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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}

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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: β($MnAl_6$), γ($MnAl_4$) and ε($MnAl_3$). 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 ±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.

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Table 1. *Unit-cell constants of* δ(Mn–Al) *and* $\mathrm{MnAl_6}$

δ(Mn–Al)

Primitive cell (*p*)

$$a = 5{\cdot}092 \pm 0{\cdot}003\ \text{Å},\ b = 8{\cdot}862 \pm 0{\cdot}005\ \text{Å},\ c = 5{\cdot}047 \pm 0{\cdot}003\ \text{Å}$$
$$\alpha = 85^\circ\ 19' \pm 5',\ \beta = 100^\circ\ 24' \pm 5',\ \gamma = 105^\circ\ 20' \pm 5'$$

Pseudo-monoclinic cell, *C*-face centred (*m*)

$$a = 5{\cdot}092 \pm 0{\cdot}003\ \text{Å},\ b = 17{\cdot}098 \pm 0{\cdot}010\ \text{Å},\ c = 5{\cdot}047 \pm 0{\cdot}003\ \text{Å}$$
$$\alpha = 92^\circ\ 52' \pm 5',\ \beta = 100^\circ\ 24' \pm 5',\ \gamma = 88^\circ\ 38' \pm 5'$$
$$a:b:c = 0{\cdot}2978 : 1 : 0{\cdot}2951$$

Optical measurements

$$\alpha = 92^\circ\ 48',\ \beta = 100^\circ\ 30',\ \gamma = 88^\circ\ 32'$$
$$a:b:c = 0{\cdot}2980 : 1 : 0{\cdot}2952$$

$\mathrm{MnAl_6}$ (Nicol, 1953)

$$a = 4{\cdot}9811 \pm 0{\cdot}0005\ \text{Å},\ b = \tfrac{1}{2}(17{\cdot}7406) \pm 0{\cdot}0005\ \text{Å},$$
$$c = 4{\cdot}9811 \pm 0{\cdot}0005\ \text{Å}$$
$$\alpha = 90^\circ,\ \beta = 98^\circ\ 34',\ \gamma = 90^\circ$$

A ternary crystal was selected for the structure determination because its shape was more suitable for the collection of accurate intensities than a thin plate of the binary compound. In addition, the composition of the ternary was known with a moderate accuracy whereas a sufficient number of binary crystals could not be obtained for chemical analysis or density determination; the electrolytic method of extraction was not successful with binary ingots containing the δ phase.

Three chemical analyses of the ternary crystals were made: the first two by Messrs Johnson, Matthey and Company Limited, and the third, using a spectrographic method, by the Admiralty Materials Laboratory. Although the crystals came from the same melt the results cover a range of compositions:

	Mn	Al	Zn	
1.	41·8	53·75	4·05†	wt. %
2.	38·2	58·2	3·8†*	wt. %
3.	35·4	61·0	3·6*	wt. %

† Neglecting trace impurities. * Avarage of two analyses.

which correspond to:

	Mn	Al	Zn	
1.	27·0	70·8	2·2	atomic %
2.	23·9	74·1	2·0	atomic %
3.	21·8	76·4	1·9	atomic %

From these estimates it is possible to give a range within which the composition of the binary must lie. Allowing for the replacement of either aluminium or manganese by zinc the extremes of the range are:

$$\mathrm{Mn_{21}Al_{79}} \qquad \mathrm{Mn_{30}Al_{70}}\ \text{atomic}\,\%\,.$$

The ideal composition obtained by crystallographic considerations (§ 3) is:

$$\mathrm{M_{26{\cdot}7}A_{73{\cdot}3}}\ \text{atomic}\,\%\,,$$

which corresponds to the formula $\mathrm{Mn_4Al_{11}}$.

A determination of the density was made by the method of flotation; the mean value of several measurements was $4{\cdot}1 \pm 0{\cdot}1$ g.cm.$^{-3}$.

3. The unit cell and symmetry

The unit-cell edges and interaxial angles of a single crystal of δ(Mn–Al) were measured with a Geiger-counter spectrometer by the method of Weisz, Cochran & Cole (1948). Alternative unit cells are listed in Table 1, together with the results of the optical observations. A primitive unit cell (*p*), space group $P\bar{1}$, has been chosen with α acute, which is unconventional but is suitable for comparison with related structures. The other cell (*m*) is *C*-face centred and pseudo-monoclinic; it is suggested by the external morphology of the crystal. Relations between these alternatives are represented by the following equivalent directions:

$$[100]_p = [100]_m; \quad [010]_p = [\bar{1}10]_m; \quad [001]_p = [001]_m\,.$$

The pseudo-monoclinic cell is more convenient for the structure determination and, except where indicated, directions, indices and atomic positions will be referred to this cell. Analysis of the intensity distribution of X-ray reflexions using the method of Howells, Phillips & Rogers (1950) supports the morphological evidence for the presence of a centre of symmetry.

Both $\mathrm{WAl_4}$ (Bland & Clark, 1958) and $\mathrm{MnAl_6}$ (Nicol, 1953) have unit cells which are closely related to the cell *m*. The primitive cell of $\mathrm{MnAl_6}$, Table 1, containing 2 Mn and 12 Al atoms, has a volume of $\frac{1}{2} \times 435{\cdot}4$ Å^3 and the δ(Mn–Al) cell (*m*) has a volume of $432{\cdot}3$ Å^3. We therefore expect the latter to contain 28, 30 or 32 atoms, and, since the manganese content is higher than that of $\mathrm{MnAl_6}$, 6 or 8 of these atoms will be manganese. One important structural feature of complex aluminium-rich alloys is that the first-order co-ordination of the transition metal atom is usually irregular, that is, a transition metal atom does not usually lie on a centre of symmetry. It follows that the most likely number of manganese atoms is 8, occupying two sets of fourfold general positions. All the chemical analyses agree that the zinc content is about 2 atomic%, but it is not known whether the zinc replaces manganese or aluminium. The calculated density on the basis of 28 atoms per cell, with zinc replacing aluminium, is $3{\cdot}85$ g.cm.$^{-3}$ and for 32 atoms per cell, with zinc replacing manganese, the density is $4{\cdot}2$ g.cm.$^{-3}$. Both values are on the limits of the range of density measurements namely, $4{\cdot}1 \pm 0{\cdot}1$ g.cm.$^{-3}$. The composition $\mathrm{Mn_8Al_{22}}$ gives a density of $4{\cdot}05$ g.cm.$^{-3}$ with zinc replacing aluminium and $4{\cdot}0$ g.cm.$^{-3}$ with zinc replacing manganese; this formula is therefore favoured by the density measurements, and is confirmed by the structure determination.

