

# Quasicrystal approximants with novel compositions and structures

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We identify several new quasicrystal approximants in alloy systems in which quasicrystals have not been previously reported. Some occur in alloys with large size contrast between the constituent elements, either containing small Boron atoms, or large Ca/Eu atoms, leading to quasicrystal structures quite different from currently known systems where the size contrast is smaller. Another group of the approximants are layered Frank–Kasper structures, demonstrating competition between decagonal and dodecagonal ordering within this family of structures.

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Axial quasicrystals are structures that possess one axis of crystallographically forbidden rotational symmetry. The structure is quasiperiodic in the plane perpendicular to this axis, but can be periodic in the direction parallel to the axis. Since they never exactly repeat, their lattice constant can be thought of as infinite within the quasiperiodic plane. Along the periodic direction the lattice constant is finite and might be fairly small.

Quasicrystal approximants are ordinary, though complex, crystals whose local structural motifs naturally extend to quasiperiodic structures with the crystallographically forbidden rotational symmetries [1]. Approximants reproduce within their unit cell a portion of an aperiodic structure, certain special fragments of which can be extended periodically while maintaining reasonable local atomic structures. Generally approximants have large lattice parameters in the directions in which the corresponding quasicrystal is quasiperiodic.

Structures that possess at least one large lattice parameter are thus candidates for being a quasicrystal approximant. If, in addition they possess a short lattice parameter orthogonal to their large one(s) this direction is a candidate for being an axis of high rotational symmetry in an axial quasicrystal.

Experimentally observed axial quasicrystal symmetries are octagonal (8x), decagonal (10x) and dodecagonal (12x). To-date decagonal quasicrystals are known in the compounds AlCoNi, AlCoCu, AlMnPd, AlCrNi, AlNiRu, AlCuRh, AlFeNi, ZnMgDy, AlCrFe, GaFeCuSi, AlCuCr and possibly others. In all these cases, the structures are believed to be layered, with a basic 4 Å unit consisting of two atomic layers that are either stacked periodically or with some modulation leading to periodicities of 4, 8, 12 and 16 Å. Perpendicular to the axis the structures are quasiperiodic. Some observed metastable dodecagonal quasicrystals occur in Ta-Te, Ni-Cr, Bi-Mn, Ni-V.

In the process of searching for bulk metallic glass-forming compounds [2, 3] we developed a database of

intermetallic structures which now contains about 1000 structures drawn mainly from standard references [4–7]. The data base contains the Pearson symbol of each structure (e.g. B<sub>4</sub>Mg<sub>2</sub>Ru<sub>5</sub> has Pearson symbol oP22 indicating an orthorhombic Primitive cell with 22 atoms), the space group (e.g. number 55, or Pbam), as well as the lattice parameters and Wyckoff coordinates.

We screened this database for structures that contain one short lattice parameter of 5 Å or less and one long lattice parameter of 8 Å or more. Owing to the presence of at least one long axis, these structures tend to have relatively large numbers of atoms per unit cell, as quoted in their Pearson symbols. We drew pictures of the structures projected along their short axis, then visually examined the picture. In many cases we observed the presence of local structural motifs of approximate 5-fold symmetry. We took special note of compounds that were chemically similar to the glass-forming compounds of interest (Al-Ca-Cu and B-Fe-Y-Zr).

When we found local 5-fold symmetry we attempted to formulate a tile decoration model that would reproduce the observed structure and allow us to extend the structure to larger approximants or a complete quasicrystalline structure. We were able to do this in several cases.

Given a proposed quasicrystal model, we carried out total energy calculations using PAW potentials [8] in the generalized gradient approximation [9] as implemented by the program VASP [10, 11]. Total energies of compounds of differing composition can be compared by measuring all energies relative to the tie-line connecting cohesive energies of pure elements. All structural energies were for fully relaxed structures and were converged to a precision of 1 meV/atom. Because we relaxed the atomic volume, these energy differences are the structural enthalpy of formation,  $\Delta H_{for}$ , evaluated at temperature T=0K.

