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Preparation and crystal structure of the novel decagonal approximant $Mn_{123}Ga_{137}$

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Abstract

A new approximant to a decagonal quasicrystal has been found in the Ga–Mn binary system. Single crystals of $Mn_{123}Ga_{137}$ were synthesised from pieces of manganese in a self flux of gallium. Still at the reaction temperature, the liquid flux and the solid $Mn_{123}Ga_{137}$ crystals were separated from each other by centrifugal action filtering. The crystal structure of $Mn_{123}Ga_{137}$ was determined from single crystal X-ray diffraction data. $Mn_{123}Ga_{137}$ crystallises in the monoclinic space group $C2/c$, $a=20.239(3)$ Å, $b=14.790(2)$ Å, $c=14.908(2)$ Å, $\beta=120.93(2)°$, $R_w=4.0\%$. The structure consist mainly of a fundamental type of wheel shaped pentagonal clusters with $5/mm$ point group pseudo symmetry. The cluster consists of seven intergrown icosahedra. Each cluster is fused to three other in the plane perpendicular to the pseudo five-fold axis. In that way they make up infinite honeycomb nets parallel to the a–b plane.

Keywords: Quasicrystal; Approximant; Mn–Ga; Intermetallic compounds; Crystal structure; Synthesis

1. Introduction

Quasicrystals are crystals whose structures can not be described within the rules of classic crystallography. They have long range order manifested in the sharp diffraction spots in the diffraction pattern, but lack translation periodicity. Thus they have no ordinary unit cell in three-dimensional space. One example is the decagonal quasicrystal [1] which has periodicity along one axis, but is quasiperiodic in the plane perpendicular to this axis. Approximants are crystals with large unit cells and diffraction patterns very similar to those of quasicrystals. They also have elemental compositions very close to those of quasicrystals. However, the approximants have atomic structures which follow the rules of classic crystallography. It is considered highly probable that approximants and quasicrystals have similar local atomic structures and contain the same types of clusters. Therefore, the study of crystal structures of approximants is of great importance for the development of models of the atomic structure and the formation of true quasicrystalline compounds.

The binary Ga—Mn alloy system is rich in intermetallic phases, several with large unit cell dimensions and unknown structures. It has won renewed interest due to its close chemical relationship to the Al–Mn system where quasicrystals first were discovered [2]. Several approximants and one decagonal quasicrystal have been identified in the Ga–Mn system with electron diffraction techniques by Wu and Kuo [3]. We here report an X-ray single crystal structure determination and refinement of the novel monoclinic decagonal approximant $Mn_{123}Ga_{137}$. The overall crystal data and intensity collection of $Mn_{123}Ga_{137}$ is given in Table 1.

2. Experimental

$Mn_{123}Ga_{137}$ exists in equilibrium with a non-stoichiometric gallium rich melt. Thus it can be synthesized from the melt by slow cooling. However, in our experiment we used a modified version of the method devised by Boström and Hovmöller [4], where the reaction took place at constant temperature in a self flux of gallium. During the reaction the manganese pieces slowly dissolved into the liquid gallium, providing conditions for slow and stable crystal growth. The non-stoichiometric synthesis mixture consisted of 0.87 g of solid approximately $3\times3\times1$ mm large manganese pieces and 1.37 g of gallium. The mixture

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Table 1
Crystal data and intensity collection for $Mn_{123}Ga_{137}$

