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Crystalline Phases Related to a Decagonal Quasicrystal. I. A Single-Crystal X-ray Diffraction Study of the Orthorhombic Al_3Mn Phase

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Abstract

Al_3Mn (with the stoichiometric composition $Al_{28.1}Mn_{10.9}$), $M_r = 1356.5$, orthorhombic, $Pn2_1a$, $a = 14.837$ (4), $b = 12.457$ (2), $c = 12.505$ (2) Å, $V = 2311.2$ (8) Å^3, atoms/cell = 4×39, $D_x = 3.90$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 65.82$ cm^{-1}, $F(000) = 2550.15$, room temperature, $R = 0.068$ for 1289 reflections. About two-thirds of Mn atoms have icosahedral coordination. In a repeat unit b, there are four interpenetrated icosahedra with two Mn and two Al atoms at their centers. This phase has a layer structure consisting of an almost 'flat' layer F sandwiched between two puckered P and p layers in the sequence $PFpP'F'p'$..., where $P'F'p'$ and PFp are related by the 2_1 axes parallel to [010]. A similar layer structure has also been found in the π-AlMnM (M = Ni, Cu, Zn) phases. Both these two crystalline structures can be obtained from that of the Al–Mn decagonal quasicrystal by substituting a rational ratio of two consecutive Fibonacci numbers for the irrational $\tau = [1 + (5)^{1/2}]/2$ in the two quasiperiodic directions.

1. Introduction

Soon after the discovery of the first icosahedral quasicrystal with $m35$ point-group symmetry, it was found that the quasicrystal and the crystalline phase of a similar composition generally have the same or

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Table 1. *Refined atomic coordinates and isotropic parameters for* Al_3Mn

The number of equivalent positions is four for all atom sites. Atoms 1–14 belong to the puckered *P* layer, 15–25 to the 'flat' *F* layer and 26–39 to the puckered *p* layer. The atoms in the puckered *P* and *p* layers have pseudo-mirror symmetry with respect to the *F* layer.

	Coordinates			Isotropic parameters		Occupancy	
Layer No.	*x*	*y*	*z*	*B* (Å^2)	CN*	Al (%)	Mn (%)
P							
Al1	0.0498 (6)	0.1197 (8)	0.2372 (9)	1.1 (4)	12	100	0
Al2	0.0505 (4)	0.1321 (5)	0.4625 (5)	0.5 (2)	12	95.0	5.0
Al3	0.0427 (4)	0.1154 (5)	0.8578 (5)	1.1 (3)	12	100	0
Al4	0.2262 (3)	0.1225 (6)	0.1597 (6)	0.6 (2)	12	100	0
Mn5	0.1789 (4)	0.0615 (13)	0.3497 (4)	0.8 (1)	12	0	100
Al6	0.2343 (3)	0.1286 (4)	0.5252 (4)	1.7 (2)	12	73.9	26.1
Al7	0.1888 (5)	0.0672 (5)	0.7307 (5)	2.2 (3)	12	100	0
Mn8	0.1826 (6)	0.0613 (7)	0.9641 (7)	0.5 (2)	14	0	100
Al9	0.3680 (4)	0.0667 (6)	0.0361 (5)	2.3 (4)	13	100	0
Al10	0.3378 (5)	0.1257 (7)	0.3354 (7)	0.8 (4)	11	100	0
Mn11	0.3735 (2)	0.0622 (3)	0.6552 (4)	1.3 (1)	14	0	100
Al12	0.3224 (5)	0.1503 (6)	0.8462 (7)	2.5 (3)	12	100	0
Al13	0.4886 (5)	0.0764 (6)	0.4430 (5)	1.3 (3)	12	100	0
Al14	0.4760 (5)	0.0686 (5)	0.8465 (7)	2.9 (4)	12	100	0
F							
Al15	0.1019 (4)	0.2613 (8)	0.0424 (5)	1.5 (3)	13	100	0
Al16	0.0964 (3)	0.2506 (11)	0.6494 (4)	1.4 (2)	13	100	0
Al17	0.1804 (4)	0.2504 (10)	0.3464 (5)	1.3 (2)	12	100	0
Mn18	0.1662 (2)	0.2473 (6)	0.8470 (3)	1.8 (1)	12	0	100
Mn19	0.2741 (2)	0.2479 (6)	0.0223 (4)	0.9 (1)	12	0	100
Mn20	0.2660 (2)	0.2513 (6)	0.6736 (2)	0.8 (1)	12	0	100
Al21	0.4063 (3)	0.2511 (11)	0.1600 (4)	1.2 (2)	13	100	0
Al22	0.3965 (4)	0.2439 (10)	0.5398 (5)	1.9 (3)	12	100	0
Mn23	0.4582 (2)	0.2517 (5)	0.3552 (3)	0.7 (1)	9	0	100
Al24	0.4424 (2)	0.2453 (6)	0.7428 (3)	1.4 (1)	12	57.3	42.7
Mn25	0.4470 (2)	0.2491 (6)	0.9544 (2)	1.0 (1)	12	0	100
p							
Al26	0.0464·(10)	0.3764 (10)	0.2390 (10)	3.0 (6)	11	100	0
Al27	0.0506 (5)	0.3787 (5)	0.4503 (6)	1.6 (3)	12	100	0
Al28	0.0401 (4)	0.3976 (5)	0.8388 (5)	1.5 (3)	11	100	0
Al29	0.2287 (5)	0.3791 (4)	0.1649 (5)	1.6 (3)	12	100	0
Mn30	0.1789 (3)	0.4468 (7)	0.3463 (4)	0.6 (1)	12	0	100
Al31	0.2349 (8)	0.3841 (6)	0.5269 (7)	2.5 (4)	12	100	0
Al32	0.1901 (4)	0.4351 (5)	0.7299 (4)	0.7 (2)	13	100	0
Mn33	0.1835 (4)	0.4379 (5)	0.9589 (5)	1.5 (3)	13	0	100
Al34	0.3720 (4)	0.4356 (6)	0.0348 (5)	2.0 (2)	13	74	26
Al35	0.3379 (10)	0.3820 (9)	0.3422 (10)	2.4 (5)	12	100	0
Al36	0.3721 (3)	0.4375 (4)	0.6614 (4)	0.6 (2)	14	97	3
Al37	0.3159 (4)	0.3523 (4)	0.8521 (5)	1.7 (3)	12	77.6	22.4
Al38	0.4748 (4)	0.4214 (5)	0.4580 (5)	1.1 (3)	11	100	0
Al39	0.4864 (3)	0.4356 (4)	0.8513 (5)	1.2 (2)	13	69 5	30.5