One interesting case is B-Mg-Ru alloys, where B<sub>4</sub>Mg<sub>2</sub>Ru<sub>5</sub>.oP22 and B<sub>11</sub>Mg<sub>5</sub>Ru<sub>13</sub>.oP62 are two observed structures [12] that we believe are approximants of a B<sub>38</sub>Mg<sub>17</sub>Ru<sub>45</sub> decagonal quasicrystal. Figure 1 shows the structure of oP22 and our proposed extension to a decagonal quasicrystal based on boat-hexagon tilings.

This compound is chemically unlike any presently

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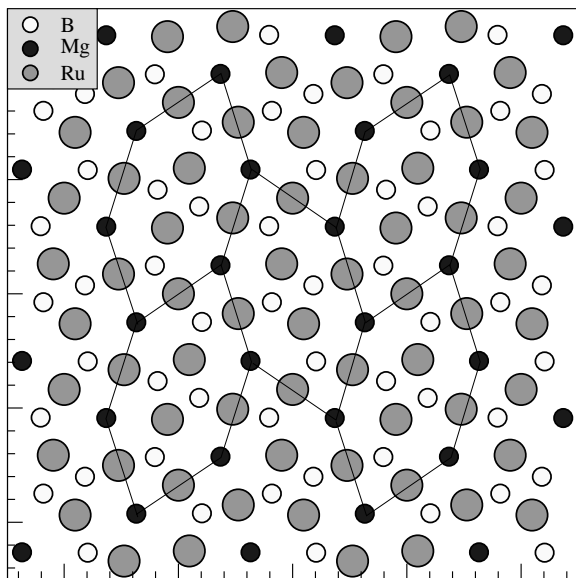


FIG. 1: (a)  $B_4Mg_2Ru_5$  approximant. (b) Proposed model quasicrystal. Large and small circles indicate upper and lower layers. Black, gray and white indicate large, medium and small atoms, respectively.

known for quasicrystal formation. Notably, it contains a fairly large concentration of Boron. Owing to the prevalence of icosahedra in elemental Boron, researchers have long suggested that icosahedral quasicrystals might occur in Boron-rich compounds [13–18], but none has yet been found.

Our proposed structure is promising because we have investigated the enthalpy of formation of other, larger hypothetical approximants. We consider how far these approximants lie from the convex hull of enthalpy versus composition for all known B-Mg-Ru structures, and find a large set of structures, nearly degenerate in energy, lying slightly above the convex hull. This is just the scenario envisioned for the entropic stabilization of quasicrystals, so we suggest that perhaps this compound will exhibit a thermodynamically stable high-temperature decagonal quasicrystal phase. We will describe the tiling energetics, including an evaluation of the energy of vertical phason stacking faults, in an upcoming publication [19].

Likewise,  $Al_8CaCo_2.oP44$  is an approximant of a hypothetical  $Al_xCa_yCo_z$  decagonal phase (Fig. 2). The structure here is quite similar to B-Mg-Ru, with the substitutions  $Mg \rightarrow Ca$ ,  $B \rightarrow Co$  exactly reproducing the B-Mg layer as a Co-Ca layer. However, the Al-content in the adjoining atomic layer is about  $3\times$  the Ru content of the adjoining layer in the B-based compound. Unlike the case of B-Mg-Ru, where the star tile is energetically unfavorable, leading to tilings of hexagons and boats only, for Al-Ca-Co the star tile is comparable in energy to the boat and hexagon tiles, leading to full HBS tilings.

