Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

A pentagonal cluster in certain approximants to decagonal quasicrystals

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Received 26 January 2001
Accepted 25 June 2001

A certain pentagonal cluster occurring in several approximants to the decagonal quasicrystal is discussed. The term 'cluster' is used here to denote a structure motif which is a certain assemblage of coordination polyhedra. The cluster resembles a wheel with an 'axis' and a 'tyre'. It is built up of seven intergrown icosahedra. The 'wheel cluster' builds up structures of infinite strands or nets perpendicular to the pentagonal wheel cluster axis. The wheel cluster is the main constituent of the decagonal approximant structure types Al_3Mn, $Al_{60}Mn_{11}Ni_4$ and $Ga_{137}Mn_{123}$.

1. Introduction

The Bergman *et al.* (1957) and Mackay (1962) clusters with 117 and $(10n^2 + 2)$, n = 3,4,5... atoms, respectively, are well known building blocks in approximants to the icosahedral quasicrystals (Shechtman *et al.*, 1984). In this paper we point out the occurrence of a pentagonal 34-atom cluster with a similar role as a building block in several approximants to decagonal quasicrystals.

A number of compounds considered to be decagonal approximants (Zhang & Kuo, 1990; Li & Kuo, 1992*a*; Kuo, 1993; Tamura, 1997) with known crystal structures were investigated. These included: $Al_{60}Mn_{11}Ni_4$ (Robinson, 1954), Al_3Mn (Taylor, 1961; Hiraga *et al.*, 1993; Shi *et al.*, 1994; Pavlyuk *et al.*, 1995), $Ga_{137}Mn_{123}$ (Boström & Hovmöller, 2001), Al_3Pd (Matsuo & Hiraga, 1994) and $Al_{13}Fe_4$ (Black, 1955).

A cluster concept for structures where icosahedra are a salient feature have been presented by Kreiner & Franzen (1995). The Kreiner cluster is made up of three vertex-sharing icosahedra and contains in total 36 atoms. This structural motif is found in vast amounts of intermetallic compounds, but cannot be used to satisfactorily describe the wheel cluster structures discussed here. Romeu (1993) proposed that decagonal quasicrystals could be generated from non-intersecting 19-atom units consisting of two intergrown icosahedra, but presented no evidence for the presence of these clusters in any solved approximant crystal structure. The wheel cluster structures discussed here cannot be described by translated Romeu 19 atom clusters.

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Table 1
Number of aluminide (Al, Ga) atoms at the different positions in the wheel clusters in structures refined from X-ray diffraction data.

Nomenclature as in Fig. 3.

Compound	Axial center	Axial apex	Outer axial pentagon	Middle axial pentagon	Circumscribing outer atoms
Sum of atoms	2	2	10	5	15
$Al_{60}Mn_{11}Ni_4$	2	0	10	2	11
T3-(AlMnZn)	2	0	9	2	9†
Al_3Mn‡	2	0	4	1	15
$Al_{61}Cr_{17}Cu_7Fe_{11}Si_3$	2	0	10	2	11
$Ga_{137}Mn_{123}$	2	0	2	0	15

† Possibly 11 if two Al atoms occupy holes in the structure. ‡ Pavlyuk *et al.* (1995).

2. Cluster description

The cluster resembles a wheel with an axis and a tyre. The 'axis' is made up of two icosahedra intergrown in such a manner that the central atom of one icosahedron is the apex atom of the other, and *vice versa*. The axis is identical to the Romeu 19 atom cluster. This axis is circumscribed by a 'tyre' of five icosahedra intergrown with each other in the same manner as the axis. One edge of each circumscribing icosahedron is made up by the two central atoms in the icosahedra of the axis. The building up of the cluster is shown in Fig. 1. In total, the cluster contains 34 atoms. The ideal, non-crystallographic point group of the cluster is D_{5h}. In this ideal case only six atoms are unique. It is noteworthy that the wheel cluster is topologically identical to one half of the inner part of the Bergman cluster, see Fig. 2.

There is a general tendency for the aluminide (Al, Ga) to occupy the axial central positions and the circumscribing outer atoms (nomenclature as in Fig. 3). The axial apex is generally occupied by a transition metal. See Table 1 for details of the atomic distributions in the wheel cluster in the known structures.

