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The Structure of $FeAl_2$ by Anomalous Dispersion Methods

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The compound '$FeAl_2$' has a triclinic unit-cell $a = 4{\cdot}878 \pm 0{\cdot}001$, $b = 6{\cdot}461 \pm 0{\cdot}002$, $c = 8{\cdot}800 \pm 0{\cdot}003$ Å, $\alpha = 91{\cdot}75 \pm 0{\cdot}05$, $\beta = 73{\cdot}27 \pm 0{\cdot}05$, $\gamma = 96{\cdot}89 \pm 0{\cdot}03°$, with approximately 6·5 iron and 11·5 aluminum atoms per cell and space group $P1$. Data collected at Mo $K\alpha$, Fe $K\alpha$ and Cr $K\alpha$ wavelengths using integrating Weissenberg photographs were analysed to yield a Patterson synthesis for the iron atoms alone, a solution of which led to direct determination of phases for most reflexions to give a Fourier synthesis of electron density showing all the atoms. The structure was refined by a full-matrix least-squares method to a final R value of 7·4% for F; departures from a centrosymmetric symmetry were only revealed on refinement. The structure is an irregular high-coordination structure, showing mixed partial occupation of some sites and shortened Fe–Al distances.

Introduction

Anomalous dispersion effects cause changes in the real ($\Delta f'$) and imaginary ($\Delta f''$) parts of the scattering power of atoms and if diffraction data for a compound are collected at wavelengths close to an absorption edge for one of its constituent atoms they show changes with wavelength which can be used in solving the structure. The techniques for exploiting changes in $\Delta f'$ alone are the same in principle as those used in isomorphous replacement techniques and it was recognized after the development of such techniques that they would be more powerful if combined with the interpretation of effects associated with changes in $\Delta f''$. An analysis of the combined use of $\Delta f'$ and $\Delta f''$ effects for both X-ray and Mössbauer resonances has been given by Black (1965) and equivalent ideas for the X-ray case have been developed by Singh & Ramaseshan (1966), Kartha & Parthasarathy (1965) and Srinivasan & Chacko (1970). The theory and practice have also been investigated for the Mössbauer application (Black & Duerdoth 1964, 1966; Parak, Mössbauer, Biebl, Formanek & Hoppe 1971; Chukhovskii & Perstnev 1972), and for the use of neutron resonances (Sikka 1969; Singh & Ramaseshan, 1968; Macdonald & Sikka 1969).

This paper describes the solution of the structure of the intermetallic compound $FeAl_2$ by use of the anomalous dispersion technique using a method of analysis which is briefly developed below, but which is equivalent to that developed by several of the authors mentioned above. $FeAl_2$, the structure of which was hitherto unknown, was chosen as a compound which promised to present a relatively simple problem, and which was an example for which isomorphous replacement is not a possible technique.

Theory

The intensity ${}_jI_H$ of spectrum H at wavelength j may be expressed in the form:

$$\begin{aligned} {}_jI_H = A_H^2 + 2A_H\alpha_H\Delta f_j' \cos \delta_H + \alpha_H^2(\Delta f_j'^2 + \Delta f_j''^2) \\ + 2A_H\alpha_H\Delta f'' \sin \delta_H \end{aligned}$$

where the atomic scattering factor appropriate to the spectrum H for one type of atom is $f_j + \Delta f_j' + \Delta f_j''$, α_H is the geometrical structure factor for atoms of this type, A_H is the amplitude for all the other atoms (assumed to give no anomalous scattering) together with the normal component for the anomalous scatterers, and δ_H is the phase angle between A_H and the real part of the anomalous atom contribution ($\alpha_H\Delta f_j'$). For a non-centrosymmetric structure, both ${}_jI_H$ and ${}_jI_{\bar{H}}$ could be measured to give

$$\begin{aligned} D = \tfrac{1}{2}[{}_jI_H + {}_jI_{\bar{H}}] = A_H^2 + 2A_H\alpha_H\Delta f_j' \cos \delta_H \\ + \alpha_H^2(\Delta f_j'^2 + \Delta f_j''^2) \end{aligned} \quad (1)$$

$$S = \tfrac{1}{2}[{}_jI_H - {}_jI_{\bar{H}}] = 2A_H\alpha_H\Delta f_j'' \sin \delta_H \,. \quad (2)$$

Examination of these equations shows that unambiguous solutions for A_H, α_H and δ_H can be obtained by measurements at three wavelengths, the solutions then being over-determined. It should be noted that A_H and α_H are reckoned positive in this formulation, all information about their relative directions being specified by δ_H.

For a centrosymmetric case

$${}_jI_H = A_H^2 + 2A_H\alpha_H\Delta f_j' + \alpha_H^2(\Delta f_j'^2 + \Delta f_j''^2) \quad (3)$$

and it is convenient to choose a zero arbitrarily for $\Delta f_j'$ (with a corresponding adjustment to f_j) at one of the wavelengths to be used so that ${}_1I_H = A_H^2 + \alpha_H^2\Delta f_1''^2$.

Measurements at three or more wavelengths should then, with perfect data, give unambiguous values for A_H and α_H. In this formulation, it is convenient to regard A_H as positive and to regard α_H as unknown in both magnitude and sign. With imperfect data, measurements at three wavelengths (which over-determine the solution) will lead to two values of α_H: a choice may be made between these either on the grounds of goodness of fit or on the criterion that it is physically impossible for α_H to be greater than the number of anomalous atoms per unit cell known to be in the crystal.

A set of values of α_H^2 can be used to give a Patterson synthesis for the anomalous scatterers alone. If this can be interpreted then a complete set of phases for the various α_H can be computed. Solutions of the equations given above give only the phase of each α_H relative to that of the A_H for the individual spectrum, but these can be combined with the inter-spectrum phases determined from the α_H solution to give the A_H phases relative to one another.

Preliminary crystallography

Crystals of the ζ-phase (nominally $FeAl_2$) of the iron–aluminum binary alloy system were prepared from the melt by P. J. Brown (see Forsyth, 1959). The composition was determined, using an X-ray microprobe analyser, as 50·5 wt.% iron, 49·4 wt.% aluminum, self-consistent absorption corrections being applied (McKinley, Heinrich & Wittry, 1966). The material was opaque and displayed no apparent external planes or cleavage faces. Thus a small (100 μm) fragment was mounted at random and oriented using the method of Brooker & Nuffield (1966), as adapted for cylindrical film (Corby, 1971). Many small fragments were examined in a search for a single crystal: only two were found and the risk of loss of fragments of the above dimensions in any grinding operation meant that a spherical crystal could not be prepared.

The unit-cell parameters were determined from measurements on a rotation photograph and a combined zero- and first-layer normal beam Weissenberg photograph, taken with Cr *Kα* radiation. The values quoted in the abstract were obtained by a least-squares fit to the $\sin^2\theta$ values for over 200 values of θ, assuming a weighted mean of $\lambda = 2{\cdot}2910$ Å and measuring weighted mean positions for high angles. This unit cell was used for indexing the reflexions and served as the coordinate frame for expressing the atomic coordinates presented later. In this paper, the cell is assumed to be in the above form, but it can be converted to 'reduced form' following Delaunay (1933) giving $8{\cdot}748 \pm 0{\cdot}003$, $6{\cdot}461 \pm 0{\cdot}002$, $8{\cdot}800 \pm 0{\cdot}003$ Å; $91{\cdot}75 \pm 0{\cdot}05$, $147{\cdot}74 \pm 0{\cdot}06$, $92{\cdot}03 \pm 0{\cdot}05°$.

The density of an 88 mg crystallite was found by a density-bottle method to be $(4{\cdot}21 \pm 0{\cdot}21) \times 10^3$ kg m^{-3}. This compares with a value of $(4{\cdot}25 \pm 0{\cdot}02) \times 10^3$ kg m^{-3} found by Forsyth (1959). Combining the density, the volume of the unit cell ($253{\cdot}7 \times 10^{-30}$ m^3) and the composition, the number of formula units per cell was found as $6{\cdot}1 \pm 0{\cdot}3$.

