Acta Cryst. (1958). **11**, 231

Studies of Aluminium-Rich Alloys with the Transition Metals Manganese and Tungsten. I. The Crystal Structure of ε(W–Al)–WAl_4

BY J. A. BLAND*

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

AND D. CLARK

Department of Metallurgy, Royal Aircraft Establishment, Farnborough, England

(*Received* 10 *December* 1956 *and in revised form* 19 *August* 1957)

The crystal structure of WAl_4 has been determined with moderate accuracy. The space-group symmetry was found to be *Cm*, and precision lattice parameters were measured as $a = 5{\cdot}272$, $b = 17{\cdot}771$, $c = 5{\cdot}218$ Å, $\beta = 100°\ 12'$. The 'heavy atom' technique was used to find the approximate structure, and F_o syntheses were used in the refinement. The atomic arrangement is non-centrosymmetrical and the cell contains 30 atoms mostly confined to eight well-defined layers perpendicular to the *b* axis. There is a close similarity between the unit cells and structures of WAl_4, $MnAl_6$ and δ(Mn–Al)–Mn_4Al_{11}.

1. Introduction

The W–Al equilibrium diagram was determined by Clark (1940), who found several phases related by peritectic reactions at the aluminium-rich end of the diagram. The crystal structures of γ(W–Al) and δ(W–Al) have been determined recently with powder photographs: γ(W–Al) (Adam & Rich, 1954) has a structural composition WAl_{12} and δ(W–Al) corresponds to WAl_5 (Adam & Rich, 1955). Clark showed that the most probable composition of ε(W–Al) is WAl_4 but no previous crystallographic data have been published. The present paper reports the determination and refinement of the crystal structure of ε(W–Al). The two authors found the approximate structure independently and it was agreed that the refinement should be completed by J. A. B., using his own data.

2. Experimental

(i) *Specimens*

The ingot containing the ε(W–Al) phase was kindly presented by Dr J. Adam. The crystals were extracted electrolytically from the alloy and were in the form of thin plates, the large faces being (010). Crystals hand picked from the residue were analysed by Messrs Johnson, Matthey and Company Limited, who found a composition corresponding to the formula WAl_4, thus confirming the analysis of Clark.

(ii) *Unit cell*

The phase WAl_4 has monoclinic symmetry; Laue photographs and systematic absences are consistent with the space groups *C*2, *Cm*, *C*2/*m*. Accurate cell dimensions of a single crystal were determined by the method of Weisz, Cochran & Cole (1948), using a Geiger-counter spectrometer. The values are:

$$a=5{\cdot}272\pm0{\cdot}003,\ b=17{\cdot}771\pm0{\cdot}010,\ c=5{\cdot}218\pm0{\cdot}003\ \text{Å},\quad \beta=100°\ 12'\pm5'.$$

This cell is nearly the same as the triclinic cell of δ(Mn–Al)–Mn_4Al_{11} (Bland, 1958), which is also similar to the cell of $MnAl_6$ (Nicol, 1953).

The density, determined by displacement, was found to be $6{\cdot}6\pm0{\cdot}2$ g.cm.$^{-3}$ whilst that calculated on the basis of 6 tungsten atoms and 24 aluminium atoms per unit cell is 6·7 g.cm.$^{-3}$. The average atomic volume is 16·0 Å^3, which is equal to the atomic volume calculated for WAl_5 (Adam & Rich, 1955).

(iii) *X-ray intensities*

Reflexions in the [100], [001], [10$\bar{1}$], and [101] zones were collected on zero-layer Weissenberg photographs from a crystal of approximately rectangular cross-section $0{\cdot}08\times0{\cdot}05$ mm. for each setting. Filtered Mo $K\alpha$ radiation and a pack of four films were used and the intensities were estimated by visual comparison with a standard scale. A Buerger precession camera was used to record the [010] reflexions. The intensities were corrected for Lorentz and polarization factors but the absorption of the X-rays in the crystal was not taken into account.

3. The approximate structure

Analysis of the 0*k*0 reflexions indicated that most of the atoms lie on eight well defined layers parallel to the (010) face of the crystal with a distance of about

* Now at the Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Ontario, Canada.

2·2 Å between successive layers. Since the area of the *ac* face of the unit cell is small, the presence of two tungsten atoms in one layer would result in a distance of about 2·6 Å between them. Such a short distance is unlikely, for transition elements tend to avoid each other in the class of compounds to which WAl_4 belongs (Black, 1956). It is probable that the tungsten atoms are distributed so that there is one on each of six layers; the remaining two layers must therefore consist entirely of aluminium atoms.

