

## The Structure of the Intermetallic Phase FeAl<sub>6</sub>

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The structure of FeAl<sub>6</sub> has been refined. The unit cell is orthorhombic and the structure is isostructural with MnAl<sub>6</sub> and with  $\alpha$ -FeCuAl, which is a copper-stabilized form of FeAl<sub>6</sub>.

### 1. Introduction

The binary phase FeAl<sub>6</sub> was first reported by Hollingsworth, Frank & Willett (1962). A copper-stabilized form of FeAl<sub>6</sub>, however, had been reported by Keller & Wilcox (1933) and was confirmed by Phragmén (1950) who investigated the aluminum-rich corner of the Al-Cu-Fe phase diagram and assigned the formula (FeCu)(CuAl<sub>6</sub>) to the  $\alpha$  phase. Phillips (1953-54) also confirmed the existence of this phase. The composition by weight of Phragmén's crystals was given as Al 70%, Cu 8% and Fe 22%. The structure of this phase was refined by Black, Edwards & Forsyth (1961) who found that the copper atoms were evenly distributed amongst the aluminum sites, the structure being isostructural with MnAl<sub>6</sub> (Nicol, 1953).

Hollingsworth *et al.* gave the cell dimensions of FeAl<sub>6</sub> as  $a=6.492$ ,  $b=7.437$ ,  $c=8.788$  Å, the unit cell being orthorhombic. These values are nearly the same as those given by Black *et al.* for the unit cell of  $\alpha$ -FeCuAl, their values being  $a=6.4343$ ,  $b=7.4604$ ,  $c=8.7768$  Å (all  $\pm 0.0010$  Å).

### 2. Material

Aluminum sheet containing crystals of FeAl<sub>6</sub> was kindly supplied by Dr E. H. Hollingsworth of the Alcoa Research Laboratories, New Kensington, Pa., U.S.A. Attempts to extract crystals of FeAl<sub>6</sub> from this sheet were unsuccessful. A crystal suitable for X-ray studies was prepared in an ingot containing 2 wt.% iron in aluminum, by annealing it at 500 °C for two hours and then quenching it in silicone oil at 20 °C. The crystal was extracted by electrolysis, 2% hydrochloric acid and a nickel cathode being used.

The crystal was acicular, the [001] zone axis being the needle axis, and it was about 0.2 mm long and 0.1 mm in diameter. Further attempts to prepare crystals of this phase by the method described above have failed.

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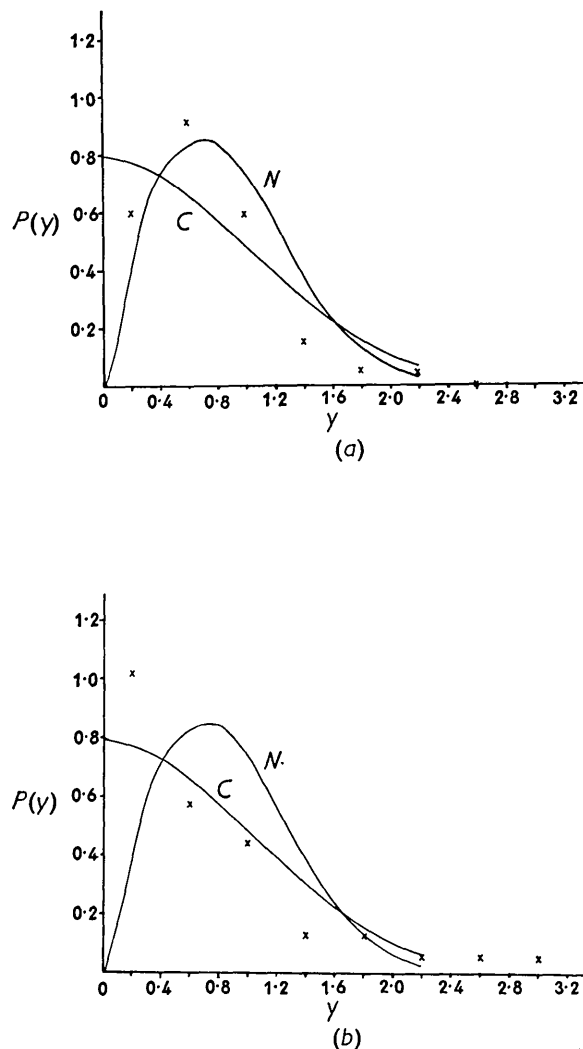