Osawa (1933) using powder photographs described the phase as rhombohedral with parameters 6·314 Å, 87°24′ 28″ (volume 251 Å^3), but this result cannot describe our single-crystal observations. Forsyth (1959) using single-crystal measurements gives a unit cell which is in good agreement with that presented here.

Collection of intensity data

An integrating Weissenberg camera was used in the equi-inclination mode to collect three-dimensional data using filtered Cr *Kα*, Fe *Kα*, Co *Kα* and Mo *Kα* radiations. A film pack containing two films only was used, with the addition of an inter-leaving Zr foil (127 μm thickness) during the Mo *Kα* exposures to increase the attenuation. The integrated reflexions were measured using a double-beam microdensitometer. Weak reflexions were estimated visually using non-integrated Weissenberg photographs; for refinement purposes the unobserved reflexions were set at 30% of the lowest detectable intensity in the preliminary stages and ignored in the later stages.

An absorption correction was made by applying the method of de Meulenaer & Tompa (1965) using a polyhedral model of the crystal derived from a set of microphotographs taken with the crystal in a variety of orientations; computations were performed using the *ABSCOR* segment of the X-RAY 63 Atlas package.* The ratio of this correction factor between any two reflexions had a maximum value for Cr *Kα* of 6:1, for Fe *Kα* of 4:1 and for Mo *Kα* of 1·5:1. The usual Lorentz and polarization corrections were made. Statistical tests following Howells, Phillips & Rogers (1950) gave indications of centrosymmetry, the whole plot lying above that expected from a centric distribution. Examination of the Mo *Kα* zero-layer film failed to reveal any apparently significant Bijvoet differences (equation 2) so the space group was assumed to be $P\bar{1}$. The reflexions were measured for exposures, taken with the crystal rotating about the *c* axis for Cr *Kα*, Fe *Kα* and Mo *Kα* radiations, of the zero, first, and second layers (these being all the layers possible for Cr *Kα*); zero-layer data for Co *Kα* were also collected at a late stage in the work.

Further extra reflexions for Mo *Kα* on the zero to seventh layers inclusive were also measured to bring the ultimate resolution of the data up to $\sin\theta/\lambda = 0{\cdot}52$. These further reflexions were only used in the later stages of the refinement and played no part in the initial solution. The individual layers were put on to a common 'absolute' scale by setting the average intensity in any layer equal to $\sum|f|^2$ (Wilson, 1942). The number of data in each layer was thought to be large enough to make the assumption of even population of reciprocal space valid in computing the expected values from the values of f at the mean position $[\frac{3}{4}(\sin\theta/\lambda)_{\rm limit}]$. The published f curves for iron (Wood & Pratt, 1957) and for aluminum (Froese, 1957) were used, and the anomalous dispersion corrections of Table 1 were included. (See *International Tables for X-ray Crystallography*, 1962; James, 1962; Miller & Black, 1970.)

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* X-RAY 63 (1969): program system for X-ray crystallography. Atlas computer laboratory, Chilton, Berkshire, England.

Preliminary solution

In the present work, the zero for $\Delta f'$ was chosen at the value of f for Mo $K\alpha$. An approximate value of A was first obtained by setting $\alpha=0$ so that $A=\sqrt{I_{\mathrm{Mo}}}$. This value was used in a least-squares fit of the equations for I for the other wavelengths used (Fe $K\alpha$, Cr $K\alpha$); in this refinement the Fe data were given twice the weighting of the Cr data because it was believed that they would be more accurate. The values of α so obtained were then used to obtain a better value of A and the cycle repeated. The equation for the sum of the squares of the residuals ($\sum$) obtained from equations of the form of (3) is a quartic in α and its turning points satisfy a cubic equation. Analysis of the coefficients of this equation for the conditions of the measurements concerned shows that it almost invariably had three real roots, two of which corresponded to minima in the residual. Data on 212 spectra were used and of these 136 gave positive values of α for both minima. Of these, 76 had only one reasonably small value of α ($\alpha \ngtr 6$ from the composition of the crystal), and for 40 more the best value of α was clearly indicated in that the values of $\sum$ for the two roots were in the ratio 5:1 or greater, with the larger being much greater than that expected from measurement errors. The remaining 20 did not satisfy this criterion; the best value was chosen in all such cases; a weighted mean of the two solutions could have been used (North, 1965) but would have made a significant difference to only a small proportion of the values used in the present problem. It can readily be shown, from the sizes of the coefficients of the cubic, that solutions giving two negative roots for α are not possible, and all the remaining 76 gave one positive and one negative root, the positive root being greater in magnitude in almost all cases: for 46 of these, the positive root was unreasonably large, while for 19 more a choice of root could be made on the basis of the size of the square of the residuals (giving 14 negative and 5 positive values for α). The remaining 11 were not clearly determined because the two roots fitted the data with less than 5:1 ratio between the $\sum$ values, although about half of these had a ratio greater than 2:1. These 11 were the only results for which the sign of α was uncertain. For many spectra, the absolute values of the best solution for α_{ll} were very small and in these cases it was clear that small errors could cause enough change in the α_{ll} to alter their signs and hence alter the signs assigned to A_{ll}. Values of A_{ll} for which α_{ll} values were less than 0·5 were excluded at early stages of the refinement.

The values of α^2 derived from the data were used for a three-dimensional Patterson synthesis, in principle the Patterson synthesis of 6 centrosymmetric iron atoms. The pattern unfortunately exhibited more than the expected 30 non-origin peaks; it was already a sharpened map in that the α values were geometric scattering factors. The main peaks were chosen and repeated trials made until tolerably good agreement existed between the vector set of six trial atoms and the Patterson synthesis. Two such solutions were found which were similar in respect of two of their iron sites but which differed significantly in the z coordinates of the third.

The α_{obs} found from the solution scheme and the values of α_{calc} obtained from the postulated iron structures were quantitatively compared using the R value:

$$\sum \big||\alpha_{\mathrm{obs}}| - |\alpha_{\mathrm{calc}}|\big| / \sum |\alpha_{\mathrm{obs}}|$$

summed over the 212 α terms. These R values were 55% and 53% respectively for the two solutions; although these values are large, the errors in the α_{obs} values were expected to be large because the solutions depended upon small differences between three different intensity measurements.

The sign of α_{calc} for each of the two solutions above was used in conjunction with the sign of the $A\alpha$ product to give the sign of A. The signed A values were then used to produce the first three-dimensional Fourier maps of electron density. These maps were satisfactory in that they gave large peaks at the positions of the three iron atoms and gave other peaks to which tentative assignments could be made for the six aluminum sites. The relationship between the two iron solutions was clarified, in that the two Fourier syntheses were essentially the same, for the third iron site of either solution was indentifiable as an aluminum site of the other.

This gave a satisfactory starting point for the refinement of the structure, but led to doubt as to the identity of the sites and to a suggestion of disorder.

Refinement

A refinement of the structure using the *ORFLS* program (Busing, Martin & Levy 1962) was attempted which produced an R value of 27% and gave a difference Fourier which confirmed the suggestion of

Table 1. *Values of the absorption coefficient and anomalous dispersion corrections used in the solution and refinement*

$\Delta f''$ values from absorption coefficients (*International Tables for X-ray Crystallography*, 1962); $\Delta f'$ values for Fe are from Miller & Black (1970), for Al from James (1962).

Wavelength		Absorption coefficient	$\Delta f'$(Fe)	$\Delta f''$(Fe)	$\Delta f'$(Al)	$\Delta f''$(Al)
Cr $K\alpha$	2·291 Å	547 cm^{-1}	−2·2	0·8	0·28	0·37
Fe Kα	1·934	337	−2·9	0·6	0·23	0·26
Co Kα	1·790	274	−4·4	0·5	0·20	0·22
Mo Kα	0·7107	93	0·3	0·9	0·05	0·03

disorder by showing that two sites contained 'atoms' intermediate in weight between iron and aluminum.

