Quasicrystals 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. One large group of approximants occur in alloys of Boron with transition metals. All these new approximants are structurally quite novel as well. While all exhibit local motifs of 5-fold symmetry, suggesting the quasicrystals should have 10-fold symmetry, it appears that in certain cases the quasicrystal might actually prefer 12-fold symmetry. SIMPLE MODELS WITH RIGID DECORATION RULES.

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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. $B_4Mg_2Ru_5$ 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 Åor 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, ΔH_{for}, evaluated at temperature T=0K.

One interesting case is B-Mg-Ru alloys, where $B_4Mg_2Ru_5$.oP22 (10.0 × 8.4 × 3.0 Å^3) and $B_{11}Mg_5Ru_{13}$.oP62 (21.9 × 10.0 × 2.9 Å^3) are two observed structures [12] that we believe are approximants of a $B_{38}Mg_{17}Ru45$ decagonal quasicrystal. Figure 1 shows the structure of oP22 and our proposed extension to a decagonal quasicrystal based on boat-hexagon tilings.

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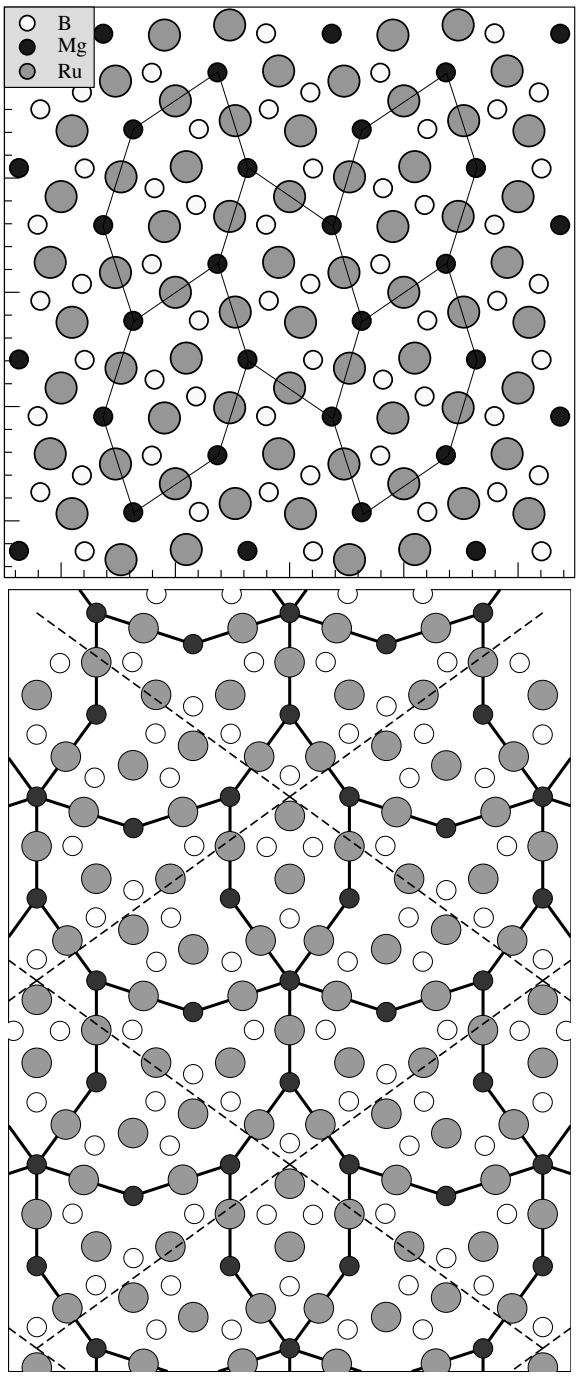

FIG. 1: (a)$B_4Mg_2Ru_5$ approximant. (b) Proposed model quasicrystal. Large and small circles indicate upper and lower layers. Black, gray and white indicate large, medium and small atoms, respectively.

This compound is chemically unlike any presently 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.

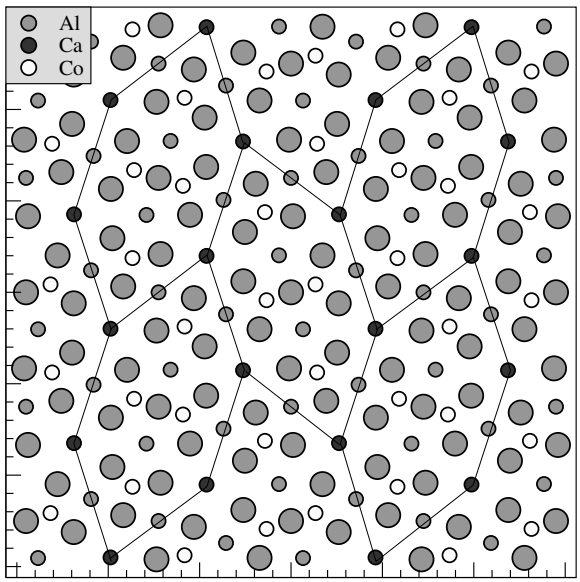

FIG. 2: B-Re-Y approximant

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 hte 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 puglication [19].

