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Crystal structure of the orthorhombic $\text{Al}_4(\text{Cr}, \text{Fe})$ approximant of the Al–Cr–Fe decagonal quasicrystal

D W Deng¹, Z M Mo and K H Kuo

Department of Materials Engineering, Dalian University of Technology, Dalian 116023, People's Republic of China

and

Beijing Laboratory of Electron Microscopy, Institute of Physics, Chinese Academy of Sciences, PO Box 2724, Beijing 100080, People's Republic of China

E-mail: d.deng@fz-juelich.de

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Abstract

The crystal structure of the orthorhombic phase $\text{Al}_4(\text{Cr}, \text{Fe})$ with a composition of $\text{Al}_{80.6}\text{Cr}_{10.7}\text{Fe}_{8.7}$ has been determined by single-crystal x-ray diffraction (table 2). There are 11 crystallographically independent Cr/Fe sites, of which 10 are icosahedrally coordinated. Of the 28 crystallographically independent Al sites 5 are icosahedrally coordinated. However, owing to the presence of many partial occupancies, caused by split atoms, some of these coordinations are only pseudo-icosahedral with effective coordination numbers $\text{CN}_{\text{eff}} \neq 12$ (section 4.3). The icosahedral and pseudo-icosahedral clusters are oriented with a two-fold axis parallel to $[100]$. They are linked either by vertex-, edge- or face-sharing or by mutual interpenetration, thus forming large clusters of icosahedra in the (100) layers with one of the five-fold axes in the $[010]$ direction. Four of the 12 atoms defining the vertices of an icosahedral cluster lie in a mirror plane (F plane), while the other atoms are in puckered layers below and above the mirror plane. Thus, the icosahedral cluster consists of layers PFP' of three atoms thick. Two such layers stack within one lattice constant $a \approx 1.25$ nm. The interconnection of icosahedra in the PFP' layer block forms large triangular and hexagonal structural motifs, though they have only two-fold rotational symmetry. Similar geometrical motifs but displaying three- or six-fold symmetry do exist in the structure of the hexagonal $\mu\text{-Al}_4\text{Mn}$, $\kappa\text{-(AlCrNi)}$, $\lambda\text{-Al}_4\text{Mn}$ and $\nu\text{-Al}_{12}\text{Cr}_2\text{Fe}$ phases.

1. Introduction

A body-centred orthorhombic phase Al_4TM (transition metal) with $a \approx 1.25$ nm, $b \approx 1.25$ nm, and $c \approx 3.05$ nm has been found to coexist with the decagonal quasicrystal having a period

¹ Address for correspondence: IFF, Forschungszentrum, Jülich GmbH, D-52425 Jülich, Germany.

Table 1. Body-centred orthorhombic (bco) Al₄TM with $a \approx 1.25$ nm, $b \approx 1.25$ nm and $c \approx 3.05$ nm in various Al–TM alloy systems.

Alloy or compound	Lattice or space group	Lattice parameters (nm)			Reference
		<i>a</i>	<i>b</i>	<i>c</i>	
η -Al ₁₁ Cr ₂ ^a	bco	1.24	1.26	3.05	Bendersky <i>et al</i> (1991)
Al ₆₅ Co ₁₅ Cu(W)	bco	1.23	1.23	3.05	Liao (1991)
Al ₆₀ Mn ₁₁ Ni ₄	bco	1.24	1.26	3.14	Singh and Ranganathan (1994)
Al ₂₄ Mn ₅ Zn ^b	bco	—	—	—	
Al ₁₂ Mn _{2.9} Zn	bco	1.24	1.26	3.05	Singh <i>et al</i> (1997)
Al ₁₂ Cr ₂ Fe	<i>Immm</i>	1.24	1.26	3.05	Sui <i>et al</i> (1995)
Al _{5.103} (Cr, Fe)	<i>Imm2</i>	1.234	1.241	3.071	Sui <i>et al</i> (1997)
Al _{77.3} Cr _{18.4} Ni _{4.3}	<i>Immm</i>	1.255	1.255	3.075	Rosell-Laclau <i>et al</i> (1996)
Al _{81.3} Cr _{11.8} Ni _{6.9}	<i>Immm</i>	1.2505	1.2619	3.0660	Deng and Kuo (2002)
Al _{80.6} Cr _{10.7} Fe _{8.7}	<i>Immm</i>	1.2501	1.2617	3.0652	Present study

^a Unstable, transforming into a monoclinic phase $a = 1.76$ nm, $b = 1.76$ nm, $c = 3.05$ nm and $\beta \approx 90^\circ$.

^b Unstable, transforming into the hexagonal λ -Al₄Mn after heating for 25.5 h at 600 °C.

of 1.25 nm along its periodic ten-fold direction in a number of Al–TM alloys by means of transmission electron microscopy (table 1). Though a structural model of the orthorhombic Al₄(Cr, Fe) phase (Sui *et al* 1997) has been given by comparing its high-resolution electron microscopy image with the well known structure of μ -Al₄Mn (Shoemaker *et al* 1989), no x-ray structural determination has been made yet. Since this orthorhombic Al₄TM has occurred in no less than six different Al–TM alloys, it must be a common structure in Al–TM alloys. Considering all of this and also its close structural relation to the Al–TM decagonal quasicrystal, it is perhaps of interest to make an x-ray single-crystal study of its crystal structure and compare its icosahedral structural motifs with those in other known Al–TM decagonal approximants. Recently, the crystal structure of the isostructural Al₄(Cr, Ni) with $R1 = 0.0728$ was briefly reported (Deng and Kuo 2002). The following is a detailed description of the structure of the orthorhombic Al₄(Cr, Fe) with $R1 = 0.0674$.

2. Experimental details

The Al₁₂CrFe₂ alloy was prepared by melting a mixture of high purity Al (99.9999 wt%), Cr (99.95 wt%) and Fe (99.9 wt%) in an electric furnace and slowly cooling it. An prismatic needle-like single crystal with the dimensions $0.04 \times 0.04 \times 0.13$ mm³ was selected in the cavities of the cast ingot. The composition of this single crystal is determined by micro-electron probe x-ray analysis and it corresponds to Al_{80.6}Cr_{10.7}Fe_{8.7}, or roughly Al₄(Cr, Fe). Using convergent-beam electron diffraction, Sui *et al* (1995) have shown earlier the body centred orthorhombic lattice and the *mmm* point group of Al₄(Cr, Fe). In the present study we have reconfirmed the (001) mirror plane by this technique so that the space group is *Immm* (no 71), but not *Imm2*.

