

# The Crystal Structure of $(\text{Ga,Zn})_{175-\delta}\text{Mg}_{97+\delta}$ – a Large 3/2-2/1-2/1 Fibonacci Approximant

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Previous investigations of the Al-Mg-Zn system succeeded in the synthesis and in single crystal structure refinement of the two Fibonacci approximants  $1/1-(\text{Al,Zn})_3\text{Mg}_2$  [1] and  $2/1-(\text{Al,Zn})_{3+\delta}\text{Mg}_{2-\delta}$  [2,3]. The fundamental structural unit of both phases was found to be the Bergman cluster (BC) consisting of successive shells of nearly icosahedral symmetry. The interior core cluster is a small icosahedron of (Al,Zn) with a vacancy at the center. It is surrounded by 20 magnesium atoms at the vertices of a pentagonal dodecahedron and 12 (Al,Zn) at the vertices of a large icosahedron. The last shell is a truncated and distorted icosahedron of soccer ball shape with  $60-n_\gamma$  (Al,Zn) and  $n_\gamma$  magnesium atoms. The interior cluster with 44 atoms of the soccer ball is known as the Pauling triacontahedron. The structure of the 1/1-approximant is simply a bcc packing of Bergman clusters as shown in Fig. 1a. Here, each cluster is connected to eight clusters along the threefold axes and to six clusters along the twofold axes of the cubic unit

cell (8+6) as shown in Fig. 1b. The former and the latter type of cluster connection are known as c and b bond, respectively [4]. The packing of the 2/1-approximant shown in Fig. 1c is more complex. The centers of the Bergman clusters define a tiling of oblate and prolate rhombohedra. In Figure 1d these rhombohedra are spanned by the c bonds shown in yellow.

The close relationship between the approximants and their respective quasicrystal may be used to model an average quasiperiodic structure using the following approach: (1) the structural units, for example, the Bergman cluster present in the crystal approximants are assumed to be the fundamental units in the related quasicrystals; (2) a rule for constructing the quasiperiodic tiling, the “quasilattice”, is extracted from the sequence of approximants; (3) decoration of the quasilattice with the fundamental units obeying the special decoration rules.

The bcc- and the rhombohedral packings turn out to be simple solutions for networks which can be derived from canonical cell tilings [4-6] after dissecting the unit cells into smaller tiles bounded by b and c edges as indicated in Fig. 1b and 1d. A canonical cell tiling (CCT) is a network of nodes with icosahedral symmetry connected by b (blue) and c (yellow) bonds and a tiling with only four kinds of cells as shown in Fig. 2, labelled A, B, C, D. These cells are bounded by three kinds of faces

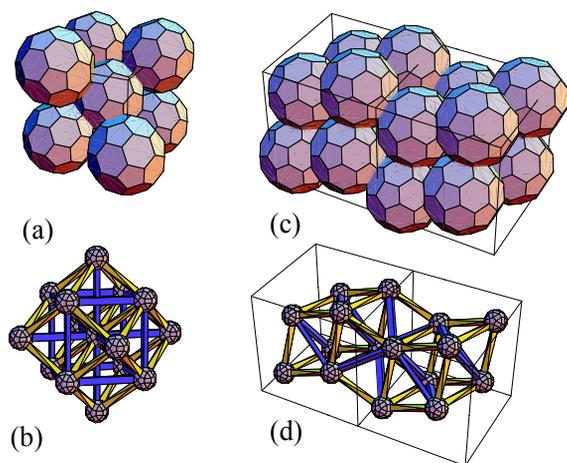


Fig. 1. The structures of two cubic Fibonacci approximants with Bergman clusters (BC) shown as solid soccer balls and the corresponding canonical cell tilings (CCT) displayed in Zometool® fashion (Zomeballs as nodes, c and b bonds as yellow and blue struts [7]): (a) bcc packing of BC's and (b) CCT for  $1/1-(\text{Al,Zn})_3\text{Mg}_2$ ; (c) rhombohedral packing of BC's and (d) CCT for  $2/1-(\text{Al,Zn})_{3+\delta}\text{Mg}_{2-\delta}$ .