Comment on novelty of structure.

Likewise, $Al_8CaCo_2.oP44$ ($14.5 \times 12.5 \times 4.0$ Å^3) is an approximant of a hypothetical $Al_xCa_yCo_z$ decagonal phase. The structure here is quite similar to B-Mg-Ru, with the substitutions Mg-¿Ca, b-¿Co exactly reproducing the B-Mg layer as a Co-Ca layer. However, the Al-content in the adjoining atomic layer is about 3× 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 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

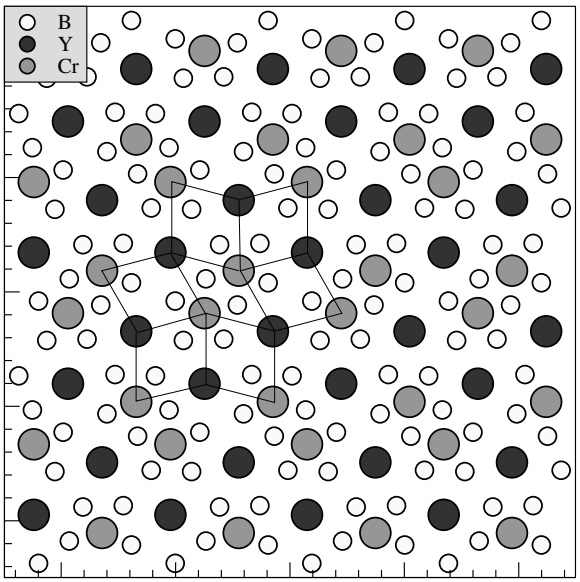

FIG. 3: B-Re-Y approximant

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.

Another curious structure is $B_2C_2Sc.oP20$, which 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 occurence 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 ($8.0 \times 4.4 \times 6.0$ Å^3) and CuEu2.oP12 ($6.4 \times 4.2 \times 15.1$ Å^3) that allow us to devise decoration rules and extend the motif to a full decagonal quasicrystal, as shown in Fig. 5. Surprisingly, one of our larger approximant structures that we produced by hand, Cu_4Eu_9, turns out also to be precited stable, though it has not been reported experimentally. The remaining approximants we tested lie slightly above the convex hull, suggesting again the likelihood of entropic stabilization.

As in the case of the B-Mg-Ru system, this new alloy system is chemicaly unlike previously known quasicrystals, this time because it is rich in a Rare Earth element. MAREK, DID YOU LOOK AT OTHER RARE EARTHS? IS IT POSSIBLE THERE COULD BE INTERESTING MAGNETIC ORDER? LET'S THINK ABOUT THIS LATER ON (AFTER THE MRS MEETING).

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× symmetric variant of the 12× 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.