4. X-ray intensity data

Reflexions from the four zones $[10\bar{1}]$, $[101]$, $[100]$ and

[001] were collected on zero-layer Weissenberg photographs from the crystal used in the determination of the cell constants; for each photograph the cross-section was rectangular with approximate dimensions $0{\cdot}04 \times 0{\cdot}09$ mm. A pack of four films was used for each exposure with Mo $K\alpha$ radiation and the intensities of the reflexions were estimated by visual comparison with an intensity scale. Lorentz and polarization corrections were applied to each reflexion.

The observed $I(hkl)$ values were placed on an approximately absolute scale and the corresponding unitary structure factors were determined using the method advocated by Lipson & Cochran (1953):

$$U(hkl) = \left(\frac{I(hkl)}{\bar{I}}\right)^{\frac{1}{2}} \left\{\sum_{j=1}^{N} n_j^2\right\}^{\frac{1}{2}},$$

where

$U(hkl)$ = unitary structure factor of a particular reflexion,

$I(hkl)$ = measured intensity of that reflexion on a relative scale,

$\bar{I}$ = average of intensities in the same region of $\sin\theta/\lambda$,

n_j = fraction of total cell content of electrons associated with jth atom,

N = number of atoms in the unit cell.

For δ(Mn–Al) we have

$$\left\{\sum_{j=1}^{N} n_j^2\right\}^{\frac{1}{2}} = 0{\cdot}27\,.$$

5. The approximate structure

(i) *The method of Harker–Kasper inequalities applied to the hkh reflexions*

There are about 15 reflexions in the $[10\bar{1}]$ zone with unitary structure factors greater than 0·25 (Table 2), and sign relations between them were found by applying the general inequality relation of Harker & Kasper (1948):

$$|U(hkl) \pm U(h'k'l')|^2 \leq \{1 \pm U(h+h',\, k+k',\, l+l')\} \times \{1 \pm U(h-h',\, k-k',\, l-l')\}\,.$$

Table 2. *Unitary structure factors and signs for fifteen reflexions in the zone* $[10\bar{1}]$

Indices	U	Douglas–Cochran signs	Harker–Kasper signs	hkl	$h'k'l'$
$3\bar{1}3$	0·65	+	+	Given	—
$2\bar{8}2$	0·59	+	+		
$0,\overline{16},0$	0·45	+	+	$0\bar{8}0$	$0\bar{8}0$
$\overline{171}$	0·41	+	+	$2\bar{8}2$	$3\bar{1}3$
$\overline{282}$	0·36	+	+	$2\bar{8}2$	$0,\overline{16},0$
$1\bar{9}1$	0·25		+	$3\bar{1}3$	$\overline{282}$
$0\bar{8}0$	0·57	a	a	Given	—
$\overline{373}$	0·50	a	a	$3\bar{1}3$	$0\bar{8}0$
$\bar{1},\overline{15},\bar{1}$	0·42	a	a	$\overline{171}$	$0\bar{8}0$
$2,\overline{16},2$	0·55	a	a	$2\bar{8}2$	$0\bar{8}0$
202	0·37	a	a	$2\bar{8}2$	$0\bar{8}0$
$3\bar{9}3$	0·54	a	a	$3\bar{1}3$	$0\bar{8}0$
$1\bar{7}1$	0·41	b	b	Given	—
$\overline{262}$	0·34		b	$1\bar{7}1$	$3\bar{1}3$
$0,\overline{14},0$	0·30	b	b	$1\bar{7}1$	$\overline{171}$

Two reflexions, $3\bar{1}3$ and $2\bar{8}2$, were given + signs, thereby fixing the origin on one of the four independent centres of symmetry, and the signs of $0\bar{8}0$ and $1\bar{7}1$ were designated a and b respectively. The remaining 11 signs were then found in terms of a and b by successive applications of the general inequality relation; they are listed in Table 2. In this way four possible sets of signs were derived, according to the signs selected for a and b, and the corresponding Fourier syntheses were computed. The coefficients were the F_o values multiplied by a converging factor which decreased linearly with decreasing $\sin\theta$. The electron-density map corresponding to $a = -$ and $b = +$ is shown in Fig. 1; the peaks A and F are identified as manganese atoms, the peaks B and E as superposed aluminium atoms, and single aluminium atoms are assigned to the peaks I and K. The arrangement of atoms at $y \sim 1/16$, peaks A and E, and at $y \sim 3/16$, peaks B and F, can be interpreted in terms of the two similar layers shown in Fig. 2(a) and 2(b), viewed in the $[10\bar{1}]$ direction. The centres of the peaks were estimated graphically and the double aluminium atoms were assumed to superpose exactly. On this basis the F_c values were found to be in reasonable agreement with the observed F_o's and the approximate structure was considered to be essentially correct. Although the superposition in peaks B and E of aluminium atoms not crystallographically related greatly simplified the determination of the approximate structure, it hindered subsequent attempts at refinement on this projection. The intensity data were therefore reserved to check the final structure obtained from the other projections.

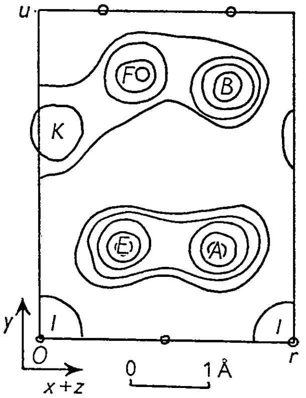

Fig. 1. The asymmetric unit of the first F_o synthesis of δ(Mn–Al) in the $[10\bar{1}]$ direction using 15 terms with signs derived by Harker–Kasper inequalities. A converging factor has been applied; the contours are at equal arbitrary intervals. or is the projection of $\frac{1}{2}(\mathbf{a}+\mathbf{c})$ and ou is the projection of $\frac{1}{4}\mathbf{b}$.