* Limited to 3.2 Å.

similar local structure. In other words, these two phases consist of the same or similar structural subunits, packed periodically in the crystalline phase and aperiodically in the quasicrystalline phase. By substituting a rational ratio of two consecutive Fibonacci numbers for the irrational $\tau = [1 + (5)^{1/2}]/2$, the characteristic number of the icosahedral symmetry, Elser & Henley (1985) recovered the cubic lattice of α-AlMnSi from the icosahedral quasilattice. Conversely, Guyot & Audier (1985) and Henley & Elser (1986) independently derived a structural model of the icosahedral quasicrystal based on the icosahedral subunits of α-AlMnSi, an approximant crystalline phase of the quasicrystal or simply an approximant. Later, this idea was extended to the case of a two-dimensional decagonal quasicrystal with a periodic tenfold axis and Kumar, Sahoo & Athithan (1986) derived a structural model of it from that of the monoclinic $Al_{13}Fe_4$ phase. Recently, Li & Kuo (1992*a*) found a new orthorhombic π-Al_4Mn phase, isostructural with $Al_{60}Mn_{11}Ni_4$ (Robinson, 1954) and T_3-AlMnZn (Damjanovic, 1961), and the structural model of the decagonal quasicrystal derived from it agrees well with that determined experimentally by Steurer (1991) for Al–Mn decagonal quasicrystals. Shoemaker (1993) recently derived a structural model of the Al–Mn decagonal quasicrystal from hexagonal μ-Al_4Mn (Shoemaker, Keszler & Shoemaker, 1989).

An orthorhombic Al_3Mn phase was discovered by Hofmann (1938), and later studied by Taylor (1960, 1961). The crystallographic data were reported as:

unit-cell parameters, $a = 14.79$ (1), $b = 12.42$ (1), $c = 12.59$ (1) Å; space groups, $Pn2_1a$ or $Pnma$; the unit-cell contents were approximately 36 Mn and 124 Al atoms (Taylor, 1961). Fitzgerald, Withers, Stewart & Calka (1988) first pointed out that the Al_3Mn phase is a close relative of the Al–Mn decagonal quasicrystal phase, and similar results were reported recently by Daulton, Kelton & Gibbons (1991). However, the structure of Al_3Mn remained unknown.

Li, Shi & Kuo (1992) recently derived a structural model of the Al_3Mn phase from the orthorhombic crystalline π-Al_4Mn phase and a comparison of this model with powder X-ray and high-resolution electron microscopy (HREM) experimental results shows good agreement.

We present here the results of a single-crystal X-ray diffraction study of the orthorhombic Al_3Mn phase (this formula has been used in the literature, though it is only an approximate composition).

2. Experimental

An Al–22 at.% Mn alloy was melted from pure Al and Mn (99.9 and 99.5%, respectively) and homogenized at 1223 K for 72 h. Single crystals of Al_3Mn can be found in the cavities of the ingot and a crystal with approximate dimensions $0.16 \times 0.25 \times 0.16$ mm was used for X-ray structural analysis.

Data were collected on a Rigaku RASA-IIS four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Lattice constants were refined from 12 reflections with 2θ in the range $19 < 2\theta < 32°$. The ω–2θ scan technique was used, scan rate $8.0° \text{ min}^{-1}$, scan width $(2.7 + 0.5\tan\theta)°$. A total of 4840 reflections were collected. Scan range: $3 \le 2\theta \le 65°$ under the following conditions: $0 \le h \le 22$, $0 \le k \le 18$ and $0 \le l \le 18$ (3087 unique reflections measured). The intensity variation of three standard reflections (060, 006, 450) measured every 100 reflections was below 1.2%. The reflections were corrected for Lorentz and polarization effects. 1289 independent reflections were used for refinement [$I > 3.5\sigma(I)$] and $R = 0.068$.

3. Structure determination and refinement

The structure of the Al_3Mn phase was determined using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined using *SHELX*76 (Sheldrick, 1976). Taylor (1961) considered *Pnma* and $Pn2_1a$ as possible space groups for the Al_3Mn phase. Both space groups have been tried in the present investigation, though $Pn2_1a$ agreed better with the experimental results. The scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71–148). The refined parameters were the scale factor, atomic coordinates and isotropic temperature factors, first assuming that all sites were occupied by Al atoms and then Al/Mn assignment was deduced from the peak height in the Fourier map. Several Fourier syntheses indicated that the peak height of Mn atoms is higher than Al atoms, though the dividing line is not very clear. During the refinement an improvement occurred when some of the Al sites with low thermal parameters were partially occupied by Mn atoms. The final refinements led to $R = 0.091$ for $39 \times 4 + 1 + 7 = 164$ parameters. The values were $R = wR = 0.068$ including anisotropic thermal parameters and occupancy [$R = 0.131$, $wR = 0.119$ for all 2539 reflections, except $I \le 0.5(I)$]. The goodness of fit (GOF) = 3.094, where GOF = $\{\sum[w(F_o - F_c)^2/\text{No. of reflections} - \text{No. of parameters}]\}^{1/2}$ and $(\Delta/\sigma)_{max} = 0.254$. Final excursions were -2.0 to $+3.5$ e Å^{-3}. The final parameters and coordination numbers (limited to 3.2 Å) are listed together with occupancies in Table 1 and bond lengths are given in the *Appendix*. The F_o and F_c data have been deposited.*

4. Description

4.1. *Layer Structure*

Fig. 1 shows the layer structure of the Al_3Mn phase consisting of three kinds of layers – one almost

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71350 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0614]

