

The Structure of FeAl₃. II

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The interatomic distances and co-ordinations in FeAl₃ are presented, and the significance of certain trends in these is discussed. The structure can be regarded as composed of mis-oriented close-packed regions, and is interpreted in terms of strong Fe-Al interactions. The occurrence of twins is related to the structural pattern. Brillouin-zone and electron-distribution data are considered; the latter show no large anomalies, but are not very reliable. Attempts to produce a low-temperature transformation reported by previous workers have failed.

1. Introduction

In a previous paper (Black, 1955*b*) the author has described the analysis of the structure of a binary Al-Fe compound, FeAl₃. That description ended with the list of the atomic parameters: it is the purpose of this paper to consider the resulting structure in detail. It has been reported that the phase undergoes certain transformations, and work to check this will also be described.

2. Interatomic distances and co-ordinations

(i) A full list of these is given in Table 1 and of their standard deviations in Table 2. The Goldschmidt radii for Fe and Al in the mean co-ordinations of this structure lead to Fe-Al and Al-Al distances of 2.60 and 2.76 Å respectively. The corresponding values found from Table 1 are 2.55 Å (taking 2.8 Å as an upper limit) and 2.77 Å (with 3.0 Å as upper limit), but the variations are so large that these means can have little significance. Most of the Fe-Al distances lie in the range 2.4–2.8 Å, and the Al-Al distances

Table 1. *Interatomic distances in FeAl₃*

All distances are in Ångström units. The first symbol in brackets after each distance specifies the neighbour concerned; the second symbol in brackets the number of such neighbours.

Fe₁: 2.429 (Al₁₇) (2); 2.513 (Al₉) (1); 2.523 (Al₈) (1); 2.538 (Al₆) (1); 2.616 (Al₁₈) (2); 2.759 (Al₉) (1); 2.771 (Al₁₉) (2); 2.839 (Al₇) (1).

Fe₂: 2.422 (Al₁₁) (1); 2.453 (Al₈) (1); 2.455 (Al₁₈) (2); 2.480 (Al₁₂) (1); 2.493 (Al₁₉) (2); 2.621 (Al₁₃) (1); 2.713 (Al₁₇) (2).

Fe₃: 2.257 (Al₁₀) (1); 2.450 (Al₆) (1); 2.502 (Al₁₅) (2); 2.528 (Al₂₀) (2); 2.556 (Al₆) (1); 2.576 (Al₇) (1); 2.758 (Al₁₆) (2); 2.906 (Fe₃) (1).

Fe₄: 2.400 (Al₁₆) (2); 2.480 (Al₂₀) (2); 2.495 (Al₁₁) (1); 2.565 (Al₁₀) (1); 2.629 (Al₁₁) (1); 2.633 (Al₁₃) (1); 2.754 (Al₁₅) (2); 3.005 (Fe₄) (1).

Fe₅: 2.306 (Al₁₄) (1); 2.463 (Al₁₁) (1); 2.476 (Al₁₅) (1); 2.514 (Al₇) (1); 2.574 (Al₁₃) (1); 2.575 (Al₁₇) (1); 2.580 (Al₁₆) (1); 2.615 (Al₉) (1); 2.644 (Al₁₈) (1); 3.472 (Fe₅) (1).

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Table 1 (cont.)

Al₁: 2.450 (Fe₃) (1); 2.538 (Fe₁) (1); 2.556 (Fe₃) (1); 2.578 (Al₇) (1); 2.829 (Al₁₇) (2); 2.868 (Al₁₅) (2); 2.937 (Al₂₀) (2).

Al₇: 2.514 (Fe₅) (2); 2.576 (Fe₅) (1); 2.839 (Fe₁) (1); 2.454 (Al₉) (1); 2.578 (Al₆) (1); 2.637 (Al₁₈) (2); 2.693 (Al₁₆) (2); 2.736 (Al₁₀) (1).

Al₈: 2.453 (Fe₂) (1); 2.523 (Fe₁) (1); 3.309 (Fe₅) (2); 2.600 (Al₉) (1); 2.700 (Al₁₉) (2); 2.752 (Al₁₃) (1); 2.879 (Al₁₇) (2); 2.978 (Al₁₉) (2); 3.003 (Al₁₇) (2).

Al₉: 2.513 (Fe₁) (1); 2.615 (Fe₅) (2); 2.759 (Fe₁) (1); 2.454 (Al₇) (1); 2.575 (Al₁₉) (2); 2.600 (Al₈) (1); 2.721 (Al₉) (1); 2.812 (Al₁₈) (2).

Al₁₀: 2.257 (Fe₃) (1); 2.565 (Fe₄) (1); 2.682 (Al₁₅) (2); 2.736 (Al₇) (1); 2.848 (Al₁₆) (2); 2.881 (Al₁₆) (2); 2.947 (Al₁₆) (2); 3.173 (Al₁₃) (1).

Al₁₁: 2.422 (Fe₂) (1); 2.495 (Fe₄) (1); 2.629 (Fe₄) (1); 2.513 (Al₁₃) (1); 2.754 (Al₁₈) (2); 2.853 (Al₁₈) (2); 2.865 (Al₂₀) (2).

