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The Crystal Structure of Os_4Al_{13}

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The crystal structure of Os_4Al_{13} has been determined and refined from three-dimensional X-ray data. The monoclinic cell dimensions are $a = 17.64$, $b = 4.228$, $c = 7.773$ Å and $\beta = 115.15°$. The space-group is $C2/m$. The atomic arrangement is related to that present in Fe_4Al_{13}. The interatomic distances in the two structures are compared.

Very little is known about the platinum metal aluminides rich in aluminum. An investigation of such alloys has been started at this Institute and has so far revealed the existence of several new phases, complex in structure and with similarities to earlier known structures like Fe_4Al_{13},[1,2] Co_4Al_{13},[3] and $Ni_4Mn_{11}Al_{60}$.[4] The simplest structure so far known in this group is represented by Os_4Al_{13}.

EXPERIMENTAL

Osmium-aluminum alloys were prepared by melting pellets, obtained by pressing osmium powder (L. Light and Co., 99.975 %) and pieces of aluminum (E. Merck A.G., at least 99.99 % pure), in an electric arc furnace under an argon pressure of 0.5 atm. The loss of aluminum from vaporization during the short melting period was determined by weighing the sample before and after the heat treatment. By comparing the X-ray powder patterns of samples of different compositions, the phase was found to exist in a pure state with a formula slightly higher in aluminum than $OsAl_3$. This preparation is grey and crystalline and contains well formed prismatic crystals very often forming aggregates. After having tried several crystals found to be twinned, a single crystal was eventually picked up from the crushed melt. The form of this crystal, which was used for the structure determination, was nearly a rectangular parallelepiped with the edges approximately 0.004, 0.008, and 0.02 mm in length. Weissenberg photographs were taken with rotation around an axis parallel to the longest edge of the crystal. CuK radiation was used and three layers were registered by the multiple-film technique. A visual estimate of 380 independent intensities was made by comparison with an intensity scale made from a suitable reflection on the zero layer.

The computational work involved in this study was to a large extent carried out using the computers BESK and FACIT EDB with the help of several computer programs.[5] The procedure of refinement by the least-squares method has been briefly described elsewhere.[6]

DERIVATION OF THE STRUCTURE

The Weissenberg photographs showed monoclinic symmetry. Guinier powder photographs, registered with monochromatized Cu$K\alpha_1$ radiation and using KCl ($a = 6.2919$ Å at 20°C) as an internal standard, gave the following monoclinic cell dimensions in Å:

$a_m = 17.64 \pm 0.01$
$b_m = 4.228 \pm 0.002$ $\quad \beta_m = 115.15 \pm 0.04°$
$c_m = 7.773 \pm 0.002$

Weissenberg photographs of the twinned crystals often looked orthorhombic. The unit cell may be described using an alternative coordinate system which reflects the pseudo-orthorhombic character actually existing in the structure:

$a_o = 15.88 \pm 0.02$
$b_o = 4.228 \pm 0.002$ $\quad \beta_o = 91.4 \pm 0.1°$
$c_o = 7.773 \pm 0.002$

The relation between the two representations of the unit are:

$$\vec{a}_o = \vec{c}_m + \vec{a}_m$$
$$\vec{b}_o = \vec{b}_m$$
$$\vec{c}_o = -\vec{c}_m$$

The reflections observed are in agreement with a highest symmetry of $C2/m$. The positions of the heavy atoms were found in the Patterson projection along [010]. These positions corresponding to an R-value of 0.26 between

Table 1. Weight analysis in Os_4Al_{13}

sin Θ-interval	$\overline{w \Delta^2}$	number of reflections in each interval
0.00—0.46	1.19	73
0.46—0.58	1.03	52
0.58—0.66	1.25	51
0.66—0.73	0.80	43
0.73—0.79	1.13	31
0.79—0.84	0.97	41
0.84—0.88	0.88	32
0.88—0.92	0.55	27
0.92—0.96	0.35	14
0.96—0.99	1.16	16
F_o-interval		
0 — 58	0.77	91
58 — 115	1.50	80
115 — 173	0.89	79
173 — 230	0.66	46
230 — 288	1.18	45
288 — 345	1.06	19
345 — 505	0.80	20