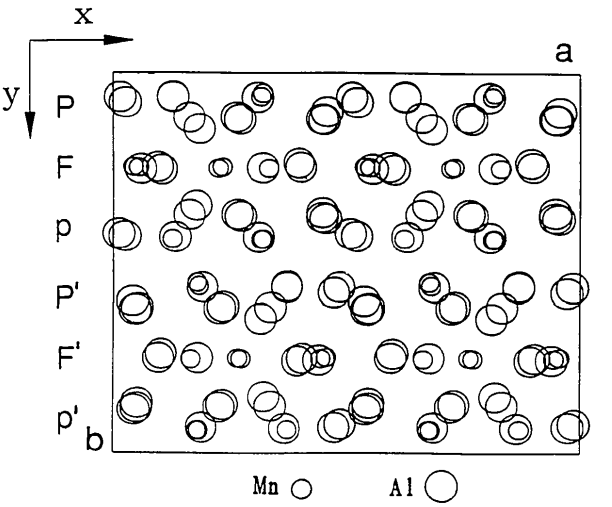
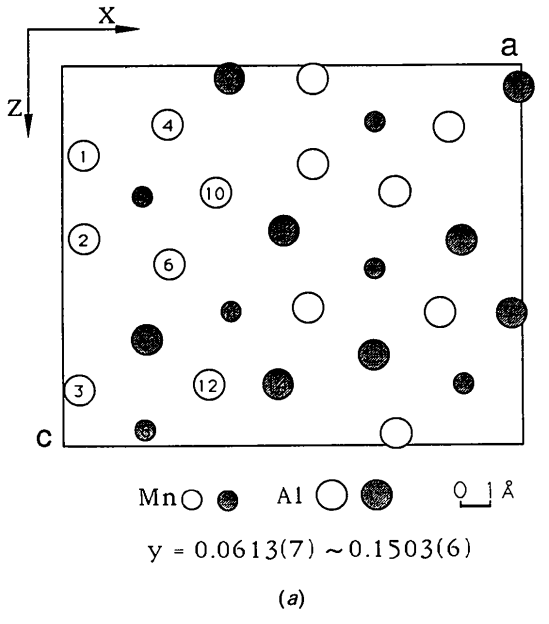


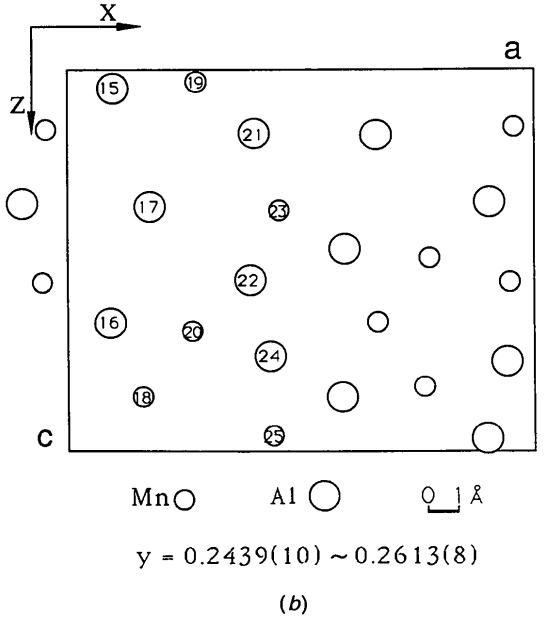
Fig. 1. The [001] projection of orthorhombic Al_3Mn. It has a layer structure consisting of almost 'flat' (F and F') and puckered (P, P', p and p') layers packed in the sequence $PFpP'F'p'$... in the [010] direction.

'flat' layer (F) sandwiched between two puckered layers (P and p). Therefore, this structure can be described in terms of these layers stacked along the b axis in $PFpP'F'p'\ldots$ sequence, where $P'F'p'$ are related to PFp by 2_1 axes parallel to [010]. The F layer deviation from planarity is about 0.2 Å, whereas the puckered layers P and p deviate by more than 1 Å. Fig. 2 shows a plan view of the 'flat' layer F (Fig. 2b) and puckered layers P and p (Figs. 2a and 2c) with their thicknesses indicated.

In the F layer, Al and Mn atoms lie alternately on the vertex of a decagon with an Al atom at its center, see Fig. 2(b). These decagons are zigzag linked in the [100] direction by edge-sharing, see the thick lines in Fig. 3 which is a [010] projection of (FPp') layers. The distance between two Mn (or Al) atoms is about 4.9 Å. The other configuration of interest is the pentagonal star with five Mn atoms forming a central pentagon (Al24 is occupied by Mn 42.7 and Al 57.3%) and five Al atoms at the apexes (shown more clearly in Fig. 3). The bond length between two Mn atoms is about 2.6 Å.

The puckered P and p' layers are more densely populated than the F layer, mainly by Al atoms. In projection they are almost the same but rotated 180° from each other around [010]. These puckered layers may be considered as consisting of two almost planar sublayers, and the atoms in the upper sublayer are indicated by open circles and the atoms in the lower sublayer by shaded circles in Figs. 2(a) and 2(c). Viewed along the b axis (see Fig. 4c), the Al and Mn atoms in these two puckered layers form mainly pentagonal antiprisms and prisms. After a rotation of 180° and a translation of $b/2$, the icosahedron with Al12 at its upper vertex in Fig. 3 will fall on an icosahedron with Al17 at its upper vertex, and *vice versa* (see Fig. 4c). The pentagons are centered by atoms located above or below the pentagon at a





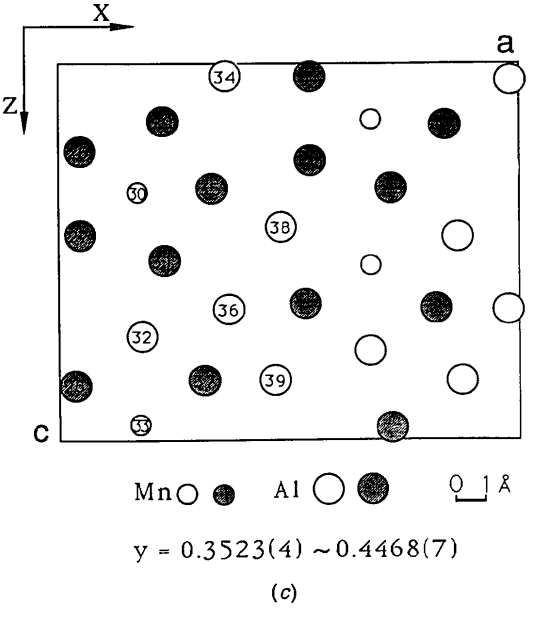


Fig. 2. Plan view of the three kinds of layer in Al_3Mn with their corrugations indicated by the y parameters. (a) Puckered layer P, (b) 'flat' layer F and (c) puckered layer p. The puckered layers consist of two almost planar sublayers indicated by open and shaded circles, respectively. There is pseudo-mirror symmetry between the puckered layers P and p. The atomic site parameters and occupancies are given in Table 1.

vertical distance of about 0.8–1.2 Å, whereas the pentagon itself is puckered by no more than 0.3 Å (see Figs. 4*a* and 4*c*).

