The Crystal Structure of Ru_4Al_{13}

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The crystal structure of Ru_4Al_{13} has been determined and refined by least-squares techniques on the basis of three-dimensional X-ray single-crystal data. The lattice parameters for the monoclinic cell are:

$$a = 15.86 \text{ Å}, \ b = 8.188 \text{ Å}, \ c = 12.74 \text{ Å}, \ \beta = 107.8°$$

The phase is isotypic with Fe_4Al_{13}, space group $C2/m$. The relations between Os_4Al_{13} and the Fe_4Al_{13}-type of structure are discussed.

In previous reports on the crystal chemistry of aluminium alloys of the group VIII metals, the structures of some phases with the composition Me_4Al_{13} have been described *viz.* FeAl₃ (of ideal composition Fe_4Al_{13}) [1,2] Co_4Al_{13} [3] and Os_4Al_{13}.[4] The structures of Fe_4Al_{13} and Co_4Al_{13} are almost identical but differ considerably from that of Os_4Al_{13}. The compound Ru_4Al_{13} described in this work is isomorphous with Fe_4Al_{13}.

EXPERIMENTAL

An alloy of the composition Ru_4Al_{13} was prepared from ruthenium powder (L. Light & Co., about 99.99 %) and aluminium ribbon (E. Merck AG, at least 99.99 %) by melting in an electric arc furnace under an atmosphere of argon. The melt formed by the alloy is very brittle and crystalline. The crystals are prismatic and almost always twinned like those found in the corresponding Fe_4Al_{13} compound.[1] A single crystal could, however, be found and this was used to collect complete X-ray single-crystal data with $CuK\alpha$ radiation. The Weissenberg photographs which were taken with [001] as the rotation axis showed monoclinic symmetry. About a thousand independent reflections from eight layer lines were estimated visually with a standard scale. The crystal was less than 0.01 mm in all dimensions and no correction for absorption was applied. The refinement of the structure was made by using a least-squares program on the computor FACIT EDB.[5]

THE REFINEMENT OF THE STRUCTURE

The structural similarity between the present phase and Fe_4Al_{13} was obvious from the X-ray data. Guinier powder photographs, registered with

Table 1. Weight analysis in Ru$_4$Al$_{13}$.

sin Θ interval	$w\Delta^2$	Number of independent reflections	$\|F_o\|$ interval	$w\Delta^2$	Number of independent reflections
0.00 — 0.46	0.88	180	0 — 45	1.16	181
0.46 — 0.58	0.78	139	45 — 90	0.98	183
0.58 — 0.66	0.67	119	90 — 135	1.36	228
0.66 — 0.73	1.45	112	135 — 180	0.76	140
0.73 — 0.79	1.18	88	180 — 225	0.93	98
0.79 — 0.84	1.04	98	225 — 270	0.72	56
0.84 — 0.88	0.80	73	270 — 315	0.49	32
0.88 — 0.92	1.11	77	315 — 360	0.33	21
0.92 — 0.96	0.76	46	360 — 405	0.59	15
0.96 — 0.99	1.70	51	405 <	0.51	33

Cu$K\alpha_1$ radiation and using KCl as an internal standard, gave the following cell dimensions in Å

$$a = 15.862 \pm 0.006$$
$$b = 8.188 \pm 0.003 \qquad \beta = 107.77° \pm 0.08$$
$$c = 12.736 \pm 0.004$$

These dimensions are similar to those reported for Fe$_4$Al$_{13}$ and Co$_4$Al$_{13}$.