Al₁₂: 2.480 (Fe₂) (2); 2.702 (Al₁₉) (4); 2.854 (Al₁₈) (4).

Al₁₃: 2.574 (Fe₅) (2); 2.621 (Fe₂) (1); 2.633 (Fe₄) (1); 2.513 (Al₁₁) (1); 2.669 (Al₁₇) (2); 2.730 (Al₁₅) (2); 2.752 (Al₈) (1); 3.173 (Al₁₀) (1).

Al₁₄: 2.306 (Fe₅) (2); 3.009 (Al₁₉) (2); 3.011 (Al₁₅) (2); 3.016 (Al₁₈) (2); 3.105 (Al₁₇) (2); 3.208 (Al₁₈) (2).

Al₁₅: 2.754 (Fe₄) (1); 2.476 (Fe₅) (1); 2.502 (Fe₃) (1); 2.663 (Al₁₆) (1); 2.682 (Al₁₀) (1); 2.730 (Al₁₃) (1); 2.840 (Al₂₀) (1); 2.845 (Al₁₇) (1); 2.868 (Al₆) (1); 2.884 (Al₁₆) (1); 2.947 (Al₁₀) (1); 3.011 (Al₁₄) (1).

Al₁₆: 2.400 (Fe₄) (1); 2.580 (Fe₅) (1); 2.758 (Fe₃) (1); 2.663 (Al₁₅) (1); 2.693 (Al₇) (1); 2.754 (Al₁₁) (1); 2.848 (Al₁₀) (1); 2.852 (Al₁₈) (1); 2.881 (Al₁₀) (1); 2.884 (Al₁₅) (1); 2.968 (Al₂₀) (1); 3.016 (Al₁₄) (1).

Al₁₇: 2.429 (Fe₁) (1); 2.575 (Fe₅) (1); 2.713 (Fe₂) (1); 2.507 (Al₁₈) (1); 2.643 (Al₁₉) (1); 2.669 (Al₁₃) (1); 2.829 (Al₆) (1); 2.845 (Al₁₅) (1); 2.879 (Al₈) (1); 2.951 (Al₁₉) (1); 3.003 (Al₈) (1); 3.105 (Al₁₄) (1).

Al₁₈: 2.455 (Fe₂) (1); 2.616 (Fe₁) (1); 2.644 (Fe₅) (1); 2.507 (Al₁₇) (1); 2.637 (Al₇) (1); 2.669 (Al₁₉) (1); 2.812 (Al₉) (1); 2.852 (Al₁₆) (1); 2.853 (Al₁₁) (1); 2.864 (Al₁₂) (1); 3.136 (Al₁₉) (1); 3.208 (Al₁₄) (1).

Al₁₉: 2.463 (Fe₅) (1); 2.493 (Fe₂) (1); 2.771 (Fe₁) (1); 2.575 (Al₉) (1); 2.643 (Al₁₇) (1); 2.669 (Al₁₈) (1); 2.700 (Al₉) (1); 2.702 (Al₁₂) (1); 2.951 (Al₁₇) (1); 2.978 (Al₈) (1); 3.009 (Al₁₄) (1); 3.137 (Al₁₈) (1).

Al₂₀: 2.480 (Fe₄) (2); 2.528 (Fe₃) (2); 2.840 (Al₁₅) (2); 2.865 (Al₁₁) (2); 2.937 (Al₈) (2); 2.968 (Al₁₆) (2).

Table 2. *Standard deviations in interatomic distances*

Pair of atoms concerned	Derivation	Result (Å)
Al $y = 0$ Al $y = 0$	$\sqrt{2} \cdot \sigma_{\text{Al}}$	0.01
Al $y = 0$ Al $y \neq 0$	$\sqrt{3} \cdot \sigma_{\text{Al}}$	0.015
Al $y \neq 0$ Al $y \neq 0$	$\sqrt{2} \cdot \sqrt{2} \cdot \sigma_{\text{Al}}$	0.02
Al $y = 0$ Fe $y = 0$	$\sqrt{(\sigma_{\text{Al}}^2 + \sigma_{\text{Fe}}^2)}$	0.01
Al $y = 0$ Fe $y \neq 0$	$\sqrt{(\sigma_{\text{Al}}^2 + 2\sigma_{\text{Fe}}^2)}$	0.01
Al $y \neq 0$ Fe $y = 0$	$\sqrt{2\sigma_{\text{Al}}^2 + \sigma_{\text{Fe}}^2}$	0.012
Al $y \neq 0$ Fe $y \neq 0$	$\sqrt{(2\sigma_{\text{Al}}^2 + 2\sigma_{\text{Fe}}^2)}$	0.013
Fe $y = 0$ Fe $y = 0$	$\sqrt{2} \cdot \sigma_{\text{Fe}}$	0.006

in two ranges, 2.60–2.75 Å and 2.83–2.95 Å. There are some extremely short distances—2.26 Å for Fe–Al and 2.45 Å for Al–Al, both shorter than any previously reported in similar structures (Nicol, 1953; Taylor, 1954).

