Bashkov, B. I., Komissarova, L. N., Spiridonov, F. M. & Shatskij, V. M. (1972). *Vestn. Mosk. Univ. Khim.* **5**, 598–600.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Dereigne, A., Manoli, J.-M., Pannetier, G. & Herpin, P. (1972). *Bull. Soc. Fr. Mineral. Cristallogr.* **95**, 269–280.
Hansson, E. (1973). *Acta Chem. Scand.* **27**, 2841–2851.
Ishakova, L. D., Gasanov, J. M., Bondar, C. A., Kleinman, I. A., Novik, B. K. & Trunov, B. K. (1988). *Neorg. Mater.* **24**, 998–1003.
Koritnaya, F. M. & Pokrovskij, A. N. (1980). *Vestn. Mosk. Univ. Khim.* **21**, 390–392.
Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.
Larsson, L. O., Linderbrandt, S., Niinisto, L. & Skoglund, U. (1973). *Suom. Kemistil. B*, **46**, 314–322.
Sizova, R. G., Voronkov, A. A. & Belov, N. V. (1974). *Dokl. Akad. Nauk. SSSR*, **217**, 1073–1076.
Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). *The XRAY76 System.* Technical Report TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
Tanaka, M. & Tsujikawa, I. (1982). *Acta Cryst.* B**38**, 2793–2797.
Valkonen, J. (1978). *Acta Cryst.* B**34**, 3064–3066.
Valkonen, J., Niinisto, L., Eriksson, B., Larsson, L. O. & Skoglund, U. (1975). *Acta Chem. Scand. Ser. A*, **29**, 866–872.
Vilminot, S., Anderson, M. R. & Brown, I. D. (1973). *Acta Cryst.* B**29**, 2628–2630.

Acta Cryst. (1995). C**51**, 177–179

$FeAl_3Si_2$

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Abstract

The title compound, iron trialuminium disilicide, is isotypic with $PdGa_5$, but presents a superstructure. All the crystals investigated were found to be twinned by pseudosymmetry. The average structure was refined in the space group *I*4/*mcm*. Then the superstructure was solved in *Pbcn*. It can be described as a succession of layers parallel to (001), made up of distorted bicapped tetragonal prisms, $Al(1)Fe_2Al(2)_4Si_4$, centred on Al(1). Each of these polyhedra is connected by sharing edges with four similar polyhedra of the same layer and by Fe-corner sharing with two polyhedra of the adjacent layers.

Comment

$FeAl_3Si_2$ is a minor phase in ferrosilicon alloys that contain about 65 wt% Si and 1–4 wt% Al. Its crystal structure was investigated as part of a study of the alloy microstructure.

The existence of $FeAl_3Si_2$ was reported by Takeda & Mutuzaki (1940). Panday & Schubert (1969) found the compound to be tetragonal with a = 6.07 and c = 9.50 Å, isotypic with $PdGa_5$ (Schubert, Lukas, Meissner & Bahn, 1959). Westgren, quoted by Panday & Schubert (1969), noted the presence of superstructure reflections which suggested order between Al and Si atoms. In fact, the formula $FeAl_3Si_2$ is a nominal one since the composition extends over a rather large range: the data of Zarechnyuk, German, Yanson, Rykhal & Muraveva (1981), Rivlin & Raynor (1981) and Anglézio (1990), along with our own electron microprobe analysis results, indicate the following composition ranges, expressed in

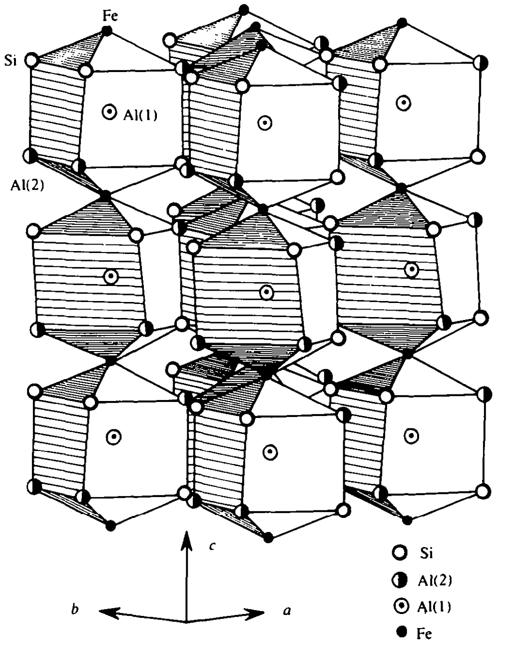

Fig. 1. Crystal structure of $FeAl_3Si_2$ viewed as an arrangement of Al-centred polyhedra.

atomic percentages: Fe 15–17, Si 27–43, Al 40–58. The composition of the investigated crystals was close to $FeAl_{2.7}Si_{2.3}$.