An empirical extinction correction $A_{\text{corr}} = A(1+gA^2)$ was made where g is the secondary extinction coefficient, chosen to be 5×10^{-6}, which improved the agreement for the bright reflexions; the effect of this correction was to increase the largest A values by about 15%. Examination of the A_{obs} and A_{calc} lists showed that the individual layers would benefit by independent scaling factors rather than a single overall factor. With these modifications R improved progressively to 19·6%.

At this stage, values of F derived from the $I_{\text{Mo }K\alpha}$ were used in place of the derived A values and all of the data measured with Mo $K\alpha$ were used, so increasing the number of F's from 212 to 476. A troublesome feature of the refinement was that one site [Al(10)] was so close to a centre of symmetry that its centrosymmetric image was at a distance from it of 1·6 Å. This impossible distance seemed to indicate that the two sites could not be simultaneously occupied, and the site did appear to have only 50% of the weight of other aluminum sites. A possible explanation of this feature was that the structure is only pseudo-centrosymmetric and so non-centrosymmetric possibilities were derived from the trial structure. Two models were formed by taking the centrosymmetric structures, deleting one member of each of two partially occupied centrosymmetric partners [one of these being Al(10)] and combining the two remaining atoms in the two independent ways to give structures which were not enantiomorphs of one another. To reduce the likelihood that oscillation problems would arise in using the least-squares refinement procedures when the structures were close to a symmetric position, all the atoms were slightly shifted before attempting the refinement and all computed shifts were reduced to 60% before application. With these changes one of the two structures became significantly better than the other giving an R value of 13·2%. This is significant improvement over the centrosymmetric structure, confidence levels exceeding 99½% (Hamilton, 1965). At this stage, two previously centrosymmetric aluminum sites (5,5′) were distinguishable as separate iron (5) and aluminum (5′). A difference Fourier synthesis still confirmed the need for disorder on three other sites and the refinement was continued with the 'occupation factors' as additional variables, using *ORFLS* as before with a full matrix and no weighting factors. The dispersion corrections of Table 1 were used in the final refinements.

The effect of allowing each atom to have individual isotropic temperature factors was also examined, but the correlation between temperature factor and occupation factor was too high to allow them both to vary simultaneously. There was however, evidence that the aluminum atoms preferred larger B values than the iron. An average value was chosen for each species and fixed; further refinement cycles then gave a minimum R value of 7·4% where R is taken as $\sum|F_o-F_c|/\sum|F_o|$, and parameters as in the Table 2. Further refinement, by allowing the B's to vary with fixed occupation factors, improved the R a little but introduced negative temperature factors for two sites and attempts to include anisotropic temperature effects similarly failed. A difference Fourier computed in the final stages of refinement showed no significant discrepancies. The expected standard deviations in the parameters were computed from the diagonal elements of the inverse matrix, and the largest shifts in the last refinement cycle were of the order of the expected standard deviations.

Table 2. *Atomic coordinates and weights*

Each x,y,z figure gives the fractional coordinate multiplied by 10^3. The figures in brackets give the standard deviation expressed in units of the last significant figure. Sites labelled M are thought to have mixed (iron and aluminum) occupation. All weight multipliers are expressed with respect to aluminum = 100 for a fully occupied site. The coordinates of Fe(1) were fixed during refinement. Pairs (*e.g.* 2,2′) indicate sites related by pseudo-symmetry.

Mean temperature factors fixed at: iron, $B=0{\cdot}33\times10^{-20}$ m^2; aluminum, $B=0{\cdot}54\times10^{-20}$ m^2.

Site Label	x	y	z	Multiplier %
Fe(1)	326	232	340	196 (6)
Fe(1′)	669 (2)	746 (2)	626 (1)	188 (4)
Fe(2)	238 (3)	582 (2)	205 (2)	188 (4)
Fe(2′)	790 (3)	427 (2)	793 (2)	180 (4)
M(3)	038 (2)	875 (2)	378 (1)	160 (4)
M(3′)	985 (2)	114 (2)	624 (2)	150 (4)
Al(4)	565 (5)	915 (4)	182 (3)	94 (6)
M(4′)	478 (3)	062 (2)	806 (2)	162 (6)
Fe(5)	122 (2)	940 (1)	085 (1)	192 (5)
Al(5′)	932 (4)	128 (3)	910 (2)	106 (5)
Al(6)	878 (5)	242 (2)	251 (2)	98 (6)
Al(6′)	111 (5)	771 (4)	736 (3)	79 (6)
Al(7′)	486 (4)	702 (3)	914 (2)	94 (5)
Al(8)	989 (5)	473 (3)	496 (3)	95 (5)
Al(9)	560 (5)	596 (3)	379 (3)	95 (5)
Al(9′)	366 (4)	402 (3)	682 (2)	106 (5)
Al(10)	882 (4)	576 (3)	046 (2)	100 (5)
Al(11)	482 (4)	011 (3)	507 (2)	93 (4)

It is clear from Table 2 that sites 3, 3′, 4′ are not fully occupied either by iron or by aluminum. From these data, each could be partially occupied by iron only, or occupied by both iron and aluminum in approximately equal proportions (corresponding to a weight of 150). A choice between the two enantiomorphic forms of the structure was made by examining the zero-layer Mo $K\alpha$ data (on which hkl and $\bar{h}\bar{k}\bar{l}$ pairs were available) and selecting reflexions in the range for which measurements of small changes could be made most accurately and which did not show large discrepancies on F_{obs} against F_{calc} for either enantiomorph. This gave a list of 13 spectra and for these the observed values of

$$\Delta I/I = 2(I_H - I_{\bar{H}})/(I_H + I_{\bar{H}})$$

were compared with corresponding values calculated

Table 3. *Observed* $|F_o|$ *and calculated* $|F_c|$ *structure factors and calculated phase angles* φ_c *for all observed spectra with* Mo $K\alpha$ *wavelength*

$|F_c|$ values calculated with the parameters of Table 2, f values quoted in the text and $\Delta f'$, $\Delta f''$ values of Table 1. $|F_o|$ values corrected and scaled to these as explained in the text. $|F_c|$ values computed for the enantiomorph of Table 2.