Table 2. Final atomic parameters and their e.s.d.'s

Atom	x	$\sigma(x)$ Å	y	z	$\sigma(z)$ Å	B Å^2	$\sigma(B)$ Å^2
Os_1	0.2940	0.0001	0	0.2915	0.0003	0.22	0.03
Os_2	0.4919	0.0001	½	0.1947	0.0003	0.22	0.03
Al_1	0.087	0.001	½	0.368	0.002	1.42	0.28
Al_2	0.257	0.001	0	0.613	0.002	1.00	0.26
Al_3	0.132	0.001	0	0.162	0.002	0.99	0.26
Al_4	0.290	0.001	½	0.087	0.002	1.60	0.29
Al_5	0.414	0.001	½	0.432	0.002	0.95	0.25
Al_6	0.409	0.001	0	0.194	0.002	1.60	0.28
Al_7	0		½	0		0.68	0.33

the $F_o(h0l)$ and $F_c(h0l)$ values, gave a starting point for the derivation of the electron density projection $\varrho(xz)$. In this way it was eventually possible to locate the sites of 8 osmium and 26 aluminium atoms all situated on mirror planes and to determine approximate positional parameters for these atoms. The suggested structure, containing two formula units Os_4Al_{13}, was then refined by least-squares method.

The weights were calculated using Hughes' weighting scheme. The final R-value is 0.103. The weight analysis obtained in the last cycle of refinement

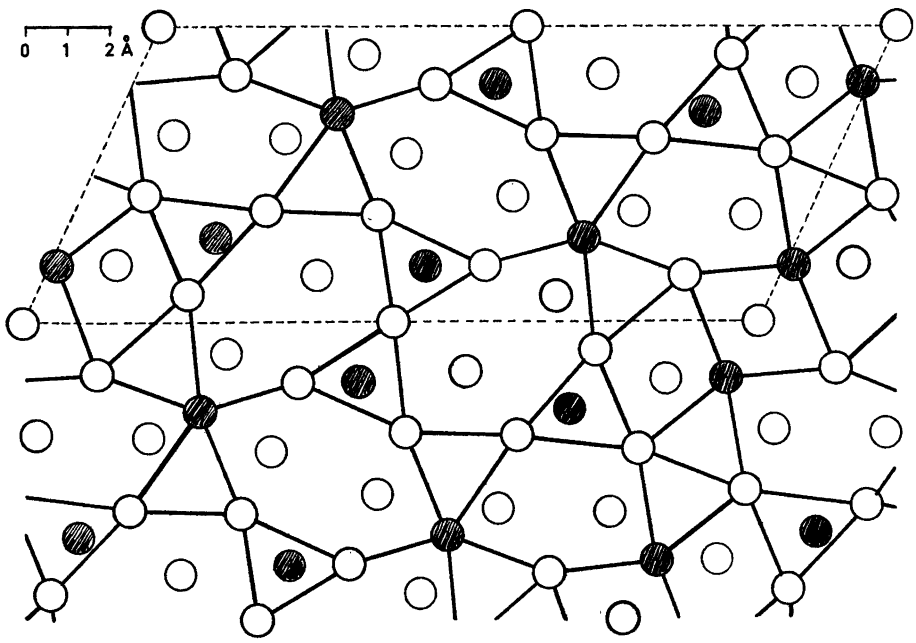

Fig. 1. The crystal structre of Os_4Al_{13} seen along the b-axis. Connected atoms at $y = 0$ and unconnected at $y = ½$. Os-atoms are shaded.

Table 3. Observed and calculated structure factors.