Crystal data	
Chemical formula	$Mn_{123}Ga_{137}$
Formula weight (g/mol)	16 309
Crystal system	monoclinic
Space group	$C2/c$ (15)
a, b, c (Å)	20.239(3), 14.790(2), 14.908(2)
β (°)	120.93(2)
V (Å^3); Z	3828; 1
Density (calculated) (g/cm^3)	7.08
Crystal form	irregular
Crystal size (mm)	0.05×0.05×0.05
Colour	lustrous metallic
Absorption coefficent (mm^{-1})	33.3
Data collection	
Diffractometer	Stoe IPDS
Radiation	Mo Kα (λ=0.71069 Å)
No. of reflections measured	12 089
No. of independent reflections	2997
No. of observed reflections	1544
Observation criterion	$I>3\sigma(I)$
Absorption correction	numerical from crystal shape
T_{min}; T_{max}	0.166; 0.437
$R_{int,obs}$; $R_{int,\ all}$	0.079; 0.093
Range of h k l	$-23\rightarrow h\rightarrow 23$ $-16\rightarrow k\rightarrow 16$ $-16\rightarrow l\rightarrow 16$
Temperature (°C)	25
Refinement	
Reflections used for cell refinement	5000
Refinement on	F
No. of reflections used in refinement	all
No. of parameters refined	148
Weighting scheme	$w=1/\sigma^2$ (F)
R_{all}; wR_{all}	0.113; 0.040
S_{all}	3.44
$(\Delta/\sigma)_{max}$	0.0001
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (eÅ^{-3})	6.38; −5.62
Extinction; extinction coefficient	gaussian isotropic; 0.0016(6)
Source of atomic scattering factors	International Tables for X-ray Crystallography (1974, Vol. IV)

was put into a quartz glass tube which was prepared with a filter made of quartz wool on top of a support of pieces of coarsely crushed quartz glass. The quartz glass tube was evacuated and sealed. The sealed quartz glass tube was then put into a quartz wool insulated cylindrical container made of stainless steel (see Fig. 1). The container was kept in a furnace at 720°C for 52 h. In the furnace the whole assemblage was kept upside down, so that the filter was at the top and the reaction mixture at the bottom of the quartz glass tube. At the end of the reaction, the steel container was turned around and transferred into a centrifuge. The melt was forced down through the quartz wool filter when the sample was centrifuged, leaving the solid crystals on top of it. Less than 10 s passed between when the sample was taken out from the furnace and the centrifuge was started. An irregular 0.05×0.05×0.05 mm large single crystal was cut from a larger crystal for the single crystal X-ray diffraction data collection. The data collection was

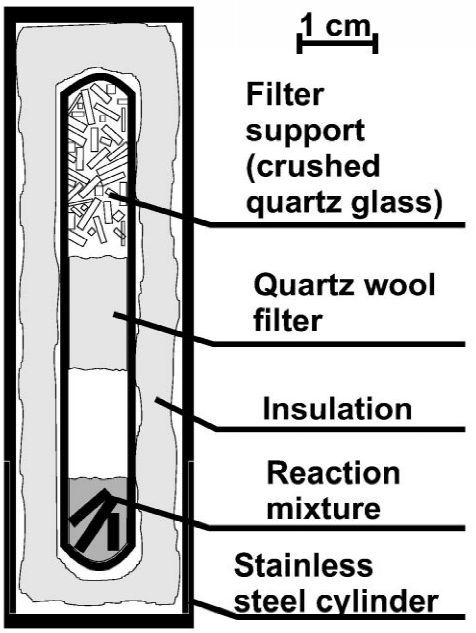

Fig. 1. The reaction ampoule with crushed quartz glass and a filter of quartz wool at the top. After annealing, the solid product was separated from the flux by turning the ampoule upside-down and centrifuging the liquid phase through the filter. The quartz glass sample container was kept inside a steel cylinder filled with quartz wool as insulation in order to keep the sample at nearly constant temperature during the centrifugation.

performed at ambient temperature with graphite monochromated $Mo_{K\alpha}$ radiation on a STOE image plate diffractometer. The data were corrected for Lorentz, polarization and absorption effects using equivalent reflections with the STOE X-RED [5] program.

The chemical composition was analyzed with EDX on freshly cut crystal surfaces in a scanning electron microscope. According to the analysis the crystal contained 47(±3) atom % Ga and 53(±3) atom % Mn.