h	k	l	$\|F_o\|$	$\|F_c\|$	ϕ_c
4	-4	0	47.6	47.7	225.
4	-3	0	49.8	46.0	229.
4	-2	0	21.8	21.5	261.
4	-1	0	11.0	11.2	330.
4	1	0	13.5	11.6	219.
4	2	0	64.9	63.5	21.
4	3	0	27.5	26.0	42.
3	-4	0	31.5	31.8	154.
3	-2	0	92.1	90.9	181.
3	1	0	32.6	31.4	88.
3	2	0	13.8	9.6	343.
3	3	0	66.7	70.4	164.
3	4	0	24.5	22.7	321.
2	-6	0	11.0	11.4	35.
2	-5	0	89.8	89.5	209.
2	-4	0	27.7	24.0	210.
2	-3	0	15.0	16.3	207.
2	-2	0	13.4	9.3	299.
2	-1	0	36.7	36.5	116.
2	0	0	34.9	33.6	351.
2	1	0	128.2	139.6	12.
2	2	0	48.4	48.7	26.
2	3	0	27.0	26.6	80.
2	4	0	23.1	21.8	155.
1	-6	0	37.1	36.1	73.
1	-5	0	31.3	30.5	139.
1	-4	0	23.9	21.6	154.
1	-3	0	96.9	103.5	173.
1	-2	0	28.8	28.8	55.
1	-1	0	22.8	15.6	38.
1	0	0	19.6	20.8	33.
1	1	0	27.2	25.8	93.
1	2	0	16.8	12.6	321.
1	4	0	42.4	40.3	193.
1	5	0	23.3	20.1	191.
1	6	0	32.3	29.7	261.
0	6	0	76.2	77.5	169.
0	4	0	15.4	15.2	262.
0	2	0	25.1	26.0	31.
-4	-2	1	39.5	40.8	202.
-4	-1	1	19.2	15.8	260.
-4	1	1	39.5	37.5	328.
-4	2	1	45.5	42.5	162.
-4	3	1	24.2	25.7	335.
-3	-4	1	10.0	11.8	286.
-3	-3	1	14.4	12.1	298.
-3	-1	1	40.0	40.8	356.
-3	0	1	105.9	96.0	176.
-3	1	1	31.1	26.2	26.
-3	2	1	4.6	5.0	315.
-3	3	1	21.4	17.3	311.
-3	4	1	21.1	18.0	164.
-3	5	1	42.7	43.3	179.
-2	-5	1	20.7	18.2	123.
-2	-4	1	40.6	41.3	195.
-2	-3	1	39.8	44.9	232.
-2	-2	1	17.8	16.3	184.
-2	-1	1	40.6	40.3	219.
-2	0	1	15.4	12.2	247.
-2	1	1	62.3	60.8	323.
-2	2	1	68.2	61.5	342.
-2	3	1	5.8	3.9	155.
-2	4	1	37.8	37.1	231.
-2	5	1	18.5	15.4	242.
-1	-5	1	80.9	80.8	30.
-1	-4	1	23.7	22.4	22.
-1	-3	1	31.4	31.6	77.
-1	-1	1	10.7	6.8	201.
-1	0	1	62.5	61.9	16.
-1	1	1	39.6	35.8	178.
-1	2	1	32.1	30.7	43.
-1	3	1	23.2	25.5	302.
-1	4	1	18.6	15.4	332.
-1	5	1	22.1	25.0	293.
-1	6	1	68.2	67.4	185.
0	-5	1	29.0	30.8	54.
0	-4	1	19.8	13.8	150.
0	-3	1	112.1	119.4	184.
0	-2	1	24.1	27.0	335.
0	2	1	23.6	25.4	13.
0	3	1	143.3	155.4	352.
0	4	1	23.4	22.3	180.
0	5	1	19.4	18.0	258.
0	6	1	20.3	22.6	214.
1	-6	1	36.8	29.9	14.
1	-5	1	21.4	19.3	39.
1	-4	1	18.7	13.8	40.
1	-3	1	54.4	54.3	58.
1	-2	1	13.2	13.9	166.
1	-1	1	40.5	36.4	162.
1	2	1	23.6	21.5	61.
1	3	1	26.6	26.1	43.
1	4	1	30.7	29.4	90.
1	5	1	43.6	42.1	320.
2	-6	1	20.4	18.6	228.
2	-5	1	10.6	14.1	40.
2	-3	1	11.6	8.8	146.
2	-2	1	161.4	176.3	195.
2	0	1	37.0	36.6	222.
2	1	1	10.9	7.5	63.
2	2	1	37.8	38.1	112.
2	3	1	19.2	18.4	19.
2	4	1	116.5	109.1	8.
2	5	1	8.2	8.1	207.
3	-5	1	82.7	82.4	11.
3	-4	1	14.5	12.8	209.
3	-3	1	25.9	26.0	50.
3	-2	1	11.7	8.4	267.
3	0	1	19.8	19.6	158.
3	1	1	55.6	50.0	173.
3	2	1	30.8	29.2	39.
3	3	1	12.8	9.0	22.
3	4	1	37.9	39.4	81.
4	-3	1	39.5	38.2	330.
4	-2	1	28.6	26.1	143.
4	-1	1	89.8	87.1	213.
4	0	1	52.2	49.3	220.
4	1	1	26.1	22.9	255.
4	2	1	14.3	10.2	337.
4	3	1	26.9	27.9	169.
-4	-1	2	45.6	44.9	327.
-4	0	2	30.7	30.1	189.
-4	1	2	11.6	13.8	145.
-4	2	2	23.4	22.6	234.
-3	-4	2	16.4	11.0	9.
-3	-3	2	87.7	83.3	358.
-3	-2	2	14.6	14.1	346.
-3	-1	2	32.6	34.2	261.
-3	0	2	13.2	8.1	73.
-3	2	2	19.8	11.9	145.
-3	3	2	114.7	106.2	167.
-2	-4	2	45.1	45.6	47.
-2	-3	2	11.8	8.4	263.
-2	-1	2	8.0	8.4	267.
-2	0	2	84.6	81.8	339.
-2	1	2	26.4	25.0	176.
-2	2	2	10.7	11.4	169.
-2	3	2	18.4	16.5	242.
-2	4	2	49.3	46.5	311.
-2	5	2	27.9	26.1	334.
-1	-5	2	25.4	26.7	139.
-1	-4	2	15.5	15.1	88.
-1	-3	2	29.0	27.8	162.
-1	-2	2	149.5	147.2	14.
-1	-1	2	21.8	24.7	257.
-1	0	2	40.3	36.2	61.
-1	1	2	12.7	19.0	184.
-1	3	2	18.7	22.9	34.
-1	4	2	86.0	85.6	181.
-1	5	2	19.0	14.5	34.
-1	6	2	34.2	33.0	265.
0	-6	2	22.2	19.9	26.
0	-5	2	82.2	82.8	180.
0	-4	2	14.1	12.3	79.
0	-3	2	28.5	24.5	54.
0	-2	2	12.8	18.7	45.
0	2	2	28.4	29.3	58.
0	3	2	4.6	12.6	134.
0	5	2	38.8	40.5	335.
0	6	2	71.5	70.1	339.
1	-6	2	34.0	35.5	226.
1	-5	2	22.7	21.5	234.
1	-4	2	16.2	11.3	116.
1	-3	2	21.7	20.8	118.
1	-2	2	11.5	7.8	135.
1	-1	2	56.9	53.9	24.
1	1	2	29.0	24.4	117.
1	2	2	40.5	43.1	157.
1	3	2	36.0	33.4	150.
1	4	2	33.9	37.2	33.
1	5	2	37.5	39.5	179.
2	-6	2	7.2	9.8	280.
2	-5	2	51.7	53.0	13.
2	-4	2	67.1	68.9	193.
2	-3	2	6.2	9.0	171.
2	0	2	10.4	11.3	304.
2	1	2	134.8	139.5	188.
2	2	2	58.8	59.6	7.
2	3	2	16.2	14.3	140.
2	4	2	29.4	26.5	68.
2	5	2	23.3	23.5	101.
3	-5	2	44.4	47.3	245.
3	-4	2	9.3	9.4	275.
3	-2	2	42.5	43.8	17.
3	-1	2	33.9	32.0	195.
3	0	2	24.8	21.7	24.
3	1	2	9.1	6.8	283.
3	2	2	12.2	13.7	244.
3	3	2	53.3	54.4	159.
3	4	2	22.7	22.8	152.
4	-4	2	68.2	66.5	31.
4	-3	2	28.5	25.6	208.
4	-2	2	10.2	8.3	95.
4	-1	2	7.1	3.1	323.
4	0	2	56.0	52.8	320.
4	1	2	22.7	20.2	189.
4	2	2	79.6	76.8	210.
5	-1	2	51.5	51.8	17.
-4	0	3	24.2	23.6	266.
-4	1	3	21.3	18.2	324.
-3	-3	3	9.4	13.3	213.
-3	-1	3	52.4	55.9	338.
-3	0	3	95.4	95.3	353.
-3	1	3	23.6	22.0	22.
-3	2	3	21.2	21.6	263.
-3	3	3	17.9	15.3	72.
-2	-4	3	19.6	19.8	176.
-2	-3	3	66.2	69.5	166.
-2	-2	3	5.4	5.7	58.
-2	-1	3	9.0	5.1	10.
-2	0	3	16.7	13.3	62.
-2	1	3	18.0	18.1	316.
-2	2	3	5.5	4.5	344.
-2	3	3	47.7	49.8	325.
-2	4	3	58.9	61.0	187.
-1	-5	3	65.5	71.6	196.
-1	-4	3	13.7	12.4	43.
-1	-2	3	11.0	17.1	162.
-1	-1	3	9.1	12.3	62.
-1	0	3	24.4	26.0	11.
-1	1	3	193.7	189.0	5.
-1	3	3	32.6	31.7	43.
-1	4	3	21.0	22.5	133.
-1	5	3	15.4	17.6	248.
-1	6	3	13.0	12.3	114.
0	-6	3	20.2	19.7	247.
0	-5	3	28.4	32.3	71.
0	-4	3	7.1	13.2	230.
0	-3	3	34.7	37.1	157.
0	-2	3	130.7	124.7	177.
0	2	3	42.4	45.6	116.
0	3	3	10.4	11.3	292.
0	4	3	12.1	15.5	308.
0	5	3	12.6	14.9	170.
0	6	3	12.7	13.8	176.
1	-6	3	22.3	24.7	324.