Fig. 1. Srinivasan statistical tests for centrosymmetry in the structure of FeAl<sub>6</sub>. (a) Distribution for the [010] zone, (b) Distribution for the [001] zone. In each diagram the theoretical distributions are drawn as full lines and the curves for a centrosymmetric and non-centrosymmetric structures are labelled C and N respectively.

### 3. Unit cell and space group

Measurements of high angle spots on zero layers of oscillation photographs were used to calculate the following cell dimensions:

$$a = 6.464, b = 7.440, c = 8.779 \text{ \AA} \text{ (all } \pm 0.005 \text{ \AA)}.$$

The density, measured by the flotation method, was found to be  $3.45 \pm 0.05 \text{ g.cm}^{-3}$ . This is in agreement with the calculated density of  $3.45 \text{ g.cm}^{-3}$  which is obtained if it is assumed that the unit cell contains six formula units. The indexing of Weissenberg photographs showed the space group to be *Ccmm*, *Ccm2<sub>1</sub>* or *Cc2m*, only the first being centrosymmetric. These space group symbols correspond to Nicol's choice of axes for MnAl<sub>6</sub> and are not those adopted in *International Tables for X-ray Crystallography* (1952). The origin of the unit cell was chosen to make  $z_1 = 0$ .

The Srinivasan test (1960) for a centre of symmetry was applied to the  $\{h0l\}$  and  $\{hk0\}$  reflexions. The distributions obtained are shown in Fig. 1. Only about fifty reflexions were available for each zone and so the distributions are probably subject to more error than is usual when this test is used. The distributions indicate that the  $[001]$  projection is probably centrosymmetric, but that the test is inconclusive for the  $[010]$  zone.

### 4. Refinement of the $[001]$ projection

Reflexions of the form  $hk0$  out to  $\sin \theta/\lambda = 1.35 \text{ \AA}^{-1}$  were collected on zero-layer normal-beam Weissenberg photographs, with filtered Mo  $K\alpha$  radiation and a multiple film technique. The intensities were measured visually with an intensity scale made by using a reflexion from this zone. The intensities were corrected for Lorentz and polarization effects.

The refinement was carried out by means of successive ( $F_o - F_c$ ) syntheses, using the atomic scattering factors given by Forsyth & Wells (1959). The structure of FeAl<sub>6</sub> was thought to be approximately the same as that of  $\alpha$ -FeCuAl, for which Black *et al.* (1961) proposed a non-centrosymmetric structure. Their deviations from a centrosymmetric arrangement were, however, small and could not be detected by any statistical test of the intensities. The centrosymmetric structure of  $\alpha$ -FeCuAl was taken as the starting point in the refinement of FeAl<sub>6</sub> so that any deviations from a non-centrosymmetric structure could be detected independently.

The atomic sites determined by Black *et al.* for the non-centrosymmetric structure of  $\alpha$ -FeCuAl are shown in Fig. 2(a). The centrosymmetric structure is obtained by changing the  $x$  coordinate of Al(1) to zero and replacing the fourfold Al(2) and Al(4) atoms by a single eightfold Al(2) atom with  $x$  coordinate at approximately the mean of the separate atom coordinates.