3. Structure analysis

The structure was solved in the space group Cc(9) with direct methods using SHELX-97 [6]. The refinement indicated a large correlation in atomic displacement factors between pairs of atoms, which indicated higher symmetry. The position of a center of symmetry was deduced from the positions of the correlated pairs. The structure was then refined with JANA98 [7] in space group $C2/c$ (15). The refined parameters were the scale factor, atomic coordinates, isotropic atomic displacement parameters, extinction coefficient and, for ten sites, occupational disorder. Attempts to refine anisotropic atomic displacement factors were made, but resulted in negative atomic displacement factor tensors for a few atoms. Despite careful absorption correction this problem could not be corrected. Therefore, the atomic displacement factors were finally refined only isotropically. Since the scattering factors for gallium and manganese are rather similar, the assignment of the

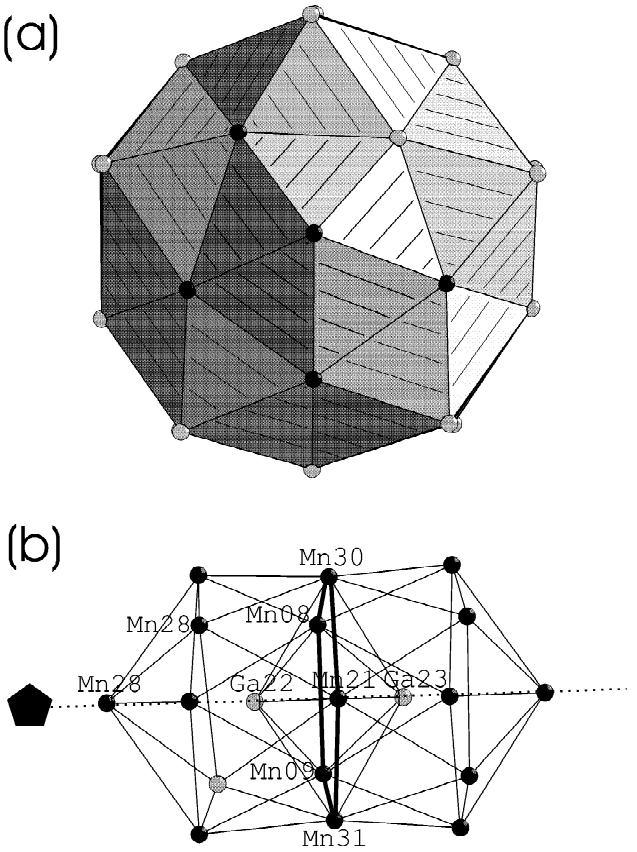

Fig. 2. (a) The complete pentagonal wheel cluster which is the fundamental structural unit in $Mn_{123}Ga_{137}$. The wheel is seen along the pseudo five-fold axis. (b) The two intergrown axial icosahedra in the pentagonal wheel cluster. The central atoms in the circumscribing icosahedra are connected by heavy lines. The central atoms of the axial and circumscribing icosahedra and the two Mn28 atoms shared by two wheels in adjacent layers are labeled. The pseudo five-fold axis is indicated with a dotted line. Atom sites more than half occupied by Ga are gray and the others are black.

element type is not completely certain. However, the assignment of elements as done in the refinement resulted in the best *R*-value. The interatomic distances within the first co-ordination sphere are widely distributed for Mn–Mn (2.7–3.6 Å), and for Ga–Ga (2.8–3.9 Å). The Mn–Ga distances have a more narrow and well defined distribution between 2.5 and 3.0 Å, with most Mn–Ga distances between 2.7 and 2.8 Å. The atoms Ga03/Mn03 and Ga04/Mn04 were refined on split positions, with the occupational sum of the atoms restrained to be one. The distance between Ga03 and Mn03 is 0.76(2) Å. The distance between Ga04 and Mn04 is 0.66(2) Å. The final atom co-ordinates are listed in Table 2.