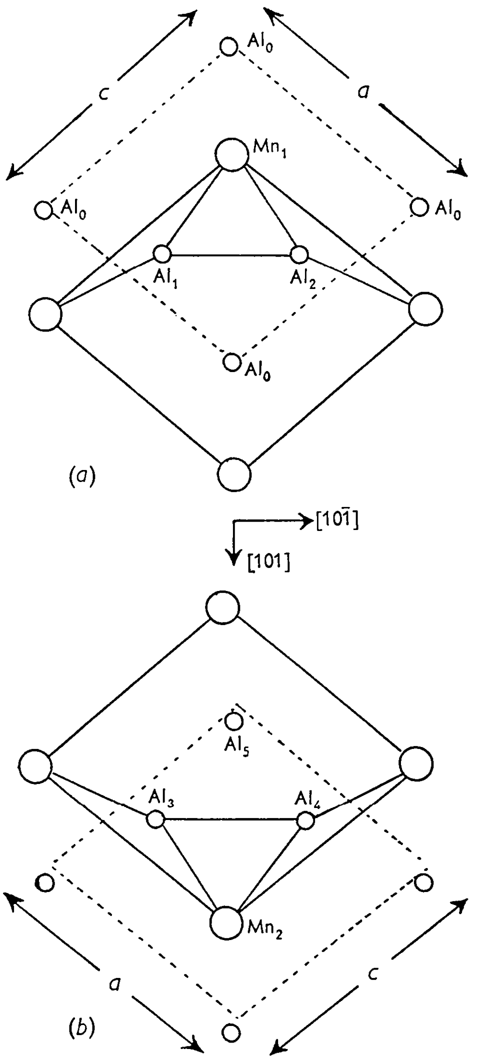

Fig. 2. The atomic arrangement in two layers of δ(Mn–Al) parallel to the *ac* face of the unit cell, (*a*) at $y \sim 1/16$ and (*b*) at $y \sim 3/16$.

(ii) *The Cochran–Douglas method applied to the hkh reflexions*

A set of signs also given in Table 2 was obtained at an earlier date by Drs A. S. and A. M. B. Douglas using the Cochran–Douglas (1955) method. The intensities were recorded using a thin plate-shaped crystal obtained from a binary alloy of aluminium and manganese. On account of this unfavourable specimen shape, the accuracy of the measurements was not high, but it was sufficiently good for the correct signs to be given to the most intense reflexions. In addition to these, the signs of some higher-order reflexions with moderate intensities were also derived. The correct sign combination thus obtained did not, at the time, lead to an acceptable Fourier synthesis. The reasons for this failure were probably (*a*) the inaccuracy of the intensities from the badly shaped crystals of the binary compound, (*b*) the use in the synthesis of all the structure factors whose signs had been determined rather than a smaller number of intense reflexions at low angles—no temperature factor was applied so that spurious ripples were obtained, and (*c*) the chemical composition and density of the crystals were then unknown and ideas concerning the most reasonable trial structure had not been fully developed.

(iii) *The method of Harker–Kasper inequalities applied to the $hk\bar{h}$ reflexions*

The signs of nine reflexions in the [101] zone were also obtained by the application of the Harker–Kasper inequality relation; they are listed in Table 3.

Table 3. *Unitary structure factors and signs for nine reflexions in the zone* [101]

Indices*	U	Harker–Kasper signs	hkl	$h'k'l'$
$0\bar{8}0$	0·69	$-$	Given on projection [10$\bar{1}$]	
$0,\overline{16},0$	0·57	$+$		
$\bar{1}\bar{1}1$	0·25	$+$	Given	—
$\bar{2}02$	0·52	$+$	Given	—
$\bar{3}\bar{1}3$	0·68	a	Given	—
$\bar{3}\bar{9}3$	0·57	$\bar{a}$	$\bar{3}\bar{1}3$	$0\bar{8}0$
$2\bar{8}\bar{2}$	0·33	$-$	$\bar{2}02$	$0\bar{8}0$
$3\bar{7}\bar{3}$	0·49	$\bar{a}$	$\bar{3}\bar{1}3$	$0\bar{8}0$
$\bar{2}82$	0·35	$-$	$20\bar{2}$	$0\bar{8}0$

* Reflexions $0\bar{8}0$ and $0,\overline{16},0$, common to Tables 2 and 3, have different U values in the two tables on account of different scaling factors.

The corresponding Fourier synthesis revealed the main features of the structure on this projection and further support was obtained for a structure consisting of successive layers of the type shown in Fig. 2. Reasonable agreement was obtained between observed and calculated structure factors.

6. Refinement of the structure

From the approximate structure it was evident that the atoms are clearly resolved on the [101] and [100] projections and the refinement process was confined to these directions. The [101] projection gave the (x–z) and y parameters while the [100] projection yielded the corresponding y and z values, and the co-ordinates of each atom were found by combining the

Table 4. *Final atomic co-ordinates in* δ(Mn–Al)

Referred to primitive cell (p)

	x	y	z
Mn_1	0·3926	0·1334	0·3390
Mn_2	0·8590	0·4022	0·7099
Al_0	0	0	0
Al_1	0·5339	0·1226	0·8462
Al_2	0·8911	0·1264	0·4906
Al_3	0·3420	0·3716	0·5778
Al_4	0·7242	0·3714	0·1960
Al_5	0·1869	0·3200	0·0574

Table 5. *List of F_o and F_c data for the* [101] *and* [100] *projections of* δ(Mn–Al)

