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The Crystal Structure of the Ternary Alloy α(AlMnSi)

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The crystal structure of the phase α(AlMnSi) has been determined, from visually estimated X-ray intensities. The atomic coordinates, obtained from a Patterson synthesis, were refined by a three-dimensional least-squares process. The approximate formula of the phase is $Mn_2Al_9Si_{1\cdot 8}$, and there are 138 atoms in the cubic unit cell, $a = 12\cdot 68$ Å, space group *Pm*3. No attempt has been made to distinguish between the two types of light atom.

Introduction

The investigation forms part of the study of aluminum-rich transition metal alloys, designed to yield information on the alloying behaviour of transition metals in association with solvents of high valency.

The phase diagram of the aluminum-rich portion of this alloy system has been investigated by Buckle (1938) and Phillips (1943). Buckle reported three ternary phases, two of which were confirmed by Phillips and labelled α and β. The structure of the β phase was determined by Robinson (1952).

Bergman (1951) reported that the α phase has 138 atoms per unit cell. Phragmen (1950) noted an isomorph in the Al–Fe–Si system with approximate composition $Fe_5Si_2Al_{20}$ and a cubic cell side of 12·523 kX. Pratt & Raynor (1951) explained the isomorphism in terms of the similar free-electron-to-atom ratios. Examination of some of their crystals, however, showed a hexagonal cell with $a = 12\cdot 3$, $c = 26\cdot 2$ Å. It seems likely that both cubic and hexagonal phases exist in this region of the Al–Fe–Si phase diagram.

Description of the α phase

The single crystals used for the refinement were provided by Aluminium Laboratories, Banbury. The composition was determined by Johnson, Matthey and Co. Ltd. as manganese 28·4%, silicon 10·7%, aluminum (by difference) 60·9% by weight. The errors were quoted as ±0·5%. According to Raynor (private communication) the phase extends up to the electron-rich limit of 27% Mn 12·5% Si by weight.

The crystals have prominent (100) faces, with a linear dimension of the order of 0·1 cm. The density was determined by flotation as $3\cdot 62 \pm 0\cdot 06$ g.cm^{-3}. This agrees with a calculated density of 3·62 g.cm^{-3} for a cell made up of 100 Al, 14 Si, and 24 Mn atoms.

The cell side was determined from a Weissenberg photograph by the method of Main & Woolfson (1963). The value obtained was $12\cdot 68 \pm 0\cdot 02$ Å in agreement with the value obtained from powder photographs. The Laue group is *m*3. No systematic absences were found, although reflexions with $h+k+l$ odd were weak. Possible space groups were *Pm*3 and *P*23. The choice of the centrosymmetric alternative, *Pm*3, was justified by the success of the refinement.

Intensity measurements and the approximate structure

The intensities of *hkl* reflexions, to a maximum *h*, *k* and *l* of 10, were estimated visually from oscillation photographs taken with Mo *Kα* radiation and a multiple-film technique. The different photographs were scaled together with the use of data from a zero-layer Weissenberg photograph. Lorentz and polarization corrections were applied; absorption was neglected at this stage for the small crystal used.

A Patterson section $P(u,v,w)$ at height $w=0$ was computed (Fig. 1). From this it was possible to fix the positions of the manganese atoms Mn(1) and Mn(2) (Table 1).

As the unit cell is almost body-centred, a difference Patterson function $P'(u,v,0)$ was next computed, where

$$P'(u,v,0) = P(u,v,0) - P(u+\tfrac{1}{2}, v+\tfrac{1}{2}, \tfrac{1}{2})$$

$P'(u,v,0)$ has positive and negative peaks arising solely from departures from body-centring. By this means atoms Al(1), Al(2), Al(3), Al(6) and Al(7) (Table 1) were located. The remaining atomic positions were determined from packing considerations.

Refinement of the structure

The structure refinement was carried out on intensity data estimated visually, Weissenberg multiple-film technique and Mo *Kα* radiation being used. Lorentz and polarization corrections were applied. The calculated absorption corrections, for the small crystal fragment used, were constant to within 2% for all reflexions observed, and were therefore not applied.

