	*m*	25·6
202	3013			0·0
031	3051	3079	*w*	5·5
211	3134	3156	*vw*	2·4
116	3538	3560	*w*	5·7
033	3612	3643	*vw*	1·2
213	3695	3727	*w*	6·4
125	3760	3795	*w*	1·7
017	3766			4·2
026	3849	3880	*mw*	9·9
204	3855			4·4
132	3944	3978	*w*−	4·2
220	4058	4093	*vw*	1·4
107	4118	4153	*vw*	1·8
222	4338	4360	*w*	2·1
008	4486	4516	*w*	2·7
035	4733			1·0
134	4786	4816	*w*+	2·8
215	4816			2·1
224	5180	5204	*s*	45·2
206	5257			0·1
040	5299	5326	*mw*	16·6
127	5443			0·2
118	5500	5526	*mw*	1·8
042	5579			0·2
231	5784	5806	*mw*−	9·2
028	5811	5845	*mw*−	11·2
019	6009			1·0
141	6062	6085	*w*	4·9
136	6188	6212	*m*	16·0
301	6219			2·1
233	6345	6389	*mw*	2·6
109	6361			5·3
037	6416	6447	*mw*	2·0
044	6421			5·4
217	6499	6522	*mw*	9·0
226	6582	6592	*m*+	20·6
143	6613			6·5
312	6760	6769	*m*	10·7
303	6780			2·2
0·0·10	7010	7023	*m*	10·7
208	7219	7228	*w*	4·8
235	7466	7473	*vw*−	2·0
321	7544	7550	*s*+	31·6
314	7602			
129	7686	7698	*vs*	47·1
145	7734	7746	*vs*	59·8
046	7823			0·2
305	7901	7907	*s*+	36·4
1·1·10	8024	8040	*s*+	7·7
240	8032			36·7
323	8105	8113	*w*	12·2
138	8150			0·2
242	8312			0·4
0·2·10	8335			0·0
051	8350			0·0
228	8544	8548	*s*+	30·1
039	8659			0·0
219	8742		trace	2·9
0·1·11	8813	8818	*vw*+	5·3
053	8911	8912	*w*	9·4
316	9004	9003	*mw*	10·2
237	9149	9152	*s*	7·6
244	9154			19·8
1·0·11	9165			1·9
325	9226	9249	*s*+	4·2
152	9243			32·0
332	9410	9406	*m*	11·4
147	9417			4·9
307	9584		*vw*	5·2
2·0·10	9743	9744	*vs*	100·0
048	9785	9778	*s**	31·9

* Coincidence with α_2 of 2·0·10.

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† Consultant to Los Alamos Scientific Laboratory.

The calculated density is 9·13 g.cm^{-3}. The space group is *Imma* and the atomic positions are

4Pu in 4(*e*): $\pm(0\ \tfrac{1}{4}\ z)$ with $z=$ 0·114
4 Ga(1) in 4(*b*): $(0\ 0\ \tfrac{1}{2})$
4 Ga(2) in 4(*e*): $\pm(0\ \tfrac{1}{4}\ z)$ with $z-0{\cdot}106$
8 Ga(3) in 8(*h*): $\pm(0\ y\ z)$ with $y=-0{\cdot}028$, $z=0{\cdot}300$

The bond lengths, accurate to about ±0·05 Å, were calculated with a Maniac program written by A. C. Larson (1964). They are as follows:

Pu–4 Ga(1)	3·11 Å	Ga(1)–4 Pu	3·11 Å
–2 Ga(2)	3·15	–2 Ga(1)	3·15
–1 Ga(2)	3·01	–4 Ga(2)	3·06
–4 Ga(3)	3·04	–2 Ga(3)	2·74
–2 Ga(3)	3·09		

Ga(2)–1 Pu	3·01 Å	Ga(3)–1 Pu	3·09
–2 Pu	3·15	–2 Pu	3·04
–4 Ga(1)	3·06	–1 Ga(1)	2·74
–4 Ga(3)	2·90	–2 Ga(2)	2·90
–2 Ga(3)	3·00	–1 Ga(2)	3·00
		–2 Ga(3)	2·58
		–1 Ga(3)	2·79

Table 1 gives the complete diffraction data for chromium *Kα* radiation, and shows the satisfactory agreement between observed and calculated values. The discrepancies between the observed and calculated $\sin^2\theta$ values are due to absorption displacement of the diffracted lines. The intensities were calculated with an IBM 7094 program written by A. C. Larson (1964).

$PuGa_6$

The diffraction lines of the $PuGa_6$ pattern correspond to a primitive tetragonal cell with

$$a=5{\cdot}942\pm0{\cdot}001,\quad c=7{\cdot}617\pm0{\cdot}001\ \text{Å}\,.$$

The cell contains two formula units, giving a calculated density of 8·11 g.cm^{-3}.