1	-5	3	21.6	21.4	348.
1	-4	3	86.6	99.7	213.
1	-3	3	4.1	7.3	130.
1	-2	3	40.1	46.0	239.
1	2	3	127.9	128.5	16.
1	3	3	11.8	13.9	356.
1	4	3	47.0	50.6	84.
1	5	3	18.3	22.9	162.
1	6	3	15.7	13.2	135.
2	-5	3	14.0	15.7	58.
2	-4	3	11.4	12.5	256.
2	-1	3	121.4	117.9	188.
2	0	3	24.2	22.1	207.
2	1	3	12.9	14.9	280.
2	2	3	14.8	15.9	67.
2	3	3	18.2	15.8	142.
2	4	3	65.6	71.2	174.
2	5	3	21.6	22.9	339.
3	-5	3	29.7	31.0	336.
3	-4	3	14.5	16.9	310.
3	-3	3	31.6	35.3	241.
3	-2	3	46.0	48.2	232.
3	-1	3	20.9	18.4	271.
3	0	3	24.6	24.3	329.
3	1	3	18.3	21.2	20.
3	2	3	5.8	5.0	334.
3	3	3	50.4	53.6	22.
3	4	3	6.5	12.9	25.
4	-4	3	9.4	10.0	92.
4	-3	3	9.2	11.4	167.
4	-1	3	54.0	56.1	21.
4	0	3	70.8	79.9	202.
4	2	3	21.8	21.7	262.
4	3	3	23.9	28.4	320.
-3	-2	4	37.4	42.2	346.
-3	-1	4	21.1	20.4	178.
-3	0	4	19.6	18.8	228.
-3	1	4	9.5	8.9	265.
-3	2	4	52.3	51.7	326.
-3	3	4	56.5	53.9	349.
-2	-4	4	60.0	62.9	35.
-2	-2	4	38.4	40.7	67.
-2	-1	4	19.2	18.7	169.
-2	0	4	38.4	32.6	159.
-2	1	4	35.7	35.7	19.
-2	2	4	8.1	12.0	161.
-2	3	4	49.1	48.4	58.
-2	4	4	17.3	16.3	305.
-2	5	4	15.6	11.9	347.
-1	-4	4	7.2	11.5	64.
-1	-3	4	40.9	39.6	160.
-1	-2	4	85.1	87.6	191.
-1	0	4	6.3	13.8	154.
-1	1	4	19.5	20.2	226.
-1	2	4	18.7	16.4	95.
-1	3	4	39.8	43.2	351.
1	4	4	100.1	100.8	358.
-1	5	4	17.2	16.2	152.
0	-5	4	54.0	54.1	8.
0	-4	4	22.0	21.5	58.
0	-3	4	10.6	7.8	44.
0	-2	4	29.8	29.9	53.
0	2	4	40.5	40.5	20.
0	3	4	17.6	14.5	75.
0	4	4	44.4	45.6	63.
0	5	4	27.9	28.7	97.
1	-6	4	36.1	38.1	219.
1	-4	4	15.4	19.6	332.
1	-3	4	10.1	8.7	347.
1	-2	4	10.1	11.8	214.
1	2	4	8.6	7.1	73.
1	3	4	26.6	28.0	122.
1	4	4	21.9	23.2	8.
1	5	4	88.9	86.1	14.
2	-5	4	23.3	22.3	340.
2	-4	4	100.3	108.9	16.
2	-3	4	13.0	9.9	78.
2	-2	4	22.2	22.8	45.
2	-1	4	6.5	4.8	240.
2	0	4	35.1	35.0	282.
2	1	4	33.0	32.6	173.
2	2	4	60.1	55.6	160.
2	4	4	16.6	13.2	34.
2	5	4	31.8	32.2	78.
3	-4	4	19.4	15.7	77.
3	-2	4	40.4	38.6	335.
3	-1	4	26.7	27.8	205.
3	0	4	91.4	87.5	218.
3	1	4	38.5	36.2	223.
3	2	4	49.1	47.5	264.
3	3	4	15.7	12.1	344.
3	4	4	9.0	9.6	90.
4	-3	4	99.1	102.0	27.
4	-2	4	24.3	23.1	43.
4	-1	4	27.1	29.6	73.
4	0	4	21.3	17.1	265.
4	1	4	13.8	15.6	262.
4	2	4	43.2	42.0	354.
4	3	4	61.3	57.8	192.
-3	-1	5	16.4	10.8	93.
-3	0	5	14.0	12.6	190.
-3	1	5	71.3	69.4	348.
-3	2	5	23.0	21.8	171.
-2	-2	5	19.8	20.2	148.
-2	-1	5	79.5	77.1	16.
-2	0	5	28.7	25.2	246.
-2	1	5	30.5	27.2	63.
-2	2	5	23.4	24.4	160.
-1	-4	5	59.5	70.7	187.
-1	-3	5	10.3	6.0	32.
-1	-2	5	23.2	19.4	80.
-1	0	5	55.2	51.4	144.
-1	1	5	29.7	30.6	205.
-1	2	5	32.5	35.2	348.
-1	3	5	21.7	21.4	74.
-1	4	5	10.4	10.0	116.
-1	5	5	13.0	12.0	78.
0	-5	5	20.9	21.2	220.
0	-4	5	31.2	35.6	219.
0	-3	5	6.6	8.1	64.
0	-2	5	21.8	24.3	22.
0	-1	5	18.9	19.1	157.
0	1	5	25.0	27.0	273.
0	2	5	25.5	26.1	122.
0	3	5	23.8	24.5	177.
0	4	5	50.9	48.3	154.
0	5	5	24.1	23.2	27.
1	-5	5	21.7	20.4	328.
1	-4	5	44.9	46.5	18.
1	-3	5	57.1	59.6	201.
1	-2	5	9.7	9.6	83.
1	2	5	105.0	104.7	195.
1	3	5	40.6	44.4	3.
1	4	5	20.6	17.8	204.
1	5	5	20.3	18.5	63.
2	-5	5	13.2	14.2	276.
2	-4	5	44.5	46.6	248.
2	-3	5	9.6	6.1	122.
2	-2	5	28.0	28.2	345.
2	-1	5	65.5	65.0	15.
2	0	5	19.7	18.9	168.
2	1	5	6.4	10.3	345.
2	2	5	23.8	23.0	261.
2	3	5	29.7	31.8	272.
2	4	5	44.3	47.5	163.
3	-4	5	11.6	12.2	311.
3	-3	5	77.7	77.9	31.
3	-2	5	38.7	36.1	216.
3	-1	5	44.8	42.6	75.
3	0	5	20.9	16.4	307.
3	1	5	44.1	41.5	333.
3	2	5	21.5	21.8	210.
3	3	5	74.3	73.6	215.
3	4	5	18.0	15.3	19.
4	-2	5	18.5	15.0	133.
4	-1	5	18.0	19.8	27.
4	0	5	74.7	69.9	24.
4	2	5	13.7	11.6	63.
-2	0	6	22.0	21.4	108.
-2	1	6	24.1	25.7	13.
-2	2	6	92.4	84.7	8.
-1	-3	6	21.9	22.8	276.
-1	-2	6	29.2	29.3	162.
-1	-1	6	105.7	104.6	183.
-1	0	6	13.4	6.3	279.
-1	1	6	9.8	6.7	195.
-1	2	6	12.5	12.0	59.
-1	3	6	33.0	33.1	131.
0	-4	6	35.1	35.1	344.
0	-3	6	71.6	71.6	217.
0	-1	6	46.1	51.8	251.
0	-2	6	21.4	18.7	75.
0	0	6	13.7	10.7	65.
0	1	6	7.8	10.8	56.
0	2	6	15.1	13.5	31.
0	3	6	63.5	67.7	22.
0	4	6	15.9	17.3	266.
1	-4	6	14.7	15.2	38.
1	-3	6	8.4	9.1	250.
1	-2	6	35.5	37.1	314.
1	-1	6	13.3	14.1	150.
1	1	6	22.8	24.1	228.
1	2	6	14.3	13.0	279.
1	3	6	14.7	13.4	324.
1	4	6	28.2	30.8	159.
2	-4	6	17.1	15.9	316.
2	-3	6	24.6	27.7	333.
2	-2	6	19.0	19.2	257.
2	-1	6	22.0	21.6	218.
2	0	6	21.2	17.7	284.
2	1	6	25.5	24.8	346.
2	2	6	39.5	40.8	3.
2	4	6	36.1	37.6	19.
3	-4	6	13.0	11.5	33.
3	-3	6	23.6	25.1	100.
3	-1	6	6.7	7.6	297.
3	0	6	57.3	54.6	24.
3	1	6	80.1	79.7	205.
3	2	6	24.1	20.2	68.
3	3	6	31.3	31.3	270.
4	-3	6	30.1	33.4	215.
4	-2	6	32.8	35.8	358.
4	-1	6	20.9	19.5	247.
4	1	6	22.6	16.5	117.
4	2	6	38.3	39.7	354.
-1	-2	7	14.1	13.0	34.
-1	-1	7	20.4	13.6	346.
-1	0	7	9.9	12.2	180.
-1	1	7	28.3	25.9	172.
-1	2	7	77.0	76.4	174.
-1	3	7	29.3	26.5	11.
0	-3	7	15.1	16.7	329.
0	-2	7	15.9	15.3	325.
0	-1	7	16.9	13.8	244.
0	0	7	105.6	93.7	205.
0	1	7	9.9	9.2	2.
0	2	7	54.8	58.8	242.
0	3	7	13.5	11.3	325.
1	-4	7	36.3	37.9	350.
1	-3	7	96.0	100.2	23.
1	-2	7	18.5	18.7	77.
1	-1	7	20.5	23.7	38.
1	1	7	36.9	42.3	302.
1	2	7	34.5	34.7	167.
1	3	7	47.5	47.3	188.
2	-4	7	21.1	18.0	245.
2	-3	7	31.7	33.7	84.
2	-2	7	10.1	11.8	334.
2	-1	7	17.6	16.4	335.
2	0	7	13.1	15.7	263.
2	1	7	57.5	59.8	223.
2	2	7	10.3	11.3	193.
2	3	7	55.9	56.8	271.
3	-3	7	15.5	16.9	27.
3	-2	7	95.5	98.0	35.
3	-1	7	26.7	25.5	54.
3	0	7	37.3	36.4	81.
3	2	7	22.4	20.5	316.
4	-2	7	8.1	8.0	102.
4	-1	7	23.0	17.9	119.