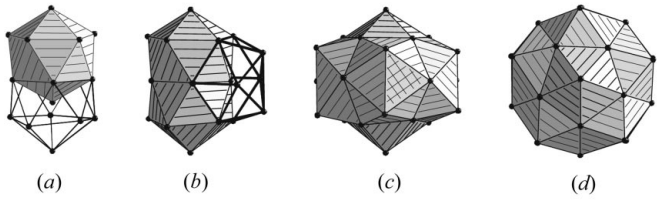

Figure 1
Wheel cluster building up sequence. (*a*) Two intergrown icosahedra make up the axis. (*b*) Side view of the wheel axis with one of the five circumscribing icosahedra drawn as a wire model. (*c*) Side view of the complete wheel cluster. One of the ten possible triangular faces that could be shared with another wheel cluster is chequered. (*d*) Top view along the fivefold axis of the complete wheel cluster.

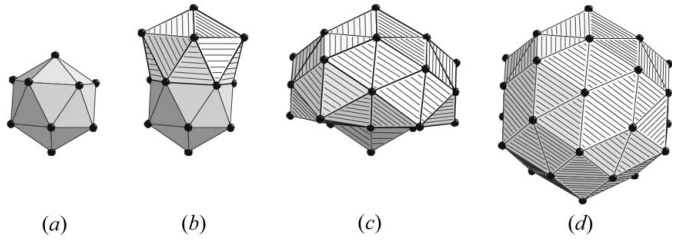

Figure 2
(*a*) Central icosahedron of the Bergman cluster. All atoms in the shell have icosahedral coordination. (*b*) When one apex atom is coordinated, the result is topologically identical to the axis in the wheel cluster. (*c*) When all atoms in the middle pentagonal ring are coordinated, the formed cluster is topologically identical to the wheel cluster. The small metric distortion is mainly in the direction along the pentagonal axis. (*d*) Inner part of the Bergman cluster where all atoms of the core icosahedron drawn in (*a*) are coordinated.

3. Cluster connectivity and layer formation

The wheel clusters build up distinct layers perpendicular to the pentagonal wheel cluster axis by sharing the three atoms of one of the outer triangular faces of the circumscribing icosahedra. An example of such a triangular face is shown chequered in Fig. 1(*c*). There are ten such faces in each wheel cluster, two of them belonging to each circumscribing icosahedron. The pentagonal axis of the wheel cluster is perpendicular to a unit cell face in all known structures.

The wheel clusters can form one-dimensional strands or two-dimensional nets by connecting to each other. A strand is formed if the wheel clusters are connected to two other wheel clusters. A net is formed if the wheel clusters are connected to three other wheel clusters.

The four possible simple types of strands are shown in Fig. 4. The connectivity can be described in a way that is analogous with the nomenclature used for derivatives of the benzene molecule in organic chemistry. The use of the nomenclature is seen in Fig. 4. The linear 1–6 strand is found in $Al_{60}Mn_{11}Ni_4$ (Robinson, 1954). The undulating 1–5 strand is found in Al_3Mn (Taylor, 1961; Hiraga *et al.*, 1993; Shi *et al.*, 1994; Pavlyuk *et al.*, 1995). The 1–4 and 1–3 arrangements have not been identified in any known structure. As will be discussed below, the 1–6 and 1–5 strands may be the only possible strands.

Three types of simple nets are possible. These are shown in Fig. 5. The smallest translational unit, the 'tile', in these nets consists of four or six connected clusters. The case when this

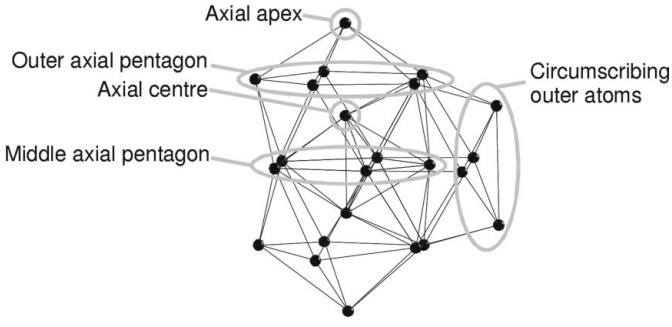

Figure 3
Notation for the different atomic positions in the wheel cluster.

tile consists of five clusters, shown in Fig. 6, could possibly be found in quasicrystals. So far, the only structure found with net-forming clusters is $Ga_{137}Mn_{123}$ (Boström & Hovmöller, 2001). In that compound each cluster has three neighbours, together forming an infinite net with the tile shown in Fig. 5(*b*).