The positions of the tungsten atoms were found from two-dimensional Patterson syntheses prepared from intensities in the [100] and [010] zones and shown in Fig. 1. Assuming that the prominent peaks correspond

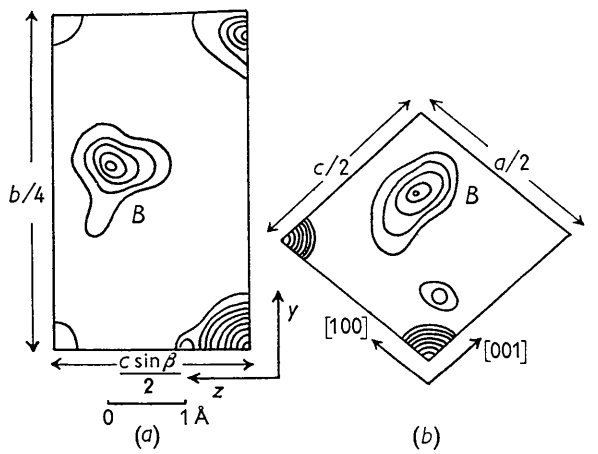

Fig. 1. Patterson functions of WAl_4 projected along (*a*) [100] and (*b*) [010]. Contours at equal arbitrary intervals in each case.

to W–W vectors, it is possible to derive both the tungsten positions and the space group. The peak *B* in the two projections has coordinates:

	[010]	[100]
x	0·330	—
y	—	0·135
z	0·330	0·330

This is taken to mean that there are at least two tungsten atoms separated by a vector with length and direction given by the point

(0·330, 0·135, 0·330)

so that not all of the tungsten atoms can be in special positions. If the space group is $C2$ or $C2/m$, both of which have a diad along the y axis, an atom in a general position (x, y, z) will be repeated to $(\bar{x}, y, \bar{z})$ and the corresponding vector in Patterson space will be in the position $(2x, 0, 2z)$. No peak appears in the [100] Patterson with co-ordinates $(0, 2z)$, so that $C2$ and $C2/m$ may be ruled out and Cm chosen. Using this non-centrosymmetrical space group, four of the six tungsten atoms were placed on the four-fold general position (0·330, 0·135, 0·330) and two on special positions (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, 0)$, and a reasonable agreement between observed and calculated Patterson functions was obtained. The structure factors for the six tungsten atoms in these positions were calculated and compared with the observed structure factors; an agreement factor $R \sim 20\%$ was obtained for reflexions with $\sin\theta/\lambda \leq 0{\cdot}5$ Å^{-1}. This confirmed the choice of space group with the tungsten atoms approximately in their correct positions but showed that the aluminium contribution to the scattering is small.

An electron-density synthesis on the [100] projection was computed, using the observed F_o values as coefficients and the phases calculated from the tungsten atoms alone. Most of the aluminium atoms were revealed as distorted peaks in the resulting map but some were obscured in the series-termination ripples from the 'heavy atom' peaks. To make certain that the positions assigned to the aluminium atoms were not spurious peaks, the process was repeated on the projections along the axes [101], [001] and [10$\bar{1}$]; no initial assumptions were made about the aluminium positions and the phases for the first F_o maps were calculated using the tungsten positions alone. The proposed structure is consistent with all four electron-density maps and is therefore considered to be correct. Additional support for the correctness of the structure is provided by packing considerations, for the interatomic distances all have reasonable values.

Lipson & Cochran (1953) have suggested that if the squares of the atomic numbers of heavy atoms and of the light atoms are approximately equal, then the 'heavy atom' method should work successfully. With WAl_4, $\Sigma f_H^2 \sim 9\Sigma f_L^2$, so that in terms of this working rule the aluminium atoms are too light, but subsequent refinement showed that aluminium atoms could be detected and their positions fixed with moderate accuracy.

4. Refinement of the structure

Refinement of the structure was carried out by means of F_o syntheses along the [100] and [101] directions. The phases corresponding to all the atoms in the structure were calculated. Only lower-order F_o's were included in the first syntheses and higher-order reflexions were introduced as refinement proceeded. Although in the final syntheses a large number of reflexions was used with $\sin\theta/\lambda \leq 1{\cdot}0$ Å^{-1}, the series-termination ripples from the tungsten atoms continued to be important and obscured or distorted the aluminium atom peaks. A converging factor $\exp[-\sin^2\theta/\lambda^2]$ was applied to the coefficients and the resulting projections are shown in Fig. 2. The centre of each atom was found by fitting a paraboloid to the nine points nearest to the peak position. The parameters of the atoms are listed in Table 1; the agreement factor R between the final F_c values and the F_o values on the same scale was about 10% on both projections. A list of observed and calculated F's is given in Table 2.