Index	F_o	F_c
$0k0$		
0		243
2		4-
4		5
6	9	17
8	86	123-
10	13	8
12	13	8
14	42	37
16	57	63
18	13	7
20	14	14
22	33	36-
24	29	27-
26		4
28		
30	30	29
32	27	22
34		6
$1k\bar{1}$		
1	41	46
3	18	15-
5	21	17
7	13	10-
9	7	6
11	5	4
13	22	20
15	33	31
17	23	24-
19	24	24
21	9	10-
23	25	25-
25	33	34
27	9	10
29	17	16
31	24	20
33	14	17-
35		7
$1\bar{k}\bar{1}$		
1	27	27
3	8	6-
5	20	25
7	17	15-
9	13	10
11	8	6-
13	33	34
15	17	20
17	20	18-
19	30	33
21	25	29-
23	9	11-
25	24	27
27	17	16-
29	27	29
31	9	9
33	7	8-
35		7
37	21	20-
$2k\bar{2}$		
0	76	70
2	22	15
4	24	17-
6	29	29
8	43	42-
10		3
12	13	11
14	23	21
16	29	30
18	7	4-
20	19	18
22	21	25-
24	12	12-
26	15	16
28		7-
30	23	26
32		10
34		2-
$2\bar{k}\bar{2}$		
2	30	26-
4	31	26
6	9	6-
8	41	27-
10	23	17
12		3
14	36	37
16	11	1
18	8	6
20	5	6
22	28	31-
24	13	16
26		2
28		6
30	26	23
32		4-
34		3
36		12-
$3k\bar{3}$		
1	96	110
3	13	13-
5	15	16
7	16	14-
9	61	71-
11	13	12
13	5	2
15	34	40
17	33	38
19		6
21	9	9
23	30	31-
25	13	9-
27		1
29		1
31	27	30
33		11
35		4
$3\bar{k}\bar{3}$		
1	28	24
3	9	8-
5	14	11
7	63	73
9	13	11-
11	7	6
13	31	30
15	42	50
17	9	10
19	13	16
21	27	30-
23	19	25-
25		1
27		3-
29	28	27
31	15	20
33		9
$4k\bar{4}$		
0	11	11
2	17	13
4	11	9-
6	8	6
8		2-
10	10	9
12		4
14	19	20
16	13	13
18	17	18-
20	18	19
22	16	19-
24	10	9-
26	23	29
28	9	12-
30	23	22
$4\bar{k}\bar{4}$		
2		2
4	14	10
6	5	5-
8	14	14
10	9	9-
12	13	17
14	17	21
16	19	23-
18	20	27
20	10	14-
22	14	16-
24	21	29
26	12	14-
28	16	19
30	13	12
32	11	12-
$5k\bar{5}$		
1	53	64
3		4-
5	5	4-
7	16	16
9	41	47-
11	9	10
13	5	7
15	13	11
17	29	32
19		4-
21	7	8
23	15	18-
25	15	14-
27		10
29		3-
31	17	21
$5\bar{k}\bar{5}$		
1	13	13-
3	8	9
5		3
7	38	38-
9	11	12
11		1-
13	19	22
15	21	20
17		
19		9
21	19	22-
23		4-
25		5
27		3
29	17	18
$6k\bar{6}$		
0	16	20
2	32	41
4		4-
6		6
8	15	17-
10	18	25-
12		4
14		5
16	25	28
18		9
20		10
22		2-
24	22	27-
$6\bar{k}\bar{6}$		
2		
4		
6	22	30-
8		7-
10		6-
12	19	23
14	23	27
16		3
18	15	20
20	20	24-
22	14	17-
24		4
$0k1$		
0	22	25-
2	13	8-
4	53	44-
6	59	59
8	24	24
10	21	18
12	37	39
14	27	26-
16	11	12-
18	14	13-
20		2
22	18	17
24	10	13
26	27	32
28		11-
30		5-
32		2-
34	17	23-
36	9	16
$0\bar{k}1$		
2	9	3
4	40	37
6	22	16
8	61	66
10	30	29-
12		2-
14	16	15
16	39	45-
18	39	39
20	13	13
22		2
24	27	25
26	21	19-
28		3
30		10-
32		
34	17	20
$0k2$		
0	15	19-
2	23	26
4	87	88
6	19	14
8	27	26
10	34	37-
12	28	26-
14		5-
16	9	13-
18	40	47
20	26	25
22	12	11
24		7
26	17	18-
28	15	18-
30	12	8-
32	12	15
34		8
36	15	18
$0\bar{k}2$		
2	34	31
4	95	106-
6	24	10
8	47	38
10	17	15-
12	84	85
14		2
16	13	10-
18		
20	33	36-
22	14	13
24		1-
26	22	23
28	16	25
30	12	11-
32		11
34	17	16-
$0k3$		
0	30	20
2	14	13-
4	20	12
6	9	6
8	9	6
10	9	8
12	16	18
14	21	18
16	17	18-
18	18	20
20		9-
22	21	19-
24	25	31
26	11	11-
28		14
30	19	19
32	12	15-
34	9	9
$0\bar{k}3$		
2	10	9
4		3
6	11	8
8	7	4
10	23	22
12	15	16-
14	27	27
16		10
18	26	25
20	29	33
22	22	20-
24		5-
26	24	27
28	12	16-
30	21	20
30	21	20
$0k4$		
0	9	7
2	30	29-
4	31	25-
6	32	27
8	9	11-
10	43	44
12	30	30
14	14	13-
16	10	7
18	20	22-
20		5-
22		2
24	14	14
26	18	23
$0\bar{k}4$		
2	12	5
4	43	46
6	15	12
8	35	30
10	12	2-
12	40	42-
14	16	15
16	15	17-
18	18	12
20	33	36
22		3
24	11	14
26	15	12-
28		9-
30	12	7-
32		4-
34	21	23
$0k5$		
0	19	15-
2		4
4		1
6	36	39
8	6	1
10		
12	27	25
14	32	40-
16	7	16
18	17	14
20	15	16-
22	26	36
24		9-
26		1-
28		7
30	14	17-
32	14	18
$0\bar{k}5$		
2		7-
4		
6	11	5
8	35	36
10	12	15
12	9	8
14	9	6-
16	12	10-
18	13	14-
20		5-
22	22	29
24		2
26	16	20
28		14
30	21	28-
$0k6$		
0	32	29
2		6
4	28	34
6	43	54-
8	22	18-
10		3-
12		4-
14	30	44
16	15	16
18	14	23
20		8-
22	19	26-
24		1-
26		19-
28	16	16
30	16	23
$0\bar{k}6$		
2	50	64
4	23	22-
6		4-
8	24	27-
10	20	29-
12	14	15
14	13	11
16	30	44
18	8	13
20		3-
22		2-
24	29	32-
$0k7$		
0		
2	27	32-
4		10
6	7	6
8		3-
10	37	46
12		10-
14		
16		4
18	21	27-
$0\bar{k}7$		
2		4-
4	17	17
6	13	21
8	8	8
10	8	19
12	23	22-
14		9-
16		3
18		4-
20	19	22
$0k8$		
0	18	16-
2	29	48
4	15	10
6	16	19
8	9	4
10	20	27-
12		5-
14	12	20-
16	12	15
18	15	24
$0\bar{k}8$		
2		
4		
6	37	47-
8	25	18
10	9	17
12	12	7
14	20	38
16	15	10-
18		2-
20	12	15-
$0k9$		
0		7-
2		7
4		6
6	17	17-
$0\bar{k}9$		
2	19	17
4		
6		4
8		2-
10		5-
12		13
14		10-
16	17	18
$0k10$		
0		4-
2	9	18-
4		3
6		5
8		10
10	17	21
$0\bar{k}10$		
2		13-
4	17	11
6	9	25
8	9	9-
10	25	23
12	17	9-