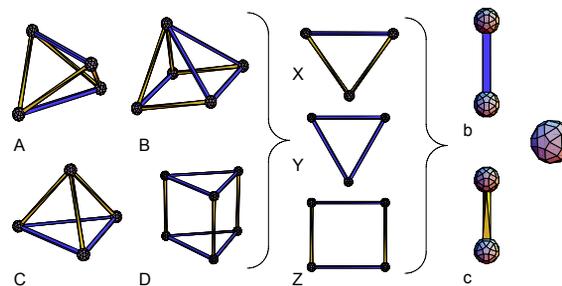


Fig. 2. Objects of canonical cell tilings [4]; four different cells: A, B, C and D; three different faces: X, Y, and Z; two different bonds b and c; one kind of node with icosahedral symmetry.

X, Y, Z, respectively. The A cell is a distorted tetrahedron, the B cell a distorted half octahedron, the C cell a trigonal pyramid and the D cell a trigonal prism. For more details about the CCT see [4] and [5].

Using the nomenclature of the canonical cell geometry the network for the 1/1-approximant, as defined by the centers of the Bergman cluster, define a simple A cell tiling with 12 A and the 2/1-approximant, an ABC tiling with 24 A, 8 B and 8 C per unit cell [4]. The decoration rules [6] for the objects of the canonical cell tilings compatible with the crystal structures of the 1/1- and the 2/1-approximant are listed as follows (R, P, and Q denote Frank-Kasper polyhedra [8] and  $\alpha$ ,  $\beta$  and  $\gamma$  Bergman cluster sites with the shell sequence  $1\alpha^0 + 12\alpha^1 + 20\beta + 12\alpha^2 + (60-n_\gamma)\alpha^3 + n_\gamma\gamma$ ):

- (C1) each CCT node is decorated with a Bergman cluster
- (C2) the central site of the Bergman cluster is empty
- (C3) two Bergman clusters are linked sharing hexagon faces (c) or edges (b)
- (C4) each b bond yields two  $\gamma$  positions edge connecting two Bergman clusters; each  $\gamma$  position has a R type coordination ( $12^{5.0}2^{6.0}$ )
- (C5) each X-face yields a position  $\delta^X$  at the center of the triangle; each  $\delta^X$  position has a P type coordination ( $12^{5.0}3^{6.0}$ )
- (C6) each Y-face yields a position  $\delta^Y$  at the center of the triangle; each  $\delta^Y$  has a Q type coordination ( $12^{5.0}4^{6.0}$ )
- (C7) each Z-face yields two  $\delta^Z$  positions between the BCs; the coordination polyhedron of each  $\delta^Z$  position is irregular with coordination number 13
- (C8) the centres of all icosahedra with CN12 ( $\alpha^2$ ,  $\alpha^3$ ), the centers of all truncated icosahedra with CN11 ( $\alpha^1$ ) and the centers of the irregular coordination type polyhedra with CN13 ( $\alpha^3$ ,  $\delta^Z$ ) are occupied with Al and Zn atoms in a disordered way
- (C9) all sites of coordination number 14 ( $\gamma$ ), 15 ( $\delta^X$ ) and 16 ( $\delta^Y$ ) are occupied with Mg atoms.

We have focused our interest on the synthesis, structural modelling and single crystal X-ray diffraction analysis of a large 3/2-2/1-2/1 approximant [6] to examine carefully the decoration rules including the D cell. An approximant of this type was discovered by W. Ohasi [9] in the Ga-Mg-Zn system using electron diffraction techniques and in

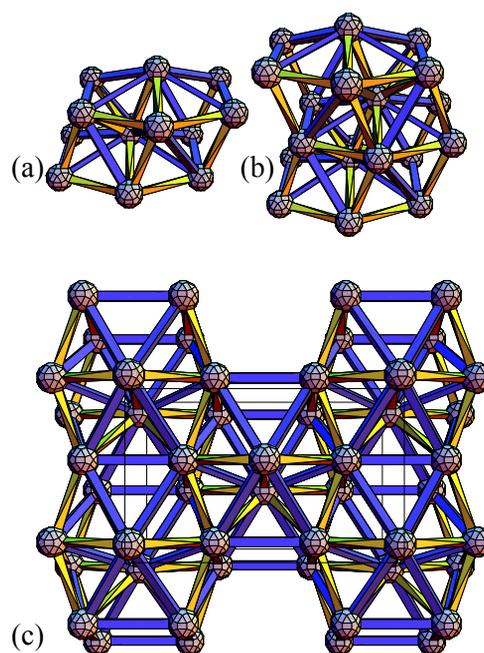


Fig. 3: The CCT network of the 3/2-2/1-2/1 orthorhombic approximant in Zometool® style: (a) the distorted hexagonal prism of 6 A, 3 B, 3 C and 1 D cell and (b) its packing along [001] with view from [201]; (c) packing along [100] and [010] with view from [001].