4. Structure description

The unit cell contains 260 atoms on 34 unique positions. Of these, eight unique atoms have icosahedral co-ordination. Another seven unique atoms have the closely related co-ordination of a bicapped pentagonal prism. The other 19 atoms have various and rather asymmetric co-ordination, with between 10 and 15 neighbours. The local icosahedral order is considered as an important feature of approximants and quasicrystals. Therefore, the structural description given here is focused on the role of the icosahedron as the basic structural element. In the following, the different icosahedra in the structure will be referred to with the name of their central atoms with the prefix ''i-'', e.g. i-Ga08 is the icosahedron around Ga08.

The fundamental structural unit in $Mn_{123}Ga_{137}$ is a pseudo five-fold wheel shaped cluster, shown in Fig. 2a. The wheel is made up of seven unique intergrown icosahedra. The pseudo five-fold axis of the wheel goes

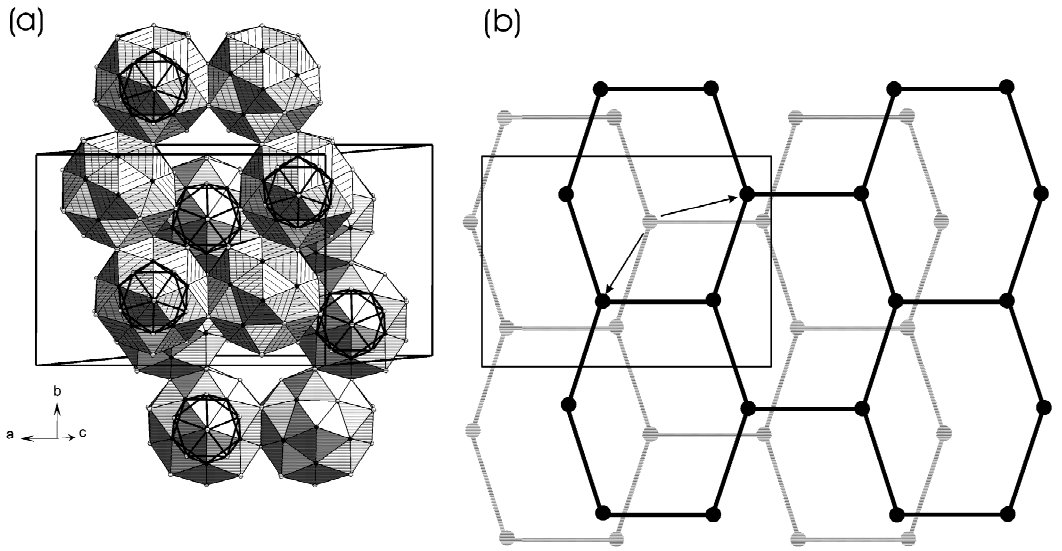

Fig. 3. (a) Packing of wheel clusters in the unit cell of $Mn_{123}Ga_{137}$. For clarity only one hexagon of each of the parallel networks is shown. The wheels in the hexagonal layer at approximately $c=1/4$ are hatched while the wheels in the layer at $c=3/4$ are solid. The prolongation of the wheel axis which penetrates into the adjacent layer is drawn as a wire model. Sites more than half occupied by Ga are gray and the others are black. (b) Schematic representation of the two adjacent hexagonal infinite layers in the cell, parallel to the a–b plane. The layer at $c=1/4$ is black while the layer at $c=3/4$ is gray. The arrows mark out the two closest 6.4 Å shifts that would superimpose the layers.