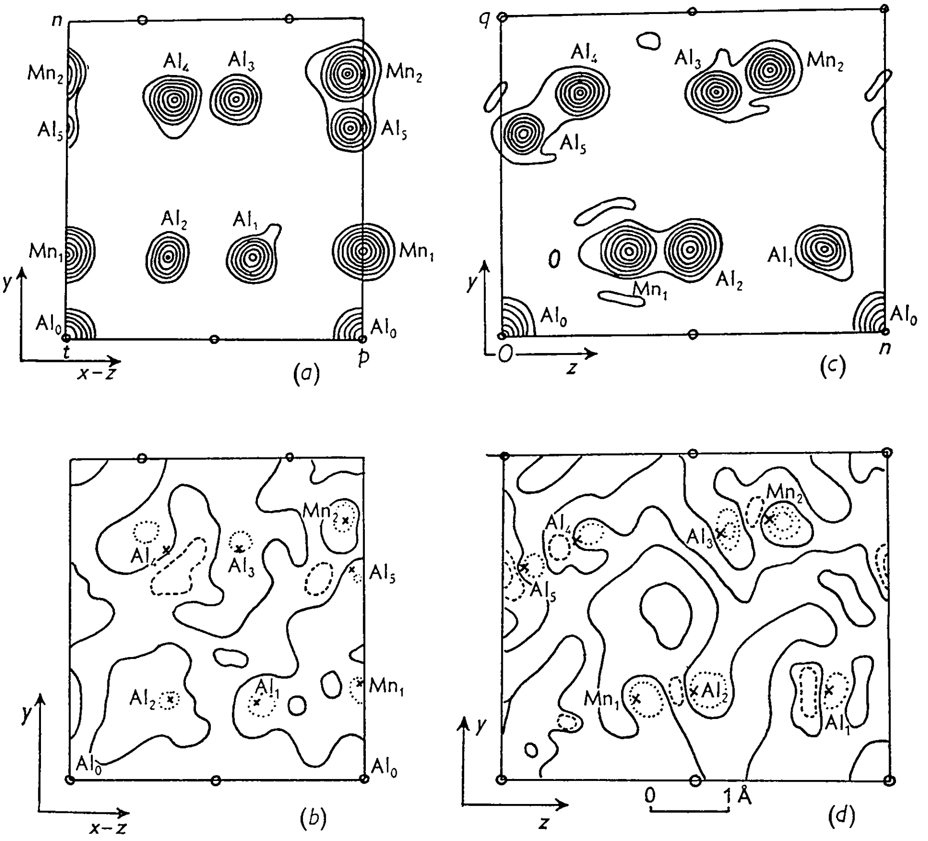

Fig. 3. The asymmetric units of the final syntheses (*a*) F_o, in the direction [101], with *tp* and *tn* as the projections of $\frac{1}{2}(\mathbf{a}-\mathbf{c})$ and $\frac{1}{2}\mathbf{b}$ respectively, (*b*) F_o-F_c, in the direction [101], (*c*) F_o, in the direction [100], with *on* and *oq* as the projections of **c** and $\frac{1}{2}\mathbf{b}$ respectively, (*d*) F_o-F_c, in the direction [100]. In (*a*) and (*c*) no $F(000)$ term is included, no converging factor has been applied and positive contours only are shown at regular arbitrary intervals (in each case), with the Mn interval twice the Al interval. In (*b*) and (*d*) the continuous line is the zero contour, the broken line the first positive and the dotted line the first negative contour. In (*b*) the interval between the contours is one-half the interval used in (*a*) for the Al contours; in (*d*) the interval is the same as that for Al in (*c*). The final atomic shifts were calculated from (*d*).

two projections. Refinement was carried out by means of F_o and F_o-F_c syntheses; low-order reflexions were used in the first few refinement cycles and higher orders were introduced at each stage until all the observed reflexions were included. The observed intensities were scaled to give F_o for comparison with F_c and an agreement factor R was progressively reduced from 30% to 15% on both projections. The co-ordinates deduced from the final F_o-F_c syntheses are given in Table 4, referred to the primitive cell (p); the matrix for transforming the atomic co-ordinates from the primitive cell to the pseudo-monoclinic cell (m) is:

$$\begin{array}{c|ccc} \downarrow\!\!\rightarrow & x_m & y_m & z_m \\ x_p & 1 & 0 & 0 \\ y_p & \bar{\tfrac{1}{2}} & \tfrac{1}{2} & 0 \\ z_p & 0 & 0 & 1 \end{array}$$

Support for the correctness of this structure is given by the low agreement factors, in the region of 15%, also obtained with reflexions in the [001] and [10$\bar{1}$] zones; a total number of about 800 reflexions was finally used. The final F_o and F_o-F_c syntheses in the [101] and [100] directions are shown in Fig. 3. A list of observed and calculated F's is given in Table 5.