A single-crystal x-ray diffraction experiment was performed at room temperature (294 ± 1 K) on a Bruker P4 diffractometer equipped with a graphite monochromator using Mo K α radiation. Its unit cell dimension was obtained and refined by 35 well centred reflections with $4.1^\circ < \theta < 26.7^\circ$. Data collection was monitored by three standards every 100th reflection. No decay was observed except the statistic fluctuation within the range of $\pm 2.8\%$. Raw intensities were corrected for Lorentz and polarization effects, and for absorption by an empirical method

based on ψ -scan data (Kopfmann and Hubber 1968). All atoms were subjected to anisotropic refinement.

Data collection was controlled by the XSCANS program. Computations were performed using the SHELXTL NT program package, version 5.10 (Sheldrick *et al* 1985) on an IBM PC 586 computer. Analytic expressions of atomic scattering factors were employed and anomalous dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1989). Crystal drawings were produced with XP (Bruker) and SCHAKAL 92 (Keller 1992).

3. Structure determination

Straightforward application of direct methods did not produce a structural model that would refine to a R factor below 50%. The hexagonal μ -Al₄Mn phase is an important approximant of the Al–Mn decagonal quasicrystal (Audier and Guyot 1986, Bendersky 1987, Shoemaker *et al* 1989, Le Lann and Shoemaker 1993, Sui *et al* 1997). The hexagonal μ -Al₄Cr (Kuo 1990, Bendersky *et al* 1991, Wen *et al* 1991, 1992, Audier *et al* 1995) is isostructural to it. In our attempt to solve the structure of the Al₄(Cr, Fe) phase, we looked at the chemically and structurally closely related compounds μ -Al₄Cr/ μ -Al₄Mn (Shoemaker *et al* 1989) and the hexagonal ν -Al₄(Fe, Cr) (Mo *et al* 2000). By analysing high-resolution electron microscopy images of the orthorhombic Al₄(Cr, Fe), its local structural arrangement (Sui *et al* 1997) was found to be similar to the projected structure along the pseudo-five-fold axis of the hexagonal μ -Al₄Mn phase. A fragment of the structure of the μ -Al₄Mn phase and the ν -Al₄(Fe, Cr) phase (see the shaded area TM(3)–Al(2)–TM(8)–Al(1)–TM(5)–Al(5)–TM(2)–Al(12) in figure 1(a)) was then used in the SHELXTL software package (Sheldrick *et al* 1985) to generate the structural model of the Al₄(Cr, Fe) phase. This allowed us to obtain a feasible structural model with a R value of about 28%. After several iterations of least-squares calculation coupled with difference Fourier syntheses, 39 independent atomic positions with a total of 253 parameters were refined by using SHELXL (Sheldrick *et al* 1985). The final refinement led to $R1 = 0.0674$ for 3206 reflections with $I > 4\sigma(I)$ and a goodness of fit $S = 0.846$. The final difference electron-density map shows no obvious features. Details of crystal parameters, data collection and structure refinements are given in table 2. The refined atom sites and isotropic displacement parameters are listed in table 3. The anisotropic displacement parameters are listed in table 4. There are 11 Cr/Fe (TM = Cr/Fe) and 28 Al independent sites in a unit cell. Two Al sites (Al(5) and Al(15)) are statistically occupied by Al (0.75) and TM (0.25) atoms (Cr and Fe atoms are not differentiated). As in many Al–TM decagonal quasicrystals (Würschum *et al* 1995) and their crystalline approximants, such as Al₆₈Pd₂₀Ru₁₂, *cP*296-46.85 (Mahne and Steurer 1996), Al_{57.3}Cu_{31.4}Ru_{11.3}, *cP*140-25.1 (Sugiyama *et al* 2000) and Al_{2.75}Ir, *cP*60-30 (Grin *et al* 1997), vacancies are also found profoundly in Al sites (Al(19)–Al(28)) and in two TM sites (TM(6) and TM(10)) in Al₄(Cr, Fe). Thus the Pearson symbol becomes *oI*366-59.56. Excluding the abnormal short distances between atomic sites of partial and/or split occupancy of 0.50–0.67, the atomic distance ranges are: TM–TM, 0.2419–0.2953 nm; Al–Al, 0.2341–0.2949 nm; and Al–TM, 0.2453–0.2980 nm.

4. Description of the structure

4.1. Layer structure

The Al–Mn and Al–Cr decagonal quasicrystals are known to have a six-layer structure with a periodicity of about 1.25 nm along its decagonal axis (Bendersky 1987, Wen *et al* 1992). Their crystalline approximants often also have a lattice parameter of this dimension and a six-layer