Fe$_4$Al$_{13}$ has been described by Black [1,2] as having the symmetry $C2/m$. The structure of Co$_4$Al$_{13}$ described by Hudd and Taylor [3] is very similar to

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

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B Å^2	$\sigma(B)$Å^2
Ru$_1$	0.0857	0.0002	0		0.3827	0.0003	0.41	0.04
Ru$_2$	0.4017	0.0002	0		0.6233	0.0003	0.52	0.04
Ru$_3$	0.0920	0.0002	0		0.9885	0.0003	0.51	0.04
Ru$_4$	0.4007	0.0002	0		0.9853	0.0003	0.56	0.04
Ru$_5$	0.3193	0.0001	0.2961	0.0002	0.2781	0.0002	0.57	0.03
Al$_6$	0.0667	0.0007	0		0.1740	0.0012	1.05	0.18
Al$_7$	0.3208	0.0007	0		0.2812	0.0013	1.13	0.18
Al$_8$	0.2383	0.0007	0		0.5354	0.0013	1.30	0.19
Al$_9$	0.0724	0.0006	0		0.5805	0.0012	0.79	0.17
Al$_{10}$	0.2396	0.0007	0		0.9565	0.0013	1.43	0.20
Al$_{11}$	0.4805	0.0006	0		0.8277	0.0011	0.55	0.15
Al$_{12}$	$\frac{1}{2}$		0		$\frac{1}{2}$		1.09	0.25
Al$_{13}$	0.3112	0.0006	0		0.7729	0.0011	0.53	0.15
Al$_{14}$	0.0834	0.0007	0		0.7874	0.0013	1.33	0.19
Al$_{15}$	0.1859	0.0005	0.2197	0.0009	0.1098	0.0009	0.99	0.12
Al$_{16}$	0.3657	0.0004	0.2168	0.0008	0.1107	0.0008	0.81	0.12
Al$_{17}$	0.1770	0.0005	0.2222	0.0010	0.3342	0.0009	1.41	0.13
Al$_{18}$	0.4909	0.0005	*0.2332	0.0009	0.3298	0.0009	1.00	0.12
Al$_{19}$	0.3639	0.0004	0.2256	0.0009	0.4822	0.0008	0.88	0.12
Al$_{20}$	0		0.2499	0.0012	0		0.69	0.16

* corresponding coordinate given by Black is probably a misprint.

Table 3. Part of the Guinier powder pattern of Ru_4Al_{13} ($CuK\alpha_1$).

h k l	$10^5 \sin^2 \Theta_{obs}$	$10^5 \sin^2 \Theta_{calc}$	I_{obs}	I_{calc}
0 0 1	—	403	—	0.3
2 0 0	—	1040	—	0.4
$\bar{2}$ 0 1	—	1048	—	0.0
1 1 0	1144	1145	vw	2.8
$\bar{1}$ 1 1	1348	1350	w	13.7
0 0 2	—	1613	—	1.3
1 1 1	1747	1746	w	8.8
$\bar{2}$ 0 1	1839	1839	vvw	1.8
$\bar{2}$ 0 2	1859	1863	vw	2.4
$\bar{1}$ 1 2	—	2363	—	0.1
$\bar{3}$ 1 1	—	3035	—	0.0
1 1 2	—	3154	—	0.5
3 1 0	—	3225	—	0.2
2 0 2	3442	3444	st	51.1
$\bar{2}$ 0 3	3482	3484	st	56.2
0 2 0	3438	3540	m	19.2
0 0 3	3626	3630	st	79.8
$\bar{3}$ 1 2	—	3652	—	0.2
$\bar{4}$ 0 1	3773	3773	m	20.2
0 2 1	3946	3943	vw	5.8
4 0 0	4164	4160	st	43.9
$\bar{1}$ 1 3	—	4181	—	0.1
$\bar{4}$ 0 2	4194	4192	st	41.9
3 1 1	—	4221	—	0.2
2 2 0	~4582	4580	vst	56.5
$\bar{2}$ 2 1		4588		42.5
$\bar{3}$ 1 3	—	5076	—	0.0
0 2 2	5154	5153	st	62.8
4 0 1		5354		19.8
1 1 3		5368		0.6
2 2 1	~5380	5378	vst	35.4
$\bar{2}$ 2 2		5402		26.9
$\bar{4}$ 0 3		5418		51.2
2 0 3	5854	5856	vw	8.9
$\bar{2}$ 0 4	5912	5912	vw	10.8
3 1 2	—	6025	—	0.4
0 0 4	6458	6453	vw	4.5
$\bar{5}$ 1 1	—	6800	—	0.0
$\bar{1}$ 1 4	—	6807	—	0.4
2 2 2	6982	6984	vw	4.4
$\bar{5}$ 1 2	—	7022	—	0.0
$\bar{2}$ 2 3	7026	7024	vw	3.3
0 2 3	1775	7170	vw	6.9

Fe_4Al_{13} but was found to have the lower space group Cm. The latter symmetry permits the separation of 8- and 4-fold positions of $C2/m$ into two sets of 4- and 2-fold positions respectively.