The different layers were scaled together using equivalent reflexions, for which the R index was approximately 0·10. No attempt was made to refine to an R value significantly lower than this. Because the number of equivalent reflexions was small, the scaling was checked at a late stage of the refinement by calculating the quantity $S=\Sigma\, F_o-F_c$, the sum being over all reflexions in that layer. S is sensibly zero for perfect scaling, if the postulated structure is substantially correct.

A three-dimensional least-squares program written by Mrs J. C. Matthewman for the EDSAC II Computer was used for the refinement. Observed reflexions out to $\sin\theta/\lambda=0{\cdot}6$ were employed, together with their equivalent reflexions. In all 148 independent non-zero reflexions were used to refine 21 parameters.

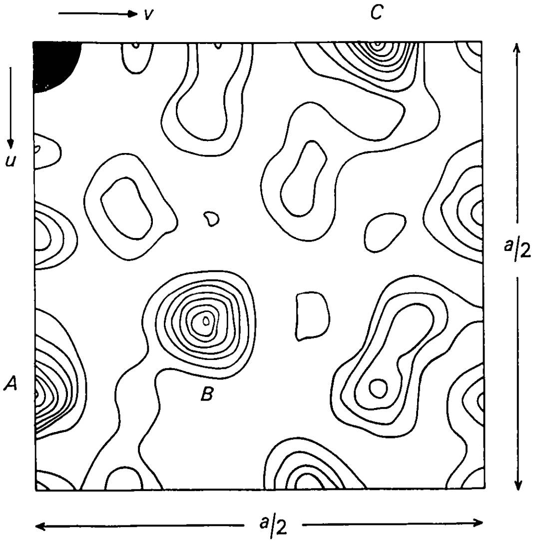

Fig. 1. Patterson section $P(u, v, 0)$ of α(AlMnSi). Peaks A, B, and C were interpreted in terms of Mn–Mn vectors.

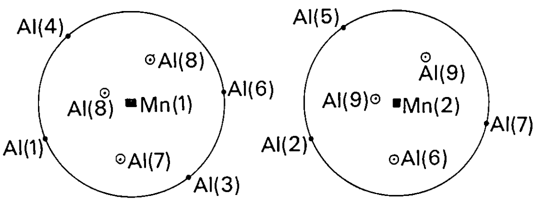

Fig. 2. Stereograms of the two types of manganese coordination polyhedron.

The atomic scattering factors were calculated from the analytic approximation of Forsyth & Wells (1959).

The program minimizes the quantity

$$R_1=\Sigma\, W_{hkl}[F_o(hkl)-F_c(hkl)]^2\,.$$

W_{hkl} is a weighting factor, chosen as

$$\frac{1}{|a|+|F_o|+|c|\,|F_o|^2},$$

where a is the minimum non-zero F_o and c the reciprocal of the maximum F_o. This scheme gives more weight to structure factors in the middle of the range of values, which are those most accurately observed (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1960).

The R index dropped to 0·16 in a few cycles, but no further progress was made until extinction was allowed for in the five strongest reflexions. All these had large F_c values when compared with the scaled F_o, the difference being statistically highly significant. The reflexions suffering severe extinction were replaced by their calculated values in the computation of atomic shifts, whilst they were omitted completely from the evaluation of the R index.

No physical significance can be attached to the temperature factors in the absence of absorption corrections. Values of 0·4 Å^2 on manganese and 0·7 Å^2 on aluminum gave the lowest difference density.

The unrefined and refined coordinates are shown in Table 1. The standard deviations are calculated from the expression given by Cruickshank (1959).

The best R value obtained was 0·098. At this stage all the shifts were much smaller than the standard deviations in atomic positions.

A three-dimensional difference map showed an electron density of 0·2 e.Å^{-3} in general positions, and higher values at special positions (e.g. 0·8 e.Å^{-3} at the origin). A rough analysis (see Cruickshank & Rollett, 1953) predicted a difference density of 0·2 e.Å^{-3} in general positions and 0·7 e.Å^{-3} at the origin. It was therefore concluded that the peaks at special positions were not physically significant.