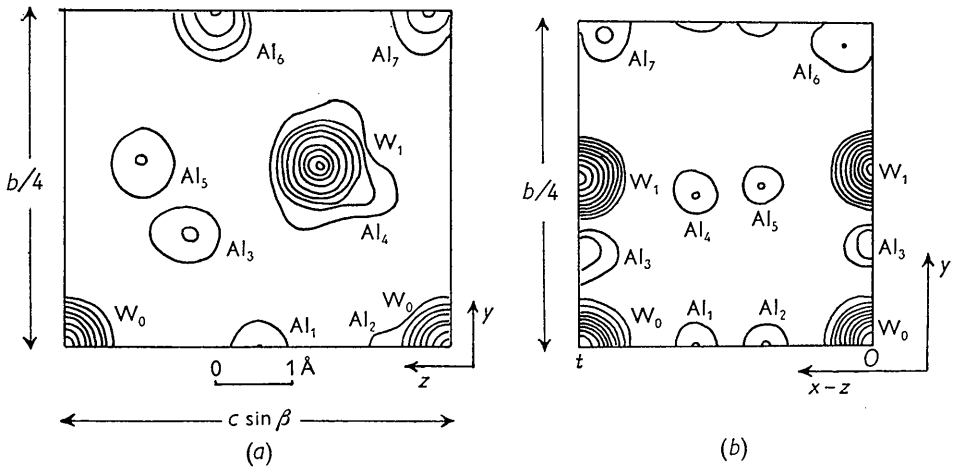

Fig. 2. Final F_o syntheses in (*a*) [100] and (*b*) [101] directions; in (*b*), the distance *ot* = projection of $\frac{1}{2}(\mathbf{a}-\mathbf{c})$. A converging factor has been introduced into both Fourier series, and the contours are plotted at equal arbitrary intervals. The $F(000)$ term has not been included. The scale shown is correct for (*a*); (*b*) is drawn on a slightly different scale.

Table 1. *Final atomic co-ordinates in* WAl_4

	x	*y*	*z*
W_0	0	0	0
W_1	0·336	0·137	0·331
Al_1	0·125	0	0·491
Al_2	0·494	0	0·129
Al_3	0·674	0·076	0·687
Al_4	0·824	0·118	0·213
Al_5	0·181	0·129	0·809
Al_6	0·682	0·232	0·583
Al_7	0·005	0·245	0·090

5. The accuracy of the structure

Inaccuracies in the determination of the atomic positions arise from: (i) Experimental errors in the observed intensities. (ii) The effect of the ripples from the tungsten atoms on the aluminium peaks and the difficulty of accurately locating the centres of distorted peaks.

It is possible to remove the second source of error by the use of F_o-F_c syntheses, but with a non-centrosymmetrical structure the method does not appear to lead to rapid refinement unless the atoms are very close to their correct positions. When the structure had reached the final stages, the accuracy of the F_o values was not considered sufficient to give a flat $\varrho_o-\varrho_c$ map near an accurately placed atom. F_o syntheses were therefore used for the refinement process, and partial allowance for the error due to the ripples was made by the use of convergence factors. Since no correction was made for the inaccuracies of the F_o's, the corresponding error in the parameters was estimated by using Booth's (1946) relation. The value of $\sigma(F_o)$ calculated from the mean of F_o-F_c was 8·0 where $F(000) \sim 252$ and this gives:

$$\text{W: } \sigma(x) = 0{\cdot}005 \text{ Å}; \quad \text{Al: } \sigma(x) = 0{\cdot}040 \text{ Å}.$$

This allows for the lack of a centre of symmetry in the crystal. It was also possible to make two independent estimates of the y parameters of the atoms from the two projections; these agreed to within 0·05 Å and it was concluded that a standard deviation of 0·10 Å in all the atomic positions is a proper estimate of the errors.

6. Description of the structure

The main feature of the structure is the sequence of eight well defined layers parallel to the (010) face of the crystal. The arrangement in each of the six layers at $y \sim 0, \frac{1}{2}, \frac{1}{8}, \frac{3}{8}, \frac{5}{8}, \frac{7}{8}$ is as shown in Fig. 3 with