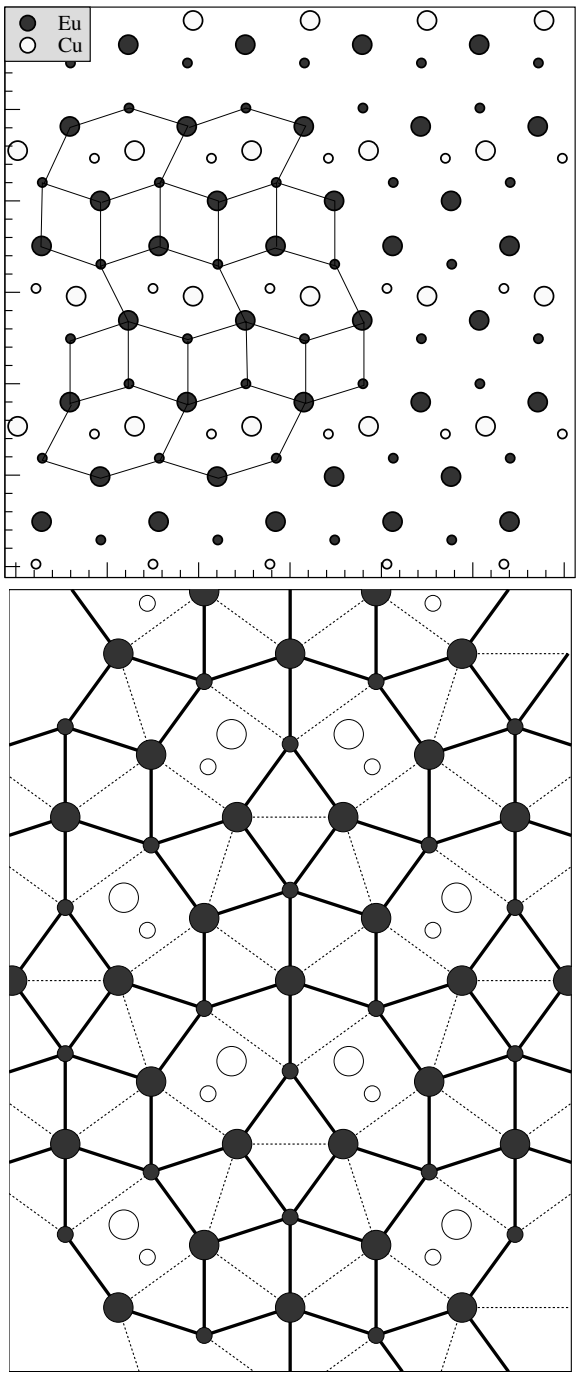

FIG. 4: (a) $CuEu_2$ approximant. (b) Cu_4Eu_9 approximant that we predict to be stable

The next class of structures we mention are based on Frank-Kasper structures. These are tetrahedrally close-packed structures. The constraints of close packing dictate that only special atomic environments occur. The basic atomic environment is the icosahedron, in which three atoms on each triangular face for a tetrahedron with the central atom. Each bond from center to shell is surrounded by five other atoms. Then there are the characteristic "defect" structures, in which 6 atoms surround a bond. This leads to coordination number 14 clusters, in which two defect bonds meet at the center, coordination 15 with three defect bonds and coordination 16 with four defect bonds.

MAREK TO WRITE

DISTINCTION BETWEEN RECTANGLE AND SQUARE (4_2 SCREW AXIS).

Mn_4Si extends to covering cluster.

Z12 dominance -¿ decagonal Z14 dominance -¿ dodecagonal

Mg4Zn7 clearly binary in sizes

Acknowledgments

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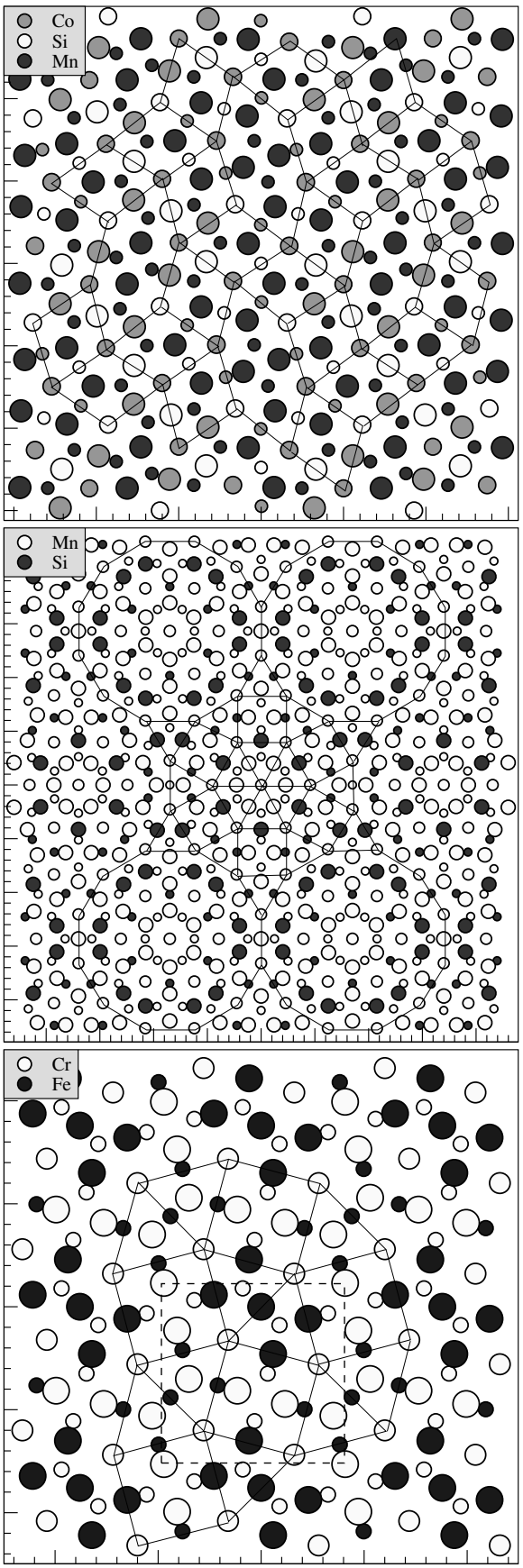

FIG. 5: (a) $CuEu_2$ approximant. (b) Proposed model quasicrystal. Replace FeCr?