for the two possible enantiomorphs. The sum of the squares of the deviations between observed and calculated values was 3·1 times greater for one enantiomorph than for the other and the lower value was approximately that expected from the overall $F_o:F_c$ agreement if allowance is made for the fact that some errors which contribute to $F_o:F_c$ discrepancies will not affect I_{hkl} and $I_{\bar{h}\bar{k}\bar{l}}$ independently: the acentric effect is marginal because the mean value of $|\Delta I/I|$ for the set selected was 0·06 and the mean value of $|I_{\text{obs}}-I_{\text{calc}}|/I$ for the same set was 0·07. Values for the enantiomorph giving the best fit are presented in Table 2 and in all the results discussed below. Table 3 gives a complete listing of $|F_o|$, $|F_c|$ and calculated phase angles of 476 spectra for Mo $K\alpha$.

Description of the structure

Table 4 gives a list of interatomic distances and summarizes the mean neighbour distances for each atom. It is evident that most sites can be classified as iron or aluminum on the basis of distances alone, and that sites 3′ and 4′ are of intermediate character; site 3 however, has neighbour distances appropriate to an aluminum atom although its weight (Table 2) must indicate partial iron occupation. An iron atom on site 3 would have iron neighbours at 2·49 to 2·54 Å: although this is shorter than any other distances of this type in this structure it may be compared with 2·51 Å for the iron–iron distance in FeAl (Pearson, 1958). If each of 3, 3′, 4′ is allotted 50% Fe and 50% Al occupation and all other sites reckoned at 100% occupation the composition becomes 6·5 Fe to 11·5 Al per cell, corresponding to 52% Fe by weight and to a density of $4{\cdot}24\times10^3$ kg m^{-3} in good agreement with experimental values quoted above. There is no indication on diffraction photographs of extra 'superlattice' reflexions corresponding to regular alternation of the occupation of the mixed sites, and no significant abnormalities in temperature factors on or near these sites which might arise from random replacement – such effects might not be specific since nearly all atoms are neighbours on one or other of the sites.

If sites 3, 3′, 4′ are ignored, the mean distances in the structure are 2·65 (Fe–Fe) 2·55 (Fe–Al) and 2·85 Å (Al–Al). These may be compared with distances in FeAl (2·55 Fe–Al, 2·90 Å Al–Al: Pearson, 1958), Fe_2Al_5 (2·52 Fe–Al, 2·81 Å Al–Al: Forsyth, 1959), Fe_4Al_{13} (2·55 Fe–Al, 2·77 Å Al–Al: Black, 1965) and Fe(Cu,Al)$_6$ (2·55 Fe–Al, 2·80 Å Al–Al: Black, Edwards & Forsyth, 1961).

The structure as a whole is an irregular close-packed arrangement. Fig. 1 shows a section of the final electron density synthesis in the (212) plane: this is one of a set of 10 sets of planes that give large diffraction intensities (absolute F between 55 and 90% of the value for all atoms exactly on the planes) and have inter-planar spacings of about 2 Å. The structure may be described as a set of interpenetrating layers of atoms with this spacing. Fig. 1 shows atomic peaks near a particular plane of the (212) type with heights above and below the mean plane level marked on each atomic peak. It can be seen that atoms 11 and 5′ lie between planes rather than on them.

The site marked 'hole' could accommodate an atom and distances from it are included in Table 4. The atoms shown form a pseudo-hexagonal layer, which is shown on a different scale in Fig. 2; the pseudo-hexagonal grid has dimensions of 2·77 and 2·50 Å as base vectors with an angle of 59°28′ between them. The location of the layer above is also shown in Fig. 2; all layers of this family are identical and the stacking displacement places iron-rich regions on one layer over the less regular aluminum-rich regions of the next. The layer above the two shown would have its pseudo-

Table 4. *Individual and mean interatomic distances*

Accuracies vary but all distances are within ±0·015 Å and most are within ±0·01 Å. Figures in parentheses identify the neighbour concerned. All distances < 3·00 Å are included.