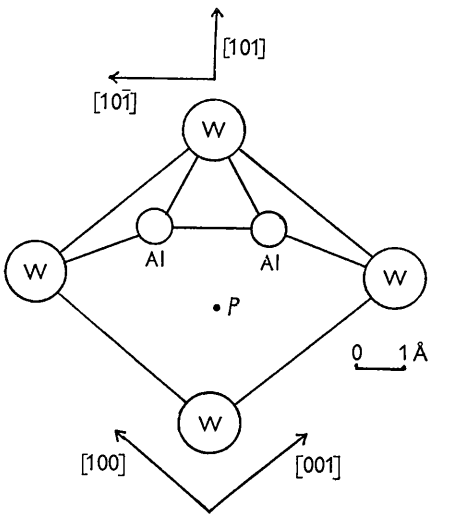

Fig. 3. The atomic arrangement in one layer of WAl_4 parallel to the *ac* face of the unit cell.

the first two layers situated on mirror planes and the other four layers slightly crumpled. There is a tungsten atom at each of the corners of the rhombus, side 5 Å and angle approximately 100°, and two aluminium atoms within the figure. The layers at 0 and

Table 2. F_o and F_c data for WAl_4

The two columns correspond to two different Weissenberg photographs; the calculated F values have been scaled to give F_c for comparison with F_o

hkl	F_o	F_c	Cos	Sin
000		252	1.00	0.00
020				
040	33	37	- 1.00	0.00
060	40	53	1.00	0.00
080	90	158	1.00	0.00
0,10,0		18	- 1.00	0.00
0,12,0				
0,14,0	72	90	1.00	0.00
0,16,0	75	85	1.00	0.00
0,18,0	36	23	- 1.00	0.00
0,20,0				
0,22,0	70	76	1.00	0.00
0,24,0	37	36	1.00	0.00
0,26,0				
0,28,0	40	28	1.00	0.00
0,30,0	48	51	1.00	0.00
001	88	73	0.00	1.00
021	54	49	0.98	0.19
041	110	100	0.80	0.59
061	52	50	0.50	- 0.86
081	57	69	0.22	- 0.96
0,10,1	58	67	0.81	0.59
0,12,1	57	69	0.77	0.64
0,14,1	30	39	- 0.14	- 0.99
0,16,1	32	43	0.65	0.77
0,18,1	59	56	0.82	0.59
0,20,1	31	32	1.00	0.00
0,22,1	42	46	- 0.28	- 0.96
0,24,1	29	30	1.00	0.00
0,26,1	50	52	0.71	0.71
0,28,1	26	27	0.62	0.79
0,30,1	27	27	- 0.10	- 0.99
0,32,1	38	37	0.93	0.37
0,34,1	28	32	0.79	0.61
0,36,1	26	22	0.08	- 0.99
002	54	39	- 0.21	0.98
022	36	35	1.00	0.00
042	140	145	0.78	- 0.64
062	55	57	0.50	0.86
082	47	41	0.20	0.98
0,10,2	55	61	0.81	- 0.59
0,12,2	76	90	0.75	0.67
0,14,2	43	48	0.14	0.99
0,16,2	17	23	0.61	0.79
0,18,2	51	64	0.79	- 0.61
0,20,2	42	43	0.97	- 0.25
0,22,2	36	37	0.12	0.99
0,24,2	27	17	0.92	- 0.39
0,26,2	45	57	0.66	- 0.75
0,28,2	21	24	0.85	0.53
0,30,2	27	30	0.34	0.94
003	108	95	0.99	- 0.06
023	24	20	0.96	- 0.28
043	32	30	1.00	0.00
063	52	46	1.00	- 0.00
083	67	65	0.99	- 0.06
0,10,3	25	17	- 0.98	0.19
0,12,3	12	11	0.41	- 0.92
0,14,3	70	68	1.00	- 0.00
0,16,3	31	30	0.97	- 0.25
0,18,3	38	36	- 0.95	0.31
0,20,3	15	17	0.90	0.45
0,22,3	50	65	1.00	- 0.00
0,24,3	9	13	0.76	- 0.66
0,26,3	24	24	- 0.94	0.35
0,28,3	38	33	0.98	- 0.19
004	74	61	- 0.21	- 0.98
024	60	59	0.85	0.52
044	68	66	0.85	0.52
064	27	31	0.84	- 0.54
084	56	57	- 0.07	0.99
0,10,4	68	75	0.77	0.64
0,12,4	54	50	0.79	0.62
0,14,4	26	26	0.44	- 0.89
0,16,4	27	26	0.45	- 0.90
0,18,4	62	62	0.81	0.59
0,20,4	20	28	0.97	0.25
0,22,4	29	34	- 0.13	- 0.99
0,24,4	25	26	0.96	0.28
0,26,4	40	52	0.76	0.65
0,28,4	10	14	0.77	- 0.64
005	56	50	0.17	0.98
025	29	24	0.98	- 0.19
045	60	52	0.59	- 0.81
065	40	32	0.58	0.81
085	52	43	0.42	0.91
0,10,5	51	43	0.79	- 0.62
0,12,5	27	34	0.42	- 0.91
0,14,5	42	39	0.09	0.99
0,16,5	24	29	0.74	0.68
0,18,5	47	58	0.82	- 0.58
0,20,5	15	12	0.86	- 0.51
0,22,5	35	39	0.05	0.99
0,24,5	16	17	0.92	- 0.40
0,26,5	37	46	0.75	- 0.67
006	74	84	1.00	- 0.00
026	30	40	1.00	0.00
046	27	43	- 0.93	0.37
066	55	53	0.99	0.06
086	62	61	0.99	- 0.06
0,10,6				
0,12,6	14	12	- 0.92	0.40
0,14,6	64	69	0.99	- 0.06
0,16,6	31	43	0.99	0.06
0,18,6	15	18	- 0.85	0.52
0,20,6	13	11	0.92	0.40
007	40	33	- 0.36	- 0.93
027	29	29	0.97	0.25
047	56	59	0.88	0.48
067	18	22	0.54	- 0.84
087	30	32	- 0.34	- 0.94
0,10,7	50	47	0.88	- 0.48
0,12,7	45	46	0.86	0.51
0,14,7	32	26	0.15	- 0.99
0,16,7		12		
0,18,7	40	47	0.89	0.47
008	46	49	- 0.09	0.99
028	24	30	0.90	0.44
048	46	55	0.81	- 0.59
068	28	36	0.95	0.31
088	32	40	0.11	- 0.99
0,10,8	32	40	0.74	- 0.68
0,12,8	24	38	0.82	- 0.58