4.2. *Coordination polyhedra*

As stated above, most atoms in Al_3Mn are at the vertices or centers of prisms and antiprisms which are related by the symmetry operations of the space group $Pn2_1a$. A detailed description of one prism and some antiprisms are given below as typical examples:

Atom Al17 in Fig. 2(*b*) centers the pentagonal prism formed between two puckered *P* and *p* layers by the atoms Al1, Al2, Al4, Al6, Al10 in Fig. 2(*a*) and atoms Al26, Al27, Al29, Al31 and Al35 in

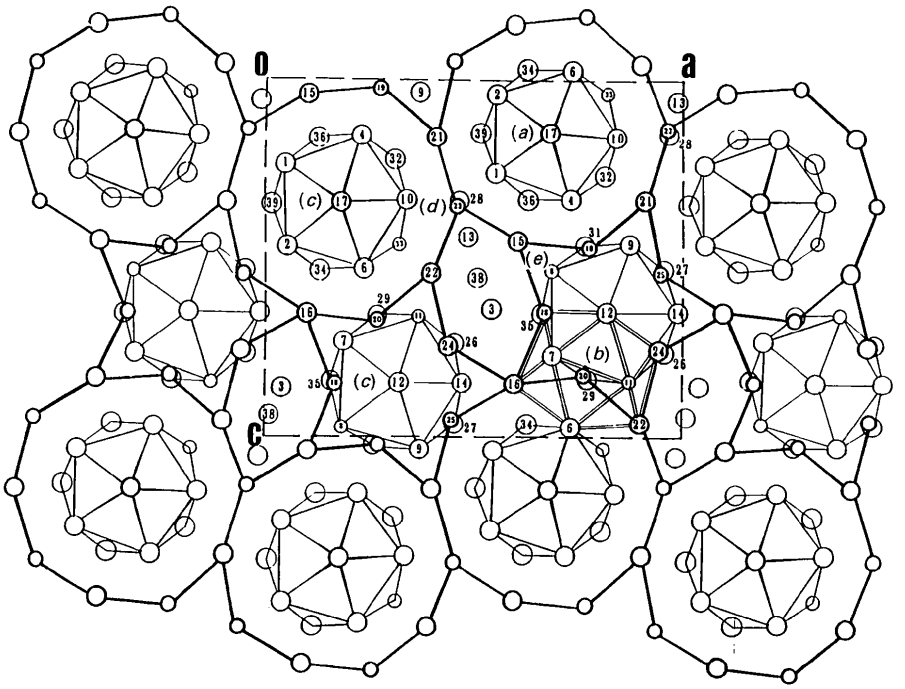


Fig. 3. The [010] projection of *FPp'* layers. Decagons and pentagonal stars shown as thick lines are on the 'flat' layer, whereas pentagons forming pentagonal antiprisms or icosahedra shown as thin lines are on the puckered *p'* and *P* layers. Another kind of icosahedron with its twofold axis parallel to [010] is outlined with double lines. (*a*)–(*e*) mark the atoms or polyhedra shown in Figs. 4(*a–e*).

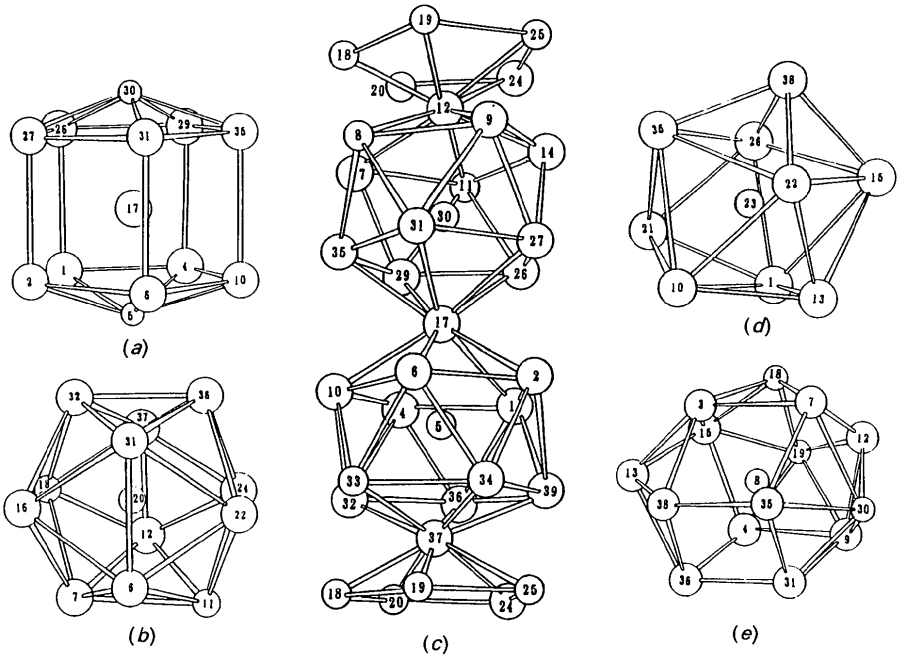


Fig. 4. Coordination polyhedra in Al_3Mn. (*a*) Capped pentagonal prism; (*b*) distorted icosahedron with a twofold axis parallel to [010]; (*c*) vertex-sharing icosahedra with their pseudo-fivefold axes parallel to [010]; (*d*) Mn23 irregular polyhedron (CN9); (*e*) Mn8 irregular polyhedron (CN14).

Table 2. *Interatomic distances in* (*a*–*g*) Al17 *pentagonal prism*, (*e*–*k*) Mn5 *and* (*i*–*o*) Al37 *icosahedra*