(ii) The co-ordinations of the Fe atoms are reviewed in Table 3. The atoms Fe₁–Fe₄ are all similar in that

Table 3. *Review of iron atom environments*

Atom	No. of Al neighbours	Mean distance (Å)
1	10	2.59 ₇
2	10	2.53 ₀
3	10	2.54 ₂
4	10	2.55 ₉
5	9	2.52 ₇

their neighbours are arranged as in the 12-fold co-ordination of a close-packed structure: the number is reduced to ten either by missing out two atoms or by missing out one neighbour and by having one atom more than 2.80 Å away. For Fe₅, with nine neighbours, the arrangement is different. Both of these are shown in Fig. 1(a) and (b). The variations in the mean Fe–Al distances may be first explained in terms of packing effects. Fe₂ has no other neighbours apart from the ten

reckoned as being in contact. Fe₃ and Fe₄ have Fe neighbours at 2.91 and 3.01 Å respectively, Fe₁ has another Al neighbour at 2.84 Å; whilst these may not be in contact, they are sufficiently near to prevent the contact atoms from moving closer to the central Fe atom. Fe₅ has about the same mean distance as Fe₂, but it has two other Al neighbours at 3.3 and 3.4 Å, and, if allowance is made for the effect of these, it can be said that the mean Fe–Al distance for nine neighbours is shorter than for ten.

With respect to their environments, the Al atoms may be divided into four types. Their co-ordinations are reviewed in Table 4 and illustrated in Fig. 1(c)–(f).

Table 4. *Review of aluminium atom environments*

Group	Atom	Fe contacts*		Al contacts†	
		No.	Mean distance (Å)	No.	Mean distance (Å)
A	8	2	2.48 ₈	8	2.80 ₁
	10	2	2.41 ₁	9	2.82 ₈
	12	2	2.48 ₀	8	2.77 ₈
	14	2	2.30 ₆	10‡	3.07
	(20)	4	2.50 ₄	8	2.90 ₃
B	6	3	2.51 ₅	7	2.83 ₅
	11	3	2.51 ₂	7	2.78 ₀
C	15	3	2.57 ₈	8	2.81 ₈
	16	3	2.57 ₉	8	2.80 ₇
	17	3	2.57 ₂	7	2.76 ₀
	18	3	2.57 ₂	7	2.74 ₁
	19	3	2.57 ₆	7	2.74 ₅
D	7	{ 3	2.53 ₅ (2.80)	7	2.63 ₃
		{ 4	2.61 ₁ (2.85)		
	9	4	2.62 ₅		
	13	4	2.60 ₁		

* Using all distances < 2.80 Å except for No. 7. There are no other contacts < 2.90 Å.

† Using all distances < 3.00 Å except for (‡) No. 14, which has no Al neighbours closer than 3.00 Å.

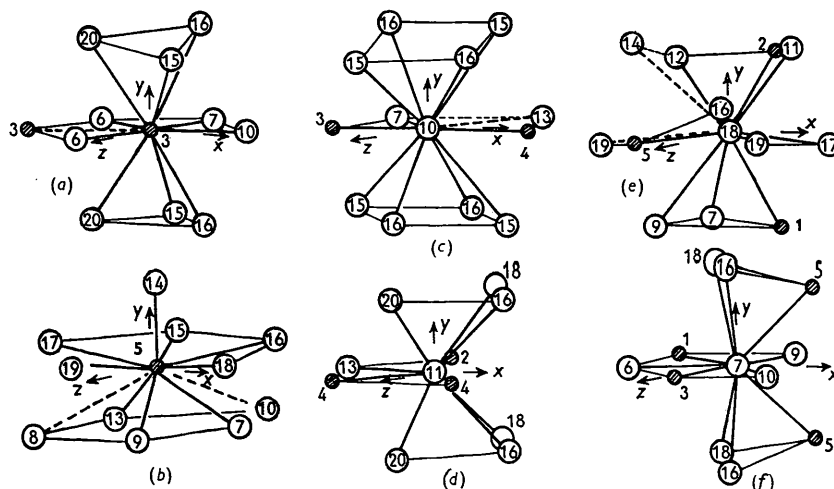


Fig. 1. Co-ordinations (a)–(b) of Fe and (c)–(f) of Al atoms. Contacts with the central atom are shown by full lines; neighbours that are not in contact are shown by broken lines. Contacts between neighbours in planes normal to the y axis are also shown. Fe atoms are shaded. For Al atoms one representative from each of the groups of Table 4 is shown.