7. Accuracy of the atomic co-ordinates

It is expected that the use of F_o-F_c syntheses should remove the major part of the errors arising from the use of a finite number of terms in the Fourier series and overlapping of atoms. Errors corresponding to uncertainties in the F_o's cannot be allowed for in this way so an estimate was made of the corresponding errors in the atomic parameters. The standard deviation $\sigma(F_o)$ in any one value of F_o calculated from the mean of F_o-F_c is 4·0, where $F(000) = 243$ on the absolute scale. Using Booth's (1946) expression this gives the following standard deviations:

$$\text{Mn: } \sigma(x) = 0{\cdot}002\ \text{Å}, \quad \text{Al: } \sigma(x) = 0{\cdot}004\ \text{Å}\,,$$

and, using Booth & Britten's equation (1948), the results are

Mn: $\sigma(x) = 0{\cdot}005$ Å, Al: $\sigma(x) = 0{\cdot}010$ Å .

The mean values of these two estimates were used. The corresponding standard deviation in the interatomic distances ranged from about 0·003 Å to 0·015 Å and a significance level of 0·04 Å was chosen, that is, if two distances differ by more than 0·04 Å then they are considered to be significantly different.

8. Description of the structure

(i) A list of the contact distances for each atom is given in Table 6. Nicol (1953) has suggested that 'normal' values of Mn–Al ~ 2·68 Å and Al–Al ~ 2·71 Å should be taken as a basis for comparison.

Table 6. *Interatomic distances in* δ(Mn–Al)

All distances are in Ångström units

Standard deviations: Al–Al 0·015 Å; Mn–Al 0·012 Å; Mn–Mn 0·010 Å

Mn_1	2·418 (Al_0);	2·498 (Al_5);	2·525 (Al_4);	2·529 (Al_3);
	2·536 (Al_2);	2·541 (Al_1);	2·600 (Al_1);	2·608 (Al_2);
	2·721 (Al_1);	2·783 (Al_2);	3·188 (Mn_1);	3·198 (Mn_2)
Mn_2	2·447 (Al_5);	2·475 (Al_4);	2·540 (Al_3);	2·557 (Al_4);
	2·660 (Al_4);	2·743 (Al_2);	2·744 (Al_3);	2·753 (Al_1);
	2·780 (Al_3);	2·815 (Al_5);	3·053 (Mn_2);	3·198 (Mn_1)
Al_0	2·740 (Al_5);	2·740 (Al_5);	2·826 (Al_2);	2·826 (Al_2);
	2·852 (Al_1);	2·852 (Al_1);	2·893 (Al_1);	2·893 (Al_1);
	2·923 (Al_2);	2·923 (Al_2);	2·418 (Mn_1);	2·418 (Mn_1)
Al_1	2·653 (Al_1);	2·682 (Al_4);	2·772 (Al_2);	2·852 (Al_0);
	2·886 (Al_3);	2·893 (Al_0);	2·932 (Al_2);	3·109 (Al_5);
	3·302 (Al_5);	2·541 (Mn_1);	2·600 (Mn_1);	2·721 (Mn_1);
	2·753 (Mn_2)			
Al_2	2·679 (Al_3);	2·749 (Al_2);	2·772 (Al_1);	2·825 (Al_0);
	2·860 (Al_4);	2·923 (Al_0);	2·932 (Al_1);	3·131 (Al_5);
	3·239 (Al_5);	2·536 (Mn_1);	2·609 (Mn_1);	2·743 (Mn_2);
	2·783 (Mn_1)			
Al_3	2·608 (Al_5);	2·625 (Al_3);	2·677 (Al_4);	2·679 (Al_2);
	2·681 (Al_5);	2·886 (Al_1);	2·978 (Al_4);	2·529 (Mn_1);
	2·540 (Mn_2);	2·744 (Mn_2);	2·780 (Mn_2)	
Al_4	2·616 (Al_5);	2·677 (Al_3);	2·682 (Al_1);	2·726 (Al_5);
	2·861 (Al_2);	2·976 (Al_5);	2·978 (Al_3);	2·475 (Mn_2);
	2·525 (Mn_1);	2·557 (Mn_2);	2·660 (Mn_2)	
Al_5	2·608 (Al_3);	2·616 (Al_4);	2·681 (Al_3);	2·726 (Al_4);
	2·740 (Al_0);	2·976 (Al_4);	3·109 (Al_1);	3·131 (Al_2);
	3·239 (Al_2);	3·302 (Al_1);	2·447 (Mn_2);	2·497 (Mn_1);
	2·815 (Mn_2)			

(ii) Both manganese atoms Mn_1 and Mn_2 have 10 aluminium neighbours if 2·82 Å is taken to be the maximum contact distance. This forms a natural limit, for the next nearest neighbour from Mn_1 is at 3·19 Å and the next nearest neighbour from Mn_2 is at 3·05 Å. The average Mn_1–Al distance, 2·58 Å, is not significantly different from the average Mn–Al distance, 2·56 Å, in $MnAl_6$, while the average Mn_2–Al distance is 2·65 Å, suggesting that the two manganese atoms have different radii in this structure.

There is a marked resemblance between the environment of Mn in $MnAl_6$, Fig. 4(*a*), and of Mn_1 in δ(Mn–Al), Fig. 4(*b*); the tenfold co-ordination group of aluminium atoms has a distinctive shape related to the icosahedron with two vertices removed. The environment of Mn_2 (Fig. 4(*c*)) is also similar to this figure but is somewhat distorted. A striking feature of this arrangement is that in each tenfold group the abnormally short distances are in the same orientation with respect to the central atom. Thus in $MnAl_6$ there are two Mn–Al_2 (2·44 Å) contacts; in δ(Mn–Al) the corresponding contacts are Mn_1–Al_0 (2·42 Å), Mn_1–Al_5 (2·50 Å) and Mn_2–Al_5 (2·45 Å), Mn_2–Al_4 (2·48 Å).