4. Wheel cluster axis extension

The axis of the wheel cluster is extended in one or both directions in all structures discussed here, in such a way that the outermost axial apex atom is coordinated by an icosahedron. Two extending icosahedra are drawn as wire models in Fig. 7. In the known structures the extension is met by the extension from another wheel cluster axis, and they share their outermost apex atom. Thus, the shared apex atom is coordinated by a pentagonal prism, since both extending icosahedra have the same orientation.

The axis extensions penetrate into the space between wheel clusters in an adjacent layer. The pentagonal prism formed by two extending icosahedra sharing an apex atom is always located in the middle of a cluster layer (Fig. 7). Each of these pentagonal prisms share two atoms with its adjacent wheel clusters in the same layer. The pentagonal prism shares pairs of atoms with three wheel clusters in the $Al_{60}Mn_{11}Ni_4$ and Al_3Mn strand structures. In the $Ga_{137}Mn_{123}$ net structure the pentagonal prism shares pairs of atoms with four wheel clusters.

There are three important center-to-center distances for the study of structures built up by the wheel cluster. The first is the perpendicular distance $d_{ll} \simeq 6.3$ Å between two adjacent wheel cluster layers, see Fig. 7. The second is the distance $d_{ww} \simeq 7.7$ Å between the centers of two adjacent wheel clusters, in the same wheel cluster layer (see Fig. 8). The third is the distance $d_{pw} \simeq 6.6$ Å between a wheel cluster and an adjacent pentagonal prism in the same wheel cluster layer, see Figs. 7 and 8. The difference between the two latter distances makes it possible to conclude from the projected structure, along the pentagonal axis, if two wheel clusters are in the same or adjacent wheel cluster layers. See Table 2 for a detailed

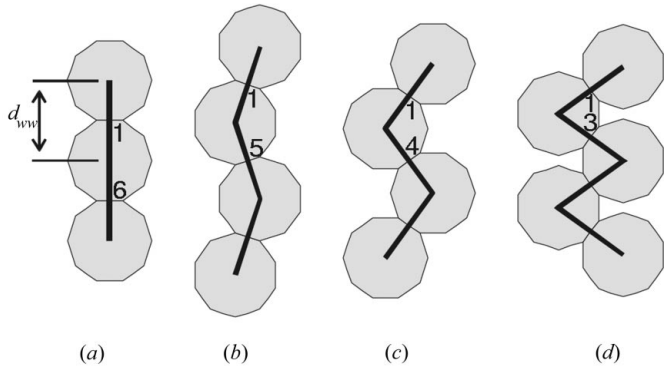

Figure 4
Hypothetical simple strands. (*a*) 1–6 strand as found in $Al_{60}Mn_{11}Ni_4$ (Robinson, 1954); (*b*) 1–5 strand as found in Al_3Mn (Pavlyuk *et al.*, 1995). The 1–4 strand (*c*) and 1–3 strand (*d*) have not been found in any known structure.

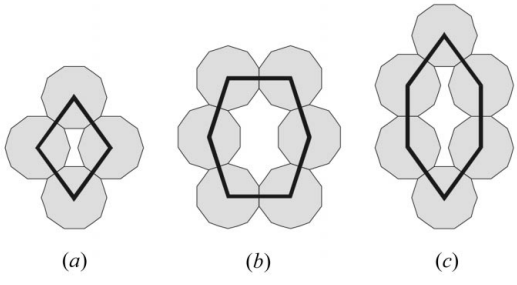

Figure 5
Hypothetical tiles with up to six wheel clusters which could form nets with only one type of tile. (*a*) 1–4–6–9 net; (*b*) 1–5–8 net, as found in $Ga_{137}Mn_{123}$; (*c*) 1–5–9 net.