Within each group the pattern of the co-ordinations is very similar, although the atoms and their neighbours are not related by symmetry; this will be discussed further in § 3. It can be seen that there is a tendency for each Al atom to have ten neighbours, the combination of seven Al's and three Fe's being the most frequent. The variations of the mean contact distances between these groups are illustrated in Fig. 2. The tendency illustrated by these may be

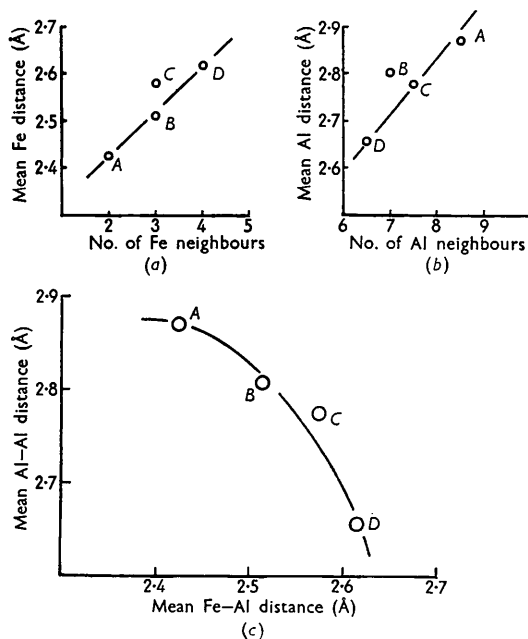


Fig. 2. Variations of mean contact distances for the neighbours of an Al atom. The lettering of each point indicates the group of Table 4.

interpreted as follows. Consider an Al atom surrounded by a polyhedron of (say) four Fe and six Al atoms. When an Fe neighbour is replaced by an Al neighbour, there is less room on the polyhedron surface, so that the mean distance from the central atom should increase. It is seen that the mean Al distance does increase, but the Fe neighbours move closer as their number decreases. Thus these trends are not explained in terms of size effects, but suggest rather some specific interaction between Fe and Al atoms. It must be emphasized that each distance plotted is the mean value of a range of distances. Thus, the three Fe neighbours of Al_{15} , Al_{16} , Al_{17} and Al_{19} could be considered in each case as two short contacts and one long contact with the near pair at a mean distance of 2.48 Å; this is still significantly longer than the mean for two Fe neighbours when there are eight or nine Al neighbours instead of seven.

(iii) Pauling (1947, 1949) has suggested a formula relating the distance between any pair of atoms and the number of electron pairs concerned in bonding between them. This relationship has been applied in

a discussion of the interatomic distances in Co_2Al_9 (Pauling, 1951). In the present structure, assuming Fe to have a valency of 5.78, the mean Fe-Al distances given by Pauling's formula for ten and nine Al neighbours are 2.557 and 2.527 Å respectively, compared with the mean observed values of 2.559 and 2.528 Å. The direct application to the mean Al-Al distance would not be very significant in view of the variation in Al co-ordinations. A direct application to the mean values of each group of Table 4, assuming Al to be trivalent and the 5.78 Fe bonds to be divided equally amongst the Al neighbours, gives Al-Al distances which are too long—between 2.9 and 3.1 Å. Alternatively, application of the formula to derive the valencies of Al atoms from the interatomic distances, assuming a single-bond radius of 1.165 Å for Fe, gives values of between 4.2 and 6.5. These might be accounted for by transfer of electrons from the transition metal (as was done for the Co_2Al_9 figures), but to give each Al atom at least one extra electron would mean the loss of three electrons per Fe atom. The single-bond radius of Fe would be changed by assuming a different percentage *d*-character for its bonds, although this would spoil the agreement of the mean Fe-Al distances given above. Detailed agreement thus does not seem possible without introducing new assumptions or modifying the existing ones.

A qualitative explanation of the interatomic distances may be given by assuming that there is a strong interaction between Fe and Al atoms which increases in strength as their separation decreases. Then the trend of Fig. 2(a) shows that the strength of the interaction with one Fe neighbour for a given Al atom increases as the number of these neighbours decreases. The Al-Al distance variations may then be due to size factors, or to interactions with Al neighbours which are also stronger as their number decreases. A fair amount of variation may be tolerated, and may be imposed by packing of the further neighbours, as outlined for the mean Fe-Al distances. A more rigid interpretation, such as Pauling's treatment gives, would mean that the very short distances have an exceptional significance, e.g. the 2.26 Å from Fe_3 to Al_{10} corresponds to 1.8 electron pairs in a bond, and the 2.45 Å from Al_7 to Al_9 gives 1.2 electron pairs. The position of Al_{14} can only be explained in terms of a strong Fe-Al interaction: for otherwise it could relax its close distances to the two Fe_5 atoms (2.31 Å) by moving out of the straight line between Fe_5 and its mirror image, as it is more than 3.0 Å from all other atoms.

Other intermetallic compounds of this type, in which there are Al atoms with different environments, show a similar variation of transition-metal-aluminium distance with the number of transition metal neighbours. The figures are reviewed in Table 5. The corresponding variation of Al-Al distances is not as regular, which may mean that the Al-Al interactions are not as important. A critical review of these data

Table 5. Variation of mean aluminium-transition-metal distances with number of transition-metal neighbours

Structure	Atom	No. of transition-metal neighbours	Distances (Å)	Mean distance (Å)
MnAl ₆ *	Al ₂	1	2.435	—
	Al ₁	2	2.60	—
	Al ₃	2	2.64, 2.54	2.59
Mn ₃ SiAl ₉ †	Al ₁	2	2.420	—
	Al ₃	3	2.67, 2.68	2.68
Co ₂ Al ₅ ‡§	Al _a	6	2.62, 2.54	2.58
	Al _d	3	2.63, 2.41	2.48
	Al _e	2	2.33, 2.53	2.43

* Nicol, 1953.