hkl	F_o	F_c	Cos	Sin
000		150	1.00	0.00
020			1.00	0.00
040	21	21	- 1.00	0.00
060	29	29	1.00	0.00
080	62	90	1.00	0.00
0,10,0			- 1.00	0.00
0,12,0			1.00	0.00
0,14,0	49	50	1.00	0.00
0,16,0	54	52	1.00	0.00
0,18,0	15	15	- 1.00	0.00
0,20,0				
0,22,0	40	43	1.00	0.00
0,24,0	20	22	1.00	0.00
0,26,0				
0,28,0	20	15	1.00	0.00
0,30,0	21	31	1.00	0.00
0,32,0				
0,34,0				
0,36,0	20	74	1.00	0.00
111	57	55	0.99	- 0.06
131	20	17	- 0.99	0.11
151	7	6	0.87	0.50
171	42	45	0.99	- 0.10
191	16	23	0.99	0.02
1,11,1	19	20	- 0.99	0.01
1,13,1	35	36	0.99	0.02
1,15,1	41	42	0.99	- 0.09
1,17,1				
1,19,1	19	21	- 0.99	0.02
1,21,1	36	37	0.99	- 0.04
1,23,1	27	27	0.99	- 0.03
1,25,1	9	8	- 0.99	0.11
1,27,1				
1,29,1	33	33	0.99	- 0.08
1,31,1				
1,33,1	10	11	- 1.00	0.00
1,35,1	10	10	1.00	0.00
1,37,1	22	30	0.99	0.16
202	79	80	0.99	- 0.12
222	17	15	0.99	0.02
242	21	21	- 0.95	0.32
262	34	26	0.99	- 0.13
282	50	56	0.99	- 0.15
2,10,2	15	9	- 0.64	0.77
2,12,2				
2,14,2	41	48	0.99	- 0.10
2,16,2	33	34	0.98	- 0.22
2,18,2	18	18	- 0.87	0.50
2,20,2	8	7	0.93	- 0.35
2,22,2	37	38	0.99	- 0.09
2,24,2	12	13	0.95	- 0.31
2,26,2	16	12	- 0.75	0.66
2,28,2	23	19	0.97	- 0.23
2,30,2	22	28	0.99	- 0.09
2,32,2				
2,34,2		6	-0.46	0.87
2,36,2	22	23	0.99	- 0.10
313	59	57	0.98	- 0.16
333	15	13	- 0.86	0.50
353		6		
373	58	62	0.98	- 0.21
393	30	33	0.99	- 0.07
3,11,3	18	12	- 0.91	0.42
3,13,3	25	23	0.99	0.03
3,15,3	44	48	0.98	- 0.20
3,17,3		5	0.95	0.32
3,19,3	8	11	- 0.92	0.39
3,21,3	27	27	0.99	- 0.14
3,23,3	25	36	0.99	- 0.13
3,25,3				
3,27,3				
3,29,3	26	27	0.97	- 0.23
3,31,3	10	16	0.99	0.08
3,33,3	10	6	- 0.97	0.26
404	44	38	0.94	- 0.34
424	16	17	0.99	0.04
444	19	19	- 0.91	0.43
464	29	28	0.98	- 0.16
484	29	27	0.92	- 0.39
4,10,4	13	18	- 0.25	0.97
4,12,4				
4,14,4	37	36	0.97	- 0.21
4,16,4	18	14	0.92	- 0.39
4,18,4	17	22	0.82	0.57
4,20,4	9	8	- 0.97	- 0.26
4,22,4	26	33	0.97	- 0.22
515	40	41	0.96	- 0.28
535	11	13	- 0.63	0.78
555	8	7	- 0.59	0.80
575	47	45	0.95	- 0.31
595	20	20	0.97	- 0.22
5,11,5	12	12	- 0.46	0.89
5,13,5	15	11	0.97	- 0.21
5,15,5	36	41	0.96	- 0.29
5,17,5				
5,19,5		11	- 0.52	0.85
5,21,5	19	20	0.94	- 0.35
5,23,5	20	33	0.96	- 0.27
606	37	34	0.90	- 0.44
626	16	16	0.99	0.01
646	13	15	- 0.77	0.64
666	26	21	0.97	- 0.21
686	27	25	0.91	- 0.43
6,10,6		6		
6,12,6		5		
6,14,6	30	33	0.94	- 0.33
6,16,6	17	18	0.95	- 0.30
6,18,6	10	11	- 0.69	0.74
6,20,6	10	7	0.98	0.16
6,22,6	24	32	0.93	- 0.37
6,24,6	10	10	0.99	0.04
717	19	23	0.91	- 0.43
737	10	11	- 0.37	0.92
757		4		
777	25	27	0.91	- 0.44
797		10	0.94	- 0.34
7,11,7		12	- 0.31	0.94
7,13,7		12	1.00	- 0.00
7,15,7	25	28	0.88	- 0.48
808	22	34	0.88	- 0.49
828				
848	14	17	0.93	- 0.37
868	20	28	0.90	- 0.46