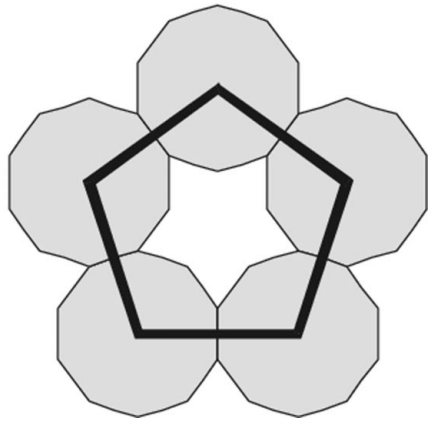

Figure 6
Pentagonal arrangement of wheel clusters. This tile cannot tile the plane itself, but it may well play a role as a tile in a decagonal quasicrystal.

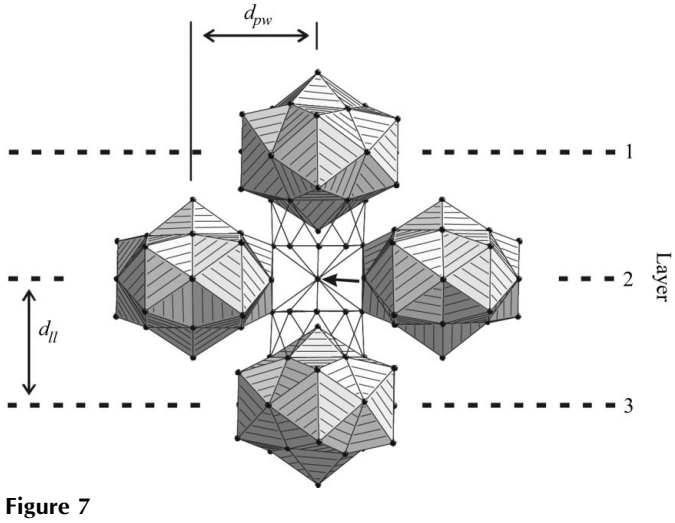

Figure 7
Two extended axes meet in a void. The shared apex atom, marked out with an arrow, is coordinated by a pentagonal prism, since the icosahedra of both extended axes have the same orientation. This arrangement is found in all known structures built up from the wheel cluster.

Table 2
The three characteristic center-to-center distances between wheel clusters.

d_{ww} = distance between the centres of two wheel clusters connected to each other in the same layer; d_{ll} = perpendicular distance between two layers of wheel clusters; d_{pw} = distance between the centre of a pentagonal prism and the wheel cluster it shares atoms with in the same layer. The distances are marked out in Figs. 7 and 8

Compound	d_{ll} (Å)	d_{ww} (Å)	d_{pw} (Å)
$Al_{60}Mn_{11}Ni_4$	6.3	7.6	6.4
T3-(AlMnZn)	6.3	7.8	6.6
Al_3Mn	6.2	7.8	6.6
$Al_{61}Cr_{17}Cu_7Fe_{11}Si_3$	6.2	7.6	6.5
$Ga_{137}Mn_{123}$	6.4	7.7	6.6

listing of these distances in the structures discussed in this paper. This knowledge could prove most useful in an attempt to solve a wheel cluster structure from high-resolution electron microscopy images taken along the pentagonal wheel cluster axis.

5. Structure description of compounds built up by wheel clusters

5.1. $Al_{60}Mn_{11}Ni_4$

Orthorhombic $Al_{60}Mn_{11}Ni_4$ (Robinson, 1954) is built up by wheel clusters in linear 1–6 strands (see Table 3 for crystallographic data). Four such strands pass through the unit cell, as shown in Fig. 9(*a*). The wheel clusters are located on mirror planes perpendicular to the wheel cluster axis. The wheel cluster axis is extended with one icosahedron in both directions. The extension of the axis is located between the strands. The unit cell of the $Al_{60}Mn_{11}Ni_4$ structure contains 156 atoms, of which 12 do not belong to wheel clusters or their extended axes. T3-(AlMnZn) (Damjanovic, 1961) is isotypic. However, in T3-(AlMnZn) one atom in the wheel cluster is missing in the structural model by Damjanovic. The position with the coordinates (1, 0.188, 0.75) that could be expected to be occupied by an atom is 2.5 Å from the nearest atom. Electron diffraction experiments indicate also that π-Al_4Mn (Li & Kuo,