Reflections *hk*0 are absent for odd $h+k$, and reflections *h*0*l* are absent for odd *h*. The suggested symmetry is thus *P*4/*nbm*, and the following structure was readily deduced.

2 Pu in 2(*c*): $(\tfrac{1}{2}\ 0\ 0)\ (0\ \tfrac{1}{2}\ 0)$
4 Ga(1) in 4(*g*): $\pm(0\ 0\ z)\ (\tfrac{1}{2}\ \tfrac{1}{2}\ z)$ with $z=0{\cdot}167\pm0{\cdot}008$
8 Ga(2) in 8(*m*): $(x,\ \tfrac{1}{2}+x,\ z)\ (x,\ \tfrac{1}{2}-x,\ \bar{z})\ (\bar{x},\ \tfrac{1}{2}-x,\ z)$
$(\bar{x},\ \tfrac{1}{2}+x,\ \bar{z})\ (\tfrac{1}{2}+x,\ x,\ \bar{z})\ (\tfrac{1}{2}+x,\ \bar{x},\ z)$
$(\tfrac{1}{2}-x,\ \bar{x},\ \bar{z})\ (\tfrac{1}{2}-x,\ x,\ z)$ with $x=0{\cdot}187\pm0{\cdot}005$, $z=0{\cdot}350\pm0{\cdot}006$.

Table 2 gives the complete set of diffraction data for Cr *Kα* radiation. The intensities were calculated from the formula

$$I\propto|F|^2pA(1+\cos^2 2\theta)/\sin^2\theta\cos\theta$$

where *p* is the permutation factor and *A* the absorption factor for a cylindrical specimen with $\mu r=5{\cdot}0$. The *f* curves of Cromer & Waber (1965) for neutral atoms were assumed, and dispersion corrections were applied using Cromer's values (1965).

The bond lengths, with extreme errors, are

Pu–8 Ga(1)	3·23 ± 0·03 Å	Ga(2)–1 Pu	3·09 ± 0·06 Å
–4 Ga(2)	3·09 ± 0·06	–2 Ga(1)	2·58 ± 0·05
		–1 Ga(2)	2·52 ± 0·11

Table 2. *Diffraction data for* $PuGa_6$ (Cr *Kα*)

	$10^4\sin^2\theta$		Intensity	
hkl	calc.	obs.	obs.	calc.
001	226	238	*vw*–	2·2
110	742	759	*vw*	2·0
002	904	926	trace	0·3
111	968	990	*w*–	3·6
200	1485	1513	*vw*+	2·3
112	1646	1672	*m*	13·1
201	1711	1735	*vs*	28·7
003	2033	2063	*w*	4·6
211	2082	2109	*m*–	7·4
202	2389	2419	*w*+	5·5
212	2760	2798	*vs*	8·4
113	2775			18·8
220	2970	2995	*s*	16·3
221	3196	3222	*w*+	4·2
203	3518	3543	*vw*+	2·3
004	3614	3635	*vvw*	0·4
310	3712	3724	*vvw*	0·8
222	3874	3902	*vw*–	1·2
213	3889			0·6
311	3938	3961	*m*	7·8
114	4356	4378	*m*–	5·7
312	4616	4639	*s*+	17·5
223	5003	5022	*w*	3·8
321	5052			0·7
204	5099	5123	*m*	8·0
214	5470	5497	*vw*	2·1
005	5647	5674	*vw*–	1·8
322	5730	5769	*s*	1·0
313	5745			11·8
400	5939	5963	*m*	5·6
401	6165	6188	*m*+	7·4
115	6389	6416	*w*	2·1
411	6536	6561	*m*	9·2
224	6584			0·6
330	6681	6702	*w*	4·9
402	6843	6864	*vw*+	2·4
323	6859			0·1
331	6907			0·6
205	7132	7148	*m*	8·9
412	7214	7230	*m*+	14·7
314	7326	7339	*vs*	30·5
420	7424	7439	*m*	14·9
215	7503	7518	*w*+	8·5
332	7585	7601	*w*	5·7
421	7650	7660	*s*	20·5
403	7972	7984	*vvw*	1·4
006	8132	8142	*m*	12·8
422	8328	8338	*m*–	7·7
413	8343			2·2
324	8440			0·8
225	8617	8626	*m*–	15·0
333	8714	8717	*vvs*	66·6
116	8874	8879	*vw*+	3·1
315	9359	9361	*m*+	14·9
423	9457	9460	*w*–	7·3
431	9506	9507	*vw*+ *	5·8
404	9553	9556	*w*+	9·2
206	9617	9617	*m*	16·7
510	9651	9651	*m*+ *	14·7
511	9877	9877	*m*	18·9

* Coincidence with α_2-line of preceding reflection.