Corrections to above table.—All reflexions in the right-hand side of the table should have indices $hk\bar{h}$, not hkh. F_c for 0,36,0 should be 24, not 74.

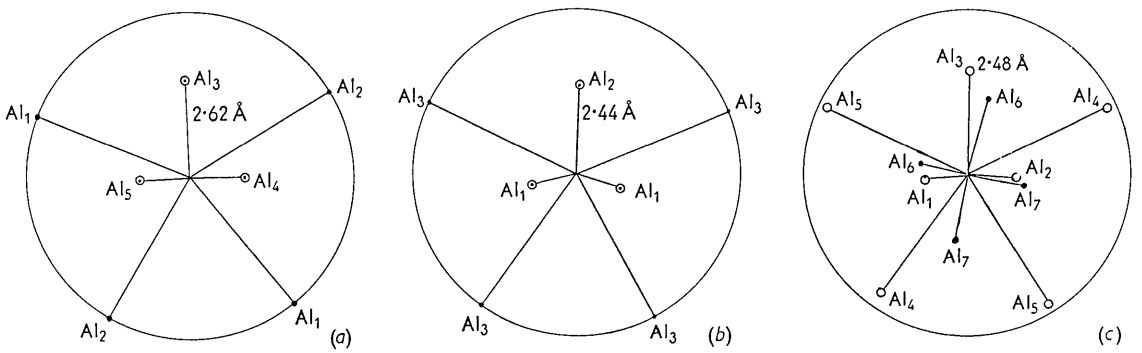

Fig. 4. Stereograms showing the environments of
(*a*) W_0 in WAl_4, 10 Al atoms; (*b*) Mn in $MnAl_6$, 10 Al atoms; (*c*) W_1 in WAl_4, 11 Al atoms.

$\frac{1}{8}$ have an atom Al_3, at $y = 0{\cdot}076$, between them, and the symmetrically equivalent layers at $\frac{1}{2}$ and $\frac{5}{8}$ are similarly separated by the atom Al_3, at $y = 0{\cdot}576$; the position of Al_3 is approximately 1·1 Å below P in Fig. 3. The remaining two layers, at $y \sim \frac{1}{4}$ and $\frac{3}{4}$, are identical and consist entirely of aluminium atoms in an approximately hexagonal net. The sequence may therefore be written:

y	$\frac{7}{8}$	0	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{3}{8}$	$\frac{1}{2}$	$\frac{5}{8}$	$\frac{3}{4}$	$\frac{7}{8}$
	$A_1 \times A_1 \times A_1$			C	$A_1 \times A_1 \times A_1$			C	A_1

← 17·8 Å →

where A_1 is the arrangement shown in Fig. 3, × represents the atom Al_3 between layers, and C is the approximately hexagonal net of aluminium atoms.

