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Re-Refinement of α-(AlMnSi)

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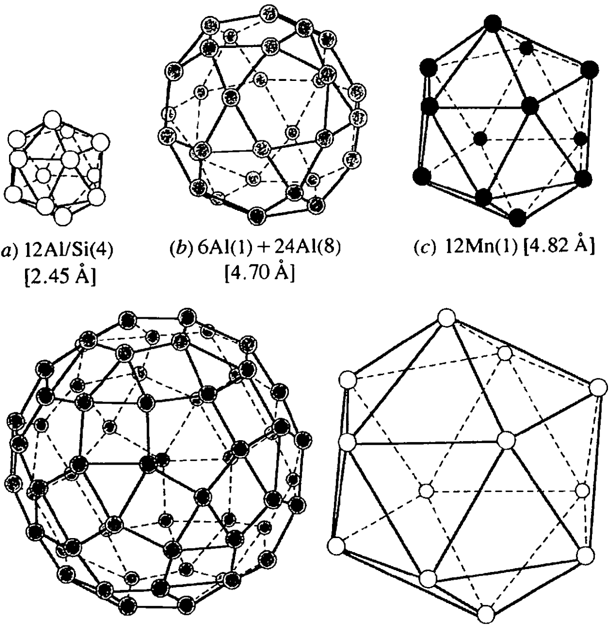
Abstract

Crystals of the α-(AlMnSi) (aluminium manganese silicon alloy, $Al_4Mn_{1.01}Si_{0.74}$) cubic 1/1 approximant phase for the icosahedral quasi-crystal were prepared from an $Al_{72}Mn_{16}Si_{12}$ alloy under an argon atmosphere. The structure is reproduced by the connection of two large atom clusters with icosahedral symmetry (a Mackay icosahedron and a double-Mackay icosahedron) [Yang (1988). *Philos. Mag.* **B58**, 47–57]. Si and Mn atoms are proposed to constitute icosahedral arrangements in the atom clusters. The crystal structure of α-(AlMnSi) was determined previously by Cooper & Robinson [*Acta Cryst.* (1966), **20**, 614–617].

Comment

The structures of crystalline approximants are frequently used for providing structural models of quasi-crystals. The α-(AlMnSi) phase is referred to as a 1/1 approximant for the Al–Mn–Si icosahedral phase in the framework of the cut-and-projection method (Elser & Henly, 1985). The crystal structure of the α-(AlMnSi) phase has been determined previously and atom clusters with icosahedral symmetry were well identified (Cooper & Robinson, 1966; Elser & Henly, 1985). These clusters are frequently discussed as a feasible structural unit of the icosahedral Al–Mn–Si quasi-crystal (Elser & Henly, 1985; Yang, 1988). In order to provide a detailed structural model for icosahedral phases, more accurate data for the α-(AlMnSi) structure were required.

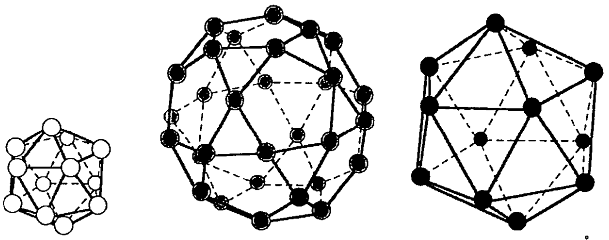
Figs. 1 and 2 indicate atom clusters with icosahedral symmetry at the origin (double-Mackay icosahedra) and the body center (Mackay icosahedra), respectively. The icosahedra shown in Figs. 1(*a*), 1(*c*), 1(*e*), 2(*a*) and 2(*c*) consist of rather small Si and Mn atoms, which are located at the centers of pentagonal arrangements of Al atoms. The sizes of the inner icosahedra in Figs. 1(*a*) and 2(*a*) may reflect the occupation probabilities of silicon at the Al/Si(4) and Al/Si(5) sites. The nearest atomic distances Al/Si(3)—Mn(1), Al/Si(4)—Mn(1) and Al/Si(5)—Mn(2) are 2.484 (1), 2.370 (1) and 2.301 (1) Å, respectively. These features correspond to those of Mn–Si pairs in the structures of β-(AlMnSi) (Robinson, 1952), $Mn_{15}Si_{26}$ (Knott *et al.*, 1967), Mn_5Si_3 (Lander & Brown, 1967) and Mn_5Si_2 (Shoemaker & Shoemaker, 1976).



(*a*) 12Al/Si(4) [2.45 Å] (*b*) 6Al(1) + 24Al(8) [4.70 Å] (*c*) 12Mn(1) [4.82 Å]

(*d*) 12Al(6) + 24Al(7) + 24Al(9) [6.71 Å] (*e*) 12Al/Si(3) [7.31 Å]

Fig. 1. Atom clusters at the origin. Clusters are classified by their radii and values in parentheses indicate the averaged distances of the constituents from the center of the clusters.