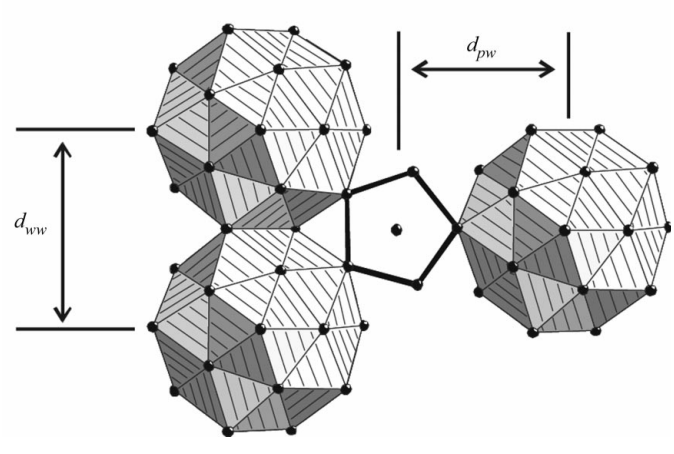

Figure 8
One pentagonal prism sharing 3 × 2 atoms with three adjacent wheel clusters in the same wheel cluster layer. The pentagonal prism is formed by two meeting icosahedral extensions of the axes of two wheel clusters in two adjacent layers. The model is seen along the pentagonal wheel cluster axis.

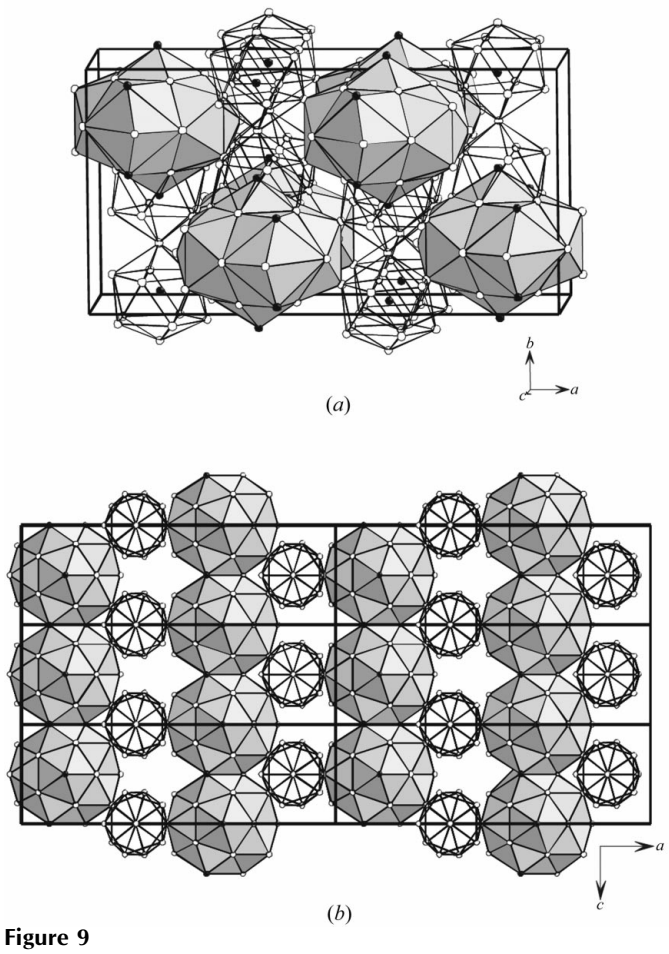

Figure 9
(*a*) One unit cell of $Al_{60}Mn_{11}Ni_4$ seen along the *c* axis. (*b*) Six unit cells of $Al_{60}Mn_{11}Ni_4$ seen along the *b* axis with $0.5 < b < 1$. The grey icosahedra build up the wheel clusters. The icosahedra drawn as wire models are extended axes of the wheel clusters in an adjacent layer. The wheel clusters build up infinite linear strands parallel to the *c* axis.