The structure can be described by the idealized formula $FeAl(1)Al(2)_2Si_2$. It is a compact arrangement in which Fe and Al(1) are tenfold and Al(2) and Si ninefold coordinated. The coordination polyhedron of Fe is a distorted bicapped tetragonal antiprism, $FeAl(1)_2Al(2)_4Si_4$, and that of Al(1) is a distorted bicapped tetragonal prism, $Al(1)Fe_2Al(2)_4Si_4$. These polyhedra strongly interpenetrate each other. The structure can be viewed as a succession of layers parallel to (001), made up of Al(1)-centred polyhedra (Fig. 1). Each polyhedron is connected by sharing edges with four similar polyhedra of the same layer, and by sharing Fe corners with two polyhedra of the adjacent layers. An alternative description of the structure can be obtained by considering a succession of layers made up of Fe-centred polyhedra.

The interatomic distances (Table 2) compare satisfactorily with the values observed in other intermetallic compounds. It can be seen that the Fe—Al(2) distances (mean value 2.563 Å) are significantly longer than the Fe—Si distances (mean value 2.461 Å), as expected for Al and Si atoms which play similar structural roles. On the other hand, the Fe—Al(1) distance (2.382 Å) is smaller; such short Fe—Al distances have been observed when the Al atom has only one or two Fe neighbours (Black, 1955; Corby & Black, 1973, 1977).

Experimental

The phase was elaborated by the Laboratoire Central de Recherche de Chedde of the Péchiney Electrométallurgie Society. A mixture of the pure elements in atomic proportion 8Al:5Fe:7Si was melted at 1400 K, annealed at 1163 K for 3 d and finally furnace-cooled to room temperature. As a consequence of temperature gradients in the furnace, segregation phenomena occurred and the final ingot was composed of two parts: one comprising two phases of nominal compositions $FeAl_3Si_2$ and $Fe_2Al_3Si_3$, the other containing $FeAl_3Si_2$ only. Small single crystals were obtained by grinding the second part of the ingot.

Crystal data

$FeAl_{2.7}Si_{2.3}$
$M_r = 193.28$
Orthorhombic
Pbcn
$a = 6.061$ (1) Å
$c = 9.525$ (1) Å
$V = 349.9$ (1) Å^3
$Z = 4$
$D_x = 3.67$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.68$–$26.45°$
$\mu = 5.47$ mm^{-1}
$T = 294$ K
Irregular polyhedron
$0.18 \times 0.07 \times 0.05$ mm
Grey

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{min} = 0.73$, $T_{max} = 0.77$
242 measured reflections
107 independent reflections
77 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.024$
$\theta_{max} = 30°$
$h = 0 \rightarrow 6$ ($h \leq k$)
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: no significant variation

Refinement

Refinement on F
$R = 0.034$
$wR = 0.037$
$S = 2.14$
77 reflections
12 parameters
Unit weights applied
$(\Delta/\sigma)_{max} < 0.01$

$\Delta\rho_{max} = 0.4$ (1) e Å^{-3}
$\Delta\rho_{min} = -0.4$ (1) e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B_{iso}
(*a*) Average structure				
Fe	0	0	1/4	0.520 (6)
Al	0	0	0	0.85 (1)
M†	0.15216 (8)	$x + 1/2$	0.14546 (7)	1.426 (7)
(*b*) Superstructure (isotropically refined)				
Fe	0	0.0109 (4)	1/4	0.19 (3)
Al(1)	0	0	0	0.58 (8)
Al(2)	0.1418 (8)	0.6345 (8)	0.8623 (3)	0.60 (6)
Si	0.1613 (8)	0.6687 (6)	0.1526 (3)	0.56 (5)

† Mixed site $Al_{0.425}Si_{0.575}$.