The investigation of Ru_4Al_{13} was started using the structure reported for Fe_4Al_{13} as a trial model. The structure was refined by the least-squares method. The weights were calculated using Hughes' weighting scheme. The final R value was 0.114. The weight analysis obtained in the last cycle of refinement is given in Table 1, the final atomic parameters in Table 2 and the Guinier pattern in Table 3.

Table 4. The interatomic distances in Ru_4Al_{13}. Upper limit 3.3 Å. The numbers represent: central atom, neighbour (number of such neighbours), followed by the distance in Å.

1—	6(1)	2.582	6—	1(1)	2.582	12—	2(2)	2.528
	8(1)	2.602		3(1)	2.514		18(4)	2.859
	9(1)	2.591		3(1)	2.727		19(4)	2.798
	9(1)	2.687		14(1)	2.573			
	14(1)	2.887		15(2)	2.902	13—	2(1)	2.712
	17(2)	2.517		17(2)	2.891		4(1)	2.644
	18(2)	2.621		20(2)	2.964		5(2)	2.583
	19(2)	2.795					8(1)	2.890
			7—	5(2)	2.425		10(1)	2.895
2—	8(1)	2.490		15(2)	3.119		11(1)	2.559
	11(1)	2.520		16(2)	3.053		15(2)	2.731
	12(1)	2.528		17(2)	3.148		17(2)	2.688
	13(1)	2.712		18(2)	3.208			
	17(2)	2.727		19(2)	3.060	14—	1(1)	2.887
	18(2)	2.507					3(1)	2.522
	19(2)	2.519	8—	1(1)	2.602		5(2)	2.579
				2(1)	2.489		6(1)	2.573
3—	3(1)	3.022		5(2)	3.255		9(1)	2.588
	6(1)	2.514		9(1)	2.860		10(1)	2.742
	6(1)	2.727		13(1)	2.890		16(2)	2.659
	10(1)	2.495		17(2)	3.049		18(2)	2.705
	14(1)	2.522		17(2)	2.894			
	15(2)	2.538		19(2)	2.943	15—	3(1)	2.538
	16(2)	2.817		19(2)	2.739		4(1)	2.758
	20(2)	2.543					5(1)	2.586
			9—	1(1)	2.591		6(1)	2.902
4—	4(1)	3.056		1(1)	2.687		7(1)	3.119
	10(1)	2.469		5(2)	2.664		10(1)	2.965
	11(1)	2.679		8(1)	2.860		10(1)	2.826
	11(1)	2.547		9(1)	2.569		13(1)	2.731
	13(1)	2.644		14(1)	2.588		16(1)	2.848
	15(2)	2.758		18(2)	2.791		16(1)	2.725
	16(2)	2.560		19(2)	2.683		17(1)	2.904
	20(2)	2.555					20(1)	2.863
			10—	3(1)	2.495			
5—	7(1)	2.425		4(1)	2.468	16—	3(1)	2.817
	8(1)	3.255		5(2)	3.298		4(1)	2.560
	9(1)	2.664		13(1)	2.895		5(1)	2.543
	10(1)	3.298		14(1)	2.742		7(1)	3.053
	13(1)	2.583		15(2)	2.965		10(1)	2.935
	14(1)	2.579		15(2)	2.828		10(1)	2.833
	15(1)	2.586		16(2)	2.935		11(1)	2.925
	16(1)	2.543		16(2)	2.833		14(1)	2.659
	17(1)	2.638					15(1)	2.848
	18(1)	2.649	11—	2(1)	2.520		15(1)	2.725
	19(1)	2.543		4(1)	2.679		18(1)	2.892
				4(1)	2.547		20(1)	2.904
				13(1)	2.559			
				16(2)	2.925			
				18(2)	2.903			
				20(2)	2.948			