accordance with the forecast of the CCT model [4] the unusual space group  $Cmc2_1$  was reported. The tiling of the orthorhombic 3/2-2/1-2/1 model is best understood as a packing of distorted hexagonal prisms which are centered and capped by two additional nodes. A prism is composed of 6 A, 3 B, 3 C and 1 D cell. A  $2_1$ -symmetry operation with the prism axis as screw axis and the translational symmetry  $oC$  generates an infinite packing. There are 24 A, 12 B, 12 C and 4 D per unit cell as illustrated in Fig. 3.

A “good” model for the 3/2-2/1-2/1 approximant should satisfy at least the criteria C1 to C9. However, the packing rules C1 to C9 obtained from the 1/1- and 2/1-approximant are not sufficient to predict a complete structure of a large approximant or a quasicrystal since D cells are included in the CCT network. A decoration of the D cell with golden rhombohedra – by way of trial – fills the gaps and creates a fragment which is similar to a Pauling triacontahedron which is shown in Fig. 4.

An algorithm for constructing decorated canonical cell tilings using these decoration rules was computer implemented with the following results

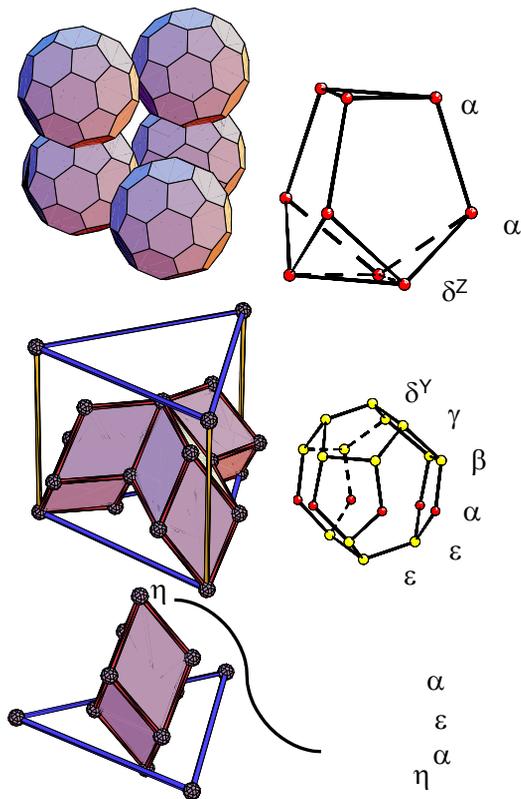


Fig. 4: The decoration of the  $D$  cell with Bergman clusters using  $C1$  to  $C9$  leaves behind large cavities without atoms; the decoration of the CCT objects with golden rhombohedra fills these gaps and creates a fragment which is similar to a Pauling triacontahedron; the additional glue atoms are labelled  $\varepsilon$  (7 Mg) and  $\eta$  (4 (Ga,Zn)).

for the  $3/2-2/1-2/1$  approximant: {24 A, 12 B, 12 C, 4 D},  $(\text{Ga,Zn})_{43}\text{Mg}_{26}$ ,  $Z = 16$ ,  $Cmc2_1$ ,  $oC1104$ ,  $a_0 = \tau^2 b$  (36.8 Å),  $b_0 = \tau b$  (22.8 Å),  $c_0 = \tau b$  (22.8 Å),  $V_{\text{cell}} = 19182 \text{ \AA}^3$ , Wyckoff sequence  $b^{124}a^{28}$  (Mg:  $b^{46}a^{12}$ ), 12 Bergman clusters per cell at positions  $4a$  in  $(0, \tau^{-2}/4, -\tau^{-1}/4)$  and  $8b$  in  $(2\tau^{-2}/4, \tau/4, -\tau^{-1}/4)$  with  $\tau = 2\cos(36^\circ) \dagger 1.618$ ,  $\langle V \rangle_{\text{atom}} = 17.375 \text{ \AA}^3$ . The idealized crystal structure is shown in Fig. 5.