Due to the interest in finding genuinely B-rich quasicrystals, we screened our database to select high B

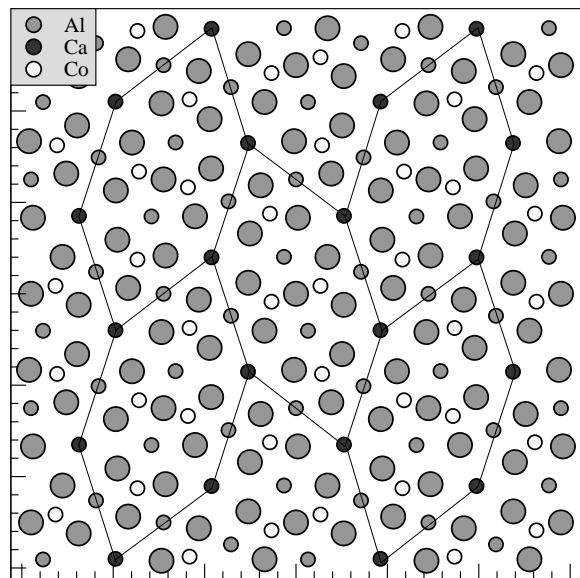
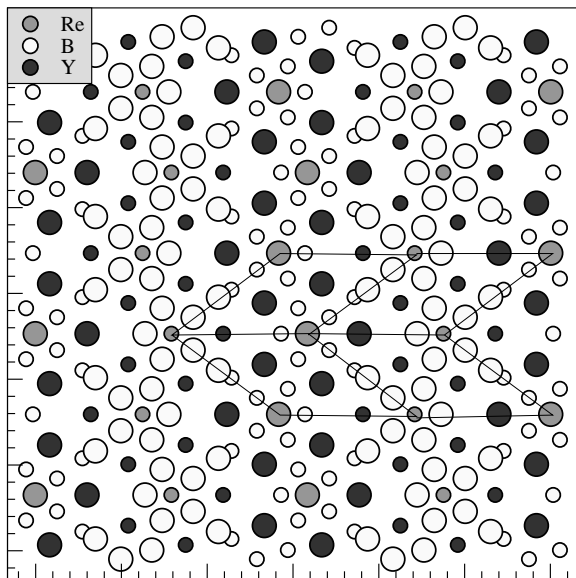


FIG. 2: Al-Ca-Co approximant

concentration and found several candidate approximants. Noteworthy cases include  $B_6ReY_2.oP36$ ,  $B_7ReY_3.oC44$  and  $B_4CrY.oP24$ . All of these feature planar Boron pentagons, centered by a medium-sized transition metal. In the first two cases, a second pentagonal ring of Y-atoms surrounds the pentagonal ring of B-atoms. Fig. 3 illustrates one of the B-Re-Y structures. We have not yet identified the proper manner to extend these structures to a full decagonal quasicrystal in a manner that achieves sufficiently low energy, but since they are all stable as BFeY alloys, and occur close-by in composition, we suspect there may be a unifying quasicrystal model to which they are approximants.

The most promising of these cases is  $B_7ReY_3$ , whose structure may be interpreted in terms of a pure tiling of skinny rhombuses (Fig. 3), with B-Y pentagonal clusters centered by Re decorating tiling vertices, and alternating heights along short periodic direction along the tiling edges. Our best attempt extending this decoration to the fat tile is unstable by a moderate 20meV/atom energy.  $B_2C_2Sc.oP20$ , another curious structure, is isostructural with  $B_4CrY.oP24$  except that the pentagonal rings contain no medium-sized transition metal. In this compound, C and B share the pentagonal rings.

Another case that we consider promising for the occurrence of an entropically stabilized decagonal quasicrystal is Eu-Cu and the isostructural compound Ca-Cu. Here again we find two experimentally observed approximants,  $CuEu.oP8$  and  $CuEu_2.oP12$  that allow us to devise decoration rules and extend the motif to a full decagonal quasicrystal, as shown in Fig. 4. Surprisingly, one of our larger approximant structures that we produced by hand,  $Cu_4Eu_9$ , turns out also to be predicted stable, though it has not been reported experimentally. The remaining approximants we tested lie slightly above