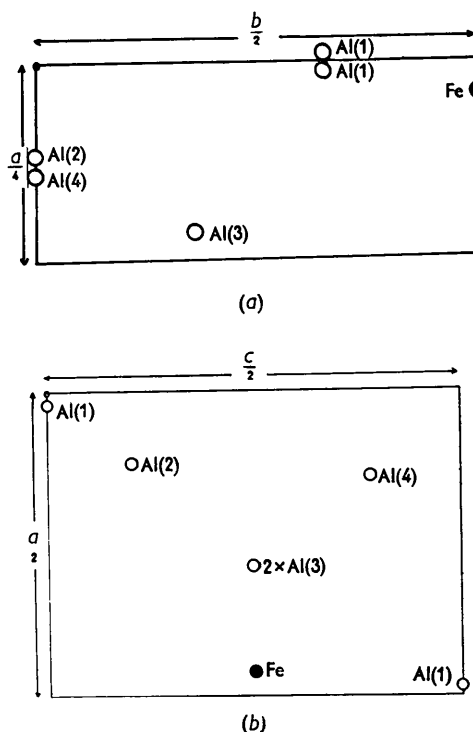


Fig. 2. Atomic positions for  $\alpha$ -FeCuAl given by Black *et al.* (a)  $[001]$  projection, (b)  $[010]$  projection.

The refinement of the structure was started with all the measured reflexions. After several cycles of refinement the  $R$  index was 21.4%. At this stage, the observed structure amplitudes were compared with the corresponding calculated structure factors and those reflexions suffering from extinction were left out of succeeding refinement cycles. The atomic parameters were refined to an  $R$  index of 13.1% on the basis of a centrosymmetric structure. An examination of the ( $F_o - F_c$ ) synthesis at this stage revealed that the Al(1) atom was elliptical but that the other atomic sites had no significant features associated with them. The Al(1) atom was therefore moved off the  $y$  axis, thereby removing the mirror plane perpendicular to  $c$  and changing the space group to *Ccm2<sub>1</sub>*, which is non-centrosymmetric. The  $[001]$  zone of this space group is, however, still centrosymmetric. The two Al(1) atoms (Fig. 2(a)) are related by the  $c$ -glide plane perpendicular to  $a$ , and they may only have equal and opposite displacements in the  $x$  direction from their original superposed positions. The refinement was continued until  $R$  was 9.7%, which was the lowest value obtained. The predicted shifts were then less than the corresponding standard deviations in the coordinates. The final  $F_o$  and ( $F_o - F_c$ ) syntheses are shown in Fig. 3 and the atomic coordinates are compared with those for  $\alpha$ -FeCuAl in Table 1.

Table 1. *The atomic parameters in FeAl<sub>6</sub> and  $\alpha$ -FeCuAl*

Parameter	FeAl <sub>6</sub>	Standard deviation	$\alpha$ -AlCuFe				Standard deviation
			A	B	C	D	
$x_0$	0.4544	0.0005	0.4612	0.4612	0.4612	0.4612	0.0003
$z_0$	0.2500	0.0006	0.2500	0.2500	0.2500	0.2500	0.0005
$x_1$	0.0200	0.0025	0.0171	0.0171	0.0171	0.0171	0.0016
$y_1$	0.3242	0.0005	0.3255	0.3255	0.3255	0.3255	0.0003
$x_2$	0.1357	0.0030	0.1455	0.1450	0.1210	0.1210	0.0022
$z_2$	0.1000	0.0015	0.1050	0.1050	0.1050	0.1060	0.0012
$x_3$	0.2842	0.0010	0.2872	0.2872	0.2872	0.2872	0.0009
$y_3$	0.3190	0.0010	0.3182	0.3182	0.3182	0.3182	0.0006
$z_3$	0.2500	0.0006	0.2410	0.2610	0.2415	0.2580	0.0005
$x_4$	0.1357	0.0030	0.1210	0.1210	0.1450	0.1450	0.0022
$z_4$	0.4000	0.0015	0.3940	0.3970	0.3970	0.3980	0.0012