These layers fit together so that the transition metal atoms avoid each other. W_0 has 10 Al neighbours with an arrangement closely similar to the co-ordination of Mn by Al in $MnAl_6$ Fig. 4(*a*) and (*b*); W_1 has 11 Al neighbours, 10 of which are approximately arranged in this distinctive way, Fig. 4(*c*).

Table 3 lists the interatomic distances. The accuracy of the structure analysis is moderate, with a standard deviation of about 0·14 Å in each distance. The atomic diameter of tungsten in the pure metal is 2·75 Å and the diameter of aluminium is 2·86 Å, so that, when allowance is made for the co-ordinations observed in this structure, the 'normal' contact distances are approximately W–Al ~ 2·72 Å and Al–Al ~ 2·71 Å. On this basis, it appears that some of the W–Al distances are contracted; the shortest, W_1–Al_3 (2·48 Å), is significantly shorter than the 'normal' distance, and is in an orientation corresponding to a short Mn–Al_2 bond (2·44 Å) in $MnAl_6$.

7. Conclusion

The structure of WAl_4 has features in common with other aluminium–transition-metal structures; there are prominent layers of atoms, the transition elements avoid each other, there is a zone of strong reflexions corresponding to interplanar spacings of about 2 Å; and there is evidence of short distances between unlike atoms (Taylor, 1954). There is a close relation between WAl_4 and the structures of $MnAl_6$ and δ(Mn–Al) which is discussed in another paper (Bland, 1958). There is no obvious structural relation between WAl_4 and $MnAl_4$.

Table 3. *Interatomic distances in* WAl_4

Standard deviation 0·14 Å in each distance
Distances in Ångström units

W_0	2·53 (Al_1); 2·57 (Al_2); 2·62 (Al_4) (2)*; 2·62 (Al_3) (2); 2·74 (Al_5) (2); 2·85 (Al_1); 2·86 (Al_2); 3·32 (W_1) (2)
W_1	2·48 (Al_3); 2·65 (Al_4); 2·66 (Al_6); 2·71 (Al_5); 2·72 (Al_7); 2·74 (Al_7); 2·74 (Al_5); 2·82 (Al_4); 2·82 (Al_6); 2·83 (Al_1); 2·87 (Al_2); 3·32 (W_0)
Al_1	2·82 (Al_5) (2); 2·87 (Al_4) (2); 2·95 (Al_2); 3·10 (Al_3) (2); 3·12 (Al_3) (2); 2·53 (W_0); 2·83 (W_1) (2); 2·85 (W_0)
Al_2	2·71 (Al_4) (2); 2·95 (Al_1); 3·00 (Al_4) (2); 3·13 (Al_3) (2); 3·13 (Al_5) (2); 2·57 (W_0); 2·86 (W_0); 2·87 (W_1) (2)
Al_3	2·79 (Al_4); 2·84 (Al_6); 2·88 (Al_5); 2·89 (Al_5); 2·90 (Al_4); 3·00 (Al_2); 3·10 (Al_1); 3·11 (Al_1); 3·13 (Al_2); 2·48 (W_1); 2·62 (W_0)
Al_4	2·58 (Al_7); 2·71 (Al_2); 2·79 (Al_3); 2·87 (Al_1); 2·87 (Al_1); 2·90 (Al_3); 2·96 (Al_7); 2·99 (Al_6); 3·08 (Al_5); 2·62 (W_0); 2·65 (W_1); 2·82 (W_1)
Al_5	2·74 (Al_6); 2·78 (Al_7); 2·82 (Al_1); 2·88 (Al_3); 2·89 (Al_3); 3·03 (Al_7); 3·08 (Al_4); 3·13 (Al_2); 2·71 (W_1); 2·74 (W_1); 2·74 (W_0)
Al_6	2·61 (Al_7); 2·71 (Al_6); 2·71 (Al_6); 2·74 (Al_5); 2·82 (Al_3); 2·89 (Al_7); 2·99 (Al_7); 2·99 (Al_4); 2·66 (W_1); 2·82 (W_1)
Al_7	2·58 (Al_4); 2·61 (Al_6); 2·64 (Al_7); 2·64 (Al_7); 2·78 (Al_5); 2·89 (Al_6); 2·96 (Al_4); 2·98 (Al_6); 3·03 (Al_5); 2·72 (W_1); 2·74 (W_1)

(2)* Indicates that there are two symmetrically related neighbours of this type.