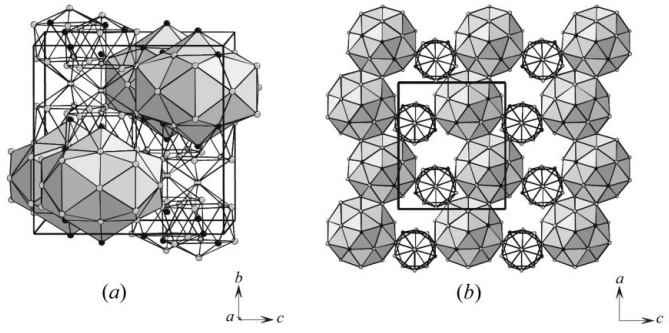

Figure 10
(*a*) One unit cell of Al_3Mn seen along the *a* axis. (*b*) Al_3Mn seen along the *b* axis with $0.5 < b < 1$. The unit cell is marked out with heavy lines. The grey icosahedra build up the wheel clusters. The icosahedra drawn as wire models are extended axes of wheel clusters in an adjacent layer. The wheel clusters build up infinite undulating rows along the *a* axis.

Table 3
Crystallographic data of phases built up by the wheel cluster, refined from X-ray diffraction data.

Compound	Space group	Cell parameters				Unique atoms	Pearson symbol	Reference
		a (Å)	*b* (Å)	*c* (Å)	β (°)			
$Al_{60}Mn_{11}Ni_4$	*Bbmm* (63)†	23.8	12.5	7.55		18	oB156	Robinson (1954)
T3-(AlMnZn)	*Cmcm* (63)	7.78	23.8	12.6		17	oC152	Damjanovic (1961)
Al_3Mn	*Pnma* (62)	14.83	12.43	12.51		25	oP156	Hiraga *et al.* (1993)
Al_3Mn	$Pn2_1a$ (33)	14.837 (4)	12.457 (2)	12.505 (2)		39	oP156	Shi *et al.* (1994)
Al_3Mn	*Pnma* (62)	14.883 (3)	12.447 (4)	12.560 (3)		25	oP156	Pavlyuk *et al.* (1995)
$Al_{61.3}Cr_{17.2}Cu_{7.4}Fe_{11.1}Si_3$	*Pnma* (62)	14.582 (1)	12.321 (1)	12.363 (1)		25	oP156	Kang *et al.* (1992)
$Ga_{137}Mn_{123}$	*C*2/*c* (15)	20.239 (3)	14.790 (2)	14.908 (2)	120.93 (2)	34	mC260	Boström & Hovmöller, 2001

† Note that with standard setting $a = 7.55$, $b = 23.8$, $c = 12.5$ Å.

1992*b*) and Mn_5Ga_6 (1/0, 2/1) (Wu & Kuo, 1997) are isostructural.

5.2. Al_3Mn

The orthorhombic crystal structure of Al_3Mn has been determined by single-crystal X-ray diffraction methods by several groups (Hiraga *et al.*, 1993; Shi *et al.*, 1994; Pavlyuk *et al.*, 1995). It is isostructural with $Al_{61.3}Cr_{17.2}Cu_{7.4}Fe_{11.1}Si_3$ (Kang *et al.*, 1992). In the Al_3Mn structure each wheel cluster is connected to two other wheel clusters, building up infinite parallel undulating strands, see Fig. 10. There are two such strands in the unit cell. The wheel clusters are located on mirror planes perpendicular to the wheel cluster axis. The wheel cluster axis is extended with one icosahedron in both directions. The extension of the axis is located between the strands. The unit cell contains 156 atoms. Only eight of these do not belong to a wheel cluster or its extended axis.

5.3. $Ga_{137}Mn_{123}$

Monoclinic $Ga_{137}Mn_{123}$ (Boström & Hovmöller, 2001) is built up by wheel clusters connected in a stretched honeycomb net (Fig. 11). The wheel cluster axis is extended with one icosahedron in only one direction. This icosahedron is met by the icosahedron extending from a wheel cluster in the layer next to the adjacent one. Since both these icosahedra have the same orientation they form a pentagonal prism (Fig. 7). This pentagonal prism is located in one of the pentagonal voids inside a hexagonal tile (Fig. 11*a*). The axial icosahedron on the opposite side of the wheel cluster shares one edge with another axial icosahedron belonging to a wheel cluster in the adjacent layer (Fig. 12). The unit cell contains 260 atoms, of which 20 do not belong to wheel clusters or their extended axes.