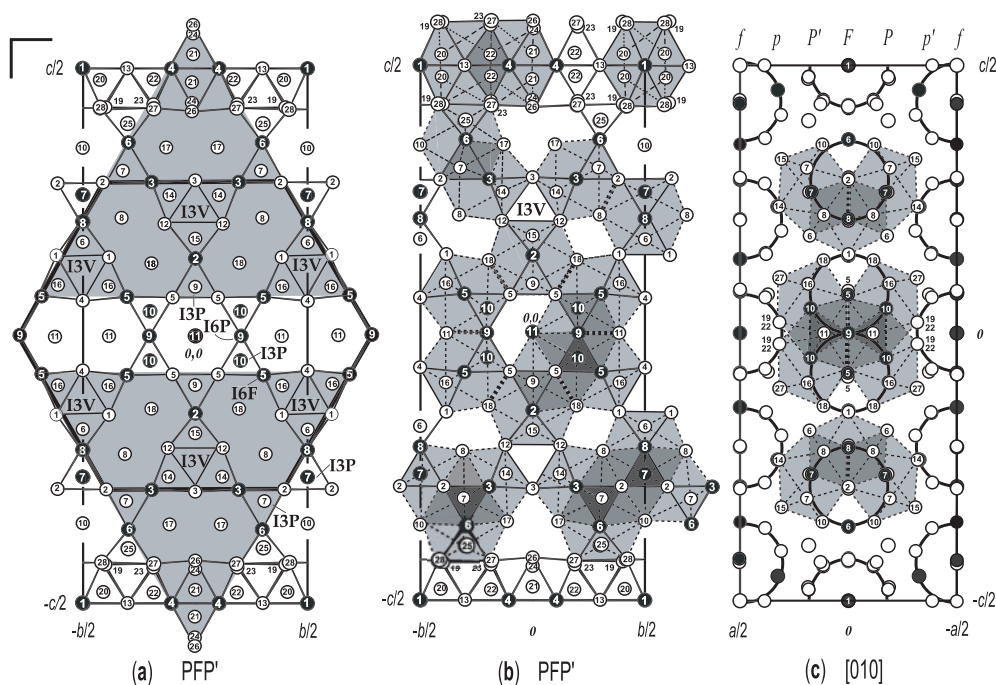


Figure 1. (a), (b) The [100] projection of the PFP' layers of the structure of $\text{Al}_4(\text{Cr, Fe})$: full circles, Cr/Fe atoms; open circles, Al atoms. Atoms in the flat layer F are connected, whereas atoms in the puckered layers P and P' across the mirror F (superimposed) are not. (a) The triangular (shaded) and hexagonal (bold lines) structural motifs; (b) icosahedra (shaded) and the icosahedral clusters I3V, I3P, I6F and I6P. (c) The [010] projection shows the PFP'pfp' six layers and the icosahedra centred at TM7 and TM10 binding together the PFP' and pfp' layer blocks.

structure PFP'pfp', whereas the pfp' layer block is related to PFP' by a symmetry operation. This six-layer structure was confirmed by Sui *et al* (1997) for orthorhombic $\text{Al}_4(\text{Cr, Fe})$ by high-resolution electron microscopy.

Figures 1(a) and (b) show the structural projection of the PFP' three layers of $\text{Al}_4(\text{Cr, Fe})$ along the a axis. For the puckered layer P', x varies from 0.1130 to 0.1915 and the atomic sites in the two puckered layers P and P' are in mirror-reflecting positions across the flat F layer at $x = 0$ (see figure 1(c)). The atoms in the F layer, open circles being Al atoms and full circles TM atoms, are connected in figures 1(a) and (b) while those in the puckered P and P' layers (superimposed on each other) are not. Figure 1(b) highlights the icosahedra (shaded, drawn in broken lines) as well as their connections in the PFP' layers, whereas figure 1(a) shows triangular (shaded area) and hexagonal (outlined in bold lines) complex motifs of interconnected icosahedra. The origin was chosen at the centre of figures 1(a) and (b) in order to show this hexagonal icosahedral cluster or structural motifs. Thus, the PFP' three-layer block, in fact, is an icosahedral compound layer with one of the two-fold axes of these icosahedra in the [100] direction. Since the layers pfp' are related to the PFP' layers by a body centred translation, we need only to discuss the structure of the PFP' three layers, though some atoms in the p layer have also been involved in some icosahedra in the FP'p layer block (see figure 1(c)). The PFP'pfp' six-layer structure can be seen clearly in it. Obviously, the F and f layers are flat mirrors at $x = 0$ and $1/2$, respectively, and the puckered P and P' layers as well as the p and p' layers are mirror images of each other. Circles of 10 atoms indicate icosahedral or pentagonal antiprisms with their five-fold axes in the [010] direction. Furthermore, the PFP'

Table 2. Details of data collection, processing and structure refinement for Al₄TM (TM = Cr/Fe).

Sample code	Al ₄ (Cr, Fe)
Molecular formula	Al _{80.6} Cr _{10.7} Fe _{8.7}
Pearson's symbol	<i>oI</i> 366-59.56
Colour and habit	Opaque needle
Crystal size	0.04 × 0.04 × 0.13 mm ³
Crystal system	Orthorhombic
Space group	<i>I</i> <i>mmm</i> (no 71)
Unit cell parameters	$a = 1.2500(6)$ nm, $\alpha = 90.00^\circ$ $b = 1.2617(2)$ nm, $\beta = 90.00^\circ$ $c = 3.0651(8)$ nm, $\gamma = 90.00^\circ$ $V = 4.8344(8)$ nm ³
Atoms/cell	306.44
Density (calc)	3.432 g cm ⁻³
Diffractometer	Bruker P4
Radiation	Graphite-monochromatized Mo K α , $\lambda = 0.71073$ Å
Temperature	295 ± 2 K
Scan type	ω -scan
Data collection range	$-18 < h < 19$, $-19 < k < 17$, $-46 < l < 38$; $\theta_{\max} = 50^\circ$
Reflections measured	
total:	4900
unique (<i>n</i>):	4900 observed [$I > 4\sigma(I)$]: 3206
Absorption coefficient	7.650 mm ⁻¹
Min. and max. transmission	0.2684, 0.5372
No. of variables, <i>p</i>	253
<i>R</i> 1	0.0674
<i>wR</i> 2	0.1253
Goof	$S = 0.846$
Residual extrema in final difference map	+1.79 to -1.46 e Å ⁻³
Number of independent atom position	39 (11TM+ 28Al)

and pfp' icosahedral layer blocks are bound together by the icosahedra (shaded in figure 1(c)) centred at TM(7) and TM(10) in layers P/p' and p/P.

4.2. Icosahedra and their connections

In figure 1(b), a large number of icosahedra with centres in the F layer are shaded and drawn in broken lines (the remaining ones can be obtained by the point group symmetry *mmm*). All these icosahedra have one of their two-fold axes perpendicular to the PFP' layers and two of their five-fold axes in the F layer. Different interconnections of these icosahedra can be noted. The three icosahedra centred at TM(3), TM(3) and TM(2) in the upper part of figure 1(b) share vertices Al(3), Al(12) and Al(12), forming an I3V cluster. Kreiner and Franzen (1995, 1997) called this an I3 cluster and have used it to discuss the structure of a large number of intermetallic compounds of transition metals. The letter V is added here to I3 to denote vertex-sharing in order to differentiate it from I3F, three face-sharing icosahedra, and I3P, three mutually (inter)penetrated icosahedra. The I3V cluster exists in a number of places in the PFP' layer block in Al₄(Cr, Fe), as can be seen in figure 1(a).

Three icosahedra centred at TM(3), TM(6) and Al(2) in the lower-right part of figure 1(b) interpenetrate into each other forming a fused I3P cluster. Two mutually interpenetrated

Table 3. Atomic sites, coordinates and equivalent isotropic displacement parameters (\AA^2) for Al_4TM (TM = Cr/Fe). (Note: $U_{\text{eq.}}$ is defined as one-third of the trace of the orthogonalized \mathbf{U} tensor.)