(*a*) 12Al/Si(5) [2.43 Å] (*b*) 24Al(9) + 6Al(2) [4.72 Å] (*c*) 12Mn(2) [4.73 Å]

○ Al/Si; ◍ Al; ● Mn

Fig. 2. Atom clusters at the body center. Clusters are classified by their radii and values in parentheses indicate the averaged distances of the constituents from the center of the clusters.

Experimental

An alloy ingot with a nominal composition of $Al_{72}Mn_{16}Si_{12}$ was prepared by melting high-purity metals in an arc furnace under an argon atmosphere. This master ingot was subsequently melted in an induction furnace, again under an argon atmosphere, followed by slow cooling at a rate of about 10 K h^{-1}. Single crystals of cubic α-(AlMnSi) and hexagonal β-(AlMnSi) phases were found in the resulting ingot. Crystals of the α phase were approximately cubic or rhombic prisms and were readily differentiated from the β phase. Electron-probe microanalysis (EPMA, JEOL JXA-8621MX) showed that the chemical composition of the α phase was about $Al_{69.6}Mn_{17.6}Si_{12.8}$, which agrees well with the chemical composition obtained by refinement ($Al_{69.7}Mn_{17.4}Si_{12.9}$).

Crystal data

$Al_4Mn_{1.01}Si_{0.74}$	Mo $K\alpha$ radiation
$M_r = 184.197$	$\lambda = 0.71069$ Å
Cubic	Cell parameters from 24 reflections
$Pm\overline{3}$	$\theta = 16.31$–$19.16°$
$a = 12.643$ (1) Å	$\mu = 4.983$ mm^{-1}
$V = 2020.9$ (3) Å^3	$T = 297$ (2) K
$Z = 24$	Irregular
$D_x = 3.632$ Mg m^{-3}	0.26 × 0.18 × 0.17 mm
D_m not measured	Metallic gray

Data collection

Rigaku AFC-6*S* diffractometer	1048 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{\rm int} = 0.049$
Absorption correction: ψ scan (North *et al.*, 1968)	$\theta_{\rm max} = 34.98°$
	$h = 0 \rightarrow 20$
	$k = 0 \rightarrow 20$
$T_{\rm min} = 0.357$, $T_{\rm max} = 0.429$	$l = 0 \rightarrow 20$
4955 measured reflections	3 standard reflections
1659 independent reflections	every 200 reflections
	intensity decay: none

Refinement

Refinement on F^2	Extinction correction: *SHELXL*93 (Sheldrick, 1993)
$R[F^2 > 2\sigma(F^2)] = 0.031$	
$wR(F^2) = 0.062$	
$S = 0.959$	Extinction coefficient: 0.00208 (11)
1472 reflections	
37 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
$w = 1/\sigma^2(F_o^2)$	
$(\Delta/\sigma)_{\rm max} < 0.001$	
$\Delta\rho_{\rm max} = 1.11$ e Å^{-3}	
$\Delta\rho_{\rm min} = -1.22$ e Å^{-3}	

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

	x	y	z	$U_{\rm iso}$
Mn(1)	0.32631 (4)	0.19779 (4)	0	0.00780 (11)
Mn(2)	0.17925 (4)	0.30790 (4)	1/2	0.00720 (11)
Al(1)	0.36784 (13)	0	0	0.0087 (3)
Al(2)	0.12429 (13)	1/2	1/2	0.0096 (3)
Al(3)†	0.28966 (12)	0	1/2	0.0104 (5)
Si(3)‡	0.28966 (12)	0	1/2	0.0104 (5)
Al(4)§	0.16552 (9)	0.10141 (9)	0	0.0077 (3)
Si(4)¶	0.16552 (9)	0.10141 (9)	0	0.0077 (3)
Al(5)**	0.33611 (8)	0.40026 (8)	1/2	0.0079 (3)
Si(5)††	0.33611 (8)	0.40026 (8)	1/2	0.0079 (3)
Al(6)	0.33135 (9)	0.40206 (9)	0	0.0103 (2)
Al(7)	0.12387 (9)	0.11768 (9)	1/2	0.0104 (2)
Al(8)	0.11798 (6)	0.18860 (6)	0.29906 (6)	0.0098 (2)
Al(9)	0.39074 (6)	0.31291 (6)	0.19617 (6)	0.0099 (2)

† Site occupancy = 0.01 (11). ‡ Site occupancy = 0.99 (11). § Site occupancy = 0.65 (6). ¶ Site occupancy = 0.35 (6). ** Site occupancy = 0.37 (6). †† Site occupancy = 0.63 (6).