Atom	Iron neighbours	Aluminum neighbours	Mixed site neighbours	Mean Fe distance	Mean Al distance	Mean mixed distance
Iron 1	2·69 (2) Å	2·44 (11), 2·48 (8), 2·51 (9), 2·53 (6), 2·56 (6), 2·66 (4) Å	2·54 (3) 2·65 (3′)	2·69 Å	2·53 Å	2·59 Å
Iron 1′	2·79 (2′)	2·42 (11), 2·43 (7′), 2·50 (9′), 2·51 (8), 2·54 (9), 2·58 (6′), 2·67 (6′)	2·49 (3) 2·64 (4′) 2·68 (3′)	2·79	2·52	2·60
Iron 2	2·69 (1) 2·79 (5)	2·49 (9), 2·51 (10), 2·52 (4), 2·56 (8), 2·59 (6), 2·64 (7′)	2·52 (3)	2·74	2·55	2·52
Iron 2′	2·79 (1′)	2·46 (5′), 2·48 (7′), 2·52 (10), 2·53 (9′), 2·53 (8), 2·54 (6′), 2·70 (9′)	2·57 (3′) 2·64 (4′)	2·79	2·54	2·61
Iron 5	2·79 (2)	2·41 (5′), 2·58 (4), 2·58 (6), 2·59 (10), 2·59 (4), 2·61 (7′)	2·53 (3) 2·64 (4′)	2·79	2·56	2·59
Mixed 3	2·49 (1′), 2·52 (2), 2·53 (5), 2·54 (1)	2·64 (4), 2·78 (3), 2·80 (11), 2·81 (8), 2·82 (11), 2·90 (6)	2·59 (3′)	2·52	2·79	2·59
Mixed 3′	2·57 (2′), 2·65 (1), 2·68 (1′)	2·46 (5′), 2·54 (11), 2·60 (8), 2·61 (9′), 2·66 (6′), 2·89 (11)	2·52 (4′) 2·59 (3)	2·63	2·63	2·56
Mixed 4′	2·64 (2′), 2·64 (5), 2·64 (1′)	2·52 (7′), 2·62 (6′), 2·62 (11), 2·62 (5′), 2·65 (5′), 2·68 (9′)	2·52 (3′)	2·64	2·62	2·52
Aluminum 4	2·52 (2), 2·58 (5), 2·59 (5), 2·66 (1)	2·71 (9), 2·80 (7′), 2·83 (11), 2·85 (5′), 2·87 (10)	2·61 (3) 2·64 (3)	2·59	2·81	2·63
Aluminum 5′	2·41 (5), 2·46 (2′)	2·80 (6′), 2·85 (4), 2·89 (9′)	2·46 (3′) 2·62 (4′) 2·65 (4′)	2·44	2·85	2·58
Aluminum 6	2·53 (1), 2·56 (1), 2·58 (5), 2·59 (2)	2·61 (4), 2·72 (8), 2·80 (11), 2·88 (10), 2·92 (9)	2·90 (3)	2·57	2·78	2·90
Aluminum 6′	2·54 (2′), 2·58 (1′), 2·67 (1′)	2·71 (11), 2·79 (9′), 2·80 (5′), 2·81 (7′), 2·87 (10), 2·95 (7′), 2·97 (8)	2·62 (4′) 2·66 (3′)	2·60	2·86	2·64
Aluminum 7	2·43 (1′), 2·48 (2′), 2·61 (5), 2·64 (2)	2·74 (10), 2·80 (4), 2·81 (6′), 2·87 (10), 2·90 (9′), 2·95 (6′)	2·52 (4′)	2·54	2·85	2·52
Aluminum 8	2·48 (1), 2·51 (1′), 2·53 (2′), 2·56 (2)	2·72 (6), 2·72 (9), 2·78 (9), 2·87 (9′), 2·97 (6′), 3·00 (9′)	2·60 (3′) 2·81 (3)	2·52	2·84	2·71
Aluminum 9	2·49 (2), 2·51 (1), 2·54 (2)	2·71 (4), 2·72 (8), 2·78 (8), 2·86 (9′), 2·90 (10), 2·92 (6), 2·93 (11)	2·78 (3)	2·51	2·83	2·78
Aluminum 9′	2·50 (1′), 2·53 (2′) 2·70 (2′)	2·79 (6′), 2·86 (9), 2·87 (8), 2·89 (5′), 2·90 (7′), 2·95 (11), 3·00 (8)	2·61 (3′) 2·68 (4′)	2·57	2·89	2·65
Aluminum 10	2·51 (2), 2·52 (2′) 2·59 (5)	2·74 (7′), 2·87 (6′), 2·87 (7′), 2·87 (4), 2·88 (6), 2·90 (9)	–	2·54	2·86	–
Aluminum 11	2·42 (1′), 2·44 (1)	2·71 (6′), 2·80 (6), 2·83 (4), 2·93 (9), 2·95 (9′)	2·54 (3′) 2·62 (4′) 2·80 (3) 2·82 (3) 2·89 (3′)	2·43	2·84	2·73
Hole	2·49 (1), 2·49 (2′), 2·51 (5), 2·52 (2)	2·60 (5′), 2·65 (10), 2·85 (4), 2·86 (6), 2·99 (7′)	2·49 (4′)	2·50	2·79	2·49

hexagonal grid in conformity with that of the base layer, but would not have identical atomic configuration, so that the stacking could be described as *ABA'*.

Appraisal of method

There are two main sources of systematic error which will affect a multiple-wavelength method for structure solution. The first of these, the absorption effect, was particularly serious in the present problem. No attempt was made to use wavelengths close to but shorter than the absorption edge; since the relevant $\Delta f'$ changes are as large for wavelengths immediately beyond the edge there is no advantage in using shorter ones unless large values of $\Delta f''$ are desired for revealing non-centrosymmetric effects: in the present case such data would have been helpful if they could have been sufficiently accurate. The absorption correction used produced substantial improvement in the data, but the R values for the chromium and iron data were still about 18 and 13% respectively for the final structure compared with the 7·5% for the molybdenum data.

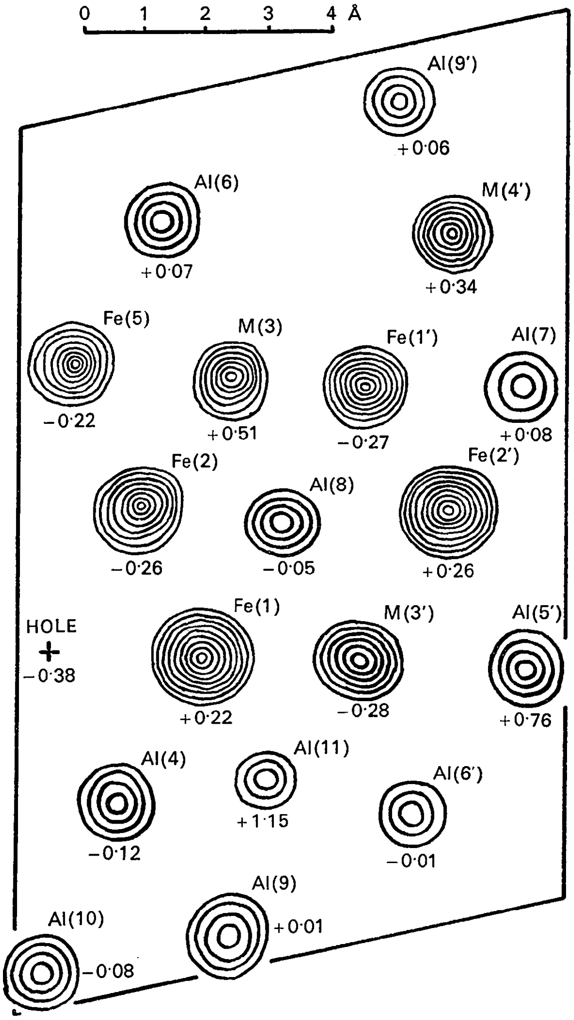

Fig. 1. Sections of the three-dimensional electron-density synthesis taken parallel to a (212) plane; each atom is represented by a section through its centre and the perpendicular height of that centre (in Å) above the mean plane of the diagram is shown along side each atomic peak. Contours are drawn at arbitrary intervals. The perimeter lines show the intersections of the cell walls by the (212) plane.