Atoms	Site	x	y	z	$U_{\text{eq.}}$	Occ.
TM(1) ^a	2b	0.0000	0.5000	0.5000	0.0245(4)	1
TM(2) ^b	4i	0.0000	0.0000	0.1448(2)	0.0239(3)	1
TM(3) ^b	8l	0.0000	0.1941(3)	0.2874(3)	0.0252(2)	1
TM(4) ^a	4h	0.0000	0.1057(4)	0.5000	0.0236(3)	1
TM(5) ^b	8l	0.0000	0.3051(3)	0.0733(1)	0.0305(2)	1
TM(6) ^a	8l	0.0000	0.2980(4)	0.3615(7)	0.0237(3)	0.70
TM(7) ^b	8m	0.3271(5)	0.0000	0.2363(2)	0.0247(2)	1
TM(8) ^b	4j	0.0000	0.5000	0.2134(3)	0.0184(3)	1
TM(9) ^b	4g	0.0000	0.2048(0)	0.0000	0.0173(5)	1
TM(10) ^a	16o	0.1742(3)	0.2018(1)	0.0460(2)	0.0266(2)	0.70
TM(11)	4e	0.1139(7)	0.0000	0.0000	0.0180(5)	1
Al(1)	8l	0.0000	0.3851(4)	0.1473(4)	0.0099(4)	1
Al(2) ^b	8l	0.0000	0.3963(8)	0.2866(6)	0.0075(3)	1
Al(3)	4i	0.0000	0.0000	0.2911(1)	0.0123(5)	1
Al(4)	4j	0.0000	0.5000	0.0652(1)	0.0118(5)	1
Al(5)/TM ^b	8l	0.0000	0.1010(1)	0.0719(8)	0.0283(4)	0.75/0.25
Al(6)	8m	0.1915(6)	0.5000	0.1749(1)	0.0142(4)	1
Al(7) ^a	16o	0.1911(7)	0.3079(5)	0.3088(6)	0.0140(3)	1
Al(8)	16o	0.1136(7)	0.3135(7)	0.2207(2)	0.0125(3)	1
Al(9) ^a	8m	0.1850(0)	0.0000	0.0917(5)	0.0225(5)	1
Al(10)	8m	0.1173(9)	0.5000	0.3507(4)	0.0194(4)	1
Al(11)	8n	0.1130(6)	0.3844(8)	0.0000	0.0125(4)	1
Al(12)	8l	0.0000	0.1224(7)	0.2095(1)	0.0124(4)	1
Al(13) ^a	4h	0.0000	0.3011(4)	0.5000	0.0313(8)	1
Al(14)	16o	0.1808(5)	0.1198(0)	0.2633(6)	0.0115(3)	1
Al(15)/TM	8m	0.1788(6)	0.0000	0.1820(7)	0.0342(4)	0.75/0.25
Al(16)	16o	0.3104(5)	0.1127(4)	0.4072(9)	0.0156(3)	1
Al(17)	16o	0.1199(9)	0.1145(7)	0.3523(3)	0.0161(3)	1
Al(18)	16o	0.3847(3)	0.3047(5)	0.3639(7)	0.0166(3)	1
Al(19)	16o	0.1286(5)	0.4013(1)	0.4276(5)	0.0208(6)	0.50
Al(20)	16o	0.3162(6)	0.0898(5)	0.0213(8)	0.0123(5)	0.50
Al(21)	8m	0.1869(2)	0.0000	0.4744(4)	0.0110(7)	0.50
Al(22)	16o	0.1824(1)	0.1849(9)	0.4796(7)	0.0097(5)	0.50
Al(23)	16o	0.1161(3)	0.1870(0)	0.4332(0)	0.0133(5)	0.50
Al(24)	8m	0.1154(3)	0.0000	0.4358(1)	0.0167(8)	0.50
Al(25)	16o	0.1835(7)	0.3013(6)	0.3965(8)	0.0291(5)	0.66
Al(26)	4i	0.0000	0.0000	0.4198(0)	0.0159(2)	0.65
Al(27)	8l	0.0000	0.1848(2)	0.4257(3)	0.0266(7)	0.67
Al(28)	8l	0.0000	0.4175(2)	0.4233(1)	0.0285(7)	0.64

^a Atoms with pseudo-icosahedral coordination.^b Atoms with icosahedral coordination.

icosahedra share a pentagon as well as their centres, or a lens-shaped pentagonal bi-pyramid, such as the shaded TM(3)–Al(2)–TM(6)–Al(17). Three mutually interpenetrated icosahedra share a triangular hexahedron (or two face-sharing tetrahedra), such as the heavily shaded Al(7)–TM(3)–Al(2)–TM(6)–Al(7). Another I3P cluster exists among the icosahedra centred at TM(8), Al(2) and Al(2) drawn in the right-hand part of figure 1(b). Other I3P clusters can be generated by the point group symmetry mmm . Such I3V and I3P clusters exist in

Table 4. Anisotropic displacement parameters (Å²) for Al₄TM (TM = Cr/Fe). (Note: the exponent takes the form: $-2\pi^2 \sum \sum U_{ij} h_i h_j \mathbf{a}_i^* \mathbf{a}_j^*$.)