Table 1. *The atomic coordinates*

The space group is $Pm3$

Atom	Initial x	Final x	$\sigma(x)$	Initial y	Final y	$\sigma(y)$	Initial z	Final z	$\sigma(z)$
Mn(1)	0·331	0·3271	0·0008	0·195	0·2006	0·0007	0	0	—
Mn(2)	0·175	0·1797	0·0008	0·305	0·3085	0·0007	0·5	0·5	—
Al(1)	0·373	0·3638	0·0019	0	0	—	0	0	—
Al(2)	0·129	0·1216	0·0022	0·5	0·5	—	0·5	0·5	—
Al(3)	0·292	0·2897	0·0021	0	0	—	0·5	0·5	—
Al(4)	0·174	0·1636	0·0015	0·108	0·0997	0·0013	0	0	—
Al(5)	0·329	0·3342	0·0015	0·406	0·3990	0·0013	0·5	0·5	—
Al(6)	0·332	0·3319	0·0014	0·398	0·4037	0·0013	0	0	—
Al(7)	0·122	0·1205	0·0015	0·107	0·1175	0·0015	0·5	0·5	—
Al(8)	0·117	0·1185	0·0010	0·188	0·1892	0·0009	0·301	0·2980	0·0009
Al(9)	0·390	0·3897	0·0010	0·314	0·3127	0·0009	0·196	0·1955	0·0009

In Table 1 no attempt is made to differentiate between aluminum and silicon – both are referred to as aluminum.

Details of observed and calculated structure factors will be included in a thesis to be submitted by one of the authors (MC) to the University of Cambridge.

Description of the structure

As noted earlier, the phase is almost body-centred. The main departure from this pattern is the aluminum atom Al(3) which has no body-centred counterpart. This results in different coordination polyhedra around the two types of manganese atom Mn(1) and Mn(2).

Taking 2·84 Å as the maximum contact distance for manganese and aluminum atoms, the coordination is described as follows.

Manganese atoms Mn(1) have ten aluminum neighbours at an average distance of 2·63 Å. This includes two short bonds to atoms Al(3) (2·46 Å) and Al(4) (2·43 Å). Manganese atoms Mn(2) have nine aluminum neighbours. The bond to atom Al(5) [which is the complement of Al(4)] is now extremely short (2·27 Å)· Abnormally short bonds are a well-known feature of manganese-aluminum polyhedra (*cf.* Black & Taylor, 1958).

The stereograms in Fig. 2 show that the rearrangement of bonds, in changing from 10-fold to 9-fold coordination mainly affects the coplanar bonds.

Two large holes in the structure, one at the origin, and the other at the centre of the unit cell, are each 12-fold coordinated by atoms of type Al(4) at 2·42 Å and Al(5) at 2·44 Å respectively. There was no evidence from the difference map that either of these sites is appreciably occupied.

The structure has been refined on the basis of 24 Mn and 14 Si atoms per cell, whereas the chemical composition corresponds to 22·6 Mn and 16·7 Si atoms per cell. Replacement occurs therefore in preference to the partial occupation of the vacant sites. A regular array of vacant sites is also found in the β phase of this alloy (Robinson, 1952).

A list of all the interatomic distances is given in Table 2. The aluminum atom environments are shown in Table 3, classified according to the number of transition metal atoms in each coordination group. This procedure was first used by Black (1955) in the study of $FeAl_3$, and has been employed by Bland (1958) in connection with the crystal structure of Mn_4Al_{11}. In these compounds, and in this alloy, the same trend is observed, namely the increase in transition metal–aluminum distance with the number of transition metal

Table 2. *Interatomic distances in* α(AlMnSi)

