Decagonal quasicrystal with novel composition and structure predicted from first principles

M. Mihalkovic* and M. Widom
Department of Physics, Carnegie Mellon University
Pittsburgh, PA 15213
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We predict the structure and possible occurence of a decagonal quasicrystal in a compound with a substantial Boron content, specifically, $B_{38}Mg_{17}Ru_{45}$. Our proposed structure, which depends on the strongly contrasting sizes of the three elements, differs considerably from the structures of previously known Aluminum-based decagonal quasicrystals. Known crystalline structures in the B-Mg-Ru alloy system prove to be quasicrystal approximants, and their experimentally observed structural disorder corresponds to phason stacking faults. Based on the approximant structures we propose a deterministic decoration of tiles by atoms. First-principles total energy calculations reveal a great many quasicrystal approximants lie close to stability at low temperatures, sugesting an entropically stabilized quasicrystal state could lie at elevated temperatures.

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While evaluating the stability of crystalline phases competing with glass formation in Al-Ca-Cu and B-Fe-Y-Zr alloys [1, 2], we discovered a number of previously unrecognized decagonal quasicrystal approximants. These are ordinary, though complex, crystals whose local structural motifs may be naturally extended to form a quasiperiodic structure with an axis of 10-fold rotational symmetry. We created a series of hypothetical approximant structures based on these motifs and calculated their total energy. Based on our findings we propose that B38Mg17Ru45 should posess a decagonal quasicrystal state that is at least metastable and potentially even thermodynamically stable.

This prediction is especially noteworthy for three reasons. (1) The compound contains a substantial amount of Boron, which has been expected to form quasicrystalline structures [3] though none are yet known. (2) The predicted structure is quite different from the established structures of Al-rich decagonal quasicrystals [4] in that it lacks a screw symmetry axis and it is an *intrinsic* ternary, while all other decagonals are essentially *pseudobinaries.* (3) We are predicting both structure and *existence* from first-principles, while in prior works [5], existence was taken as a crucial experimental input for structure prediction.

Two B-Mg-Ru decagonal approximants are known experimentally [6] $B_4Mg_2Ru_5$ (Pearson symbol oP22) and $B_{11}Mg_5Ru_{13}$ (Pearson symbol oP62). Already a relationship to quasicrystals is evident in the Fibonacci numbers of Mg and Ru atoms in each crystal's stoichiometry. These crystal structures are illustrated in Fig. 1. Hexagon (H) and boat (B) tiles [5] are inscribed on these figures to show how the atoms decorate a set of tiles that can be arranged to cover the plane quasiperiodically with 10-fold rotational symmetry. The tile edge length a_q=4.5 Å is known as the *quasilattice constant.* We call the $B_4Mg_2Ru_5$ tiling H2, because each unit cell contains two hexagons. Similarly we call the $B_{11}Mg_5Ru_{13}$ tiling B2H2.

In $B_4Mg_2Ru_5$ only the H tile appears, and it is decorated deterministically with every site is fully occupied by a unique atomic species. The determinism of this decoration reflects the strong size contrasts between atomic species. Nominal atomic diameters are [7], respectively, 1.8, 2.7 and 3.2 Å for B, Ru and Mg. That is the sense in which we refer to BMgRu as an *intrinsic* ternary. Other decagonal-forming ternaries, e.g. Al-Co-Ni are pseudobinaries because at least two of the elements readily substitute for each other.

All atoms lie on two flat layers, all the medium sized Ru atoms occupy one layer (z=0), while the large and small Mg and B atoms occupy the other (z=1/2). We will refer to this pair of adjacent layers as a *bilayer.* Bilayers are stacked along the c axis with a 3 Å periodicity.