(iii) The aluminium-atom environments and contact distances are discussed by dividing them into classes according to the number of transition metals in each co-ordination group (Table 7); this procedure was used by Black (1955) for the analysis of the aluminium co-ordinations in $FeAl_3$. The atom Al_0 in class *A* has 2 manganese and 10 aluminium contacts; Al_5 in class *B* has 3 manganese and 8 aluminium contacts; and each of the remaining aluminium atoms (Al_1, Al_2, Al_3, Al_4) has 4 manganese and 7 aluminium contacts.

The variation in the interatomic distances for each of these classes is compared with the corresponding curve for $FeAl_3$ in Fig. 5. In both compounds there is the same trend, namely, when the number of transition-metal neighbours increases so does the mean transition-metal–aluminium distance. The opposite trend would be expected if size factor alone were important, and Black has discussed this effect in terms

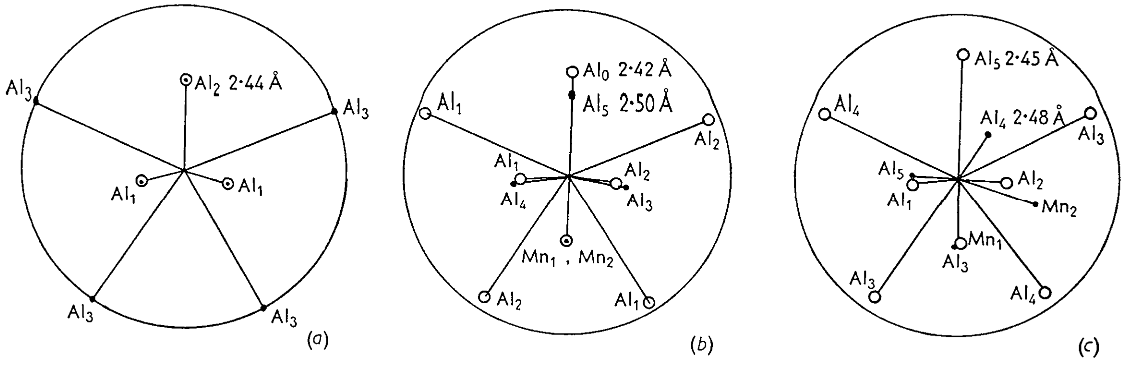

Fig. 4. Stereograms showing the environments of (*a*) Mn in $MnAl_6$, 10 Al atoms; (*b*) Mn_1 in δ(Mn–Al), 10 Al and 2 Mn atoms; (*c*) Mn_2 in δ(Mn–Al), 10 Al and 2 Mn atoms.

of a strong bond between unlike atoms; the data given here support this hypothesis.

Table 7. *Aluminium atom environments in* δ(Mn–Al)

		Mn contacts*		Al contacts†	
Group	Atom	No.	Mean contact distance	No.	Mean contact distance
A‡	Al_0	2	2·418 Å	10	2·847 Å
B	Al_5	3	2·586	6 or 8	2·724 2·823
C	Al_1	4	2·654	7	2·810
	Al_2	4	2·668	7	2·820
	Al_3	4	2·648	7	2·733
	Al_4	4	2·554	7	2·788

* Using all distances $< 2·83$ Å.

† Using all distances $< 3·00$ Å, except for Al_5 (8 neighbours), which has two neighbours at 3·109 Å and 3·131 Å.

‡ Groups according to number of Mn contacts.

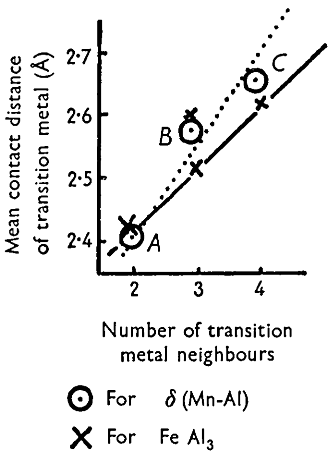

Fig. 5. The variation of the mean contact distances for the neighbours of an aluminium atom in δ(Mn–Al) and $FeAl_3$.

It is of interest to note that aluminium both in δ(Mn–Al) and in $MnAl_6$ has 11 or 12 neighbours, whereas in $FeAl_3$ (Black, 1955) and in Co_2Al_9 (Douglas, 1950) an environment of 10 atoms round each aluminium is most frequent.

(iv) The sequence of well-defined planes of atoms parallel to the (010) face of the crystal is a prominent feature of the structure; there are eight of these layers separated from each other by approximately 2·1 Å. Layers at $y \sim 1/16, 7/16, 9/16, 15/16$ are symmetrically equivalent, each with the arrangement shown in Fig. 2(*a*); the atom Al_0 at $y = 0$ is midway between the layers at $y \sim 15/16$ and $1/16$ and the atom Al_0 at $y = 1/2$ is between the layers at $y \sim 7/16$ and $9/16$. The arrangement in the layers at $y \sim 3/16, 5/16, 11/16, 13/16$ is shown in Fig. 2(*b*). This differs from Fig. 2(*a*) in that Al_5 may be considered as belonging to the layer; it is about 0·4 Å from the mean level of the other atoms. The sequence may therefore be written:

y 15/16 1/16 3/16 5/16 7/16 9/16 11/16 13/16 15/16
$A_1 \times A_1$ A_2 A_2 $A_1 \times A_1$ A_2 A_2 A_1
——————17·1 Å——————

where A_1 is the arrangement shown in Fig. 2(*a*) with the shared atom Al_0 represented by ×, and A_2 is the slightly crumpled layer shown in Fig. 2(*b*). Thus A_1 is obtained from A_2 by removing one aluminium atom, Al_5.