Table 2. *Selected bond lengths (Å)*

Mn(1)—Al/Si(4)	2.3701 (13)	Al/Si(3)—Al(6$^{\rm xii}$)	2.5625 (15)
Mn(1)—Al/Si(3$^{\rm i}$)	2.4843 (10)	Al/Si(3)—Al(7$^{\rm xiii}$)	2.570 (2)
Mn(1)—Al(1)	2.5552 (7)	Al/Si(3)—Al(9$^{\rm xii}$)	2.8542 (9)
Mn(1)—Al(6)	2.5834 (13)	Al/Si(4)—Al/Si(4$^{\rm vi}$)	2.564 (2)
Mn(1)—Al(8$^{\rm ii}$)	2.6121 (9)	Al/Si(4)—Al/Si(4$^{\rm iii}$)	2.5846 (13)
Mn(1)—Al(8$^{\rm iii}$)	2.6260 (10)	Al/Si(4)—Al(8$^{\rm v}$)	2.9249 (13)
Mn(1)—Al(7$^{\rm i}$)	2.8124 (9)	Al/Si(5)—Al/Si(5$^{\rm x}$)	2.522 (2)
Mn(1)—Al(9)	2.9890 (9)	Al/Si(5)—Al/Si(5$^{\rm xii}$)	2.5577 (13)
Mn(2)—Al/Si(5)	2.3014 (12)	Al/Si(5)—Al(9$^{\rm v}$)	2.9414 (13)
Mn(2)—Al(7)	2.5049 (13)	Al/Si(5)—Al(9$^{\rm i}$)	2.9563 (11)
Mn(2)—Al(2)	2.5262 (8)	Al(6)—Al(6$^{\rm xiv}$)	2.477 (2)
Mn(2)—Al(9$^{\rm iv}$)	2.5958 (9)	Al(6)—Al(8$^{\rm iii}$)	2.6791 (13)
Mn(2)—Al(6$^{\rm i}$)	2.5995 (8)	Al(6)—Al(9)	2.8259 (10)
Mn(2)—Al(9$^{\rm v}$)	2.5999 (10)	Al(6)—Al(7$^{\rm iii}$)	3.3592 (15)
Mn(2)—Al(8)	3.0544 (9)	Al(7)—Al(8)	2.6952 (9)
Al(1)—Al(7$^{\rm i}$)	2.7310 (14)	Al(7)—Al(9$^{\rm xii}$)	2.9335 (13)
Al(1)—Al/Si(4$^{\rm vi}$)	2.861 (2)	Al(7)—Al(7$^{\rm xiii}$)	2.976 (2)
Al(1)—Al(8$^{\rm vii}$)	2.9440 (10)	Al(7)—Al(7$^{\rm xv}$)	3.132 (2)
Al(1)—Al(1$^{\rm viii}$)	3.342 (3)	Al(8)—Al(9$^{\rm v}$)	2.7252 (11)
Al(2)—Al(9$^{\rm ix}$)	2.8861 (10)	Al(8)—Al(9$^{\rm i}$)	2.7458 (11)
Al(2)—Al(6$^{\rm i}$)	2.9240 (14)	Al(8)—Al(8$^{\rm i}$)	2.8266 (14)
Al(2)—Al/Si(5$^{\rm x}$)	2.960 (2)	Al(8)—Al(8$^{\rm xv}$)	2.983 (2)
Al(2)—Al/Si(3$^{\rm v}$)	3.089 (2)	Al(9)—Al(9$^{\rm xvi}$)	2.763 (2)
Al(2)—Al(2$^{\rm xi}$)	3.143 (3)	Al(9)—Al(9$^{\rm v}$)	3.0329 (14)

Symmetry codes: (i) z, x, y; (ii) $z, x, -y$; (iii) $y, z, -x$; (iv) $z, x, 1-y$; (v) y, z, x; (vi) $x, -y, -z$; (vii) $z, -x, -y$; (viii) $1-x, -y, -z$; (ix) $z, 1-x, 1-y$; (x) $x, 1-y, 1-z$; (xi) $-x, 1-y, 1-z$; (xii) $y, z, 1-x$; (xiii) $x, -y, 1-z$; (xiv) $x, 1-y, -z$; (xv) $-x, y, z$; (xvi) $1-x, y, z$.

The initial parameters for the refinement were taken from the structural model of Cooper & Robinson (1966). The present analysis refined isotropic displacement parameters only. Following on from the discussion of the β phase (Robinson, 1952), the distances of the Al/Si(3), Al/Si(4), Al/Si(5) and Al(6) atoms from their neighboring Al sites are appreciably less than those between any other pairs of Al atoms. Therefore, these sites are considered to be occupied by Al and Si atoms statistically. Introduction of three Al/Si mixed sites of Al/Si(3), Al/Si(4) and Al/Si(5) sucessfully converged to give a final R value of 0.031. Further refinement including other Al/Si mixed sites did not lead to an improved model. The maximum and minimum residuals of difference electron density were located 0.50 and 0.38 Å, respectively, from the Mn(2) site.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1991). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OH1107). Services for accessing these data are described at the back of the journal.

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