In our deterministic decoration, large Mg atoms occupy every tile vertex. Ru atoms occupy two topologically distinct sites: tile edge midpoints "Ru_α"), and tile interior sites "Ru_β". B atoms form a network of pentagons and skinny rhombi similar to the Co network in flat layers of o-Al13Co4. All B atoms center trigonal prisms formed by Ru atoms. Ru_β atoms belong to the shared faces of the pairs of trigonal prisms inside the tiles, while Ru_α atoms belong to shared edges of trigonal prisms in adjacent tiles. Mg atoms serve to cap non-shared faces of trigonal prisms. These trigonal prisms are common motif in amorphous and related crystalline compounds [8]. In particular, the BRe3.oC16 structure features trigonal prisms with Re at the vertices centred by B, stacked periodically on the top of each other just like in the present case.

The experimentally determined atomic positions agree very accurately with our the idealized tiling model, in which all atoms sit at tile vertices, mid-edges or special points reached by dividing edges or tile diagonals in the

*Also at Slovakian Address

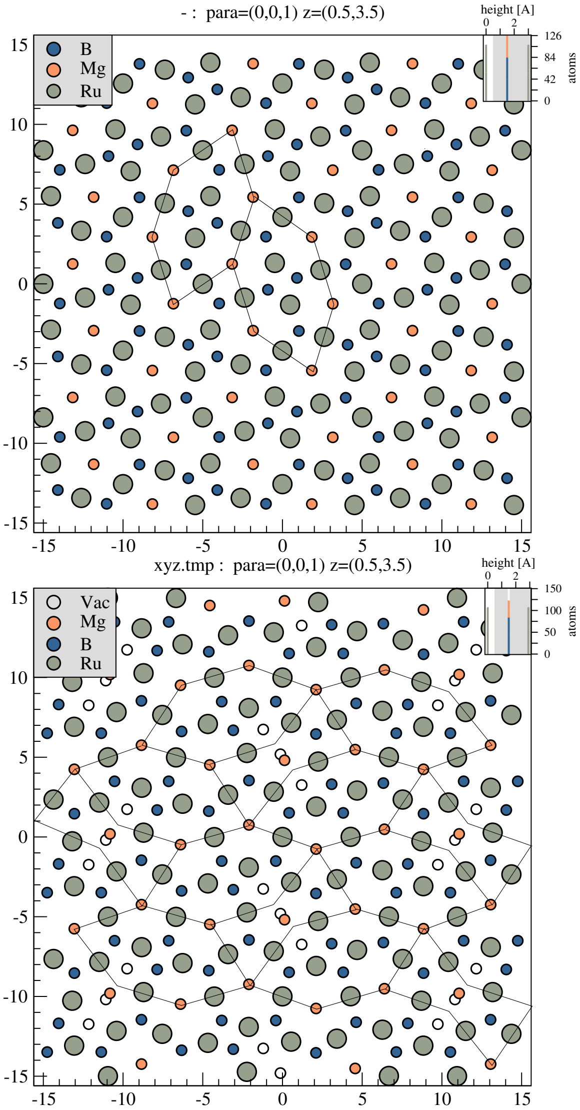

FIG. 1: top: $B_4Mg_2Ru_5$ (oP22) bottom: $B_{11}Mg_5Ru_{13}$ (oP62). Color coding Blue=B, Orange=Mg, Green=Ru, Empty=Vacancy. Size coding Large=lower plane, small=upper plane. Shading indicates 1/2 atomic occupancy. Dashed lines indicate uncertain tile edges. Bold lines outline HB pair showing deterministic atomic decoration.

powers of the golden mean $\tau = (1 + \sqrt(5))/2$. The RMS displacements of the experimentally determined positions from the ideal positions in 0.086 Å. The maximum displacement is 0.14 Å found for Ru_α atoms.

Remarkably, a very similar structure is found for the crystal Al8CaCo2 (Pearson symbol oP44), which exhibits an H2 tiling. In this case, Co, Al and Ca atoms respectively play the role of the small, medium and large B, Ru and Mg atoms. While the Co and Ca atom positions are equivalent to the B and Mg positions, the medium-sized Al atoms are more numerous than the Ru atoms, and they occupy sites in both levels of the bilayer.