Atoms	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
TM(1)	0.0211(7)	0.0263(8)	0.0260(7)	0.000	0.000	0.000
TM(2)	0.0221(5)	0.0254(5)	0.0242(5)	0.000	0.000	0.000
TM(3)	0.0230(4)	0.0218(4)	0.0309(4)	0.0006(3)	0.000	0.000
TM(4)	0.0213(5)	0.0225(5)	0.0268(5)	0.000	0.000	0.000
TM(5)	0.0423(4)	0.0262(4)	0.0229(4)	-0.0010(3)	0.000	0.000
TM(6)	0.0170(5)	0.0235(5)	0.0306(5)	0.0019(5)	0.000	0.000
TM(7)	0.0222(4)	0.0263(4)	0.0255(4)	0.000	0.0016(3)	0.000
TM(8)	0.0182(5)	0.0180(5)	0.0189(5)	0.000	0.000	0.000
TM(9)	0.0128(9)	0.0250(10)	0.0142(8)	0.000	0.000	0.000
TM(10)	0.0333(4)	0.0225(3)	0.0241(3)	0.0019(3)	-0.0102(3)	-0.0027(4)
TM(11)	0.0122(9)	0.0208(9)	0.0209(9)	0.000	0.000	0.000
Al(1)	0.0145(7)	0.0095(6)	0.0058(6)	-0.0032(6)	0.000	0.000
Al(2)	0.0071(6)	0.0079(6)	0.0074(6)	-0.0007(6)	0.000	0.000
Al(3)	0.0138(10)	0.0087(9)	0.0145(10)	0.000	0.000	0.000
Al(4)	0.0092(9)	0.0087(9)	0.0175(10)	0.000	0.000	0.000
Al(5)/TM	0.0311(7)	0.0253(7)	0.0287(7)	0.0004(6)	0.000	0.000
Al(6)	0.0173(7)	0.0145(7)	0.0110(7)	0.000	0.0001(6)	0.000
Al(7)	0.0145(5)	0.0110(5)	0.0164(5)	0.0022(4)	0.0010(4)	-0.0003(5)
Al(8)	0.0112(5)	0.0130(5)	0.0134(5)	0.0018(4)	-0.0016(4)	-0.0005(4)
Al(9)	0.0138(7)	0.0409(9)	0.0127(7)	0.000	-0.0004(7)	0.000
Al(10)	0.0100(7)	0.0387(9)	0.0094(7)	0.000	0.0020(6)	0.000
Al(11)	0.0107(6)	0.0097(6)	0.0171(7)	0.000	0.000	0.0024(6)
Al(12)	0.0100(7)	0.0147(7)	0.0125(7)	-0.0001(6)	0.000	0.000
Al(13)	0.0131(11)	0.0115(11)	0.0694(18)	0.000	0.000	0.000
Al(14)	0.0101(4)	0.0111(5)	0.0134(5)	-0.0022(4)	0.0008(4)	0.0005(4)
Al(15)/TM	0.0280(7)	0.0408(8)	0.0338(7)	0.000	0.0001(7)	0.000
Al(16)	0.0189(5)	0.0159(5)	0.0134(5)	-0.0026(4)	-0.0003(4)	0.0024(5)
Al(17)	0.0208(5)	0.0145(5)	0.0144(5)	-0.0007(4)	0.0025(5)	0.0008(5)
Al(18)	0.0162(5)	0.0148(5)	0.0157(5)	-0.0011(4)	0.0017(5)	0.0019(5)
Al(19)	0.0113(9)	0.0114(9)	0.0144(9)	-0.0045(9)	0.0035(9)	-0.0021(9)
Al(20)	0.0139(14)	0.0048(12)	0.0142(14)	0.000	-0.0044(13)	0.000
Al(21)	0.0106(9)	0.0091(9)	0.0095(8)	0.0034(8)	-0.0005(8)	-0.0017(9)
Al(22)	0.0122(9)	0.0167(1)	0.0108(9)	0.0017(9)	0.0004(8)	0.0007(9)
Al(23)	0.0148(1)	0.0158(1)	0.0194(1)	0.000	-0.0029(1)	0.000
Al(24)	0.0192(1)	0.0213(1)	0.0220(1)	-0.0013(1)	-0.0072(1)	-0.0063(1)
Al(25)	0.0129(1)	0.0193(1)	0.0143(1)	-0.0015(1)	0.000	0.000
Al(26)	0.0122(9)	0.0245(1)	0.0110(8)	-0.0069(8)	-0.0035(8)	-0.0009(9)
Al(27)	0.0143(1)	0.0193(1)	0.0194(1)	0.0042(12)	0.000	0.000
Al(28)	0.114(3)	0.066(2)	0.102(3)	0.000	0.000	0.000

many hexagonal intermetallic phases, such as Al₉Mn₃Si (Robinson 1952, Kripjakevich 1977), μ-Al₄Mn (Shoemaker *et al* 1989), κ-AlCrNi (Sato *et al* 1997), λ-Al₄Mn (Kreiner and Franzen 1997) and ν-Al₄(Fe, Cr) (Mo *et al* 2000).

Around TM(11) at the centre of figure 1(b), there is a ring of six icosahedra, centred at TM(2) and TM(5) atoms, respectively, sharing a triangular face (drawn in thick dotted lines) between two neighbouring icosahedra. This ring of six face-sharing icosahedra is called here an I6F cluster. As pointed out by Higashi *et al* (1981) in Mg₅₁Zn₂₀, this is the outer ring of six icosahedra around TM(11). In addition, there is also an inner ring of six icosahedra with centres at TM(9) and Al(5), respectively (for clarity, only two of them are drawn in figure 1(b)).

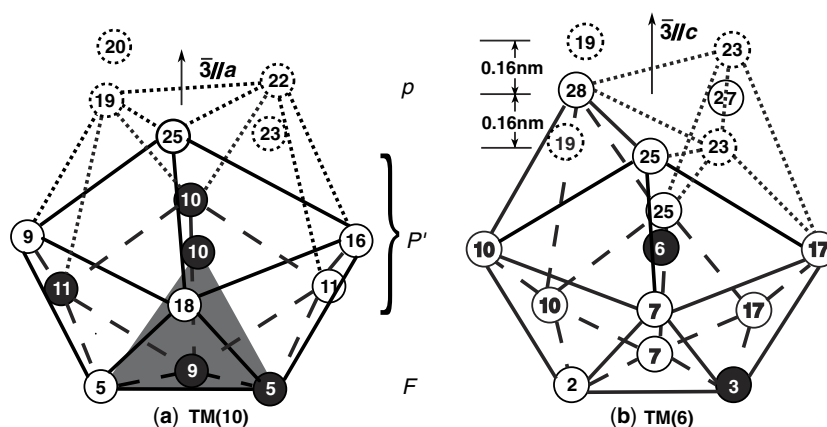


Figure 2. (a) The pseudo-icosahedron centred at TM(10) in FP'p layers with the partially occupied site Al(25) in the P' layer and the split sites Al(19), Al(20), Al(22) and Al(23) in the p layer, $CN_{\text{eff}} = 11.4$. The shaded region is a tetrahedron. (b) The pseudo-icosahedron centred at TM(6) in the PFP' layers with the partially occupied Al(27) and Al(28) sites in the F layer and the split sites Al(19) and Al(23) in the P and P' layers; $CN_{\text{eff}} = 11.6$.