$k = 0$

h	l	F_o	F_c	h	l	F_o	F_c
2	0	37	34	$\bar{10}$	3	94	81
4	0	298	335	$\bar{8}$	3	375	−322
6	0	131	126	$\bar{6}$	3	220	12
8	0	95	106	$\bar{4}$	3	180	−139
10	0	405	408	$\bar{2}$	3	279	−248
12	0	< 29	27	0	3	52	− 49
14	0	289	274	2	3	368	−398
16	0	30	45	4	3	42	49
18	0	< 30	14	6	3	261	−275
$\bar{20}$	0	145	155	8	3	155	−153
$\bar{20}$	1	182	−190	10	3	104	− 97
$\bar{18}$	1	136	130	12	3	247	−227
$\bar{16}$	1	195	−189	14	3	< 25	− 13
$\bar{14}$	1	43	37	16	3	182	−192
$\bar{12}$	1	114	−128	$\bar{20}$	4	63	70
$\bar{10}$	1	87	− 94	$\bar{18}$	4	232	252
$\bar{8}$	1	259	247	$\bar{16}$	4	< 31	9
$\bar{6}$	1	185	−165	$\bar{14}$	4	353	360
$\bar{4}$	1	241	235	$\bar{12}$	4	< 28	43
$\bar{2}$	1	15	− 14	$\bar{10}$	4	93	90
0	1	18	17	$\bar{8}$	4	164	136
2	1	226	292	$\bar{6}$	4	< 22	− 17
4	1	83	− 86	$\bar{4}$	4	395	384
6	1	434	460	$\bar{2}$	4	63	− 55
8	1	< 24	10	0	4	67	62
10	1	144	157	2	4	52	44
12	1	165	170	4	4	154	−157
14	1	44	53	6	4	187	194
16	1	279	278	8	4	177	−169
$\bar{20}$	2	144	−146	10	4	151	127
$\bar{18}$	2	139	−142	12	4	134	−121
$\bar{16}$	2	< 31	− 26	14	4	121	−111
$\bar{14}$	2	356	−360	$\bar{22}$	5	245	234
$\bar{12}$	2	< 27	5	$\bar{20}$	5	< 25	16
$\bar{10}$	2	294	−295	$\bar{18}$	5	129	135
$\bar{8}$	2	126	−112	$\bar{16}$	5	104	103
$\bar{6}$	2	175	−171	$\bar{14}$	5	< 31	19
$\bar{4}$	2	359	−364	$\bar{12}$	5	378	410
$\bar{2}$	2	35	24	$\bar{10}$	5	28	3
0	2	362	−390	$\bar{8}$	5	397	415
2	2	49	− 38	$\bar{6}$	5	90	79
4	2	76	− 79	$\bar{4}$	5	127	117
6	2	153	−162	$\bar{2}$	5	305	281
8	2	< 27	24	0	5	88	79
10	2	255	−222	2	5	392	420
12	2	104	98	4	5	44	46
14	2	< 29	− 24	6	5	104	113
16	2	54	− 39	8	5	180	171
$\bar{22}$	3	96	− 81	10	5	< 25	6
$\bar{20}$	3	139	122	12	5	254	238
$\bar{18}$	3	109	−104	$\bar{18}$	6	149	−170
$\bar{16}$	3	< 31	21	$\bar{16}$	6	126	128
$\bar{14}$	3	< 29	− 33	$\bar{14}$	6	104	−100
$\bar{12}$	3	156	−143	$\bar{12}$	6	< 31	2

h	l	F_o	F_c
$\bar{10}$	6	60	50
$\bar{8}$	6	119	−106
$\bar{6}$	6	330	257
$\bar{4}$	6	129	−125
$\bar{2}$	6	194	207
0	6	82	81
2	6	< 31	30
4	6	202	196
6	6	< 28	− 23
8	6	258	240
$\bar{18}$	7	114	−125
$\bar{16}$	7	144	−166
$\bar{14}$	7	43	− 48
$\bar{12}$	7	283	−304
$\bar{10}$	7	< 30	0
$\bar{8}$	7	154	−149
$\bar{6}$	7	133	−135
$\bar{4}$	7	54	− 60
$\bar{2}$	7	217	−236
0	7	30	46
2	7	153	−151
$\bar{18}$	8	89	97
$\bar{16}$	8	90	−102
$\bar{14}$	8	55	− 62
$\bar{12}$	8	< 29	− 30
$\bar{10}$	8	195	−187
$\bar{8}$	8	79	57
$\bar{6}$	8	232	−229
$\bar{4}$	8	< 29	− 25
$\bar{2}$	8	107	−114
0	8	189	−185
$\bar{16}$	9	171	198
$\bar{14}$	9	< 22	15
$\bar{12}$	9	196	193
$\bar{10}$	9	< 24	33
$\bar{8}$	9	< 34	− 29
$\bar{6}$	9	126	132
$\bar{4}$	9	75	− 70
$\bar{2}$	9	188	185