In the experimentally refined $B_{11}Mg_5Ru_{13}$ structure [6], neither the atomic occupation nor the decomposition

FIG. 2: Perp space atomic surface figure.

into H and B tiles is uniquely determined. The atomic occupation is not unique because certain B and Mg atoms (shaded) have occupancy 0.5. The decomposition into H and B tiles is not unique because an HB pair (e.g. those shown in bold in Fig. 1) can be interchanged by means of a *bowtie flip* [5] (see dashed lines in Fig. 1). Because the atomic decoration is not determined, there is no guide as to how to resolve the region covered by an HB pair into its separate tiles. The bowtie flip is an example of a localized *phason* fluctuation [9].

The occupancy of the partially occupied sites must be highly correlated. For example, pairs of 50% occupied Mg sites are only 0.5 Å apart. Surely in reality a single Mg atom occupies precisely one out of the two sites at any instant in time. We find in addition, through our total energy calculations described below, that the nearby partially occupied B sites are strongly correlated with the Mg position in such a manner that when the B atom is in its prefered site relative to the Mg atom, the HB pair resolves uniquely into an H tile decorated as found previously in the $B_4Mg_2Ru_5$ structure plus a B tile decorated as shown in Fig. 1. We believe the experiment reveals partial occupancy as a result of phason disorder. This disorder could be planar in nature, with the HB pairs resolved randomly within a single bilayer, but these random layers stacked with perfect periodicity. Alternatively (and more likely, as we show below) the disorder could be truly three dimensional, with an HB pair in a given bilayer possibly resolving oppositely to the same pair in an adjacent bilayer, creating a phason stacking fault.

One additional tile type, a star (S), is often included along with H and B tiles [5]. Stars are not necessary to tile the plane with 10-fold symmetry because bowtie phason flips can convert an HS pair into a BB pair. However, for completeness we consider the possibility they are present.

The decoration rules can be conveniently described in terms of atomic surfaces as illustrated in Fig. 2. Cutting through hyperspace in the usual fashion creates a perfectly quasiperiodic HBS tiling, with each tile decorated exactly as described above. The structure exhibits space group 10/mmm, which is strikingly different from previously known decagonal quasicrystals in that it lacks a 10_5 screw axis.

The composition is rigidly fixed by the perp space areas of the atomic surfaces, which in turn are governed by the ideal atomic decorations of the tiles. We find the factions of atomic species as B ($1/\tau^2 = 0.382$), Mg ($1/(\tau^2 + 2\tau) = 0.171$) and Ru ($\tau/(\tau + 2) = 0.447$). Owing the the intrinsic ternary nature of BMgRu, there is no room to adjust these compositions to optimize quasicrystal formation, in contrast to the case of the pseudobinaries, where adjustments of the composition can move the Fermi level to a pseudogap, for example. If we wished to make comparable adjustments for BMgRu it would be necessary to move to a quatenary (pseudoternary) system such as B-(Mg,Sc)-Ru, for example.

Now we turn to a study of structural stability. Our first-principles total energy calculations are based on electronic density functional theory using the program VASP [10]. We employ the GGA approximation and use the VASP-supplied PAW potentials [11]. Our energy cutoff and k-point densities are chosen to achieve convergence of energy to an accuracy of 1 meV/atom. For all structures examined we relax atomic positions and lattice parameters while maintaining their starting symmetries. We calculate the energies of all known structures in the B-Mg-Ru ternary system and a large number of hypothetical structures including quasicrystal approximants in addition.

The known binary phase diagrams of B-Mr and Mr-Ru are reproduced exactly in the sense that all known stable phases lie on the convex hull of energy versus compositions, and all *unknown* structures lie above the convex hull. In the case of B-Ru, all unknown stuctures correctly lie above, and most known structures lie on the convex hull. However, two phases, B3Ru7 and B8Ru11 lie far above the convex hull (by 66 and 143 meV/atom, respectively). Introducing partial occupancy can lower the energy considerably but we have not yet found structures whose energy reaches the convex hull. These phases require further theoretical and experimental study.