† Robinson, 1952.

‡ Bradley & Cheng, 1938.

§ These figures may not be as accurate as the more recent (single-crystal) results for other compounds. The parameters are being re-determined in this laboratory.

is given by Taylor (1954). Vousden (1954) has presented other evidence favouring the hypothesis of a strong aluminium-transition-metal interaction in these compounds.

3. Description of the structure

The structure is described in terms of the alternate flat and puckered layers of atoms perpendicular to the monoclinic *b* axis. The general plan of the two layers is shown in Figs. 3 and 4. The flat layer is com-

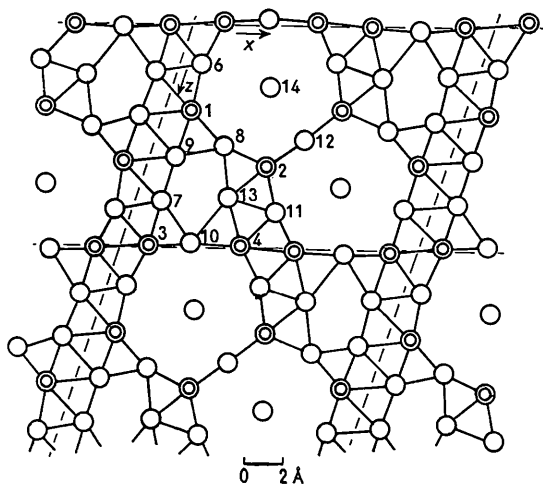


Fig. 3. Pattern of atoms in the flat layer at $y = 0$. Fe atoms are double circles, Al atoms single circles.

posed of close-packed regions—continuous chains along the *c* edge of the cell and more isolated patches between them. These two types are oriented at 30° to each other, and with such a relationship between close-packed regions there must be a region of 'misfit' whose simplest form is that of decagons or pentagons. The pentagons of the puckered layer are connected

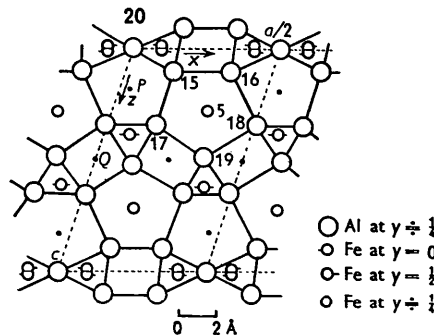


Fig. 4. Pattern of atoms in the puckered layer about $y = \frac{1}{2}$. Fe-Al contacts are not marked. The Fe atoms of neighbouring layers are also shown.

with these, but there is no obvious relationship between the pattern of this latter layer and that of the close-packed areas.

The structure may be interpreted by assuming that it must give the Fe atoms nine or ten (preferably ten) Al neighbours. This cannot be done with continuous close-packed regions and the misfit regions allow for the necessary gaps in the Fe co-ordination; Fe₅ then fits in these gaps. The puckered layer is controlled by this atom having five neighbours at about the same height, and these five fix the orientation of triangles which lie above and below the Fe's of the flat layer (Fig. 4). This prevents those triangles linking up to form a close-packed configuration. At all points marked, like *P* and *Q*, in the puckered layer, there are sites which are more than 2 Å from any neighbours, whilst Al₁₄ in the flat layer is not in contact with any atoms of that layer. It seems that such vacant regions and inefficient packing are tolerated, whilst the arrangement of Fe-atom neighbours dominates the structural pattern. At the same time, each Al atom is fitted approximately symmetrically between its Fe neighbours, the worst deviations from this being atoms Al₆ and Al₁₁ (see Fig. 1(d)). The shortest interatomic distances are between atoms in the flat layer. The shortest Fe-Al distances are for atoms Al₈, Al₁₀ and Al₁₂, which are the links between the close-packed regions.

4. The twinning

The diffraction data show that twin components can be related in two ways, by reflexions across the (100) plane and the (001) plane, or across planes perpendicular to these. To interpret such effects with a known structure, it is necessary to find a composition plane across which components related by this reflexion can be joined without large changes in the interatomic environments. Attempts to do this for a simple reflexion across the above planes were unsuccessful.

The possibility of the twin components being related by a glide plane, as in the Baveno law found for orthoclase (Bragg, 1937), was then considered. This presents a large number of alternatives as there are