		Interatomic distances (Å)
a		
Mn30	Al26	2.537 (4)
Mn30	Al27	2.456 (8)
Mn30	Al31	2.530 (6)
Mn30	Al35	2.494 (5)
Mn30	Al29	2.530 (7)
b		
Al26	Al27	2.642 (9)
Al27	Al31	2.898 (6)
Al31	Al35	2.769 (6)
Al35	Al29	2.746 (6)
Al29	Al26	2.860 (5)
c		
Al17	Mn30	2.446 (8)
Al17	Al26	2.867 (4)
Al17	Al27	2.819 (4)
Al17	Al31	2.919 (6)
Al17	Al35	2.855 (5)
Al17	Al29	2.870 (7)
d		
Al1	Al26	3.198 (10)
Al2	Al27	3.077 (9)
Al4	Al29	3.197 (11)
Al6	Al31	3.183 (10)
Al10	Al35	3.194 (10)
e		
Al17	Al1	2.876 (5)
Al17	Al2	2.828 (4)
Al17	Al4	2.908 (6)
Al17	Al6	2.818 (6)
Al17	Al10	2.808 (5)
f		
Al1	Al2	2.822 (9)
Al2	Al6	2.838 (5)
Al6	Al10	2.827 (7)
Al10	Al4	2.751 (6)
Al4	Al1	2.791 (5)
g		
Mn5	Al17	2.354 (8)
Mn5	Al2	2.530 (4)
Mn5	Al1	2.485 (4)
Mn5	Al6	2.488 (6)
Mn5	Al10	2.495 (5)
Mn5	Al4	2.591 (7)
h		
Al1	Al36	2.720 (6)
Al1	Al39	2.754 (7)
Al2	Al34	2.852 (7)
Al2	Al39	2.868 (7)
Al4	Al32	2.787 (7)
Al4	Al36	2.727 (7)
Al6	Mn33	2.797 (7)
Al6	Al34	2.878 (7)
Al10	Al32	2.824 (1)
Al10	Mn33	2.822 (7)
i		
Mn5	Al34	2.896 (7)
Mn5	Al32	2.915 (4)
Mn5	Mn33	2.899 (4)
Mn5	Al36	2.916 (7)
Mn5	Al39	2.912 (5)
j		
Al32	Al32	2.866 (9)
Mn33	Mn33	2.953 (5)
Al34	Al34	2.855 (6)
Al39	Al39	2.919 (6)
Al36	Al36	2.832 (5)
k		
Al37	Al39	2.735 (5)
Al37	Al33	2.604 (4)
Al37	Al36	2.740 (7)
Al37	Al34	2.643 (6)
Al37	Al32	2.623 (4)
Al37	Mn5	2.607 (9)
l		
Mn20	Al36	2.807 (7)
Mn20	Al32	2.646 (7)
Mn18	Al32	2.783 (7)
Mn18	Mn33	2.769 (7)
Mn19	Mn33	2.835 (7)
Mn19	Al34	2.757 (7)
Mn25	Al34	2.765 (9)
Mn25	Al39	2.721 (7)
Al24	Al39	2.809 (7)
Al24	Al36	2.803 (7)
m		
Al37	Mn20	2.667 (6)
Al37	Mn25	2.659 (4)
Al37	Al24	2.678 (4)
Al37	Mn18	2.578 (4)
Al37	Mn19	2.571 (6)
n		
Mn20	Mn18	2.626 (6)
Mn18	Mn19	2.714 (6)
Mn19	Mn25	2.703 (5)
Mn25	Al24	2.648 (8)
Al24	Mn20	2.758 (5)
o		
Al12	Al37	2.519 (8)
Al12	Mn25	2.600 (4)
Al12	Al24	2.498 (4)
Al12	Mn18	2.613 (5)
Al12	Mn19	2.616 (6)
Al12	Mn20	2.635 (6)

Fig. 2(*c*), see the capped pentagonal prism in Fig. 4(*a*). The interatomic distances between the atoms of the Al17 pentagonal prism are summarized in Table 2(*a*)–2(*g*).

In fact, this capped pentagonal prism links two icosahedra centered by Mn5 and Mn30, respectively, with their pseudo-fivefold axis in the [010] direction, and Al12 and Al37, in turn, also have icosahedral coordination, see Fig. 4(*c*). The bond lengths in Mn5 and Al37 icosahedra are summarized in Table 2(*e*)–2(*k*) and 2(*i*)–2(*o*). As in the π-Al_4Mn crystalline phase and the Al–Mn decagonal quasicrystal (Li & Kuo, 1992*a*), there are four interpenetrated icosahedra or one pentagonal prism (2.9 Å thick) and four antiprisms (2.4 Å each) in a repeat unit $b \simeq 1 \times 2.9 + 4 \times 2.4 = 12.5$ Å (Shoemaker, 1993).

It is of interest to note that another kind of distorted icosahedra exists with its twofold axis parallel to the [010] axis. These icosahedra are centered by Mn18, Mn19, Mn20, Mn25 and Al24 (42.7% Mn and 57.3% Al), respectively, located at the vertices of the central pentagon of a pentagonal star (see Figs. 2*b* and 3). Only the icosahedron around Mn20 is outlined by double lines in Fig. 3. As shown in Fig. 4(*b*), Al16, Mn18, Al22 and Al24 are on the same *F* layer, Al6, Al7, Mn11 and Al12 are at the *P* layer, and Al31, Al32, Al36 and Al37 (partially occupied by Mn) are at the *p* layer. This kind of icosahedron links the distorted double icosahedra, shown in Fig. 4(*c*), forming an icosahedral net in the (010) plane. In Al_3Mn about 2/3 of Mn atoms and 1/3 of Al atoms have icosahedra coordination.

In addition to these pentagonal prisms and icosahedra, there are some irregular polyhedra as well. The irregular polyhedron with Mn23 at its center (Fig. 4*d*) has a coordination number (CN) of 9. It links the two neighboring icosahedra by vertex sharing (Al1 and Al10, respectively). As pointed out by Shoemaker *et al.* (1989), this CN9 polyhedron can be visualized as a trigonal prism with three additional Al atoms capped on its three rectangular prismatic faces. Fig. 4(*e*) shows the Mn8 irregular polyhedron with a CN14 coordination, and the Mn11 and Mn33 polyhedra have a CN13 coordination of similar nature (see the bond lengths in the *Appendix*).

5. Related phases

5.1. Al_3Mn *and* π-Al_4Mn

In a transmission electron microscopic study of the crystalline approximants of the decagonal quasicrystal in the AlMnCu system, the structural relationship of the orthorhombic π-$Al_{20}Mn_3Cu_2$ and Y-AlMnCu phases has been discussed (Li & Kuo, 1992*b*). The electron diffraction patterns and lattice images show that the two phases are probably constructed of the same structural subunits (flattened hexagons) but packed differently, see Fig. 5. This is possibly also the case in the π-AlMn and Al_3Mn phases since they are isostructural with the two orthorhombic phases, respectively, in the AlMnCu system.

In the π-AlMn case, all the hexagons have the same orientation and they form a *B*-centered rectangular lattice in the (010) plane, see the lower part of Fig. 5. In the Al_3Mn phase, the hexagon slabs alternate between two different orientations at 36° with each other, see the upper part of Fig. 5. The vertices of this flattened hexagon superimpose on the centers of icosahedra in Fig. 3. In other words, the different orthorhombic lattices of these two phases are derived from the two different periodical tilings of the same subunit of flattened hexagon consisting of distorted icosahedra. This explains why these two phases frequently intergrow.