To examine the proposed model a  $3/2-2/1-2/1$  approximant of the Ga-Mg-Zn system was prepared and investigated by single crystal X-ray diffraction [6]. The refinement of the model using X-ray diffraction data of a suitable single crystal was started with the composition  $(\text{Ga,Zn})_{43}\text{Mg}_{26}$  using the scattering factors of Zn and Mg. During the refinement 44 (Ga,Zn) atoms (4% of all atoms in the unit cell) were deleted and 28 (Ga,Zn) atoms (2.5%) were relocated and inserted by the difference-fourier

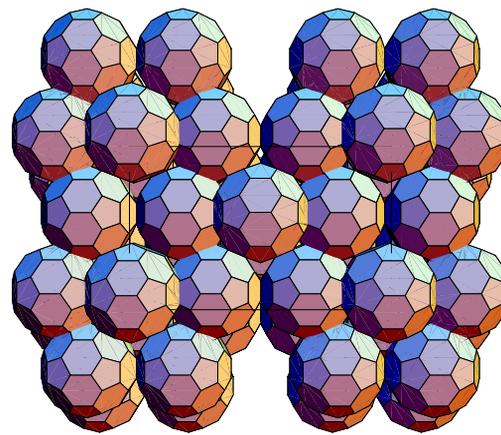


Fig. 5: Parts of the idealized structure of the  $3/2-2/1-2/1$  approximant  $(\text{Ga,Zn})_{43}\text{Mg}_{26}$  obtained by the decoration of the CCT with Bergman clusters.

techniques, respectively. 36 (3.3%) (Ga,Zn) and 64 (5.8%) Mg atoms were exchanged and a small set of positions with coordination number 13 was randomly occupied with (Ga,Zn) and Mg atoms. The average shift of all stable atomic positions in the unit cell was only 0.19 Å pm ( $(\text{Ga,Zn})_{67}\text{Mg}_{37}$ ,  $x_{\text{Ga}} \dagger 0.09-0.19$ ,  $oC1088$ ,  $Z = 4$ ,  $Cmc2_1$ ,  $a = 36.840(7) \text{ \AA}$ ,  $b = 22.782(5) \text{ \AA}$ ,  $c = 22.931(5) \text{ \AA}$ ,  $N_{\text{ind}} = 23398$  ( $9105 > 2\sigma(F^2)$ );  $N_{\text{var}} = 576$ ,  $R1/wR2 = 0.170/0.154$ ).

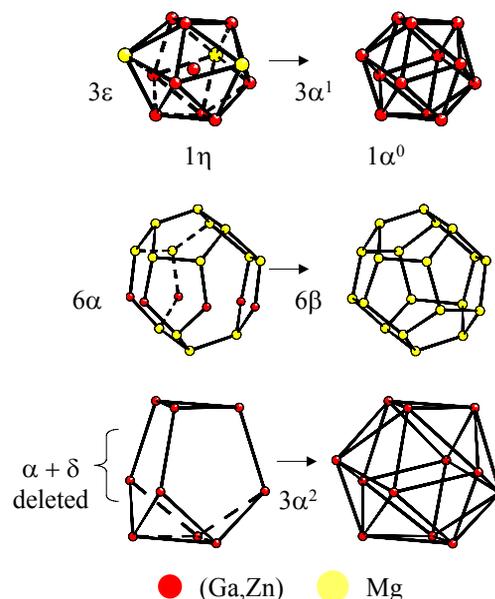


Fig. 6: Differences between the model and the refined structure: the distorted fragment (left) transforms to a nearly icosahedral Pauling triacontahedron (right); for each shell the major differences are indicated.

The crystal structure of  $(\text{Ga,Zn})_{175-\delta}\text{Mg}_{97+\delta}$  is close to the proposed model and the underlying cluster network is that of the 3/2-2/1-2/1 canonical cell tiling. The fundamental units occupying the nodes represent Bergman clusters, albeit distorted. However, there are some significant differences as illustrated in Fig. 6. The incomplete and distorted Pauling triacontahedron in the interior of the D cell is transformed during the refinement to a nearly perfect Pauling triacontahedron with the position of the cluster very close ( $\Delta \dagger 4$  pm) to the idealized site at  $4a$  ( $0, 3/2-3\tau/4, 3/4-\tau/4$ ). The  $(\text{Ga,Zn})$  atoms, which occupy the center of these Pauling triacontahedra, are removed leaving a vacancy similar to the vacancies at the nodes of the CCT. The transformation effects some  $\alpha, \beta, \gamma$  and  $\delta$  positions of the surrounding Bergman clusters. Those positions which are not compatible with the additional Pauling triacontahedra were shifted up to 50 pm or were even deleted. The crystal structure is now best described as a packing of 16 Pauling triacontahedra per unit cell with nearly icosahedral symmetry, twelve of them occupying the nodes of the canonical cell tiling and four of them the common tips of the rhombohedra in the D cells. The Pauling triacontahedron inside the D cell is surrounded by six