One of us (J. A. B.) wishes to thank Prof. N. F. Mott and Dr W. H. Taylor for the provision of facilities and for guidance, and Dr P. J. Black and Dr M. M. Woolfson for advice and helpful criticism. J. A. B. is indebted to the Department of Scientific and Industrial Research for a Senior Award, and also acknowledges grants from the Ministry of Supply (Basic Properties of Metals Committee) and from a fund provided by Messrs Imperial Chemical Industries Limited.

We should like to thank Dr M. V. Wilkes, Director of the Cambridge University Mathematical Laboratory, for allowing time on the EDSAC digital computer, and to acknowledge the help of Miss H. M. Bolton and Miss P. A. Dixon, who carried out the hand calculations.

References

ADAM, J. & RICH, J. B. (1954). *Acta Cryst.* **7**, 813.
ADAM, J. & RICH, J. B. (1955). *Acta Cryst.* **8**, 349.
BLACK, P. J. (1956). *Acta Met.* **4**, 172.
BLAND, J. A. (1958). *Acta Cryst.* **11**, 236.
BOOTH, A. D. (1946). *Proc. Roy. Soc.* A, **188**, 77.
CLARK, W. D. (1940). *J. Inst. Met.* **66**, 271.
LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures.* London: Bell.
NICOL, A. D. I. (1953). *Acta Cryst.* **6**, 285.
TAYLOR, W. H. (1954). *Acta Met.* **2**, 684.
WEISZ, O., COCHRAN, W. & COLE, W. F. (1948). *Acta Cryst.* **1**, 83.

Acta Cryst. (1958). **11**, 236

Studies of Aluminium-Rich Alloys with the Transition Metals Manganese and Tungsten. II. The Crystal Structure of δ(Mn–Al)–Mn_4Al_{11}

BY J. A. BLAND*

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 10 *December* 1956 *and in revised form* 19 *August* 1957)

Crystals of the triclinic alloy phase δ(Mn–Al) with an ideal formula Mn_4Al_{11} have been isolated from a ternary melt containing zinc. The space-group symmetry was found to be $P\bar{1}$, and the precision lattice constants measured as $a = 5{\cdot}092$, $b = 8{\cdot}862$, $c = 5{\cdot}047$ Å, $\alpha = 85°\ 19'$, $\beta = 100°\ 24'$, $\gamma = 105°\ 20'$. The approximate structure has been determined by direct methods and has been refined by difference syntheses. Abnormally short distances occur in the same orientation as in $MnAl_6$, relative to the transition metal atom. The relationship between the crystal structures of δ(Mn–Al), $MnAl_6$ and WAl_4 is considered in terms of similarly shaped co-ordination groups and well defined layers of atoms; the pattern of sites in each layer is derived from a crumpled 5-connected net. Related structures in the Fe–Al and Co–Al systems are discussed.

1. Introduction

The Mn–Al system was investigated crystallographically by Hofmann (1938), who found the cell constants of three phases: $\beta(MnAl_6)$, $\gamma(MnAl_4)$ and $\varepsilon(MnAl_3)$. Complete data have not previously been available for δ(Mn–Al) although Hofmann examined this phase and suggested that it is monoclinic or triclinic with two repeats of approximately 5 Å at an angle of about 101°. No determination of the chemical composition of this phase has been reported, but Raynor & Wakeman (1947) suggest that it may be $MnAl_4$. As a result of the present work it has been found that the structural formula of δ(Mn–Al) is Mn_4Al_{11}, so that the aluminium content is lower than that previously suggested.

2. Specimens

The following materials were used in the preparation:

(i) Pure zinc. The elements detected spectrographically were lead, cadmium, iron and calcium; the amount of each did not exceed 0·001%. This material was kindly presented by the Imperial Smelting Corporation Limited, of Avonmouth.
(ii) Super-purity aluminium kindly presented by the British Aluminium Company Limited.
(iii) Pure electrolytic manganese obtained from Messrs Johnson, Matthey and Company Limited.

The specimens were prepared by the method described by Raynor & Wakeman (1947). Single crystals were extracted electrolytically from slowly cooled zinc-rich alloys containing aluminium and manganese. I am indebted to Dr P. Vousden for making the ingot which contained crystals of the δ phase. The crystals have a tabular habit with well formed, highly reflecting faces, and an initial study of the morphology was made with an optical goniometer. The measurements of angles are consistent to within $\pm 3'$ so that an accurate determination of the cell constants and symmetry could be made (Table 1). The symmetry is triclinic but pseudo-monoclinic, and most of the faces have opposites which suggests the presence of a centre of symmetry.

The X-ray photographs obtained from a δ(Mn–Al) crystal containing a small amount of zinc were shown to be identical with those recorded using a single crystal of δ(Mn–Al) obtained from a binary melt.

* Now at the Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Ontario, Canada.