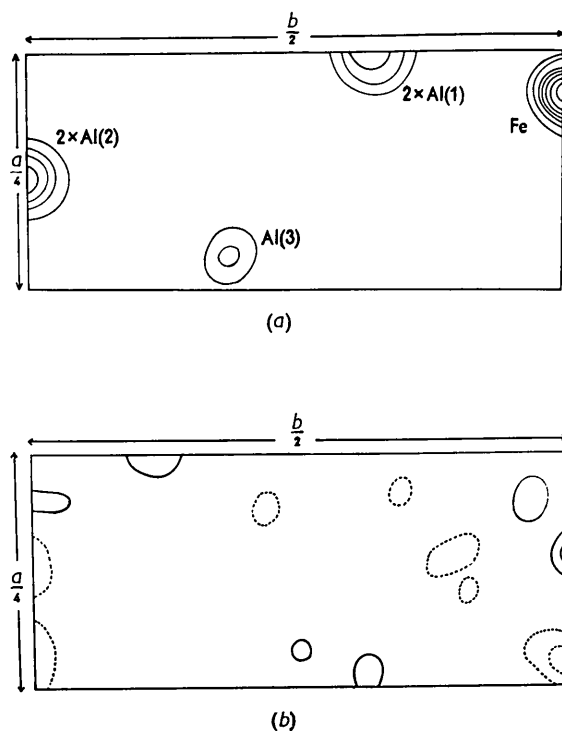


Fig. 3. (a) Final  $F_o$  synthesis of [001] projection of FeAl<sub>6</sub>. The contours are at equal arbitrary intervals. (b) Final  $(F_o - F_c)$  synthesis for the [001] projection of FeAl<sub>6</sub>. The contour intervals are one eighth those in (a); negative contours are shown as broken lines and the zero contour is omitted.

### 5. Refinement of the [010] projection

Reflexions of the form  $h0l$  were collected and measured as described in § 4. The crystal was not small enough in the  $z$  dimension for the absorption to be assumed to be a smooth function of  $\sin \theta/\lambda$ , and so absorption corrections were calculated on the EDSAC II electronic computer with a program devised by Wells (1960). The linear absorption coefficient was calculated to be  $42.6 \text{ cm}^{-1}$ .

The [010] projection is centrosymmetric if the space group is  $Ccmm$  and non-centrosymmetric if

the space group is  $Ccm2_1$ . The atomic sites in the asymmetric unit for the non-centrosymmetric structure of  $\alpha$ -FeCuAl are shown in Fig. 2(b).

The initial coordinates used in the refinement were those given by Black *et al.* for the centrosymmetric structure of  $\alpha$ -FeCuAl. The atomic coordinates were refined, using all the measured reflexions, to an  $R$  value of 16.0%. The difference Fourier synthesis again indicated that the Al(1) atom should be moved

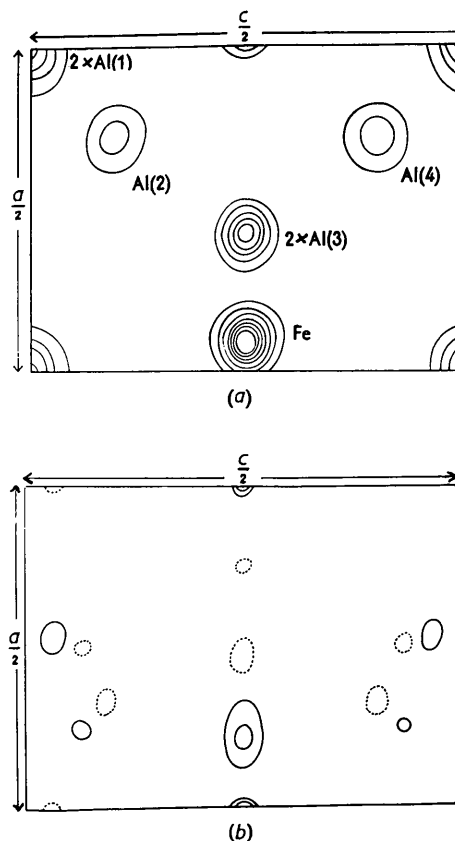


Fig. 4. (a) Final  $F_o$  synthesis of [010] projection of FeAl<sub>6</sub>. The contours are at equal arbitrary intervals. (b) Final  $(F_o - F_c)$  synthesis for the [010] projection of FeAl<sub>6</sub>. The contour intervals are one eighth those in (a); negative contours are shown as broken lines and the zero contour is omitted.

in the  $x$  direction, but predicted no shifts of the Al(2) and Al(4) atoms from their apparently equivalent positions. At this stage those reflexions suffering from extinction were discarded. The refinement was continued until  $R$  was 14.2% which was the lowest value obtained. The final  $F_o$  and  $(F_o - F_c)$  syntheses are shown in Fig. 4. The displacement of the Al(1) atoms from the centrosymmetric arrangement is too small to be detected on the  $F_o$  map. The atomic coordinates are compared with those for  $\alpha$ -FeCuAl in Table 1. A list of  $F_o$  and  $F_c$  values is given elsewhere (Walford, 1963).