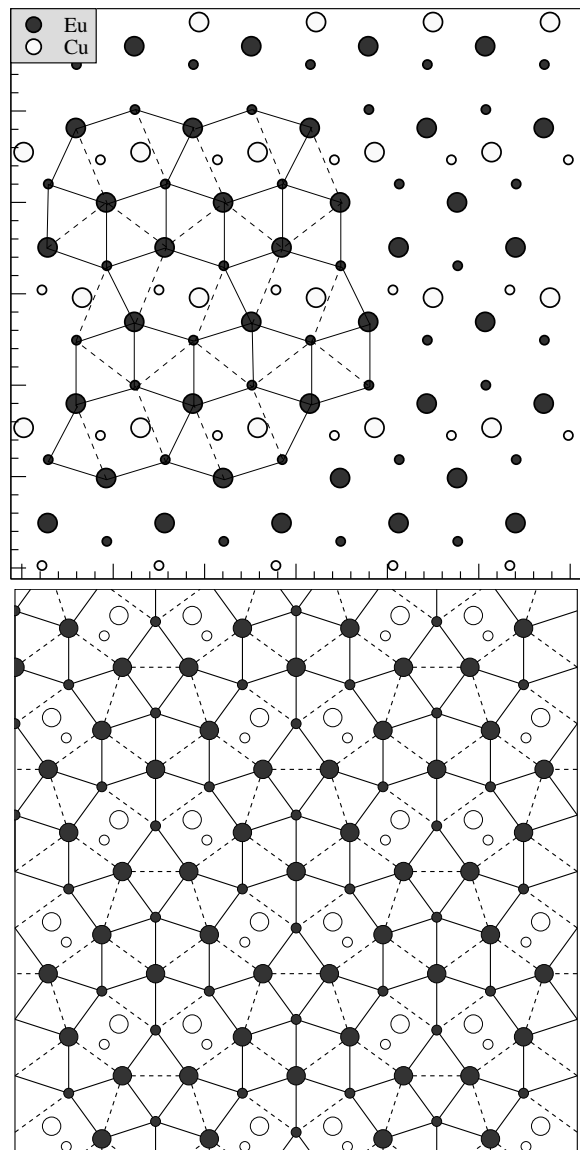
FIG. 3:  $B_7ReY_{3.o}C_{44}$  structure.

the convex hull. In order for the quasicrystal to be stabilized entropically a mechanism is needed to reduce the phason stacking fault energy, such as addition of a third element.

As in the case of the B-Mg-Ru system, this new alloy system is chemically unlike previously known quasicrystals, this time because it is rich in a Rare Earth element. A unique feature of this potential quasicrystal is striking simplicity of the decoration, with tiling edge length equal to the nearest neighbor interatomic distance. The small tile size is responsible for the large composition range of the family of approximants, spanning  $x_{Eu}=0.5 \rightarrow 1$  range of the Eu/Ca content (interestingly, both orthorhombic and monoclinic CaCu structures, as well as CuEu with BFe structures, are valid approximants of the same quasicrystal family).

Unlike the previous structures, where the basic tiles were drawn from HBS tilings, for Cu-Eu the basic structure is based on a decoration of the rectangle-triangle (RT) tiling. The rectangle-triangle tiling is a  $10\times$  symmetric variant of the  $12\times$  symmetric square-triangle tiling which form dodecagonal quasicrystals. Interestingly, both these models have exact solutions for their entropy and phason elastic constants. They also share the property that their phason degrees of freedom in general are quite complex involving non-local “zipper” updates.

The next class of structures we mention belong to Frank-Kasper family with tetrahedral close-packing. The constraints of close packing dictate that only special atomic environments with triangulated shells occur. The basic atomic environment is the icosahedron, coordination number  $Z=12$ , in which three atoms on each triangular face form a tetrahedron with the central atom. Each bond from center to shell is surrounded by five other atoms. Then there are the characteristic “defect” struc-

FIG. 4: (a)  $CuEu_2$  approximant. (b)  $Cu_4Eu_9$  approximant that we predict to be stable

tures, in which 6 atoms surround a bond. This leads to coordination number  $Z=14$  clusters, in which two defect bonds meet at the center, coordination  $Z=15$  with three defect bonds and coordination  $Z=16$  with four defect bonds.