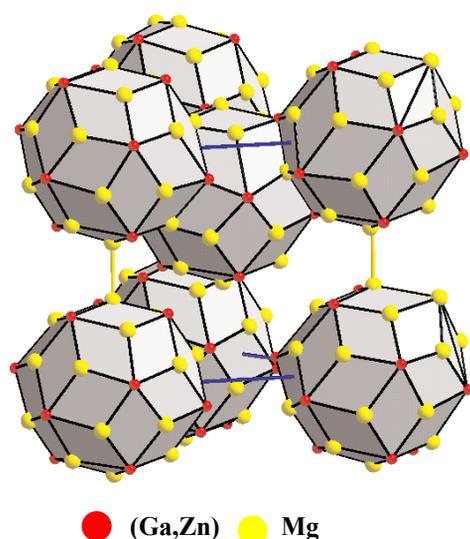


Fig. 7. The decoration of the D cell with Pauling triacontahedra; the idealized distances between the interior cluster and the node clusters of the CCT are  $b$  and  $b/\tau$ ; the latter distance is short enough for a face-to-face connection of the Pauling triacontahedra.

nearest neighbours close to the idealized distances  $3 \times b$  (14.1 Å) and  $3 b/\tau$  (8.7 Å). The latter distance is short enough to allow a face-to-face connection of the Pauling triacontahedra as shown in Fig. 7.

The experimental findings support the following conclusions. The structures of new approximant phases as well as the quasicrystals of the systems Al-Mg-Zn and Ga-Mg-Zn and related systems represent packings of Pauling triacontahedra occupying the nodes of canonical cell tilings and the common tips of the rhombohedra in the D cells. Thus, it appears that the fundamental structural unit of related primitive hypercubic icosahedral quasicrystals of the Bergman class is given by the Pauling triacontahedron and the underlying network is of a canonical cell tiling type. The driving force of the quasicrystal and approximant formation probably is the optimized packing density of the Pauling triacontahedra caused by the CCT and the well known stabilisation of the Pauling triacontahedron as basic cluster by a magic electron number with 92 electrons per 44 atoms and  $e/a \dagger 2.09$  [10,11]. The  $(\text{Ga,Zn})$  disorder at the centers of the small polyhedra permits the compound to optimize its free electron concentration as a Hume-Rothery compound.

## References

- [1] G. Bergman, J.L.T. Waugh and L. Pauling, *Acta Crystallogr.* **10**, 254 (1957).
- [2] S. Spiekermann, *Zur Strukturchemie von Approximanten ikosaedrischer Quasikristalle*, Dissertation, Universität Dortmund, Germany, 1998.
- [3] K. Sugiyama, W. Sun and K. Hiraga, *J. Alloys Comp.* **342**, 139 (2002).
- [4] C.L. Henley, *Phys. Rev. B* **43**(1), 993 (1991).
- [5] M.E.J. Newman, C.L. Henley and M. Oxborrow, *Phil. Mag.* **B71**, 991 (1995).
- [6] G. Kreiner, *J. Alloys Comp.* **338**, 261 (2002).
- [7] Mathematica 4.0, Wolfram Research, Part of the notebook code is IQtools1.618 written by V. Elser.
- [8] F.C. Frank and J.S. Kasper, *Acta Crystallogr.* **11**, 184 (1958).
- [9] W. Ohasi, *Icosahedral and approximant crystals in the Ga-Mg-Zn system*, Doctoral thesis, Harvard University, Cambridge, USA, 1989.
- [10] H. Sato, T. Takeuchi and U. Mizutani, *Phys. Rev. B-Cond. Mat.* **64**, 94207 (2001).
- [11] C.-S. Lee and G.J. Miller, *Inorg. Chem.* **40**, 338 (2001).