Two neighbouring icosahedra of this ring interpenetrate into each other. Following the name used for I3P, this ring of six interpenetrated icosahedra is called here an I6P cluster. Between the inner and outer rings of six icosahedra, there are further six I3P clusters and one of these (icosahedra centred at TM(5), TM(9) and Al(5) surrounding TM(10) with the overlapped region heavily shaded in figure 1(b)) is marked in figure 1(a). The TM(11) atom is located at the centre of a hexagonal antiprism. Such a hexagonal configuration of icosahedra with six-fold symmetry occurs frequently as a real hexagonal motif in hexagonal intermetallic phases, such as λ -Al₄Mn (Kreiner and Franzen 1997). The large I6F cluster in figure 1(a) is connected to other icosahedral clusters, I3V and I3P, in the PFP' layer block by pentagonal prisms centred at Al(1), Al(4) and Al(12).

Thus, it becomes clear that all TM atoms in Al₄(Cr, Fe), except TM(11) at the centre of a hexagonal antiprism, have icosahedral (coordination number $CN = 12$) or pseudo-icosahedral coordination (effective $CN_{\text{eff}} \approx 12$) and most of them have their centres in the F and f layers. However, the icosahedra centred at TM(1), TM(4), TM(6) and TM(10) as well as the TM(11) polyhedron all consist of Al sites of split occupancy (see figure 2) and this will be further discussed below.

4.3. Partial and/or split occupancy

Partial and/or split occupancy is a common phenomenon in Al–TM intermetallic compounds and sometimes more than 15% of the atomic sites are unoccupied. This is shown by their Pearson symbol: Al₆₈Pd₂₀Ru₁₂, *cP*296-49.15 (Mahne and Steurer 1996), Al_{57.3}Cu_{31.4}Ru_{11.3}, *cP*140-25.1, calculated from table 2 of Sugiyama *et al* (2000) and Al_{2.75}Ir, *cP*60-30, calculated from table 2 of Grin *et al* (1997). From table 3 it can be seen that the split atomic sites with 1/2 occupancy (Al(19)–Al(24)) and partial (about 2/3) occupancy (Al(25)–Al(28)) are located close to the (002) plane with a dense population of triangles, figures 1(a) and (b). In the structure of the cubic Al₆₈Pd₂₀Ru₁₂, there is also such a dense packing of triangles in the (001) plane and many partial and split atomic sites, see figure 3(b) in Mahne and Steurer (1996).

A part of the partial and split atomic sites in figure 1(b) is enlarged in figure 3, in which the split atomic sites Al(19)–Al(24) in the P and P' layers are drawn in dotted circles. These

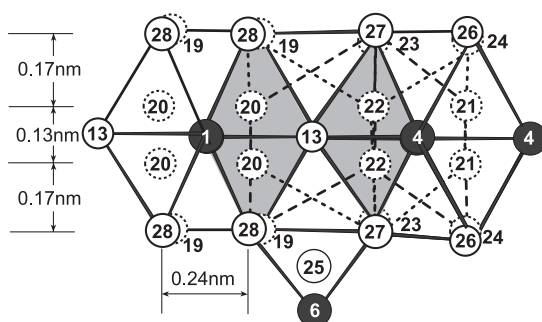


Figure 3. Enlarged part of the top-left corner of figure 1(b) showing the pseudo-icosahedra centred at TM(4) and Al(13) as well as the split atomic sites Al(19)–Al(24) in the P and P' layers (drawn in dotted circles).

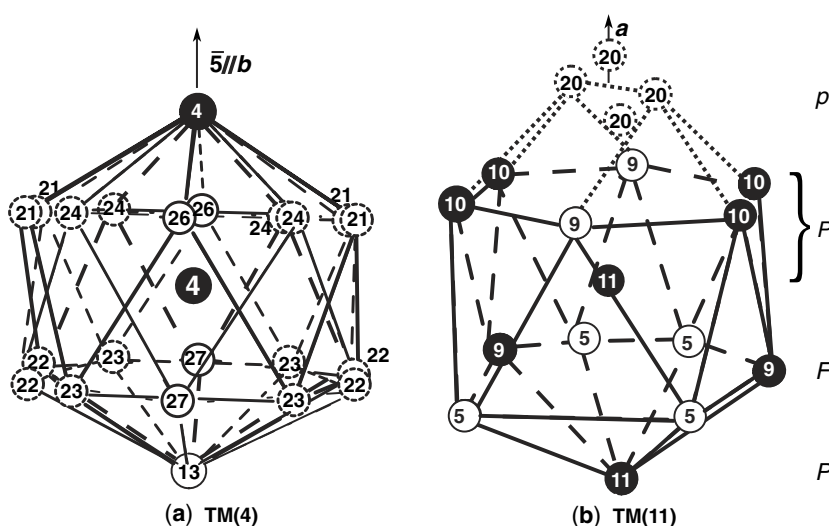


Figure 4. (a) Two alternative pseudo-icosahedra centred at TM(10) drawn in thick and thin lines. $CN_{\text{eff}} \approx 12.7$. (b) The polyhedron surrounding the TM(11) atom at 0.1139, 0, 0 with four symmetrical, split atomic sites Al(20) in the p layer; $CN_{\text{eff}} = 15$.

atomic sites are too closely located to be fully occupied, such that the distance between two split Al(20) sites is only 0.13 nm and that between Al(19) and Al(20) is 0.17 nm. The distance between Al(19) in the P or P' layer and Al(28) in the F layer is 0.1629 nm (not given in figure 3, see figure 2(b)). The two sets of pentagonal antiprisms centred at Al(13) and TM(4) are drawn in different broken lines. Figure 4(a) shows the configuration of two sets of icosahedral sites around TM(4), one set drawn in full lines and the other in dotted lines. Either set of icosahedral sites can be occupied provided that the other set is vacant, i.e. 0.50 occupancy for the Al(19) to Al(24) sites in the P/P' layers. For the Al(26) to Al(28) sites in the F plane, the partial occupancy is 0.64–0.67 (for such a pair of Al sites, one is in this unit cell and the other one is in the neighbouring cell). This also applies to the icosahedra surrounding TM(1) and Al(13). However, instead of a CN of 12, TM(1), TM(4) and Al(13) have an effective $CN_{\text{eff}} \approx 2 + 16 \times 1/2 + 4 \times 2/3 \approx 12.7$. These icosahedra form a chain along the [010] direction in the (002) plane. It is of interest to note in figure 3 that the occupancy drops from