All distances are in Å

Standard deviations of individual bonds: Mn–Al 0·03 Å, Al–Al 0·04 Å

Atom	Neighbours	Already quoted	Coordination Number
Mn(1)	1 Al(1) at 2·58; 1 Al(3) at 2·46 1 Al(4) at 2·43; 1 Al(6) at 2·57 2 Al(7) at 2·84; 2 Al(8) at 2·61 2 Al(8) at 2·64		10
Mn(2)	1 Al(2) at 2·53; 1 Al(5) at 2·27 2 Al(6) at 2·60; 1 Al(7) at 2·53 2 Al(9) at 2·62; 2 Al(9) at 2·59		9
Al(1)	2 Al(4) at 2·83; 4 Al(7) at 2·74 4 Al(8) at 2·95	2 Mn(1)	12
Al(2)	1 Al(2) at 3·08; 2 Al(3) at 3·08 2 Al(5) at 2·98; 4 Al(6) at 2·90 4 Al(9) at 2·90	2 Mn(2)	15
Al(3)	2 Al(6) at 2·57; 2 Al(7) at 2·61 4 Al(9) at 2·86	2 Mn(1); 2 Al(2)	12
Al(4)	4 Al(4) at 2·56; 1 Al(4) at 2·53 2 Al(8) at 2·94; 2 Al(8) at 2·95	1 Mn(1); 1 Al(1)	11
Al(5)	4 Al(5) at 2·59; 1 Al(5) at 2·56 2 Al(9) at 2·94; 2 Al(9) at 2·95	1 Mn(2); 1 Al(2)	11
Al(6)	1 Al(6) at 2·44; 2 Al(8) at 2·71 2 Al(9) at 2·83	1 Mn(1); 2 Mn(2); 2 Al(2) 1 Al(3)	11
Al(7)	1 Al(7) at 2·98; 1 Al(7) at 3·05 2 Al(8) at 2·72; 2 Al(9) at 2·98	2 Mn(1); 1 Mn(2); 2 Al(1) 1 Al(3)	12
Al(8)	2 Al(8) at 2·81; 1 Al(8) at 3·00 2 Al(9) at 2·73	2 Mn(1); 1 Al(1); 2 Al(4) 1 Al(6); 1 Al(7)	12
Al(9)	1 Al(9) at 2·79; 2 Al(9) at 3·03	2 Mn(2); 1 Al(2); 1 Al(3) 2 Al(5); 1 Al(6); 1 Al(7) 2 Al(8)	13

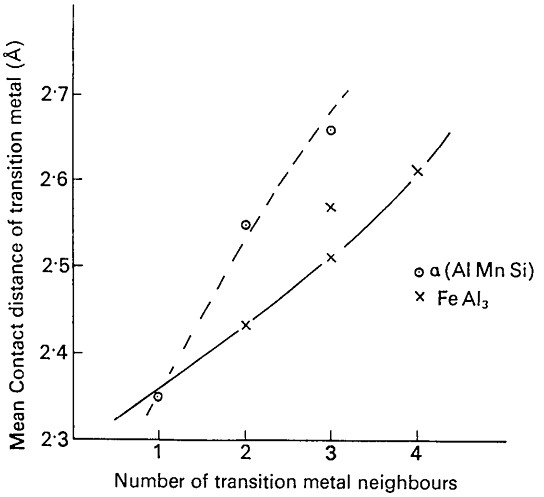

Fig. 3. Variation of the mean contact distances for neighbours of an Al atom in α(AlMnSi) and FeAl$_3$.

neighbours. The results are displayed in Fig. 3, together with those of Black for FeAl$_3$. Black discusses the trend in terms of a strong bond between unlike atoms.

The structure is a three-dimensional network of polyhedra. It can alternatively be described in terms of layers of manganese atoms parallel to the (100) planes, and linked by aluminum atoms, but in this case the layering is not as marked as in other aluminum alloys of transition metals.

Table 3. *Analysis of aluminum atom environments*

The standard deviation of a single Mn–Al bond is 0·03 Å

	Manganese contacts		
Atom	Number	Mean distance	Average
Al(4)	1	2·43	
Al(5)	1	2·27	2·35
Al(1)	2	2·58	
Al(2)	2	2·53	
Al(3)	2	2·46	
Al(8)	2	2·63	
Al(9)	2	2·60	2·55
Al(6)	3	2·59	
Al(7)	3	2·73	2·66

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The Crystal Structure of Al$_2$Se$_3$

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The crystal structure of Al$_2$Se$_3$ has been determined from X-ray powder diffraction data. The unit cell is monoclinic, being centred on the *C* face, with parameters $a=11{\cdot}68_0$, $b=6{\cdot}73_3$, $c=7{\cdot}32_9$ Å and $\beta=121{\cdot}1_2°$. The space group is *Cc* and the structure is similar to that of α-Ga$_2$S$_3$.

Introduction

The crystal structure of Al$_2$Se$_3$ was examined by Schneider & Gattow (1954), who used X-ray diffraction data obtained with a Debye–Scherrer camera of 5·74 cm diameter. They proposed a wurtzite-type structure which was deficient in cations, the parameters of the hexagonal cell being $a=3{\cdot}89$, $c=6{\cdot}30$ Å.