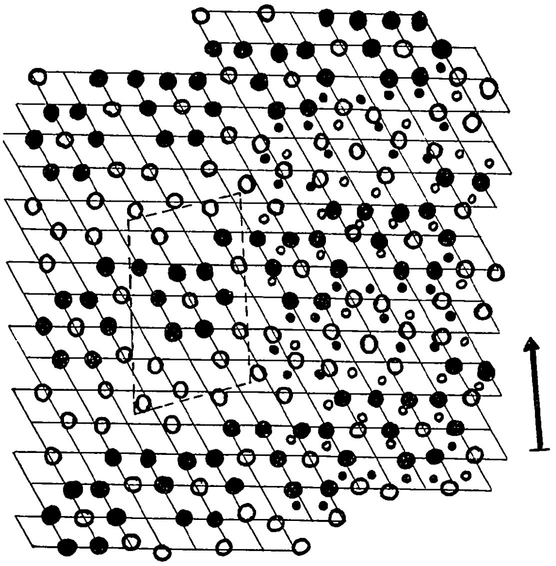

Fig. 2. Long-range pattern of the (212) plane array; the broken lines indicate the intersection with one unit cell as in Fig. 1. Full lines show the pseudo-hexagonal net. The atomic pattern of part of an adjacent layer at 2·1 Å above the one shown, is indicated by the smaller circles; this second layer is identical in pattern to the first and related to it by the shift vector as shown. (Open circles aluminum sites; full circles iron or mixed sites.)

The second main problem concerns the scaling between data at different wavelengths. The Wilson statistical method used for both interlayer scaling for any one wavelength and for inter-wavelength scaling seemed to be satisfactory, in that a repeat of the calculation of the α values and the $A\alpha$ signs after scaling the various data from the F_c's of the finally refined structure showed that α results did not suffer very large changes because of inaccurate scaling and that hardly any $A\alpha$ signs were affected. There were significant errors in the scale factors between layers because individual layers of the reciprocal lattice did show significant departures from the Wilson average, but since the error from this cause affected all three wavelengths in a similar way it did not seriously affect the α-solutions. A possible way of determining scale factors would be to vary them with respect to some error criterion for the α solutions, *e.g.* the estimated deviations from the least-squares fitting procedures or excursions of the best values of α above the physically reasonable limits set by the known composition. A test of such possibilities with the present data showed that these two criteria were relatively insensitive to scale-factor variations but the method might be useful with better data. A rough appraisal shows that other methods of scaling (Singh & Ramaseshan 1966) or of avoiding scaling problems (Unangst, Muller, Müller & Keinert, 1967) would not have produced better results in this problem.

The main difficulty with the present problem arose because of departures from centrosymmetry that were not sufficiently well marked to be detected at an early stage, combined and interacting with partial or multiple occupation of certain sites by both types of atom involved. This latter feature led to effects, on the Patterson of the α^2 values, which were attributed to faulty data, but which could have led more rapidly to the solution if they had been interpreted for what they were – real effects of the distribution of iron atoms in the structure.

All the 65 strongest reflexions show phase angles which are within $\pi/4$ of the phase direction for the pseudo-centrosymmetric structure, and calculations from the final structure confirmed that the differences between inverse pairs of spectra would be too small to detect with confidence with molybdenum radiation. The method of solution led to correct prediction of the approximate phases (nearest value either 0 or π) for over 90% of all reflexions with a true phase within $\pi/4$ of the 0 or π directions of the pseudo-centrosymmetric structure, whilst if all reflexions were included this proportion drops to 70%.

The arrangements of the iron atoms, deduced from the α^2 Patterson synthesis, gave R values of about 55%; this may be compared with (*a*) a value obtained by comparing the experimental α data with values derived from the nearest centrosymmetric equivalent of the final structure (53%) and (*b*) values expected from the effect of errors in the separate data (final R values for Mo $K\alpha$, Fe $K\alpha$, Cr $K\alpha$ data were 7·5, 13 and 18% respectively) on the experimental values derived from them, estimated to lead to an R value of about 45% if the structure had been centrosymmetric. Thus poor agreement of α values for the intermediate solution is mainly explained by data errors but has a substantial contribution from the acentric effects. If the longer wavelength (Cr $K\alpha$) data could have been as accurate as the Mo $K\alpha$ or Fe $K\alpha$ data, then a 'refined' set of α values could have attained an R value as low as 30%. Substantially better results would have been obtained if Co $K\alpha$ had been used throughout in place of Cr $K\alpha$ (collection of data with this radiation had not proceeded beyond the zero layer when the main solution was achieved).

Conclusions

The determination of this structure was achieved by use of the multiple-wavelength technique: the only step in the solution which was not automatic was the determination of the arrangement of the iron atoms from a Patterson synthesis of those atoms. The structure was selected as a potentially simple problem because of the small unit cell and the high proportion of iron atoms, but in the event was complicated by the effect of pseudo-symmetry and mixed-site occupation. The effects being exploited were comparatively large because of the high proportion of anomalous atoms (although this also enhances absorption problems) but the fact that these atoms were of sufficient weight to dominate the phases in this structure (most $A\alpha$ signs positive) is not directly relevant to the success of the method, although it does mean that other techniques might have been equally or more effective.

There is clearly scope for testing the method with structures of much greater complexity. Most of the absorption effects encountered could be removed and the optimum choice of wavelengths could provide enhancement to offset the reduction of the inter-wavelength changes which would follow from a reduced proportion of the anomalous atoms in a complex structure.

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The Crystal Structure of $CsMn_4Cl_9$

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The crystal structure of $CsMn_4Cl_9$ is tetragonal with $a = 11{\cdot}62$ (2) and $c = 10{\cdot}28$ (2) Å. The space group is $I4_1/a$ and $Z = 4$. The Cs and Cl atoms are cubic close-packed and the Mn atoms are octahedrally coordinated by Cl atoms. Each $MnCl_6$ octahedron is linked to six neighbouring octahedra by sharing five edges and one vertex.

Introduction

The authors have recently completed a study of the crystal structures of compounds in the CsCl–$MnCl_2$ system and the crystal structure of $CsMnCl_3$, which is related to that of $CsNiCl_3$, has already been described (Goodyear & Kennedy, 1973). The structures of Cs_2MnCl_4 and Cs_3MnCl_5 have been found to be similar to those of Cs_2MnBr_4 (Goodyear, Steigmann & Kennedy, 1972) and Cs_3CoCl_5 (Powell & Wells, 1935) respectively, and details of these will shortly be submitted for publication. $CsMn_4Cl_9$, however, is unique in that no other caesium complex halide of similar composition has previously been reported.

The material was prepared by heating a mixture, containing 4 molar parts of $MnCl_2$ and 1 of CsCl, in an evacuated silica tube until molten and then cooling the specimen to room temperature at the rate of about 5°/h. Red plate-like crystals were formed which were suitable for X-ray analysis. As was found with all the compounds in the series, the material was very hygroscopic and hence single crystals were examined and selected in a stream of dry nitrogen prior to mounting in sealed Lindemann-glass tubes. The density of the material was determined by weighing a sample quickly in air and in toluene.

X-ray data

The unit-cell dimensions were determined from oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation about an axis which turned out to be the a axis. The symmetry was tetragonal and the observed density could be accounted for by assigning four molecules of $CsMn_4Cl_9$ to the unit cell. The complete crystal data are shown in Table 1.

Table 1. *Crystal data*

Formula, $CsMn_4Cl_9$;	F.W. 671·78
Tetragonal;	$a = 11{\cdot}62$ (2), $c = 10{\cdot}28$ (2) Å
	$Z = 4$, $D_o = 3{\cdot}26$, $D_x = 3{\cdot}22$ g cm^{-3}
Mean r (cm):	0·0096
μ (cm^{-1}):	80·3 ($\lambda = 0{\cdot}7107$ Å)

Intensity data were collected from equi-inclination Weissenberg photographs taken about the a axis with Mo $K\alpha$ radiation. The intensities of 417 reflexions, on layer lines 0 to 5, were measured from multiple-film exposures using a Joyce–Loebl flying-spot microdensitometer; of these 318 were symmetrically independent. 118 reflexions were too weak to be observed.

The intensity data were corrected with the Lorentz–polarization factor and for absorption using the factors given by Bond (1959) for a cylindrical specimen. The observed reflexions satisfied the conditions $h+k+l = 2n$ for hkl, $h = 2n$ for $hk0$ and $l = 4n$ for $00l$, which suggested $I4_1/a$ (No. 88) as the only possible space group.

Determination of the structure

The initial structure was determined from packing considerations and a knowledge of the space group.