(v) *Related structures.*—The similarity of the unit cells of δ(Mn–Al) and $MnAl_6$ (Table 1) may be associated with the occurrence of the A_1 net, Fig. 2(*a*), in both structures. In $MnAl_6$ there is a sequence of layers at intervals of 2·2 Å parallel to the (010) face of the primitive unit cell:

y 0 1/4 1/2 3/4 0
$B \times A_1 \times B \times A_1 \times B$
———½(17·7 Å)———

where B is the arrangement shown in Fig. 2(*a*) with the manganese atoms removed. Thus $MnAl_6$ consists of an alternation of A_1 sheets with other layers, B, consisting entirely of aluminium atoms; the layers are separated by single aluminium atoms, ×.

WAl_4 (Bland & Clark, 1958), has been discussed in terms of A_1 layers in which manganese is replaced by tungsten; these layers also have single aluminium atoms between them and there are additional sheets of aluminium atoms arranged in an approximately hexagonal net.

Schubert (1953) has pointed out that Fe_2Al_5 is related to $MnAl_6$. The proposed structure is more closely related to δ(Mn–Al)–Mn_4Al_{11} for it contains a sequence of A_1 layers in which manganese atoms are replaced by iron atoms with single aluminium atoms midway between the layers. Phragmen (1950) has suggested that a phase with the formula $(FeCu)(AlCu)_6$, with a very small copper content, may be isomorphous with $MnAl_6$. No detailed structure analysis of this compound has been made, but it seems likely that it contains layers similar to A_1.

The occurrence of similar tenfold polyhedra of aluminium atoms in $MnAl_6$, δ(Mn–Al) and WAl_4 has been noted previously. The same shape is found in the proposed structure of Fe_2Al_5 and a closely related, tenfold polyhedron is observed round Co in Co_2Al_5 (Bradley & Cheng, 1938) and round Mn in β(MnSiAl) (Robinson, 1952). In the ternary, the short distances are again in the same orientation as the short distances in $MnAl_6$.

9. Discussion

The significance of the A_1 and A_2 layers, Fig. 2, in relation to the classification of intermetallic compounds is clear when it is realized that the A_2 layer is a crumpled 5-connected net; this array is shown in Fig. 6 extending over several unit cells. An ideal 5-connected net with aluminium atoms on the lattice points has a two-dimensional unit cell which is square

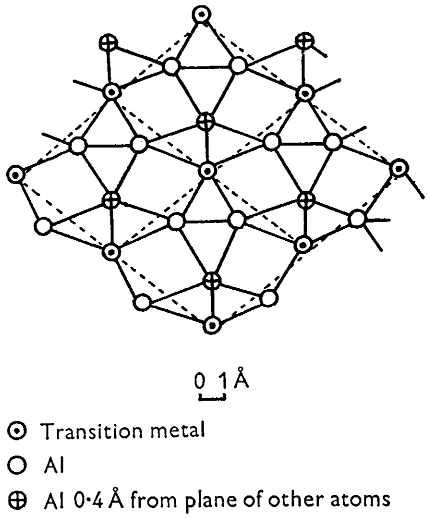

Fig. 6. The A_2 layer consisting of transition metal and aluminium atoms; a crumpled 5-connected net. The A_1 pattern is obtained by removing the aluminium atoms marked with a cross.

with 6 Å sides (Black, 1956). If some of the aluminium atoms are replaced by transition-metal atoms and the net is allowed to crumple, the A_2 pattern is obtained in which the square is replaced by the rhombus with sides 5 Å × 5 Å at an angle of 101°; this is the *ac* unit of the three structures $MnAl_6$, δ(Mn–Al) and WAl_4. Black has shown that the plane 5-connected net is present in a large number of intermetallic compounds and that it forms a convenient basis for the classification of aluminium-rich structures with eight- and nine-fold co-ordination of the transition-metal atoms. The present work shows how the scheme can be extended to structures in which the transition-metal atoms have higher co-ordination numbers.

δ(Mn–Al) exhibits characteristics common to other transition-metal–aluminium alloys; these include prominent layering, a zone of strong reflexions with spacings corresponding to about 2 Å and short inter-atomic distances (Taylor, 1954). The successful application of direct methods to the determination of this structure may be attributed to the well defined atomic layers associated with reflexions having large unitary structure factors. Cochran & Douglas (1955) have already shown that the application of direct methods leads to the correct solution for the (known) structure of Co_2Al_9.

The structure of $\gamma(MnAl_4)$ is not known; there is no obvious relationship between its unit cell and those of either of the adjacent phases, $\beta(MnAl_6)$ and $\delta(Mn_4Al_{11})$ in the Mn–Al system.

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References

Black, P. J. (1955). *Acta Cryst.* **8**, 175.
Black, P. J. (1956). *Acta Met.* **4**, 172.
Bland, J. A. & Clark, D. (1958). *Acta Cryst.* **11**, 231.
Booth, A. D. (1946). *Proc. Roy. Soc.* A, **188**, 77.
Booth, A. D. & Britten, K. H. V. (1948). *Proc. Roy. Soc.* A, **193**, 305.
Bradley, A. J. & Cheng, C. S. (1938). *Z. Kristallogr.* **99**, 480.
Cochran, W. & Douglas, A. S. (1955). *Proc. Roy. Soc.* A, **227**, 486.
Douglas, A. M. B. (1950). *Acta Cryst.* **3**, 19.
Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.
Hofmann, V. (1938). *Aluminium, Berl.* **20**, 867.
Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210.
Lipson, H. & Cochran, W. (1953). *The Determination of Crystal Structures*, London: Bell.
Nicol, A. D. I. (1953). *Acta Cryst.* **6**, 285.
Phragmen, A. (1950). *J. Inst. Met.* **77**, 489.
Raynor, G. V. & Wakeman, D. (1947). *Proc. Roy. Soc.* A, **190**, 82.
Robinson, K. (1952). *Acta Cryst.* **5**, 397.
Schubert, K. (1953). *Naturwissenschaften*, **16**, 437.
Taylor, W. H. (1954). *Acta Met.* **2**, 684.
Weisz, O., Cochran, W. & Cole, W. F. (1948). *Acta Cryst.* **1**, 83.