Table 2. *Interatomic distances* (< 3.1 Å)

For the Al(2) and Si environments, distances written on the same horizontal line refer to interatomic vectors which are symmetry equivalent in the average structure.

Fe environment			Al(1) environment		
Fe—Al(1)	2.3822 (1)	×2	Al(1)—Fe	2.3822 (1)	×2
Fe—Al(2^{i})	2.550 (5)	×2	Al(1)—Al(2^{xi})	2.714 (4)	×2
Fe—Al(2^{ii})	2.576 (5)	×2	Al(1)—Al(2^{xii})	2.664 (4)	×2
Fe—Si^{iii}	2.474 (4)	×2	Al(1)—Si^{iii}	2.665 (4)	×2
Fe—Si^{iv}	2.448 (4)	×2	Al(1)—Si^{xiii}	2.715 (4)	×2

Al(2) environment		Si environment	
Al(2)—Fe^{i}	2.550 (5)	Si—Fe^{xiv}	2.474 (4)
Al(2)—Fe^{v}	2.576 (5)	Si—Fe^{xv}	2.448 (4)
Al(2)—Al(1^{i})	2.714 (4)	Si—Al(1^{xiv})	2.665 (4)
Al(2)—Al(1^{vi})	2.664 (4)	Si—Al(1^{xvi})	2.715 (4)
Al(2)—Al(2^{vii})	2.745 (5)	Si—Si^{xvii}	2.696 (6)
Al(2)—Si^{viii}	2.717 (5)	Si—Al(2^{xviii})	2.717 (5)
Al(2)—Si^{ix}	2.615 (5)	Si—Al(2^{xix})	2.615 (5)
Al(2)—Si^{i}	2.602 (6)	Si—Al(2^{i})	2.602 (6)
Al(2)—Si^{x}	2.775 (4)	Si—Al(2^{xx})	2.775 (4)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x, y-1, z$; (iv) $x-\frac{1}{2}, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (vii) $-x, y, \frac{3}{2}-z$; (viii) $x, 1-y, \frac{1}{2}+z$; (ix) $\frac{1}{2}-x, \frac{3}{2}-y, \frac{1}{2}+z$; (x) $x, y, 1+z$; (xi) $x, y-1, z-1$; (xii) $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$; (xiii) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (xiv) $x, 1+y, z$; (xv) $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$; (xvi) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (xvii) $-x, y, \frac{1}{2}-z$; (xviii) $x, 1-y, z-\frac{1}{2}$; (xix) $\frac{1}{2}-x, \frac{3}{2}-y, z-\frac{1}{2}$; (xx) $x, y, z-1$.

A preliminary investigation of several crystals by Weissenberg and precession techniques led to the following conclusions: (i) all the crystals showed the 4/*mmm* Laue symmetry, (ii) the presence of weak reflections with $h + k + l = 2n + 1$ indicated a superstructure with a primitive unit cell.

In the first stage, the superstructure reflections were neglected and the average structure was refined in the space group *I*4/*mcm* using the structure of $PdGa_5$ as an initial model (Table 1*a*).

Because of their consecutive atomic numbers, aluminium and silicon are difficult to distinguish precisely. Nevertheless, the site labelled Al appeared to be occupied – at least predominantly – by aluminium. For the mixed site, the occupancies of Si and Al were chosen to fit the empirical formula $FeAl_{2.7}Si_{2.3}$.

In the second stage, the superstructure was investigated. As the observed reflection conditions ($hk0$: $h + k = 2n$; $00l$: $l = 2n$; $0kl$: $k = 2n$ and/or $l = 2n$) did not match any of the diffraction symbols, the crystal was considered to be twinned by pseudosymmetry. Among the subgroups of *I*4/*mcm*, the space group *Pbcn* was consistent with all the observed conditions. The two components of the twin could be related either by a (110) symmetry plane or by a [001] fourfold axis. The perfect 4/*mmm* symmetry observed led us to suppose that the crystal was polysynthetically twinned, *i.e.* constituted of numerous small domains of the two components *A* and *B* with virtually equal volumes V_A and V_B. Then the observed intensity of an *hkl* reflection is the half-sum of the *hkl* and *khl* reflection intensities of a similar untwinned crystal. The superstructure was refined using the average structure as an initial model. Only reflections unaffected by the twinning were used:

(*a*) the *hhl* reflections: 34 of the substructure ($l = 2n$) and 15 of the superstructure ($l = 2n + 1$);

(*b*) among the $h0l$ (and $0kl$) reflections, two sets satisfying the condition (i) h (or k) $= 2n + 1$ and $l = 2n$, and the condition (ii) h (or k) $= 2n$ and $l = 2n + 1$; the reflections of the two sets were considered as $h0l$ and $0kl$, respectively, and their intensities were multiplied by two.