Icosahedral quasicrystal Frank-Kasper phases, represented by prototype  $\alpha$ -AlZnMg phase [20] are pseudo binary structures, in which larger Mg atoms center higher-coordinated polyhedra  $Z=14,15,16$ , while smaller (Al,Zn) atoms have icosahedral  $Z=12$  coordination. In the binary Mg-Zn system, the  $Mg_4Zn_7$  phase is an approximant of a decagonal quasicrystal, and in both icosahedral and decagonal cases the content of  $Z=12$  coordinated smaller atoms is about 60%. The close relationship between decagonal and icosahedral FK structures was discussed by Roth and Henley [21].

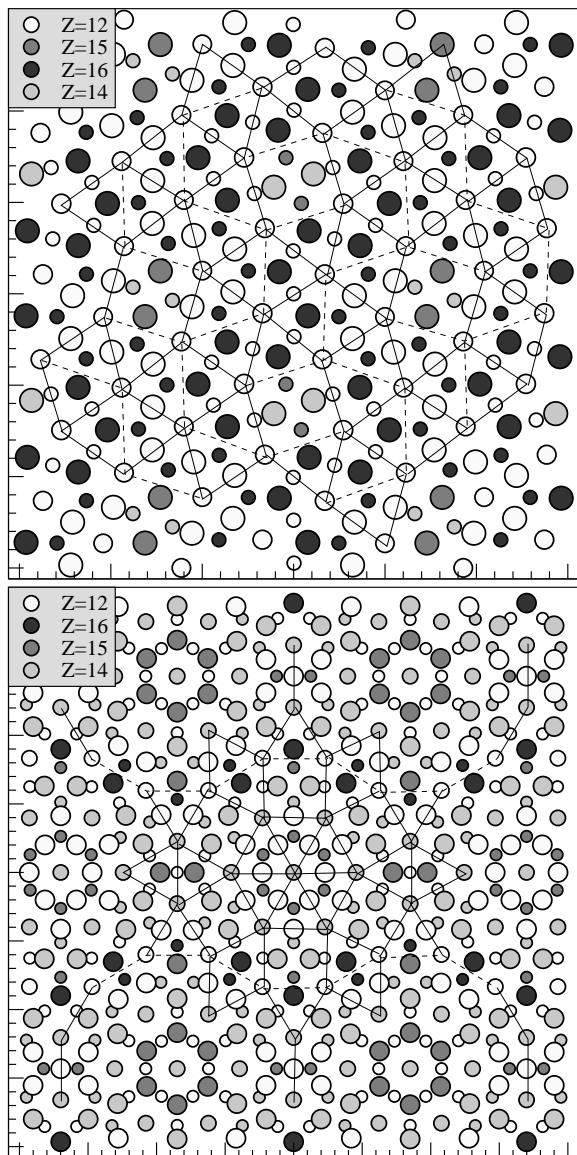


FIG. 5: (a)  $\text{Co}_8\text{Mn}_9\text{Si}_3$  and (b)  $\text{Mn}_4\text{Si}$  structures

As a result of our search, we identified a family of layered (short axis  $c \sim 5\text{\AA}$ ) close-packed structures that interpolate between approximation of decagonal and dodecagonal ordering. In both cases, the structures may be viewed as simple decorations of square-triangle tiling; for the moment, we don't distinguish between isosceles/equilateral (60deg/72deg) triangles and between squares/rectangles. Tiling vertices are associated with pairs of atoms at  $\pm 0.25$ ; no other atoms are aligned along  $c$  axis. Two kinds of tiling bonds connect nearest-neighbor vertices:  $b_1$  with an atom decorating the bond midpoint;  $b_2$  without any atom associated with it. Each triangle is decorated by one interior atom, each rectangle by four.