$k = 1$

h	l	F_o	F_c
1	0	155	168
3	0	291	360
5	0	< 18	18
7	0	376	411
9	0	27	49
11	0	135	114
13	0	160	163
15	0	< 34	25
$\bar{17}$	0	231	202
$\bar{19}$	1	130	−180
$\bar{17}$	1	113	−108
$\bar{15}$	1	< 34	48
$\bar{13}$	1	287	−257
$\bar{11}$	1	102	95
$\bar{9}$	1	125	−106
$\bar{7}$	1	< 21	2
$\bar{5}$	1	126	87
$\bar{3}$	1	146	−171
$\bar{1}$	1	233	285
1	1	111	−109
3	1	117	116
5	1	235	222
7	1	< 26	12
9	1	344	296
11	1	104	−106
13	1	301	255
15	1	123	92
17	1	84	86
$\bar{21}$	2	264	−244
$\bar{19}$	2	29	− 34
$\bar{17}$	2	329	−272
$\bar{15}$	2	104	−103
$\bar{13}$	2	102	− 92
$\bar{11}$	2	304	−315
$\bar{9}$	2	< 25	6
$\bar{7}$	2	505	−603
$\bar{5}$	2	72	− 49
$\bar{3}$	2	196	−201
$\bar{1}$	2	172	−149
1	2	65	− 58
3	2	376	−463
5	2	< 25	10
7	2	235	−196
9	2	56	− 48
11	2	78	127
13	2	268	−189
15	2	112	89
17	2	176	−161
$\bar{15}$	3	328	−273
$\bar{13}$	3	< 32	42
$\bar{11}$	3	222	−180
$\bar{9}$	3	59	− 59
$\bar{7}$	3	< 23	− 15
$\bar{5}$	3	356	−402
$\bar{3}$	3	70	46
$\bar{1}$	3	434	−515
1	3	40	− 41
3	3	143	−156
5	3	254	−230
7	3	79	− 80
9	3	433	−380
11	3	< 34	− 32
13	3	173	−172
15	3	155	−138
$\bar{21}$	4	265	248
$\bar{19}$	4	< 30	− 18
$\bar{17}$	4	190	200
$\bar{15}$	4	69	78
$\bar{13}$	4	74	82
$\bar{11}$	4	296	258
$\bar{9}$	4	109	− 94
$\bar{7}$	4	267	221
$\bar{5}$	4	< 25	6
$\bar{3}$	4	< 25	19

h	l	F_o	F_c
$\bar{1}$	4	145	137
1	4	147	−141
3	4	206	190
5	4	198	−170
7	4	< 34	− 33
9	4	< 34	4
11	4	136	−129
$\bar{19}$	5	164	168
$\bar{17}$	5	< 33	− 33
$\bar{15}$	5	240	272
$\bar{13}$	5	< 34	40
$\bar{11}$	5	153	140
$\bar{9}$	5	208	193
$\bar{7}$	5	90	75
$\bar{5}$	5	363	373
$\bar{3}$	5	< 30	2
$\bar{1}$	5	201	219
1	5	160	158
3	5	90	91
5	5	245	242
7	5	< 34	16
9	5	198	186
$\bar{21}$	6	164	−174
$\bar{19}$	6	< 27	− 15
$\bar{17}$	6	< 31	− 29
$\bar{15}$	6	68	− 90
$\bar{13}$	6	69	83
$\bar{11}$	6	217	−210
$\bar{9}$	6	117	86
$\bar{7}$	6	< 33	34
$\bar{5}$	6	< 33	14
$\bar{3}$	6	199	183
$\bar{1}$	6	145	−129
1	6	217	220
3	6	< 34	− 43
5	6	140	127
7	6	175	164
$\bar{19}$	7	304	−302
$\bar{17}$	7	< 29	− 19
$\bar{15}$	7	243	−247
$\bar{13}$	7	101	− 89
$\bar{11}$	7	91	− 70
$\bar{9}$	7	247	−259
$\bar{7}$	7	34	− 42
$\bar{5}$	7	268	−322
$\bar{3}$	7	34	− 48
$\bar{1}$	7	< 33	2
1	7	171	−168
$\bar{17}$	8	93	− 99
$\bar{15}$	8	56	61
$\bar{13}$	8	240	−269
$\bar{11}$	8	31	42
$\bar{9}$	8	161	−167
$\bar{7}$	8	85	−108
$\bar{5}$	8	31	− 42
$\bar{3}$	8	233	−238
$\bar{9}$	9	180	183