The distribution of the Al and Si atoms on the two 8(*d*) sites corresponds to the lowest *R* factor for the stoichiometric formula $FeAl_3Si_2$ (Table 1*b*). No attempt was made to fit the empirical formula $FeAl_{2.7}Si_{2.3}$ by refining the Al(2) site as a mixed $(Al_{1-x}Si_x)(2)$ site.

All the programs used belong to the *SDP* system (B. A. Frenz & Associates, Inc., 1982). The absorption corrections were applied using the *ABSCOR* program (Coppens, Leiserowitz & Rabinovich, 1965).

We thank the Laboratoire Central de Recherche de Chedde of the Péchiney Electrométallurgie Society for crystal preparation.

Lists of structure factors, anisotropic displacement parameters, experimental details for the average structure and complete geometry have been deposited with the IUCr (Reference: DU1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Anglézio, J. C. (1990). Thèse de Doctorat en Sciences, Univ. Paris-Sud, Orsay, France.

B. A. Frenz & Associates, Inc. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.

Black, P. J. (1955). *Acta Cryst.* **8**, 43–48.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Corby, R. N. & Black, P. J. (1973). *Acta Cryst.* B**29**, 2669–2677.

Corby, R. N. & Black, P. J. (1977). *Acta Cryst.* B**33**, 3468–3475.

Panday, P. K. & Schubert, K. (1969). *J. Less-Common Met.* **18**, 175–202.

Rivlin, V. G. & Raynor, G. V. (1981). *Int. Met. Rev.* **3**, 133–152.

Schubert, K., Lukas, H. L., Meissner, H. G. & Bahn, S. (1959). *Z. Metallkd.* **50**, 534–540.

Takeda, S. & Mutuzaki, K. (1940). *Tetsu To Hagane*, **26**, 335–361.

Zarechnyuk, O. S., German, N. V., Yanson, T. I., Rykhal, R. M. & Muraveva, A. A. (1981). *Faz. Ravnoves. Met. Splav.* pp. 69–73.

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$KAlAs_2O_7$

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Abstract

Potassium aluminium pyroarsenate, $KAlAs_2O_7$, is isostructural with $RbAlAs_2O_7$. Although these two structures are not isotypic with structures of the series $M^IM^{III}P_2O_7$ form I, they are closely related to them. Relevant discussion and references are given in a previous paper [Boughzala, Driss & Jouini (1993). *Acta Cryst.* C**49**, 425–427].

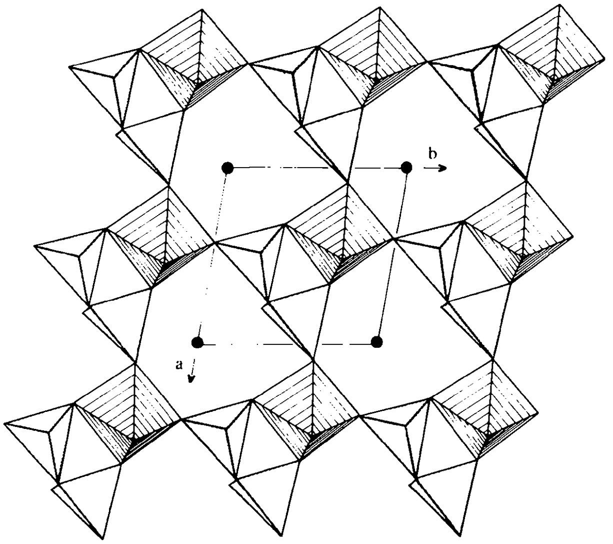

Fig. 1. Projection of half of the unit-cell contents of the title structure onto the (001) plane showing a layer of connected polyhedra.

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