5.2. Al_3Mn *and* $Al_{13}Fe_4$

The structure of the orthorhombic Al_3Mn phase is also closely related to that of the monoclinic $Al_{13}Fe_4$ phase (Black, 1955). First, the structures of these two crystalline phases are both composed of flat (not exact in the Al_3Mn case) and puckered layers. Secondly, the heavy atoms (Mn, Fe) in the flat layer form a net of pentagons and rhombi, and the Al atoms together with the heavy atoms form the centered decagons and pentagonal stars. The local structural subunits in both of the 'flat' and puckered layers are alike and the relationship between adjacent layers is similar in the two phases. Recently, the structure of $Al_{13}Fe_4$ has also been shown to consist of icosahedral subunits (Barbier, Tamura & Verger-Gaugry, 1993).

5.3. Al_3Mn *and* μ-Al_4Mn

Recently, the structure of hexagonal μ-Al_4Mn has been analyzed as an approximant of a decagonal quasicrystal (Shoemaker, 1993). This crystalline phase consists of layers perpendicular to the pseudo-

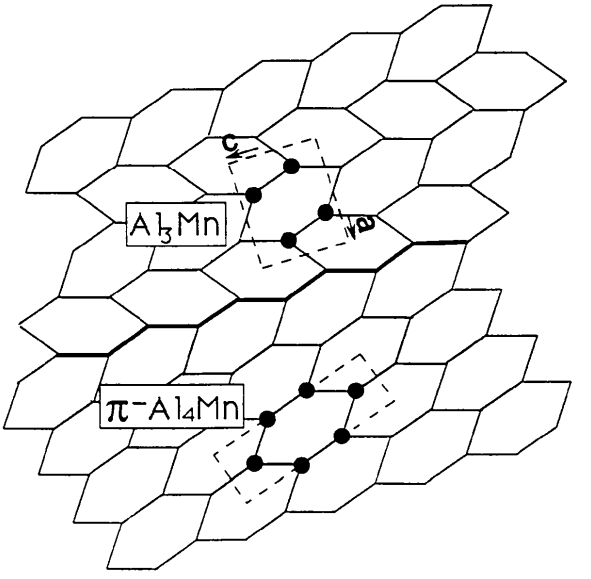


Fig. 5. Schematic diagram showing the lattice correspondence between the two orthorhombic approximants, Al_3Mn and π-Al_4Mn, in (010) orientation. Both consist of the same subunit of flattened hexagons, but in different tessellations, and are in the same orientation in π-Al_4Mn and two different orientations in Al_3Mn. The vertices of this flattened hexagon in a unit cell (drawn as solid circles) superpose on the centers of icosahedral chains in Fig. 3.

fivefold [100] axis of the hexagonal cell. Atoms on these layers in the μ-Al_4Mn structure form centered pentagonal prisms and antiprisms (or icosahedra), which are analogous to Al_3Mn.

5.4. Al_3Mn *and* Al–Mn *decagonal quasicrystal*

A structural model of the Al–Mn decagonal quasicrystal has been proposed based on the structure of the π-AlMn phase (Li & Kuo, 1992*a*). The flattened hexagon in the structure of the π-AlMn phase (and also Al_3Mn) can be further broken into four kinds of Penrose-type rhombus tiles with different decorations. Starting with any one of them and following the given matching rules, the aperiodic flat and puckered layer of the Al–Mn decagonal quasicrystal can be constructed. With the structure of Al_3Mn solved, a better structural model of the Al–Mn decagonal quasicrystal might be derived from it, as was demonstrated recently by Shoemaker (1993) based on the structure of μ-Al_4Mn. On the other hand, the lattice parameters of π-Al_4Mn and Al_3Mn have been recovered by substituting a rational ratio of two consecutive Fibonacci numbers F_{n+1}/F_n for τ in two quasiperiodic directions of the decagonal quasicrystal (Zhang & Kuo, 1990).

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Note added in the revised copy: After first submission of this paper in April 1992, we learned that Hiraga, Kaneko, Matsuo & Hashimoto (1993) and Kang, Malaman, Venturini & Dubois (1992) have also studied the structure of Al_3Mn.

APPENDIX

Selected interatomic distances (Å) limited to d = 3.2 Å in the Al_3Mn phase

Al1 polyhedron		Al2 polyhedron		Al3 polyhedron		Al10 polyhedron		Mn11 polyhedron		Al12 polyhedron	
Al39	2.754 (7)	Mn5	2.530 (4)	Mn8	2.554 (4)	Al17	2.808 (5)	Mn20	2.855 (6)	Mn30	2.536 (8)
Al17	2.876 (5)	Mn25	2.359 (4)	Al24	2.533 (4)	Al4	2.751 (6)	Al29	2.742 (6)	Mn25	2.600 (4)
Al4	2.791 (5)	Al21	3.020 (5)	Al7	2.754 (4)	Mn23	2.391 (4)	Al14	2.836 (7)	Al24	2.498 (4)
Al15	3.104 (7)	Al34	2.852 (7)	Mn11	2.602 (5)	Mn33	2.822 (7)	A38	3.186 (5)	Mn18	2.613 (5)
Mn5	2.485 (4)	Al27	3.077 (9)	Al14	2.801 (7)	Al21	2.877 (6)	Al13	3.160 (7)	Mn19	2.616 (6)
Mn23	2.426 (4)	Al6	2.838 (5)	Al16	3.204 (5)	Al35	3.194 (10)	Al7	2.899 (5)	Mn20	2.635 (6)
Al21	2.978 (4)	Al14	2.748 (7)	Al38	2.735 (7)	Al32	2.824 (1)	Al22	2.706 (7)	Mn8	2.777 (4)
Al2	2.822 (9)	Al16	2.847 (7)	Al13	2.662 (7)	Al22	3.075 (7)	Al6	2.756 (5)	Mn11	2.736 (7)
Al28	3.216 (8)	Al9	2.826 (5)	Mn18	2.465 (4)	Al6	2.827 (7)	Al26	2.805 (6)	Al14	2.495 (10)
Al36	2.720 (6)	Al39	2.868 (7)	Al15	3.066 (6)	Mn5	2.495 (5)	Mn30	2.896 (7)	Al9	2.680 (7)
Al13	2.488 (7)	Al17	2.828 (4)	Al22	2.985 (5)	Al13	2.683 (4)	Mn33	3.022 (10)	Al37	2.519 (8)
Al26	3.198 (10)	Al1	2.822 (9)	Al26	3.475 (9)			Al3	2.602 (5)	Al7	2.663 (4)
								Al12	2.736 (7)		
								Al24	2.729 (6)		
Al4 polyhedron		Mn5 polyhedron		Al6 polyhedron							
Mn19	2.428 (5)	Al2	2.530 (4)	Al34	2.878 (7)						
Al29	3.197 (11)	Al34	2.896 (7)	Al7	2.764 (8)						
Al17	2.908 (6)	Al32	2.915 (4)	Al22	2.808 (5)						
Al15	2.922 (5)	Al6	2.488 (6)	Mn5	2.488 (6)						
Al10	2.751 (6)	Mn33	2.899 (4)	Mn20	2.450 (5)						
Al1	2.791 (5)	Al36	2.916 (7)	Mn11	2.756 (5)						
Al21	3.115 (5)	Al39	2.912 (5)	Al31	3.183 (10)						
Al36	2.727 (7)	Al17	2.354 (8)	Al2	2.838 (5)						
Al32	2.787 (7)	Al4	2.591 (7)	Al17	2.818 (6)						
Mn5	2.591 (7)	Al10	2.495 (5)	Al10	2.827 (7)						
Mn8	2.642 (7)	Al37	2.607 (9)	Mn33	2.797 (7)						
Al9	2.702 (4)	Al1	2.485 (4)	Al16	2.984 (5)						
Al7 polyhedron		Mn8 polyhedron		Al9 polyhedron							
Al34	3.083 (7)	Al3	2.554 (4)	Mn8	2.896 (5)						
Al35	2.726 (7)	Al9	2.896 (5)	Al14	2.861 (7)						
Al6	2.764 (8)	Al7	2.921 (9)	Al39	3.051 (4)						
Mn20	2.661 (6)	Al35	2.721 (6)	Al32	3.051 (7)						
Mn8	2.921 (9)	Mn30	2.903 (4)	Mn30	2.889 (7)						
Mn11	2.889 (5)	Al38	2.916 (2)	Mn25	2.754 (6)						
Al29	2.769 (7)	Al12	2.777 (4)	Al27	2.844 (6)						
Al3	2.754 (4)	Al36	3.021 (7)	Al21	2.829 (7)						
Mn18	2.694 (7)	Al13	3.109 (6)	Al12	2.680 (7)						
Mn30	2.861 (2)	Mn18	2.751 (7)	Al2	2.826 (5)						
Al16	2.851 (6)	Mn19	2.788 (6)	Mn19	2.659 (6)						
Al12	2.663 (4)	Al31	2.644 (6)	Al31	2.742 (6)						
		Al4	2.642 (7)	Al4	2.702 (4)						
		Al15	2.932 (7)								