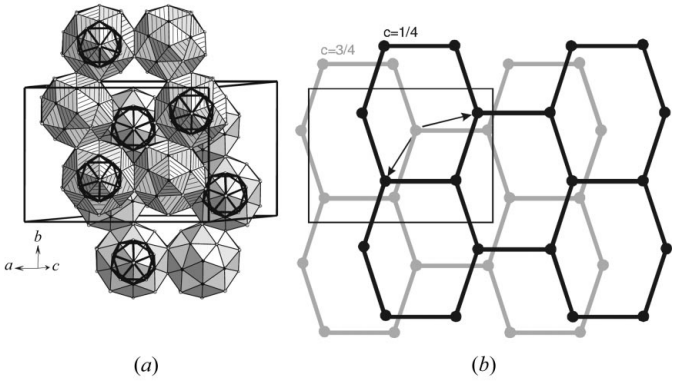

Figure 11
(*a*) Packing of wheel clusters in the unit cell of $Ga_{137}Mn_{123}$. For clarity, only one hexagonal tile from each of two adjacent layers are shown. The wheel clusters in the hexagonal layer at approximately $c = \frac{1}{4}$ are drawn hatched, while the wheel clusters in the layer at $c = \frac{3}{4}$ are drawn solid. The extensions of the wheel cluster axes which penetrate into the adjacent layer are drawn as wire models. (*b*) Schematic representation of the two adjacent hexagonal infinite layers in the cell, parallel to the *ab* plane. The layer at $c = \frac{1}{4}$ is black while the layer at $c = \frac{3}{4}$ is grey. The arrows mark out the two closest 6.4 Å shifts that would superimpose the layers.

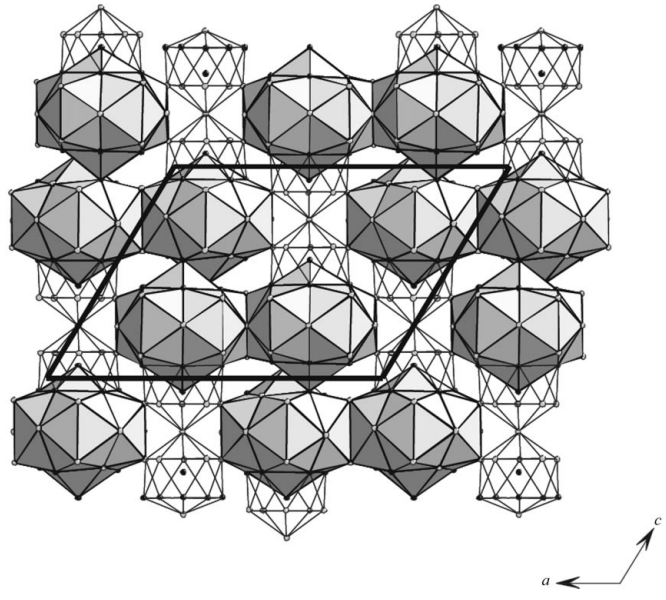

Figure 12
Unit cell of $Ga_{137}Mn_{123}$ seen along the *b* axis with $-0.1 < b < 0.6$. The grey icosahedra build up the wheel clusters. The icosahedra drawn as wire models are extended axes of wheel clusters. Each wheel cluster has only one extension of the axis, which is met by an extended axis from a wheel cluster in an adjacent layer. The axis on the opposite side of the wheel cluster is not extended, but shares an edge with an axis of a wheel cluster in another adjacent layer.

6. Discussion

The wheel cluster can be used to describe several complicated decagonal approximants, including $Al_{60}Mn_{11}Ni_4$, Al_3Mn and $Ga_{137}Mn_{123}$. However, the structures of Al_3Pd (Matsuo & Hiraga, 1994) and $Al_{13}Fe_4$ (Black, 1955) belong to different classes of decagonal approximants and they cannot be described with the wheel cluster.