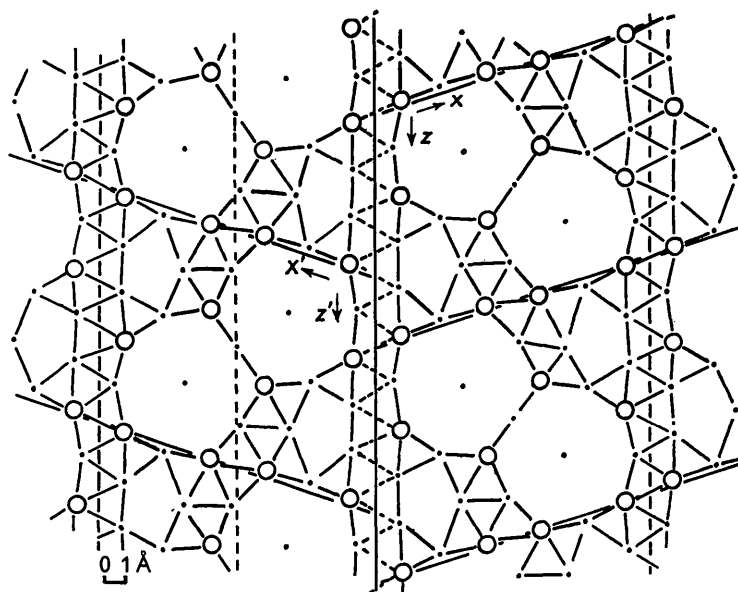


Fig. 5. Plan of layers at $y = 0$ (or $y = \frac{1}{2}$) for a twin crystal of the first type. Either the full or the broken line is the trace of the composition plane. Unit cells are outlined with respect to the first possibility. Fe atoms are circles, Al atoms dots.

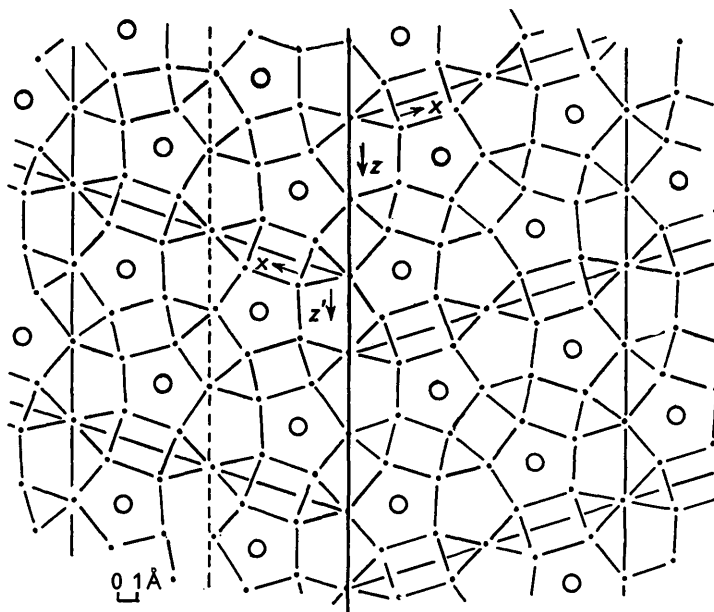


Fig. 6. Plan corresponding to Fig. 5 for the layer near $y = \frac{1}{4}$.

four possible planes, which only specify direction, not position, for possible composition planes, and a glide component for each, which can be quite arbitrary. For each of the twin relationships, only one satisfactory scheme was found, but it cannot be claimed that all possible combinations have been explored.

In the first type, the twins are related by the operation of reflexion across the A face of the cell, followed by a translation of 3.9 \AA in the negative z direction. The effect of this on the two layers is shown in Figs. 5 and 6. In each case, the region

between full and broken lines (of width 7 \AA) is common to the two structures and there are no changes in nearest-neighbour environments. For the second type, there is a reflexion across the C face followed by a translation of $\frac{1}{2}a$ in the x direction. The effect of this for the flat layer is shown in Fig. 7; again, there are no nearest-neighbour changes, and the region between the broken lines (12 \AA wide) is common to both components. For the puckered layer, this glide-plane operation is already present as a symmetry operation of the structure and the diagram of Fig. 4 would serve

to fit over Fig. 7. These features have all been established by careful graphical methods, and no detailed calculations of the new interatomic distances across the composition planes have been attempted. It is not possible to determine by direct calculation either the

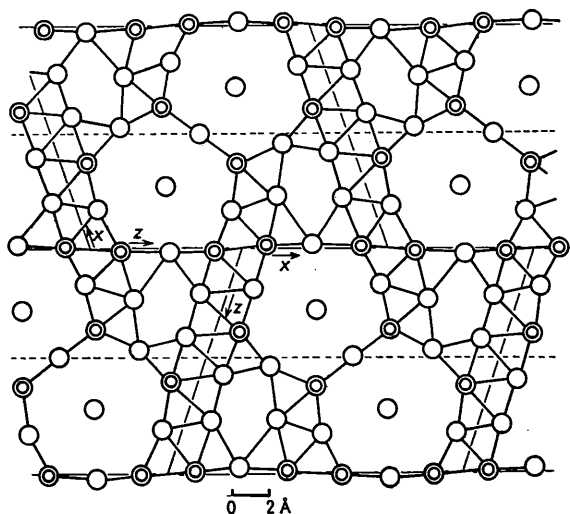


Fig. 7. Plan of layer at $y = 0$ for a twin crystal of the second type.

exact placing of atoms on or very near these planes, or, in at least one case, the exact length of the translation component of the glide.