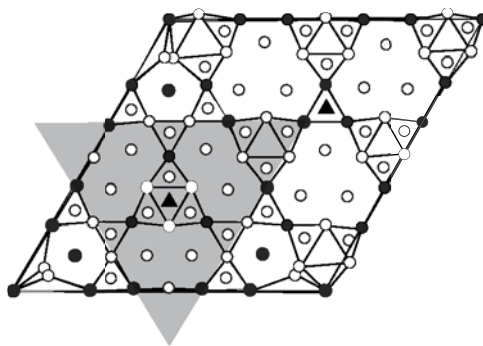


Figure 5. Triangular structural motif (shaded) in the PFP' layers of the hexagonal μ -Al₄Mn with F at $z = 1/4$ (calculated from the data of Shoemaker *et al* (1989)).

about 2/3 for the TM(6) and Al(25)–Al(28) sites to 1/2 for the Al(19)–Al(24) sites as they approach the (002) plane.

Another icosahedron in the PFP' layer block having similar partial and split atomic sites is that surrounding TM(6), figure 2(b). In addition to the partial atomic sites Al(27) and Al(28) in the F layer, there are also split atomic sites Al(23) and Al(19) in the P and P' layers falling at the same positions as Al(27) and Al(28), respectively, in the [100] projection, see figure 3. The distance between Al(19) and Al(28) shown in figure 2(b) is too short to be occupied simultaneously. One possibility is the top triangle switching between Al(28)–Al(23)–Al(23) and Al(27)–Al(19)–Al(19). This pseudo-icosahedron has a $CN_{\text{eff}} = 11.6$. On the other hand, the icosahedron with its centre at TM(10) in the FP'p layer block, figure 2(a), has only split atomic sites of Al(19), Al(20), Al(22) and Al(23) in the p layer. It has a $CN_{\text{eff}} = 11.4$.

Finally, the polyhedron surrounding TM(11) is shown in figure 4(b). If one single atom in the p layer were located directly above the TM(11) atom, then it would be a $CN = 14$ Kasper polyhedron of $\bar{6}$ symmetry. However, there are instead four symmetric Al(20) atomic sites and one possibility is to choose a diagonal pair to form a $CN_{\text{eff}} = 15$ polyhedron.

4.4. Triangular and hexagonal motifs

There are two large structural motifs in figure 1(a): one is the shaded triangular area consisting of I3V and I3P icosahedral clusters; the other is the hexagonal area within the bold lines consisting of I6F and I6P as well as I3P clusters. However, these structural motifs have only two-fold rotational symmetry in Al₄(Cr, Fe). After ordering, such structural motifs may display three- or six-fold symmetry and are naturally expected to exist in hexagonal approximants with a large a parameter. In fact, a triangular motif with three-fold symmetry has indeed been found in the PFP' layer block (F at $z = 1/4$) around the three-fold axis in μ -Al₄Mn, figure 5 (Shoemaker *et al* 1989). Since the family of hexagonal κ -Al(Cr, Ni), λ -Al₄Mn and ν -Al₄(Cr, Fe) phases are structurally related to μ -Al₄Mn (Mo *et al* 2000), this structural motif should also appear in these structures too. Indeed, one such motif appears in κ -Al(Cr, Ni) around the three-fold axis (Li *et al* 1997a, Sato *et al* 1997) and figure 6 is the PFP' layer block calculated from their data. Moreover, the c parameter of the orthorhombic Al₄(Cr, Fe), as mentioned above, is closely related to the a parameter of the hexagonal κ -Al(Cr, Ni). In λ -Al₄Mn (Kreiner and Franzen 1997), the three triangular structural motifs around a three-fold axis partly overlap each other, figure 7 (also calculated). Moreover, there is also a larger hexagonal structural motif, outlined in bold lines, geometrically similar to that

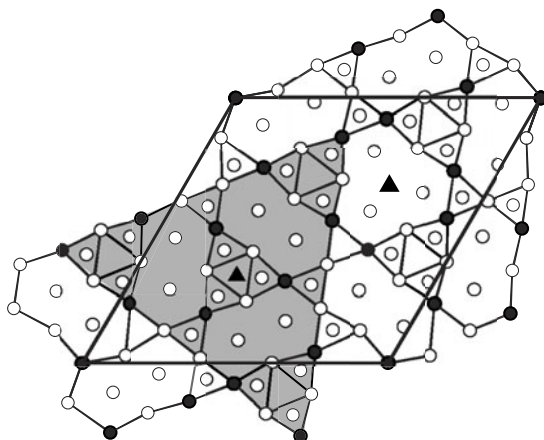


Figure 6. Triangular structural motif (shaded) in the PFP' layers of the hexagonal κ -Al(Cr, Ni) with F at $z = 1/4$ (calculated from the data of Sato *et al* (1997)).

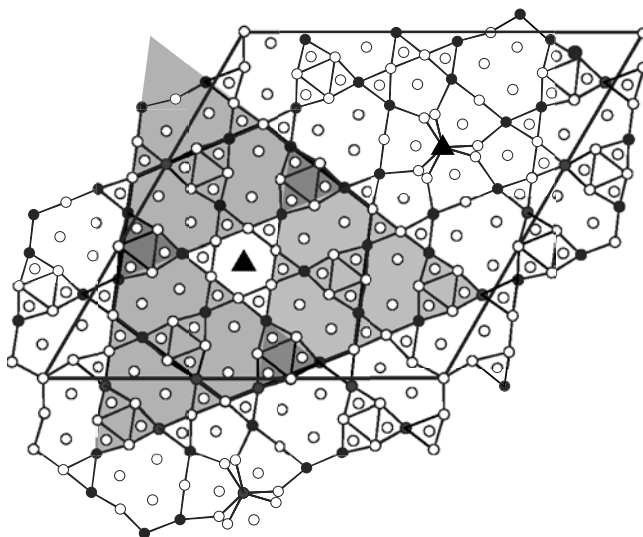


Figure 7. Triangular (shaded) and hexagonal (bold lines) structural motifs in the PFP' layers of the hexagonal λ - Al_4Mn with F at $z = 1/4$ (calculated from the data of Kreiner and Franzen (1997)).

shown in figure 1(a). In the hexagonal ν - $\text{Al}_4(\text{Cr, Fe})$ having an even larger a parameter (Mo *et al* 2000), these three triangular structural motifs are completely separated, figure 8. It is of interest to note that the hexagonal κ , λ and ν phases all have a c parameter of about 1.25 nm and six layers PFP'pfp' stacked in a c period, but the pfp' layer block in these cases is related to the PFP' one by a 6_3 screw axis. However, the triangular structural motif in these hexagonal phases, unlike μ - Al_4Mn , is skew with respect to the a_1 and a_2 axes (Mo and Kuo 2000).