## 6. Discussion

The structure of FeAl<sub>6</sub> is essentially the same as that of  $\alpha$ -FeCuAl and as that of MnAl<sub>6</sub>. The latter has been fully described by Nicol (1953).

Accurate measurements on MnAl<sub>6</sub> have been carried out by Forsyth (1959). Effects similar to those in  $\alpha$ -FeCuAl were observed but were very much smaller in magnitude and were of the correct order for anisotropic thermal vibrations. No definite choice was made between a structure with anisotropic vibrations and one based on a departure from centrosymmetry.

The present work on FeAl<sub>6</sub> indicates that the deviations from centrosymmetry are less than those in  $\alpha$ -FeCuAl and greater than those in MnAl<sub>6</sub>.

In their refinement of  $\alpha$ -FeCuAl, Black *et al.* described the structure in terms of the four possible non-centrosymmetric structures with space group  $Ccm2_1$  which are produced if the mirror plane perpendicular to the  $c$  axis of the space group  $Ccmm$  is removed. No decision could be taken on which of these four was the correct structure. Low temperature

Table 2. *Interatomic distances for FeAl<sub>6</sub> and for the four possible structures for  $\alpha$ -FeCuAl*

Atom	Bonded to	Number of bonds	FeAl <sub>6</sub>		$\alpha$ -AlCuFe				Standard deviation	
			Length (Å)	Standard deviation	A	B	C	D		
Fe	Al(1)	2	2.590	0.005	2.576	2.576	2.576	2.576	0.003	
	Al(1)	2	2.561	0.005	2.555	2.555	2.555	2.555	0.003	
	Al(2)	1	2.445	0.025	2.400	2.400	2.532	2.527	0.015	
	Al(3)	2	2.616	0.010	2.626	2.626	2.626	2.625	0.007	
	Al(3)	2	2.522	0.010	2.499	2.500	2.499	2.499	0.007	
	Al(4)	1	2.448	0.025	2.527	2.541	2.409	2.414	0.015	
Al(1)	Fe	1	2.561	0.005	2.555	2.555	2.555	2.555	0.003	
	Fe	1	2.590	0.005	2.576	2.576	2.576	2.576	0.003	
	Al(1)	1	2.616	0.007	2.603	2.603	2.603	2.603	0.004	
	Al(2)	1	2.941	0.017	2.877	2.877	> 3	> 3	0.013	
	Al(2)	1	2.674	0.007	2.724	2.724	2.682	2.685	0.004	
	Al(3)	1	2.782	0.015	2.795	2.930	2.794	2.909	0.010	
	Al(3)	1	2.877	0.015	2.811	2.671	2.807	2.692	0.010	
	Al(3)	1	2.749	0.015	2.738	2.876	2.741	2.855	0.009	
	Al(3)	1	2.947	0.015	> 3	2.870	2.997	2.889	0.009	
	Al(4)	1	2.725	0.017	2.825	2.817	2.690	2.690	0.013	
	Al(4)	1	2.672	0.007	2.748	2.739	2.793	2.793	0.004	
	Al(2)	Fe	1	2.445	0.025	2.400	2.400	2.532	2.527	0.015
Al(1)		2	2.674	0.007	2.724	2.724	2.682	2.685	0.004	
Al(1)		2	2.941	0.017	2.877	2.877	> 3	> 3	0.013	
Al(3)		2	2.878	0.017	2.810	2.889	2.866	2.935	0.013	
Al(3)		2	2.951	0.017	2.962	> 3	2.808	2.869	0.013	
Al(4)		1	2.639	0.020	2.541	2.567	2.567	2.567	0.015	
Al(4)		1	2.639	0.030	2.521	2.502	2.502	2.509	0.018	
Al(3)		1	2.522	0.010	2.499	2.500	2.499	2.499	0.007	
Al(3)	Fe	1	2.616	0.010	2.626	2.626	2.626	2.625	0.007	
	Al(1)	1	2.877	0.013	2.811	2.671	2.807	2.692	0.010	
	Al(1)	1	2.782	0.015	2.795	2.930	2.798	2.909	0.010	
	Al(1)	1	2.947	0.013	> 3	2.870	2.997	2.889	0.009	
	Al(1)	1	2.749	0.013	2.738	2.876	2.741	2.855	0.009	
	Al(2)	1	2.878	0.017	2.810	2.889	2.866	2.925	0.013	
	Al(2)	1	2.951	0.017	2.926	> 3	2.808	2.869	0.013	
	Al(3)	1	2.694	0.015	2.712	2.712	2.712	2.712	0.012	
	Al(4)	1	2.954	0.018	2.929	2.864	2.887	2.825	0.013	
	Al(4)	1	2.881	0.018	2.873	2.806	> 3	2.937	0.013	
	Al(4)	Fe	1	2.448	0.020	2.527	2.541	2.409	2.414	0.015
		Al(1)	2	2.672	0.006	2.748	2.739	2.793	2.790	0.004
		Al(1)	2	2.725	0.018	2.825	2.817	2.690	2.687	0.013
		Al(2)	2	2.639	0.020	2.541	2.567	2.567	2.567	0.015
Al(2)		2	2.639	0.025	2.521	2.502	2.502	2.502	0.018	
Al(3)		1	2.954	0.018	2.929	2.864	2.887	2.825	0.013	
Al(3)		1	2.881	0.018	2.873	2.806	> 3	2.941	0.013	