17—	1(1)	2.517
	2(1)	2.727
	5(1)	2.638
	6(1)	2.891
	7(1)	3.148
	8(1)	3.049
	8(1)	2.894
	13(1)	2.688
	15(1)	2.904
	18(1)	2.957
	19(1)	2.988
	19(1)	2.645
18—	1(1)	2.621
	2(1)	2.507
	5(1)	2.649
	7(1)	3.208
	9(1)	2.791
	11(1)	2.903
	12(1)	2.859
	14(1)	2.705
	16(1)	2.892
	17(1)	2.957
	19(1)	3.197
	19(1)	2.771
19—	1(1)	2.795
	2(1)	2.519
	5(1)	2.543
	7(1)	3.060
	8(1)	2.943
	8(1)	2.739
	9(1)	2.683
	12(1)	2.798
	17(1)	2.988
	17(1)	2.645
	18(1)	3.120
	18(1)	2.771
20—	4(2)	2.544
	5(2)	2.555
	7(2)	2.963
	11(2)	2.948
	15(2)	2.863
	16(2)	2.904

Table 5. Distances in Me_4Al_{13} compounds and their elements.

Compound	Bond	CN	Range of distance in Å	Average distance in Å
Al fcc	Al—Al	12		2.86
Fe bcc 20°C	Fe—Fe	8		2.48
Fe fcc 916°C	Fe—Fe	12		2.57
Ru hcp	Ru—Ru	6 + 6	2.65 — 2.71	2.68
Os hcp	Os—Os	6 + 6	2.68 — 2.74	2.71
Fe_4Al_{13}	Fe—Al	~10	2.26 — 2.84	2.55
	Al—Al		2.45 —	
Ru_4Al_{13}	Ru—Al	~10	2.43 — 2.89	2.60
	Al—Al		2.56 —	
Os_4Al_{13}	Os—Al	10, 11	2.46 — 2.86	2.65
	Al—Al	~10	2.57 — 2.96	2.79

The non-centrosymmetric Co_4Al_{13} was then taken as a trial structure in a second calculation but the result showed no indications of Ru_4Al_{13} having a lower symmetry than $C2/m$.

Several aluminium sites of Fe_4Al_{13} and Co_4Al_{13} are reported to be partially occupied by 30—70 % aluminium. According to the B values given in Table 2 there seems to be no such extensive partial occupation by aluminium in Ru_4Al_{13}.

DISCUSSION

The interatomic distances are given in Table 4. The standard deviations for these are less than 0.02 Å. The numbering of the atoms in this table and in Table 2 is the same as used by Black in the first paper on Fe_4Al_{13}.[1] In the second paper on Fe_4Al_{13},[2] where the interatomic distances are given, the atoms Al_7 and Al_{14} have been interchanged.

A comparison between the atomic distances of Fe_4Al_{13} and Ru_4Al_{13} shows that the coordinations around equivalent atoms in the two structures are the same. However, the ranges of distance are different as shown in Table 5. This is because of the extremely short distances found in Fe_4Al_{13}. On the other hand, the ranges of distance found in Ru_4Al_{13} are almost identical to those found in Os_4Al_{13}, except for the upper limit of the Al—Al distances (*cf.* Table 5). According to the distribution of Al—Al distances around 3 Å found in Ru_4Al_{13} there is no definite upper limit like that found for Al—Al distances in Os_4Al_{13}. Well defined coordination shells indicating close packing are formed around all the atoms of Os_4Al_{13} and all the ruthenium atoms of Ru_4Al_{13}. This is not the case with all the aluminium atoms of Ru_4Al_{13} and is caused by the aluminium atom numbered 7 which has only two contacts closer than 3.0 Å.