Ga(1)–4 Pu	3·23 ± 0·03 Å	–4 Ga(2)	3·06 ± 0·02
–1 Ga(1)	2·54 ± 0·13	–1 Ga(2)	3·15 ± 0·07
–4 Ga(2)	2·58 ± 0·05	–2 Ga(2)	3·19 ± 0·10

The mean value Pu–12 Ga = 3·18 Å is considerably larger than the distance Pu–13 Ga = 3·08 Å observed in $PuGa_4$, and suggests that the effective valence of plutonium is four in $PuGa_6$ and closer to five in $PuGa_4$.

In gallium metal each atom forms seven bonds, one of length 2·44 Å and six in the range 2·71–2·80 Å. Short Ga–Ga bonds of 2·45 Å also occur in $PuGa_2$ (Ellinger, Land & Struebing, 1965).

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Hybrid solid solution.

By GABRIELLE DONNAY, *Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C., U.S.A.*

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The purpose of this note is to draw the attention of crystallographers to the existence of an unusual kind of solid solution, which was discovered by Kushiro & Schairer (1963). Forsterite, Mg_2SiO_4, an orthosilicate (isolated tetrahedra), forms a limited solid solution in diopside, CaMg Si_2O_6, a metasilicate (chains of tetrahedra). Such a solid solution, which not only involves the usual topological rearrangements of the crystal structure of the solvent, but also requires changes in the anionic building blocks themselves, is here called a *hybrid solid solution*. In the three common types of solid solution, substitution, addition and omission, minor structural rearrangements accompany the variations in composition; no strong linkages, such as Si–O bonds, are broken. In the present case the ratio of tetrahedrally coordinated cation to oxygen changes from 1:3 in diopside towards 1:4 in forsterite. Drastic structural rearrangements must take place, which will be shown to involve more than one type of solid solution. The three most likely hypotheses will be discussed in turn. A fourth one, involving cation vacancies at the centers of oxygen tetrahedra will be presented by Kushiro & Schairer in the forthcoming publication of their phase-diagram study.

Above 1300°C and up to the melting point, forsterite can amount to about 5 weight per cent of the solid solution in diopside, so that the composition can be written in moles per cent: $Di_{93}Fo_7$. For reference in the subsequent discussion we write:

$$CaMgSi_2O_6 + 0{\cdot}08\ Mg_2SiO_4 = CaMg_{1{\cdot}16}Si_{2{\cdot}08}O_{6{\cdot}32}\ .$$

1. If *the number of silicon atoms is considered constant*, the formula becomes $Ca_{0{\cdot}96}Mg_{1{\cdot}12}Si_{2{\cdot}00}O_{6{\cdot}08}$ or, for x moles of forsterite to one mole of diopside, $(Ca_{1-y}Mg_y)\ Mg_{1+2y}\ Si_2\ O_{6+2y}$, where $y = x/(2+x)$.

The Si/O ratio is now less than $\frac{1}{3}$ and some of the silicon tetrahedra must share only one corner instead of two. This would result from breaking one Si–O bond in the $Si_2O_6^{4-}$ chain, and adding one oxygen atom to the depleted tetrahedron. The broken ends of the chain must move apart and one of the added magnesium ions would fit between them. Moreover, for every two such magnesium ions, one more magnesium ion is added, which substitutes for calcium. The cells where the breaks occur must be randomly distributed. Since there are four diopside formula units per cell, the maximum number of chain-breaks is $4 \times 0{\cdot}08 = 0{\cdot}32$, or about one in every three unit cells.

2. If *the number of oxygen atoms is considered constant*, the formula becomes $Ca_{0{\cdot}95}Mg_{1{\cdot}10}Si_{1{\cdot}97}O_{6{\cdot}00}$.

Table 1. *Calculated densities of diopside-forsterite solid solution in the three structural interpretations*

	Type	Formula	Formula weight	Density, calc.
End member	Diopside	$CaMgSi_2O_6$	216·56	3·275* g.cm⁻³
Hybrid solid solution	Substitution and double addition: broken chains	$(Ca_{0{\cdot}96}Mg_{0{\cdot}04})Mg_{1{\cdot}08}$ $Si_2O_{6{\cdot}08}$	219·18	3·315
	Double substitution and addition: Si-Mg chains	$(Ca_{0{\cdot}95}Mg_{0{\cdot}05})Mg_{1{\cdot}02}$ $(Si_{1{\cdot}97}Mg_{0{\cdot}03})O_6$	216·145	3·269
	Double substitution and omission: crosslinked Si-Mg chains	$(Ca_{0{\cdot}94}Mg_{0{\cdot}06})Mg$ $(Si_{1{\cdot}96}Mg_{0{\cdot}04})O_{5{\cdot}96}$	214·88	3·250

* Observed densities for diopside, quoted from the literature by Deer, Howie & Zussman (1963), range from 3·22 to 3·38 g.cm⁻³. No densities have been determined for the solid solutions.