In the limit of “pure” dodecagonal order, *all* tiling linkages are of type  $b_1$ . Since all edges are equivalent, the

TABLE I: Dodecagonal and decagonal Frank-Kasper approximants

structure	$N_3$	$N_3/N_4$	$\zeta$
$\text{Mg}_4\text{Zn}_7$	32	16	0
$\text{Co}_{17}\text{Si}_{13}\text{V}_{20}$	12	6	0
$\text{Co}_8\text{Mn}_9\text{Si}_3$	20	10	0
$\text{Al}_3\text{Nb}_{10}\text{Ni}_9$	8	2	0
$\text{Cr}_9\text{Mo}_{21}\text{Ni}_{20}$	8	2	0.5
$\text{Mn}_4\text{Si}$	14	2.333	0.692
$\text{CrFe}$	4	2	1

triangles become equilateral and the rectangles are actually square. In the opposite limit of “pure” decagonal order, each triangle has two  $b_1$  and one  $b_2$  edge (so it is isosceles), and each rectangle has two  $b_1$  and two  $b_2$  edges, which imposes a packing rule for rectangles and triangles to share the same kinds of linkages. Squares possess a  $4_2$  screw axis that rectangles lack.

Conversion of  $b_2$  linkages into  $b_1$  by placing extra atoms on the linkage midpoints converts  $Z=12$  vertex polyhedra into  $Z=14$ . We define a parameter to measure the degree of dodecagonal *vs.* decagonal order in a layered FK approximant. First, identify the tile vertices by locating atom pairs at  $\pm 0.25$  along the short axis. They must have coordination polyhedron  $Z=12$  or  $Z=14$ . Then, define

$$\zeta = N_{v14}/(N_{v12} + N_{v14}) \quad (1)$$

where  $N_{vZ}$  denote numbers of tiling vertices with  $Z=12$  or  $Z=14$  coordination. A structure is pure dodecagonal for  $\zeta=1$ , and pure decagonal for  $\zeta=0$ . Conversion of  $b_2 \rightarrow b_1$  cannot be done locally, as it produces  $c$ -height alternation conflicts for neighboring atoms inside the tiles.

Table I summarizes our results for several structures. Besides the  $\zeta$  parameter, we provide numbers of triangles per unit cell  $N_3$  and the  $N_3/N_4$  ratio, where  $N_4$  is number of “squares”. The ideal  $N_3/N_4$  ratios for decagonal and dodecagonal quasicrystal are  $2(\sqrt{5}+1) \sim 6.47$  and  $4/\sqrt{3} \sim 2.31$ . Structures with  $\zeta > 0$  have  $N_3/N_4$  close to 2, while the ratio is much larger than 2 for all but the smallest structures with  $\zeta = 0$ .

Fig. 5 shows  $\text{Co}_8\text{Mn}_9\text{Si}_3$  as an example decagonal structure, and as an example  $\text{Mn}_4\text{Si}$  dodecagonal. The  $b_1$  linkages are shown as solid lines,  $b_2$  dashed. While the  $\text{Mn}_4\text{Si}$  structure exhibits some icosahedra at the tiling vertices ( $\zeta \sim 0.7$ ), we regard it as a prominent dodecagonal approximant, due to the presence of large 12-fold clusters. These clusters actually extend beyond the dodecahedra outlined in the figure, so the clusters overlap and *cover* entire structure.

Finally, we remark that the decagonal limit of this family of structures is optimal for (pseudo)binary compounds with contrast in atomic sizes, and about  $\sim 40\%$  content of large and  $60\%$  of small ( $Z=12$ ) atoms. In the compounds listed in Table I with  $\zeta=0$ , Mg, Nb, V and Mn indeed play role of the larger atoms, and occupy centers of  $Z > 12$  polyhedra. As  $\zeta \rightarrow 1$ , fraction of  $Z=12$  polyhedra decreases to about  $1/3$ , by convert-

ing  $Z=12$  to  $Z=14$ . Meanwhile, volumes of the higher-coordinated polyhedra are only marginally bigger than that of icosahedron, so that the dodecagonal structures are (pseudo)monoatomic, by which we mean the atomic size contrast is small.

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