The orthorhombic ε - Al_4Cr (Wen *et al* 1992, Li *et al* 1997b) is structurally closely related to the hexagonal μ - Al_4Mn (Shoemaker *et al* 1989): $a_\varepsilon = a_\mu$, $b_\varepsilon = \sqrt{3}b_\mu$ and $c_\varepsilon = 1/2c_\mu$. Two such triangular structural motifs can be found in the [001] projection of ε - Al_4Cr , figure 9 (also calculated). It is of interest to note that these triangular motifs expand vertically in figure 9 to include a heavily shaded region in figure 9 which is geometrically the same as that

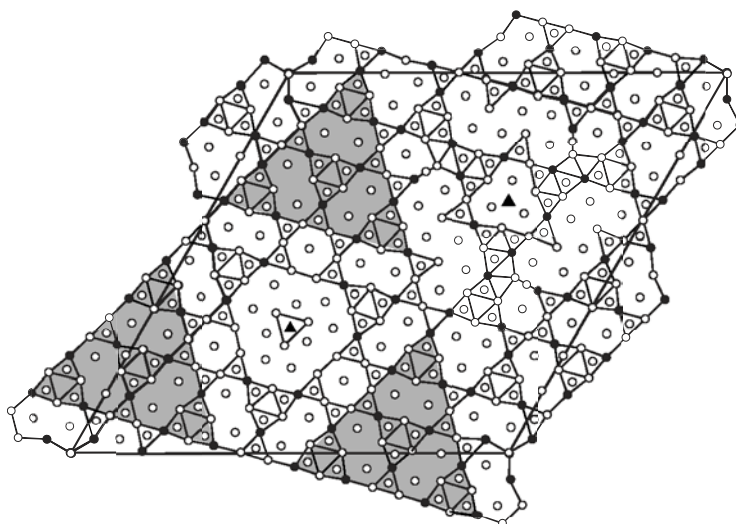


Figure 8. Triangular structural motif (shaded) in the PFP' layers of the hexagonal ν -Al₄(Cr, Fe) with F at $z = 1/4$ (calculated from the data of Mo *et al* (2000)).

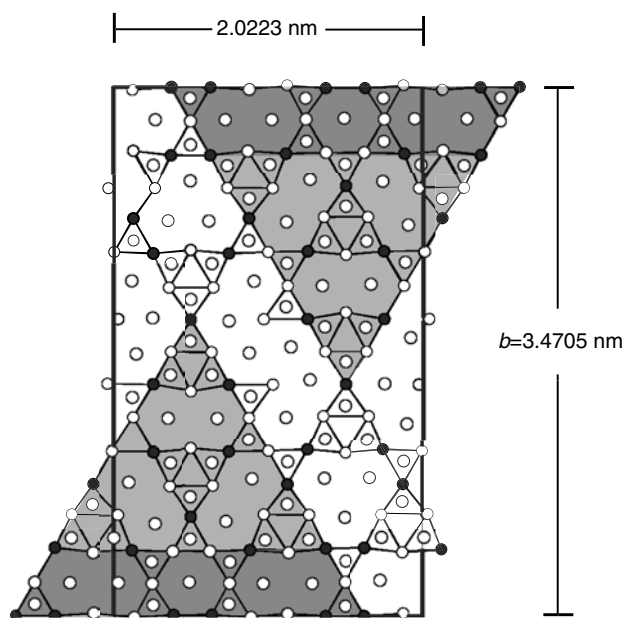


Figure 9. Triangular structural motif (shaded) in the PFP' layers (F at $x = 0$) of the orthorhombic ϵ -Al₄Cr (full circles) related to the hexagonal μ -Al₄Cr/ μ -Al₄Mn (calculated from the data of Li *et al* (1997b)).

between the two triangular motifs in Al₄(Cr, Fe) shown in figure 1(a). In other words, both the orthorhombic Al₄(Cr, Fe) and the hexagonal ϵ -Al₄Cr consist of two similar triangular motifs. However, the triangular motifs in ϵ -Al₄Cr move sidewise and expand vertically so that both the lattice parameters shown in figure 9 are somewhat larger than their counterparts in Al₄(Cr, Fe).

Since μ -Al₄Mn and λ -Al₄Mn are well known quasicrystalline approximants of the Al–Mn decagonal quasicrystal (Audier and Guyot 1986, Bendersky 1987), these relatively large structural motifs in the orthorhombic Al₄(Cr, Fe) might also occur in the structure of Al–TM decagonal quasicrystals.

5. Concluding remarks

- (1) The crystal structure of the orthorhombic phase Al₄(Cr, Fe) has been determined by single-crystal x-ray diffraction. There are 39 (28Al + 11Cr/Fe) independent atoms in a unit cell. A number of Al sites in the cell have partial or split occupancies. Accordingly, the effective coordination numbers of the pseudo-icosahedral are $CN_{\text{eff}} \neq 12$.
- (2) In the orthorhombic Al₄(Cr, Fe), there are six layers, PFP'pfp', along the *a* axis. F and f are flat layers at $x = 0$ and $1/2$, respectively, and they are related by a body centred translation. Both F and f layers are sandwiched between two puckered layers, P/P' and p/p', respectively, in mirror reflection positions.
- (3) As an important structural character of the Al–TM alloys, the icosahedral connection in the orthorhombic Al₄(Cr, Fe) is discussed in detail. In addition, two large triangular icosahedral clusters are drawn and compared with the related Al–TM phases with different symmetries.
- (4) Geometrically, the large icosahedral clusters in orthorhombic Al₄(Cr, Fe) and related phases have triangular and/or hexagonal shapes, but chemically they do not have three- or six-fold symmetry, as can be seen from the point group symmetry *mmm* of this structure. By means of ordering, however, icosahedral clusters of three- and six-fold symmetry can exist and various hexagonal structures can result.

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