Table 2
Positional and thermal parameters for $Mn_{123}Ga_{137}$

Atom	Wyck.	Occ.	*x*	*y*	*z*	U_{eq} (Å^2)	Type[a]
Mn01	8f	0.56(4)	−0.1173(1)	0.0084(2)	−0.0579(2)	0.009(1)	
Ga01	8f	0.44(4)	−0.1173(1)	0.0084(2)	−0.0579(2)	0.009(1)	
Mn02	8f	1	0.2553(2)	0.0094(2)	−0.0736(2)	0.0057(7)	
Mn03	8f	0.754(8)	0.5099(3)	0.0326(5)	0.5801(4)	0.031(1)	
Ga03	8f	0.246(8)	0.4968(6)	−0.016(1)	0.5762(9)	0.031(1)	
Mn04	8f	0.323(9)	−0.3710(6)	−0.005(1)	0.4161(7)	0.0083(9)	
Ga04	8f	0.677(9)	−0.3907(2)	0.0324(3)	0.4123(2)	0.0083(9)	
Mn05	4e	1	0.5	0.0323(3)	0.75	0.004(1)	
Ga06	8f	1	−0.3642(1)	0.0438(2)	0.1069(2)	0.0080(5)	
Ga07	8f	1	0.2591(1)	0.0445(2)	0.1066(2)	0.0092(5)	
Mn08	8f	1	−0.1219(2)	0.0491(2)	−0.2462(2)	0.0005(6)	c
Mn09	8f	1	0.2540(2)	0.0527(2)	−0.2559(2)	0.0068(7)	c
Ga10	8f	1	0.0213(1)	0.0529(2)	0.1213(2)	0.0116(5)	p
Ga11	8f	1	0.1186(1)	0.0549(2)	0.3772(2)	0.0096(5)	p
Ga12	4e	1	0	0.0839(2)	0.75	0.0090(7)	p
Ga13	8f	1	−0.3819(1)	0.0968(2)	−0.2467(2)	0.0166(5)	
Ga14	8f	1	0.1885(1)	0.1002(1)	0.2521(2)	0.0105(5)	p
Ga15	8f	1	−0.4340(1)	0.1027(2)	0.2330(2)	0.0225(6)	
Mn16	8f	0.60(5)	0.1406(1)	0.1195(2)	−0.0808(2)	0.010(1)	
Ga16	8f	0.40(5)	0.1406(1)	0.1195(2)	−0.0808(2)	0.010(1)	
Mn17	8f	0.69(5)	−0.0009(1)	0.1259(2)	−0.0599(2)	0.008(1)	
Ga17	8f	0.31(5)	−0.0009(1)	0.1259(2)	−0.0599(2)	0.008(1)	
Mn18	8f	1	−0.3749(2)	0.1271(2)	0.5715(2)	0.0043(7)	
Mn19	8f	0.73(5)	−0.2365(2)	0.1276(2)	−0.0600(2)	0.012(1)	
Ga19	8f	0.27(5)	−0.2365(2)	0.1276(2)	−0.0600(2)	0.012(1)	
Ga20	8f	1	0.4490(1)	0.1547(2)	0.6216(2)	0.0209(6)	
Mn21	8f	1	0.3102(2)	0.1696(2)	0.2531(2)	0.0019(5)	c
Ga22	8f	1	0.2291(1)	0.1739(1)	−0.1492(2)	0.0088(5)	a
Ga23	8f	1	0.1484(1)	0.1760(2)	0.6393(2)	0.0098(5)	a
Ga24	4e	0.40(5)	0	0.1819(2)	0.25	0.002(1)	p
Mn24	4e	0.60(5)	0	0.1819(2)	0.25	0.002(1)	p
Mn25	8f	0.57(4)	−0.0722(2)	0.1833(2)	0.0605(2)	0.012(1)	p
Ga25	8f	0.43(4)	−0.0722(2)	0.1833(2)	0.0605(2)	0.012(1)	p
Ga26	8f	0.18(4)	−0.3077(1)	0.1867(2)	0.0621(2)	0.004(1)	
Mn26	8f	0.82(4)	−0.3077(1)	0.1867(2)	0.0621(2)	0.004(1)	
Mn27	8f	1	−0.4519(2)	0.1872(2)	0.0592(2)	0.0049(7)	
Mn28	8f	1	0.3069(1)	0.1879(2)	0.0614(2)	0.0030(7)	
Ga29	8f	0.49(4)	−0.1729(1)	0.1960(2)	0.4177(2)	0.008(1)	
Mn29	8f	0.51(4)	−0.1729(1)	0.1960(2)	0.4177(2)	0.008(1)	
Mn30	8f	1	0.0797(1)	0.2235(2)	−0.2549(2)	0.0058(6)	c
Mn31	8f	1	0.2971(1)	0.2260(2)	−0.2534(2)	0.0010(6)	c
Ga32	8f	1	0.4426(1)	0.2260(1)	0.1027(2)	0.0058(5)	
Ga33	8f	1	0.1632(1)	0.2337(1)	0.3809(2)	0.0094(5)	p
Ga34	8f	1	−0.0626(1)	0.2394(1)	0.3787(2)	0.0094(5)	p