The twin relationships involve only a change in the long-range pattern of the structure, so that it can be understood why growth twins of this type should occur frequently. The structure has well marked layers in several directions, giving rise to very strong (Brillouin zone) reflexions corresponding to spacings of about 2 Å. These reflexions from a twin pair are in approximate coincidence: this can be compared with similar results for the Fe-Al-Be ternary (Black, 1955*a*) and a Ni-Mn-Al ternary (Robinson, 1952). It can be shown by a detailed analysis (Black, 1954) that in the present case the layers of one component are joined without discontinuity to parallel planes of similar spacing in the other, so that reflexions from the two are almost superposed.

5. The Brillouin zone

The crystals give a set of very strong reflexions with values of $p (= 1/2d_{(hkl)})$ in the range 0.24–0.26 Å⁻¹. If this is assumed to be an electron compound, it must have an electron: atom ratio in the range 1.7–2.0, the limiting values corresponding to filling of the Fermi (inscribed) sphere and of the whole Brillouin zone respectively. Correspondingly, iron must be assumed to absorb between 2.5 and 1.0 electrons. This result, and similar results for other iron compounds, are discussed elsewhere (Black, 1954, 1955*c*).

6. Electron counts

Previous workers have considered the possibility of electron transfer in aluminium-rich transitional-metal compounds (see Taylor, 1954), and have used F_o and $(F_o - F_c)$ syntheses to investigate this transfer. A critical discussion of these results is given elsewhere (Black, 1955*c*). In the present work, no experimental measurements have been made to put the intensities on an absolute scale, and in the refined projection most atoms have two or three neighbours at about 0.9 Å so that overlap effects will be serious. In Table 6,

Table 6. Review of counts on iron-atom peaks

Synthesis	Atom No.					
	1	2	3	4	5a	5b
F_o (a)	30.9	15.5	32.3	34.5	20.3	22.6
$F_o - F_c$ (b)	+0.3	-0.2	+0.8	+2.6	+1.1	-0.1
$F_o - F_c$ (c)	+1.3	-0.3	+1.3	+3.3	-0.1	-0.8

(a) Assuming zero electron density between the atoms.

(b) Using Fermi-Thomas scattering factors for iron.

(c) Using Viervoll & Ögrim (1949) factors for iron-normal + 3 (3*d*) electrons (see Black, 1955*c*).

The scale is arbitrary, obtained by making the mean of the iron counts on the F_o equal to 26.0.

counts for iron atom peaks on the F_o and $(F_o - F_c)$ syntheses are reviewed. The $(F_o - F_c)$ counts do not reproduce the large variations of the F_o , but show a mean count of one extra electron per iron atom. This effect is about the same size as an estimated standard deviation for counts of this nature (Black, 1955*b*). The effect is thus too small to be significant and its interpretation is ambiguous in the absence of absolute scaling.

7. The related phases

(i) The first reliable investigations of the aluminium-rich end of the Fe-Al system were made by Gwyer & Phillips (1927) and Ageev & Vher (1930). Bradley & Taylor (1938, 1940) studied this system and the ternary Al-Fe-Ni system, and Bradley & Goldschmidt (1939) studied the Al-Fe-Cu system. In the work of Bradley and his collaborators, powder photographs were used to examine slow-cooled and quenched alloys. It was reported that in the binary system, the FeAl₃ phase could be obtained by quenching from above 600° C., whilst a slightly different compound, Fe₂Al₇, appeared in slow-cooled alloys. This latter transformed to give the FeAl₃ pattern when heated above 600° C. No powder photographs or measurements thereon were published; it was stated that the differences between the two phases were clearly defined second-order effects. Cooling curves showed no sign of discontinuity in the region where the transformation was supposed to occur. In both of the ternary systems mentioned above, these two phases were found, together with a third phase which showed only differences of a secondary character with respect to

the other two. Nowotny, Komarek & Kromer (1951), working on the Al-Fe-Si system, published powder photographs labelled FeAl_3 and Fe_2Al_7 . As far as can be seen, none of the latter came from alloys free from silicon, and no reason for identifying them with a binary compound was given. Raynor, Faulkner, Noden & Harding (1953) have shown that there is evidence that FeAl_3 crystals extracted from Al-Fe-Zn alloys show some change as the Zn content of the alloys is increased. For alloys with more than 80% Zn, there is a sudden decrease in the Zn content of the crystals, although this is always less than $2\frac{1}{2}\%$ by weight.

The formula FeAl_3 corresponds to 40.8% Fe by weight. Raynor & Pfeil (1946-7) measured the composition of extracted crystals and found 37.2 wt. % Fe for samples annealed at 500° C., and 38.1% for those quenched from 670° C. Armand (1952) found only crystals of composition near Fe_2Al_7 in binary specimens. Thus other workers have not obtained crystals with the composition FeAl_3 and their results suggest that the composition is variable.