measurements by Williams (1961) also failed to produce a definite solution.

A comparison of the bond lengths in FeAl<sub>3</sub> and  $\alpha$ -FeCuAl (Table 2) reveals that the largest differences between the two structures occur when an Al(2) or Al(4) atom is involved. This suggests that it is these sites which are affected most when the Cu atoms are introduced into the structure and thus it seems likely that these are the sites which are occupied by the Cu atoms in  $\alpha$ -FeCuAl. This deduction is in agreement with the conclusions of Phillips (1953-54) although Black *et al.* (1961) were unable to detect Cu atoms in these sites.

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### Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

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#### On the detection of cyanide-ion rotation in potassium cyanide by neutron diffraction. By

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Recently, considerable interest has been shown in the study of the crystal structure of cyanides by neutron diffraction, in view of the fact that the neutron scattering amplitudes of carbon and nitrogen, apart from being significantly unequal, are comparable to and often exceed those of the metal atoms in contrast to their X-ray scattering factors (Bacon, 1963). This enables the carbon and nitrogen atoms to be distinguished and also accurately located in the presence of metal atoms. One of these investigations has been on potassium cyanide by Elliott & Hastings (1961), who, from a study of the neutron-diffraction powder data, concluded that at room temperature the cyanide ions in this cubic crystal (space group  $Fm\bar{3}m$ ) are freely rotating (Pauling, 1930), rather than disordered, *i.e.* oriented at random along the eight [111] directions (Frenkel, 1935). This distinction in favour of the dynamic model against the static disordered model seemed somewhat surprising in view of the considerable difficulty we had in choosing between several models for cubic  $K_2Zn(CN)_4$ , even using single-crystal neutron data. The structure-factor calculations

of Elliott & Hastings on the basis of the static disordered model seem, however, to be in error.\*

\* *Note added on 1 September:* Elliott & Hastings in their reply to the editor say that there is indeed an arithmetical error in the calculation of their 111 intensities, but that correction of this would not have altered their conclusions. They also point out that they did not apply any Debye-Waller correction. While with the temperature factors used by us, our  $F_c$ 's on the basis of the dynamic model are in approximate agreement with the intensities calculated by Elliott & Hastings, removal of the temperature factors takes the calculated values for the dynamic model once again close to those for the static disordered model without temperature factors. In short, with or without Debye-Waller correction, distinction between the two models on the basis of powder neutron data seems difficult. It may be mentioned here that from the point of view of a diffraction experiment, it is not also possible to distinguish between a static disordered model and one in which the cyanide ions are undergoing hindered rotation and therefore the latter model can also be considered consistent with our data.