[a] a = Central atom of axial icosahedron in wheel, c = central atom of circumscribing icosahedron in wheel, b = central atom in icosahedron prolonging axial icosahedra in wheel, p = central atom in pentagonal prism.

through two intergrown icosahedra; i-Ga22 and i-Ga23. In these two axial icosahedra, the central atom in one icosahedron is the apex atom of the other, and vice versa, as shown in Fig. 2b. Five icosahedra circumscribe and are intergrown with the axial icosahedra and complete the picture of a wheel with the non-crystallographic point group pseudo symmetry $5/mm$. The central atoms in the circumscribing icosahedra are the same as those in the central pentagonal ring (drawn with heavy lines in Fig. 2b) of the two intergrown axial icosahedra. The five circumscribing icosahedra share surfaces with each other. The outermost perimeter of the wheel is bound by ten triangular surfaces parallel to the pseudo five-fold axis, two belonging to each circumscribing icosahedron. Both of the axial icosahedra are centered by Ga. The circumscribing icosahedra are completely centred by Mn. The mean diameter of the wheel is 8.2 Å.

Three out of the ten triangular surfaces on the outermost perimeter of one wheel are each shared with one other wheel. The wheels are in this way fused, forming infinite honeycomb type layers parallel to the a–b plane, as shown in Fig. 3. In each cell there are two such parallel layers at approximately $c = 1/4$ and $c = 3/4$. The distance between two layers is 6.4 Å and the two closest shifts parallel to the

a–*b* plane to superimpose two layers are both 6.5 Å, as indicated with arrows in Fig. 3b.

The eighth unique icosahedron, i-Mn25, is not included in the above description, even though it is intergrown with the wheel. Mn25 is the apex atom of the axial i-Ga23. The reason to exclude i-Mn25 from the description of the cluster is that it has no connections with other wheels within the hexagonal layer. The icosahedron i-Mn25 is partly penetrating into one of the two pentagonal voids inside the rings formed by six fused wheels of an adjacent hexagonal layer, as shown in Fig. 4. Pairs of i-Mn25 icosahedra (drawn as wire models in Fig. 4) meet, and share an apex in the middle of the pentagonal void. The only atoms shared between wheels in adjacent layers are the two Mn28 atoms. These atoms constitute an edge of the axial i-Ga22.

Seen perpendicular to the *a*–*b* plane, i.e., along the [001] direction, the wheels and the i-Mn25 icosahedra nearly superimpose in pentagonal columns. However, there is a small shift, caused by the fact that the two axial i-Ga22 share an edge, rather than a single apex atom. As a result, these infinite columns are tilted 4° with respect to the [001] direction. The repeating unit in the column is ''wheel–wheel–i-Mn25–i-Mn25'' (see Fig. 4).

Mn03, Mn04 and Mn05 are the only unique atoms which are not part of any icosahedra. All of them fill up the pentagonal void not occupied by i-Mn25.