The ternary diagram is correctly reproduced in the sense that the two known phases and no others lie on the convex hull. We resolved the partial occupancy of $B_{11}Mg_5Ru_{13}$ in many diffferent ways to find the lowest energy. It turns out that introduction of phason stacking faults is favored, with the the stacking fault energy $E_{sf} \approx$ -0.15 eV per fault [12]. In addition we detect stacking fault interaction energies of about 0.025 eV per pair of faults. Starting from our ideally decorated B2H2 tiling with the maximal number of stacking faults (2 per double heigh unit cell) we find significant atomic relaxation in the stacking fault regions. In particular, the Mg atom displaces by over 1 Å towards the bowtie center. Adjacent Ruα atoms relax towards the now-vacant vertex. Our relaxed positions are very close to the experimentally determined atomic positions.

Our calculated cohesive energies show that the known stable ternary phases are only marginally stable, lying just a few meV/atom below the weighted average of adjacent stable compounds. Furthermore, many of the unobserved unstable approximant structures lie just a few meV/atom above the convex hull. In other words, we find a cluster of many distinct but very nearly degenerate structures in the vicinity of the ideal quasicrystal composition. At other compositions no unknobserved structure lies less than 20 meV/atom above the convex hull.

The unique association between tiles and atomic positions captures configurational degrees of freedom intrinsic to the quasicrystal structures. Tile flips guarantee controlled and plausible local reshufflings of the structure. The key to the thermodynamic properties, and useful ingredient of the structure refinements, is "tiling Hamiltonian", associating energy terms with tiling objects, and their local mutual relationships. [Cite previous works: energy based diffraction refinement, and ab-initio tile-hamiltonian fits for ANC].

FIG. 3: Simulations of the random tiling model governed by our tile hamiltonian. (top) ground state (bottom) T=1000K state

We attemtped to extract the significant tile-hamiltonian terms from ab-initio calculations, relaxing structures resulting from the application of the same decoration rule to a number of tilings, with or without the stacking faults. All the SF calculations were for cells doubled along c-direction (ei 4 atomic layers); this only provides an initial estimate of the actual energetics when the configurational and displacive freedom due to the stacking disorder are not subject to such a short-length restriction.

We find the by far strongest tile-hamiltonian term is B2-¿HS rearrangement (3A bilayer); this costs 1.18 eV. We point out the set of nearest-neighbor distances after the flip is exactly the same as before. Probably this means that pentagons of B atoms stacked with 3A separation are highly unfavourable. Interestingly, the second largest term we identified was due to a different packing of pure Hexagons. The packing mode seen in the $B_4Mg_2Ru_5$ approximant is according to our calculation stable, but the packing mode in which H tiles are placed side by side cost 0.52 eV per Hexagon pair.

Carrying out simulations using this tile hamiltonian we find the ground state structure consists of domains of the $B_{11}Mg_5Ru_{13}$-like order (i.e. B2H2 tilings with a maximal density of stacking faults) separated by regions of $B_4Mg_2Ru_5$-like order (H2 tilings). At elevated temperatures around T=1000K we find instead a decagonal quasicrystal consisting of bilayers of random HB tilings with stacking faults inserted randomly between adjacent bilayers. If the compound actually possesses an equilibrium quasicrystal state, it will most likely be stabilized by the configurational entropy of this random tiling model. Actually reaching this state experimentally may be difficult owing to the much lower melting temperature of Mg compared with B and Ru.

In conclusion, we employ analogies with known crystal structures together with accurate first-principles total energy calculations to propose the existence of a previously unknown decagonal quasicrystal-forming compound. Our proposed structure is quite unlike previously known decagonal phases because it is an intrinsically ternary structure. It lacks a screw axis, consisting instead of an alternation of two dissimilar atomic layers, each with 10-fold symmetry.

Perhaps the most remarkable aspect of this compound is its high Boron content. Elemental Boron is known to form structures containing many icosahedra, and tits true low temperature equilibrium structure is unknown. What are the prospects for finding a quasicrystal containing an even high Boron fraction? It is interesting to note that B4CrY.oP24 and B6ReY2.oP36 both form H2 approximant phases, on different length scales. More surprises may lie in wait in other Boron-rich compounds.

Acknowledgments

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