(ii) The work of preparing specimens described here was done in co-operation with Dr A. R. Harding in the Department of Metallurgy at Birmingham University. A check was made on the composition of the phase by analysing crystals extracted by electrolysis of alloys quenched from several temperatures between 900° C. and 600° C. The analyses were performed by Messrs Johnson Matthey and Co. All the specimens contained between 38.5 and 39 wt. % Fe. Preliminary photographs showed no difference between these specimens and crystals which had been slow-cooled to lower temperatures. Crystals obtained by quenching a small (20 g.) specimen from 900° C. were then compared with crystals annealed at 470° C. for ten weeks. No differences could be detected on powder photographs. Some specimens were more critically examined, by single-crystal complete-rotation and Weissenberg photographs, and again no difference could be found. One specimen was quenched from above the liquidus and annealed at 470° C., so that no crystals were grown at higher temperatures. Powder photographs of a crystal-rich extract of very small crystals again showed no differences. Thus the transformation reported by Bradley & Taylor could not be reproduced. The composition found structurally corresponds to 39.2 wt. % Fe, and the best approximate formula is $\text{Fe}_4\text{Al}_{13}$. The formula FeAl_3 has been retained merely for convenient reference.

(iii) Examination of results obtained by Robinson (1952, 1954) for the ternary phase $\text{Ni}_4\text{Mn}_{11}\text{Al}_{60}$ shows that its structure is related to that of FeAl_3 . This will be discussed elsewhere when work on the ternary structure has been completed.

8. Conclusion

One of the most important features of the FeAl_3 structure is its extreme complexity, in comparison

with the structures of other aluminium-transition-metal compounds previously described: in such a complex structure there is a much greater range of variation in interatomic distances and in atomic coordinations, which has already (Fig. 2 and Table 5) been shown to give an indication of very suggestive new relationships for a number of compounds of various transition metals with aluminium. The attempt to interpret these relationships has led to re-examination of a variety of other known structures; a full discussion of the important features which emerge will be given later, but it is already clear that one of the most valuable consequences of the analysis of this complex alloy may prove to be the enhanced understanding of the fundamental significance of the geometry of a variety of alloy-phase structures.

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The Crystal Structure of Indanthrone

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The crystal structure of the α form of indanthrone has been determined by two-dimensional Fourier projections on (010) and three-dimensional line syntheses parallel to [010]. The interatomic distances and inter-bond angles have been calculated, and a slight departure from planarity of the molecule has been established.

The crystals are monoclinic; $a = 30.83$, $b = 3.833$, $c = 7.845$ Å, $\beta = 91^\circ 55'$; space group $P2_1/a$; two molecules in the unit cell.

Introduction

The structure of indanthrone is of particular interest because of its commercial significance as a vat dyestuff. Many complex organic compounds whose structures have been determined are of industrial importance, but, with the exception of the phthalocyanines (Robertson, 1935), few crystal structures have been determined in the dyestuffs field. Indanthrone is known to exist in several polymorphic forms (B.I.O.S., 1945; F.I.A.T., 1948) and the present paper describes the crystal-structure determination of the stable α form.

Experimental

Dendritic clusters of single crystals were grown by vacuum sublimation of pure δ indanthrone, and were identified as the α form by X-ray powder photographs. The individual crystals were very elongated [b] laths, platy on {100}, with small {001}, and very poorly defined terminal faces. They have excellent fibrous cleavage along the lath. The unit-cell dimensions were measured from Weissenberg photographs and the angle β was determined goniometrically:

$$a = 30.83, b = 3.833, c = 7.845 \text{ \AA}; \beta = 91^\circ 55'.$$

Monoclinic, holosymmetric class; space-group $P2_1/a$. There are two centrosymmetrical molecules $C_{28}H_{14}O_4N_2$ in the unit cell. Density by flotation = 1.60 g.cm.^{-3} ; calculated density = 1.58 g.cm.^{-3} .

Weissenberg photographs using $\text{Cu } K\alpha$ radiation were taken of the zero, first, second, and third layers of the b axis, and the zero layer of the c axis; and the intensities were estimated visually by comparison with a calibrated scale of time exposures of one reflection from the same crystal. The appropriate geo-

metrical correction factors were applied and the relative structure amplitudes were calculated. The absolute scale and a temperature factor

$$\exp(-4.0 \sin^2 \theta / \lambda^2)$$

were obtained graphically from a comparison of the observed and calculated structure factors.

Structure determination

Assuming the molecule to be approximately planar, its tilt from the (010) plane was limited to less than 30° by the short b -axis length of 3.833 Å. There were several possible ways of packing the molecules in this plane, and indication of the correct one was given by the unusually large structure factors of several high-order planes, which had spacings corresponding to the 1.20 and 2.08 Å spacings in the molecule formed by the regular repetition of hexagonal rings.

The initial ($h0l$) structure-factor calculations were made assuming a planar molecule, built of regular hexagons of side 1.39 Å; and the x and z coordinates were then refined by successive Fourier projections on (010). The final projection (Fig. 1) included 165 observed reflexions and was summed at intervals of $1/120$ and $1/60$ along the a and c axes respectively. All the atoms were resolved, and the x and z coordinates corresponding to the centres of the peaks were located analytically by least squares, assuming a Gaussian electron-density distribution of the form

$$\rho(x, z) = \exp(r - sx^2 - tz^2 - ux - vz - wxz).$$

Since the (311) and (410) planes gave the strongest (hkl) reflexions, trial y coordinates were calculated for the molecule in these and intermediate planes, and the