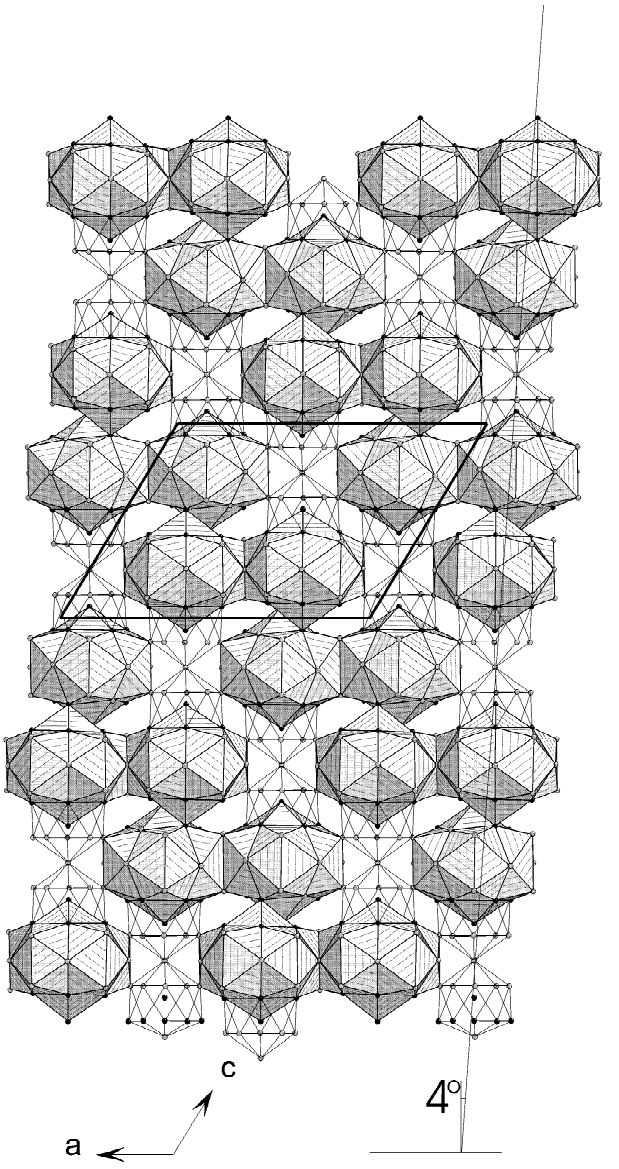

Fig. 4. The unit cell seen along the *b*-axis with $0<b<0.5$. The wheel clusters are drawn hatched and the i-Mn25 icosahedra are drawn as wire models. The column is tilted 4° in the *a*-axis direction, from being perpendicular to the *a*–*b* plane. Atom sites more than half occupied by Ga are gray and the others are black.

5. Discussion

According to the refinement, $Mn_{123}Ga_{137}$ contains 53 atom% Ga and 47 atom% Mn. This deviates somewhat from the composition according to the EDX analysis. There are several reasonable explanations for such a discrepancy. Manganese and gallium differ only by six in atomic number, and thus their scattering factors for X-rays are rather similar. The relative amounts of elements on positions with mixed occupancy are in this case not very accurately determined with X-ray diffraction methods. The linear absorption coefficient is very high – more than 30 mm^{-1}. This makes the absorption correction most crucial. Even very small imperfections in the absorption correction can be expected to give problems with the atomic displacement parameters, which are intimately related to the type of atom at the position.

There are several phases with compositions very close to that of $Mn_{123}Ga_{137}$. We have chosen to name the title compound by the total unit cell content according to the refinement. Even in the case of a certain solid solubility, changing the element proportions, the phase will then be identified by the atom sum in the unit cell.

The structure of $Mn_{123}Ga_{137}$ is closely related to the structure of $MnAl_3$ [8–11]. The $MnAl_3$ structure can be described as completely built up from wheel clusters. However, in $MnAl_3$ each wheel is fused to only two other wheels. The wheels thus build up infinite parallel strands. The wheel cluster can also be identified in the tetragonal approximant Mn_3Ga_5 [4], but there the wheel clusters occur isolated from each other. $Mn_{123}Ga_{137}$ can be classified as an approximant to the decagonal quasicrystal [1] based on the pseudo decagonal [001] diffraction pattern and the presence of a decagonal quasicrystal with a similar composition [3]. The crystal structure of $Mn_{123}Ga_{137}$ has an abundance of icosahedral local order, which is considered to be fundamental in the structure of quasicrystals. We consider it probable that the wheel shaped cluster presented here is a fundamental structural unit in a structure class containing several other decagonal approximants and perhaps also decagonal quasicrystals.

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