It should be noted that the centres of the wheel clusters are clearly distinguished in high-resolution electron microscope (HREM) images taken along the pentagonal wheel cluster axis. The distances 6.6 and 7.6 Å have repeatedly been reported as distances in HREM images between prominent objects recognized here as the wheel cluster. Examples are found in Li *et al.* (1992), Hiraga *et al.* (1993) and Wu *et al.* (1998). The difference in projected distances d_{ww} and d_{pw} along the pentagonal wheel cluster axis between wheel clusters in the same and in adjacent layers is clearly distinct. Thus, it should be possible to determine the full three-dimensional atomic structure of wheel cluster compounds, from HREM images taken along the direction of the pentagonal wheel cluster axis.

We believe that the 1–4 and 1–3 strands cannot exist in structures analogous to the structures with 1–6 ($Al_{60}Mn_{11}Ni_4$ type) and 1–5 strands (Al_3Mn type). The inward bend of the 1–3 strand cannot accommodate a pentagonal prism. While the inward bend of the 1–4 strand can accommodate a pentagonal prism, the adjacent strand in the same layer does not fit to the prism. Only the simple net 1–5–8 shown in Fig. 5(*b*) can accommodate a pentagonal prism in the layer of the tile. The pentagonal arrangement of wheel clusters shown in Fig. 6 makes up a full shell of a pentagonal prism by itself. This prism is identical to the one formed by two meeting axis extensions with icosahedra of the same orientation.

It seems possible that the wheel cluster is also the fundamental unit in some decagonal quasicrystals with compositions close to the approximants discussed here. We believe that an attempt to solve the structure of such a decagonal quasicrystal from HREM images might be facilitated by the knowledge of the structural principles discussed in this paper.

This work was carried out with economical support from the Swedish Natural Science Research Council.

References

Bergman, G., Waugh, J. L. T. & Pauling, L. (1957). *Acta Cryst.* **10**, 254–259.
Black, P. J. (1955). *Acta Cryst.* **8**, 43–48.
Boström, M. & Hovmöller, S. (2001). *J. Alloys Compd*, **314**, 154–159.
Damjanovic, A. (1961). *Acta Cryst.* **14**, 982–987.
Hiraga, K., Kaneko, M., Matsuo, Y. & Hashimoto, S. (1993). *Philos. Mag. B*, **67**, 193–205.
Kang, S. S., Malaman, B., Venturini, G. & Dubois, J. M. (1992). *Acta Cryst.* B**48**, 770–776.
Kreiner, G. & Franzen, H. F. (1995). *J. Alloys Compd*, **221**, 15–36.
Kuo, K. H. (1993). *J. Non-Cryst. Solids*, **153/154**, 40–44.
Li, X. Z. & Kuo, K. H. (1992*a*). *Philos. Mag. B*, **66**, 117–124.
Li, X. Z. & Kuo, K. H. (1992*b*). *Philos. Mag. B*, **65**, 525–533.
Li, X. Z., Shi, D. & Kuo, K. H. (1992). *Philos. Mag. B*, **66**, 331–340.
Mackay, A. L. (1962). *Acta Cryst.* **15**, 916–918.
Matsuo, Y. & Hiraga, K. (1994). *Philos. Mag. Lett.* **70**, 155–161.
Pavlyuk, V. V., Yanson, T. I., Bodak, O. I., Cerny, R., Gladyshevskii, R. E., Yvon, K. & Stepien-Damm, J. (1995). *Acta Cryst.* C**51**, 792–794.
Robinson, K. (1954). *Acta Cryst.* **7**, 494–497.
Romeu, D. (1993) *Philos. Mag. B*, **67**, 77–96.
Shechtman, D., Blech, I., Gratias, D. & Cahn, J. W. (1984). *Phys. Rev. Lett.* **53**, 1951–1953.
Shi, N. C., Li, X. Z., Ma, Z. S. & Kuo, K. H. (1994). *Acta Cryst.* B**50**, 22–30.
Tamura, N. (1997). *Philos. Mag. A*, **76**, 337–356.
Taylor, M. A. (1961). *Acta Cryst.* **14**, 84–84.
Wu, J. S. & Kuo, K. H. (1997). *Metall. Mater. Trans. A*, **28**, 729–742.
Wu, J. S., Li, X. Z. & Kuo, K. H. (1998). *Philos. Mag. Lett.* **77**, 359–370.
Zhang, H. & Kuo, K. H. (1990). *Phys. Rev. A*, **42**, 8907–8914.