The average distances in the elements are given in Table 5. Os and Ru have about the same size and are considerably larger than Fe. According to this and the fact that Os_4Al_{13} is better packed, Ru_4Al_{13} should have the Os_4Al_{13} structure from geometrical reasons. This is, however, not the case and the Ru_5 atom seems to play an important role in this connection. The arrangement around Ru_1—Ru_4 is very similar to the arrangement around the Os atoms
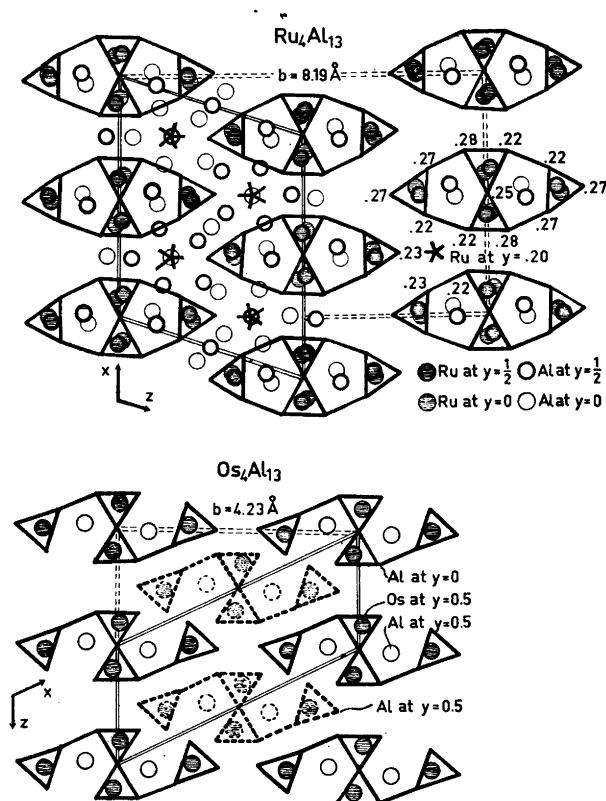
Fig. 1. The atomic arrangements in Os_4Al_{13} and Ru_4Al_{13}. There is an aluminium atom at each corner of the triangles. These aluminium atoms form a puckered net at around $y = 1/4$ in Ru_4Al_{13}. The deviation from planarity is indicated in one of the figures of Ru_4Al_{13}. The cell dimensions for Os_4Al_{13} are: $a = 17.64$ Å, $b = 4.228$ Å, $c = 7.773$ Å, $\beta = 115.15°$.

in Os_4Al_{13} but differs completely from that around Ru_5. This fact is illustrated in Fig. 1. Os_4Al_{13} may be described as built up from column-like arrangements of the composition Os_4Al_{13} the projections of which are indicated in the figure. Very similar units of the same composition and containing $Ru_1 - Ru_4$ are found in the ruthenium phase. The Ru_5 atoms, at the asterisk-like positions in the figure, form almost straight $Ru_5 - Al_7 - Ru_5$ bonds along [010] and force Al_7 to have no other contact closer than 3.0 Å.

No explanation why the composition is the same in the two compounds has been found.

When looking at a three-dimensional model of Ru_4Al_{13} the most striking feature is the regular arrangement of the Ru atoms. Ru_5 is in the centre of a deformed petagonal prism formed by the other ruthenium atoms. Only fragments of this pattern are found in Os_4Al_{13}.

Compounds of similar composition and structures seem to exist in the rhodium and palladium systems. The crystals of these form very complicated twins but give a zero layer Weissenberg photograph around a rotation axis of 16.6 Å, which, as far as the strong reflections are concerned, is very like the corresponding zero layer photograph of Ru_4Al_{13}. The strong spots are approximately arranged in a 5-fold symmetry but this is more exactly so in the Pd and Rh compounds and these have much larger unit cells.

It seems likely that the approximately five-fold symmetry observed in the single-crystal patterns of these new, very complicated phases reflects an even more regular transition-metal structure than that found in Ru_4Al_{13}.

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