h	l	F_o	F_c
		$k = 2$	
2	0	< 38	28
4	0	244	275
6	0	105	113
8	0	92	91
10	0	335	357
12	0	37	21
14	0	265	248
$\bar{16}$	0	32	42
$\bar{18}$	1	136	115
$\bar{16}$	1	198	−172
$\bar{14}$	1	< 26	32
$\bar{12}$	1	108	−109
$\bar{10}$	1	86	− 85
$\bar{8}$	1	233	210
$\bar{6}$	1	134	−140
$\bar{4}$	1	175	189
$\bar{2}$	1	< 10	− 9
0	1	< 10	13
2	1	208	237
4	1	73	− 73
6	1	320	391
8	1	< 23	8
10	1	133	141
12	1	167	158
14	1	< 74	45
$\bar{16}$	1	266	254
$\bar{20}$	2	137	−136
$\bar{18}$	2	138	−132
$\bar{16}$	2	< 25	− 24
$\bar{14}$	2	334	−326
$\bar{12}$	2	< 25	− 1
$\bar{10}$	2	232	−260
$\bar{8}$	2	109	−101
$\bar{6}$	2	146	−141
$\bar{4}$	2	285	−303
$\bar{2}$	2	20	24
0	2	261	−321
2	2	34	− 33
4	2	66	− 70
6	2	160	−145
8	2	< 25	27
10	2	215	−202
12	2	88	89
14	2	< 22	− 25
$\bar{16}$	2	39	− 37
$\bar{20}$	3	123	114
$\bar{18}$	3	96	− 97
$\bar{16}$	3	< 25	20
$\bar{14}$	3	< 26	− 32
$\bar{12}$	3	134	−130
$\bar{10}$	3	84	73
$\bar{8}$	3	279	−279
$\bar{6}$	3	< 19	11
$\bar{4}$	3	136	−123
$\bar{2}$	3	181	−209

h	l	F_o	F_c	h	l	F_o	F_c
0	3	38	− 41	$\bar{8}$	5	169	156
2	3	279	−344	$\bar{18}$	6	164	−156
4	3	32	42	$\bar{16}$	6	119	115
6	3	234	−248	$\bar{14}$	6	98	− 92
8	3	158	−139	$\bar{12}$	6	< 26	4
10	3	89	− 88	$\bar{10}$	6	65	47
$\bar{12}$	3	227	−208	$\bar{8}$	6	109	− 97
$\bar{20}$	4	59	67	$\bar{6}$	6	220	231
$\bar{18}$	4	212	228	$\bar{4}$	6	129	−111
$\bar{16}$	4	< 26	9	$\bar{2}$	6	179	185
$\bar{14}$	4	289	324	0	6	69	74
$\bar{12}$	4	< 25	37	2	6	< 25	25
$\bar{10}$	4	100	84	4	6	196	181
$\bar{8}$	4	165	122	6	6	< 20	− 21
$\bar{6}$	4	< 22	− 17	8	6	263	221
$\bar{4}$	4	332	329	$\bar{18}$	7	102	−116
$\bar{2}$	4	53	− 41	$\bar{16}$	7	140	−154
0	4	72	58	$\bar{14}$	7	32	− 40
2	4	54	39	$\bar{12}$	7	270	−275
4	4	150	−137	$\bar{10}$	7	< 26	0
6	4	183	172	$\bar{8}$	7	138	−139
8	4	191	−155	$\bar{6}$	7	134	−125
10	4	128	112	$\bar{4}$	7	57	− 51
$\bar{12}$	4	113	−110	$\bar{2}$	7	195	−215
$\bar{18}$	5	128	126	0	7	23	42
$\bar{16}$	5	89	96	2	7	147	−139
$\bar{14}$	5	< 26	20	$\bar{16}$	8	87	− 97
$\bar{12}$	5	333	366	$\bar{14}$	8	54	− 55
$\bar{10}$	5	26	2	$\bar{12}$	8	< 21	− 27
$\bar{8}$	5	360	366	$\bar{10}$	8	178	−171
$\bar{6}$	5	92	73	$\bar{8}$	8	54	52
$\bar{4}$	5	127	107	$\bar{6}$	8	196	−210
$\bar{2}$	5	264	252	$\bar{4}$	8	< 21	− 24
0	5	81	67	$\bar{2}$	8	97	−106
2	5	341	376	0	8	179	−170
4	5	52	43	$\bar{12}$	9	136	179
6	5	109	106				

is given in Table 1 and the final atomic parameters and their e.s.d.'s are given in Table 2. The observed and calculated F-values are given in Table 3.