Al13 polyhedron		Al14 polyhedron		Al15 polyhedron	
Mn11	3.160 (7)	Mn11	2.836 (7)	Mn18	2.630 (7)
Al38	2.358 (5)	Al16	2.887 (6)	Mn19	2.572 (5)
Al36	2.995 (5)	Al9	2.861 (7)	Al29	2.836 (5)
Al15	2.856 (6)	Al26	2.766 (7)	Al38	2.745 (5)
Al22	2.772 (6)	Mn30	2.754 (5)	Al4	2.922 (5)
Al1	2.488 (7)	Mn25	2.658 (5)	Al1	3.104 (7)
Mn23	2.485 (6)	Al3	2.801 (7)	Al13	2.856 (6)
Mn8	3.109 (6)	Al27	2.726 (9)	Al26	2.963 (7)
Mn33	3.089 (3)	Al12	2.495 (10)	Mn33	2.720 (6)
Al3	2.662 (7)	Al24	2.603 (6)	Al28	3.195 (7)
Al28	2.615 (6)	Al2	2.748 (7)	Mn23	2.490 (4)
Al10	2.683 (4)	Al34	3.168 (5)	Mn8	2.932 (7)
		Al7	3.302 (6)	Al3	3.066 (6)
Al16 polyhedron		Al17 polyhedron		Mn18 polyhedron	
Al14	2.887 (6)	Al29	2.870 (7)	Mn19	2.714 (6)
Al39	2.824 (6)	Al4	2.908 (6)	Al15	2.630 (7)
Al32	2.869 (6)	Al10	2.808 (5)	Al16	2.680 (7)
Mn18	2.680 (7)	Al1	2.876 (5)	Al12	2.613 (5)
Mn20	2.535 (5)	Al35	2.855 (5)	Al32	2.783 (7)
Mn25	2.569 (5)	Al26	2.867 (4)	Mn33	2.769 (7)
Al31	3.056 (5)	Mn30	2.446 (8)	Al7	2.694 (7)
Al24	2.653 (5)	Al27	2.819 (4)	Al28	2.650 (5)
Al2	2.847 (7)	Al6	2.818 (6)	Mn20	2.626 (6)
Al27	3.035 (7)	Mn5	2.354 (8)	Mn8	2.751 (7)

Al7	2.851 (6)
Al6	2.984 (5)
Al28	3.109 (7)

Mn19 polyhedron

Mn18	2.714 (6)
Al29	2.510 (7)
Al4	2.428 (5)
Al15	2.573 (5)
Mn25	2.703 (5)
Al34	2.757 (7)
Al21	2.611 (5)
Al12	2.616 (6)
Mn33	2.835 (7)
Mn8	2.788 (6)
Al9	2.659 (6)
Al37	2.571 (6)

Mn20 polyhedron

Mn11	2.855 (6)
Al31	2.513 (6)
Al37	2.667 (6)
Al7	2.661 (6)
Al36	2.807 (7)
Al22	2.561 (5)
Al6	2.450 (5)
Al16	2.535 (5)
Al24	2.758 (5)
Al32	2.646 (7)
Mn18	2.626 (6)
Al12	2.635 (6)

Al21 polyhedron

Mn23	2.560 (8)
Mn25	2.642 (8)
Al34	2.828 (6)
Al2	3.020 (5)
Al35	2.980 (7)
Mn19	2.611 (5)
Al29	3.080 (5)
Al27	3.003 (7)
Al4	3.115 (5)
Al10	2.877 (6)
Al9	2.829 (7)
Al26	2.890 (4)
Al1	2.978 (4)

Al22 polyhedron

Al38	2.699 (6)
Al36	2.875 (7)
Al6	2.808 (5)
Mn20	2.561 (5)
Mn11	2.706 (7)
Al31	2.971 (5)
Al13	2.772 (6)
Al10	3.075 (7)
Mn23	2.484 (7)
Al3	2.985 (5)
Al24	2.628 (8)
Al35	3.133 (7)

Mn23 polyhedron

Al21	2.560 (8)
Al35	2.418 (4)
Al10	2.391 (4)
Al13	2.485 (6)
Al26	2.349 (4)
Al38	2.486 (6)
Al15	2.490 (4)
Al22	2.484 (7)
Al1	2.426 (4)

Al24 polyhedron

Mn25	2.648 (8)
Al3	2.533 (4)
Al12	2.498 (4)
Al28	2.597 (5)
Mn20	2.758 (5)
Mn11	2.729 (6)
Al14	2.603 (6)
Al16	2.653 (5)
Al39	2.809 (7)
Al37	2.678 (4)
Al36	2.803 (7)
Al22	2.628 (8)

Mn25 polyhedron

Al34	2.765 (9)
Al21	2.642 (8)
Al12	2.600 (4)
Al24	2.648 (8)
Al2	2.359 (4)
Mn19	2.703 (5)
Al27	2.529 (4)
Al14	2.658 (5)
Al16	2.569 (5)
Al39	2.721 (7)
Al9	2.754 (6)
Al37	2.659 (4)

Al26 polyhedron

Mn11	2.805 (6)
Al29	2.860 (5)
Al14	2.766 (7)
Al38	2.741 (7)
Al17	2.867 (4)
Al15	2.963 (7)
Al1	3.198 (10)
Mn23	2.349 (4)
Al21	2.890 (4)
Mn30	2.537 (4)
Al27	2.642 (9)

Al27 polyhedron

Mn30	2.456 (6)
Mn25	2.529 (4)
Al34	2.750 (5)
Al31	2.898 (6)
Al21	3.003 (7)
Al2	3.007 (9)
Al14	2.726 (9)
Al9	2.844 (6)
Al17	2.819 (4)
Al16	3.035 (7)
Al39	2.751 (7)
Al26	2.642 (9)

Al28 polyhedron

Mn33	2.651 (4)
Al24	2.597 (5)
Al10	3.370 (8)
Mn18	2.650 (5)
Al38	2.735 (8)
Al36	2.543 (5)
Al13	2.615 (6)
Al15	3.195 (7)
Al16	3.109 (7)
Al39	2.551 (7)
Al32	2.651 (4)

Al29 polyhedron

Mn11	2.742 (6)
Mn19	2.510 (7)
Al17	2.870 (7)
Al4	3.197 (11)
Al15	2.836 (5)
Al34	2.768 (5)
Al21	3.080 (5)
Al7	2.769 (7)
Al35	2.746 (6)
Al26	2.860 (5)
Mn30	2.530 (7)
Mn33	2.761 (8)

Mn30 polyhedron

Al27	2.456 (8)
Al12	2.536 (8)
Al31	2.530 (6)
Mn8	2.903 (4)
Mn11	2.896 (7)
Al29	2.530 (7)
Al14	2.754 (5)
Al9	2.889 (7)
Al17	2.446 (8)
Al7	2.861 (2)
Al35	2.494 (5)
Al26	2.537 (4)

Al31 polyhedron

Mn20	2.513 (6)
Mn30	2.530 (6)
Al27	2.898 (6)
Mn36	2.722 (5)
Al22	2.971 (5)
Al6	3.183 (10)
Al16	3.056 (5)
Al35	2.769 (6)
Al32	2.699 (8)
Mn8	2.644 (6)
Al9	2.742 (6)
Al17	2.919 (6)

Al32 polyhedron

Al16	2.869 (6)
Al39	3.188 (6)
Mn5	2.915 (4)
Mn18	2.783 (7)
Al9	3.051 (7)
Mn20	2.646 (7)
Al31	2.699 (8)
Al4	2.787 (7)
Al10	2.824 (1)
Al37	2.623 (4)
Mn33	2.866 (9)
Al36	2.832 (5)
Al28	2.651 (4)

Mn33 polyhedron

Al28	2.651 (4)
Al10	2.822 (7)
Al37	2.604 (4)
Mn5	2.899 (4)
Mn18	2.769 (7)
Mn11	3.022 (10)
Mn19	2.835 (7)
Al29	2.761 (8)
Al13	3.089 (3)
Al15	2.720 (6)
Al34	2.953 (5)
Al32	2.866 (9)
Al6	2.797 (7)

Al34 polyhedron

Mn25	2.785 (9)
Al21	2.828 (6)
Al7	3.083 (7)
Al6	2.878 (7)
Mn5	2.896 (7)
Mn19	2.757 (7)
Al29	2.768 (5)
Al27	2.750 (5)
Al2	2.852 (7)
Al39	2.855 (6)
Al37	2.643 (6)
Mn33	2.953 (5)
Al14	3.168 (5)

Al35 polyhedron

Mn23	2.418 (4)
Al21	2.980 (7)
Al7	2.726 (7)
Mn8	2.721 (6)
Al29	2.746 (6)
Al17	2.855 (5)
Al10	3.194 (10)
Al31	2.769 (6)
Al26	3.257 (6)
Mn30	2.494 (5)
Al38	2.542 (4)
Al22	3.133 (7)

Al36 polyhedron

Al38	2.971 (7)
Al13	2.995 (5)
Al22	2.875 (7)
Mn20	2.807 (7)
Al31	2.722 (5)
Al39	2.919 (6)
Al4	2.727 (7)
Al37	2.740 (7)
Al1	2.720 (6)
Mn5	2.916 (7)
Mn8	3.021 (7)
Al28	2.543 (5)
Al24	2.803 (7)
Al32	2.832 (5)

Al37 polyhedron

Mn30	2.667 (6)
Al39	2.735 (5)
Mn33	2.604 (4)
Al36	2.740 (7)
Mn25	2.659 (4)
Al34	2.643 (6)
Al12	2.519 (8)
Al24	2.678 (4)
Al32	2.623 (4)
Mn5	2.607 (9)
Mn18	2.578 (4)
Mn19	2.571 (6)

Al38 polyhedron

Mn11	3.186 (5)
Al36	2.971 (7)
Al13	2.358 (5)
Al15	2.745 (5)
Al22	2.699 (6)
Al26	2.741 (7)
Mn8	2.916 (2)
Al3	2.735 (7)
Al28	2.735 (8)
Mn23	2.486 (6)
Al35	2.542 (4)

Al39 polyhedron

Al16	2.824 (6)
Al32	3.188 (6)
Al37	2.735 (5)
Al1	2.754 (7)
Al9	3.051 (4)
Al36	2.919 (6)
Mn25	2.721 (7)
Al34	2.855 (6)
Al24	2.809 (7)
Mn5	2.912 (5)
Al27	2.751 (7)
Al2	2.868 (7)
Al28	2.551 (7)

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