THE STRUCTURE

The structure thus derived is built up of plane nets of atoms, illustrated by the connected atoms at $y = 0$ in Fig. 1. The nets are repeated along [010] by a 2_1 axis of $C2/m$.

The interatomic distances shorter than 3.5 Å are listed in Table 4. The mean distances and the coordinations around the various atoms are shown in Table 5, atoms at larger distances than 3 Å being disregarded.

The standard deviations in the interatomic distances are:

Os—Al_7	0.004 Å
Os—Al_{1-6}	0.03 Å
Al_7—Al_{1-6}	0.03 Å
Al_{1-6}—Al_{1-6}	0.04 Å

Table 4. Interatomic distances in Os_4Al_{13} (Å).

Os_1—	Al_6	2.457		Os_2	2.587
	$2Al_2$	2.531		Os_2	2.675
	Al_1	2.565		Al_4	2.825
	Al_3	2.586		$2Al_2$	2.894
	$2Al_4$	2.627		$2Al_1$	2.962
	Al_4	2.654		$2Al_7$	2.983
	Al_2	2.846		$(2Al_6$	3.299)
	$2Al_5$	2.855	Al_4—	$2Os_1$	2.627
Os_2—	$2Al_6$	2.570		Os_1	2.654
	Al_3	2.587		$2Al_4$	2.573
	Al_5	2.637		Al_5	2.623
	$2Al_7$	2.639		Al_2	2.794
	$2Al_1$	2.667		Al_3	2.825
	Al_3	2.675		$2Al_6$	2.835
	Al_5	2.738		$(Al_6$	3.221)
	$(Os_2$	3.161)		$(Os_2$	3.285)
	$(Al_4$	3.285)	Al_5—	Os_2	2.637
Al_1—	Os_1	2.565		Os_2	2.738
	$2Os_2$	2.667		$2Os_1$	2.855
	Al_7	2.588		Al_4	2.623
	$2Al_5$	2.628		$2Al_1$	2.628
	Al_2	2.693		Al_5	2.733
	Al_6	2.823		$2Al_6$	2.787
	$2Al_3$	2.962		Al_2	2.888
	$(Al_6$	3.376)	Al_6—	Os_1	2.457
	$(2Al_4$	3.485)		$2Os_2$	2.570
Al_2—	$2Os_1$	2.531		Al_7	2.639
	Os_1	2.846		$2Al_5$	2.787
	$2Al_2$	2.693		Al_1	2.823
	Al_1	2.693		$2Al_2$	2.835
	Al_4	2.794		$(Al_4$	3.221)
	Al_5	2.888		$(Al_1$	3.376)
	$2Al_3$	2.894	Al_7—	$4Os_2$	2.639
	$(Al_3$	3.232)		$2Al_1$	2.588
	$(2Al_1$	3.485)		$2Al_6$	2.639
Al_3—	Os_1	2.586		$2Al_3$	2.983

Table 5. Coordination and mean values of interatomic distances (in Å) in Os_4Al_{13}.

	Os_1— 11 Al	2.649	
	Os_2— 10 Al	2.639	
Al_1— 3 Os	2.633	— 7 Al	2.755
Al_2— 3 Os	2.636	— 7 Al	2.793
Al_3— 3 Os	2.616	— 7 Al	2.929
Al_4— 3 Os	2.646	— 7 Al	2.723
Al_5— 4 Os	2.771	— 7 Al	2.725
Al_6— 3 Os	2.532	— 6 Al	2.784
Al_7— 4 Os	2.639	— 8 Al	2.798
Al— Os mean dist.	2.645	Al—Al mean dist.	2.787

The Os—Al distances are in the range 2.46—2.86 Å and the Al—Al distances in the range 2.57—2.96 Å. The mean values of the Os—Al and Al—Al distances are 2.65 Å and 2.78 Å. These mean distances are in excellent concordance with those found in Fe_4Al_{13}, *viz.* 2.55 Å for the Fe—Al distances and 2.77

Å for the Al—Al distances, taking into consideration the fact that the radius of Os should be about 0.1 Å larger than that of Fe. It is, however, worth mentioning that no extremely short distances, as those found for some Fe—Al and Al—Al contacts in Fe_4Al_{13}, are present in Os_4Al_{13}. Thus while in the former compound the Al—Al distances fall into two ranges (2.60—2.75 Å and 2.83—2.95 Å), a similar division of these distances is not present in the osmium phase.

This structure will be further discussed when other structures of this type, now under study, have been determined.

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