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First-principles prediction of a decagonal quasicrystal containing Boron

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We interpret experimentally known B-Mg-Ru crystals as quasicrystal approximants. These approximant structures imply a deterministic decoration of tiles by atoms that can be extended quasiperiodically. Experimentally observed structural disorder corresponds to phason (tile flip) fluctuations. First-principles total energy calculations reveal that many distinct tilings lie close to stability at low temperatures. Transfer matrix calculations based on these energies suggest a phase transition from a crystalline state at low temperatures to a high temperature state characterized by tile fluctuations. We predict $B_{38}Mg_{17}Ru_{45}$ forms a decagonal quasicrystal that is metastable at low temperatures and may be thermodynamically stable at high temperatures.

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While evaluating the stability of crystalline phases competing with metallic glass formation [1], we discovered a number of previously unrecognized decagonal quasicrystal approximants [2]. 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 quasicrystal approximant structures based on these motifs and calculated their total energy. Based on our findings we propose that $B_{38}Mg_{17}Ru_{45}$ should posses a decagonal quasicrystal state that is at least metastable, and potentially even thermodynamically stable at high temperature.

This prediction is noteworthy because: (1) the compound contains a substantial amount of Boron, which has been speculated to form quasicrystalline structures [3–6] though none are yet known; (2) the predicted structure is quite different from the established structures of Al-rich decagonal quasicrystals [7, 8] in that it is an *intrinsic* ternary, while known Al-rich decagonals are essentially *pseudobinaries*; (3) we predict both structure and *existence* from first-principles, while in prior work [8], existence was taken as a crucial experimental input for structure prediction; (4) first-principles total energy calculations confirm the feasibility of entropic stabilization [9].

Two experimentally known B-Mg-Ru crystals [10, 11], $B_4Mg_2Ru_5$ (Pearson symbol oP22, space group Pbam) and $B_{11}Mg_5Ru_{13}$ (Pearson symbol oP62, space group Pbam), are decagonal approximants. These compounds form through solid state transformation at an annealing temperature of T_a=1323K. 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 [8] are inscribed on these figures to show how the structures can be interpreted as quasicrystal approximants. The tile edge length a_q=4.5 Å is known as the *quasilattice constant*.

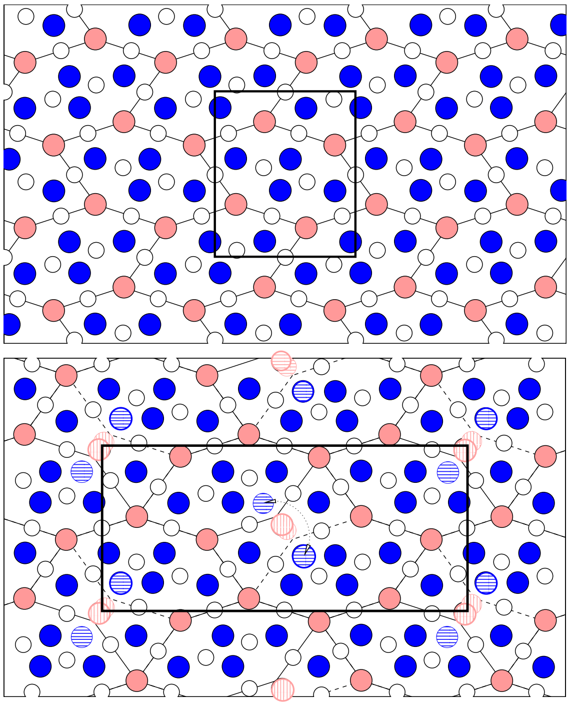

FIG. 1: top: $B_4Mg_2Ru_5$ (oP22) bottom: $B_{11}Mg_5Ru_{13}$ (oP62). Color coding: Blue=B, Orange=Mg, White=Ru. Size coding: Large=upper plane, small=lower plane. Shading indicates 1/2 atomic occupancy. Solid lines outline outline optimal tiling $\mathcal{O}$. Dashed lines indicate possible phason tiling flips leading to tiling $\mathcal{O}'$.

In $B_4Mg_2Ru_5$ only the H tile appears, and it is decorated deterministically with every site fully occupied by a unique atomic species. The determinism of this decoration reflects the strong size and chemistry contrast between atomic species. That is the sense in which we refer to B-Mg-Ru as an *intrinsic* ternary. Other ternaries that form decagonal quasicrystals are pseudobinaries because at least two of the elements readily substitute for

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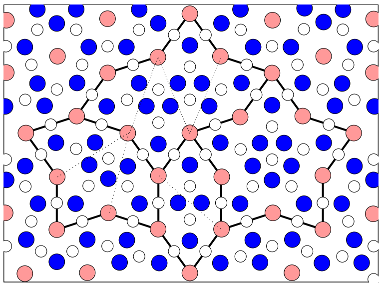

FIG. 2: Ideal tiles and decorations. Tiles shown are H, B, S and E. Prototiles for the generalized 2-level tiling [13] are shown with dashed lines.

each other (e.g. Co and Ni in Al-Co-Ni).

All atoms lie on two flat layers. 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 refer to this pair of adjacent layers as a *slab*. Slabs 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 thin rhombi. All B atoms center trigonal prisms formed by Ru atoms [10]. 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 [1, 12].

The experimentally determined atomic positions of $B_4Mg_2Ru_5$ agree very accurately with the deterministic decoration of our idealized tiling model. The RMS displacements of the experimentally determined positions from the ideal positions is 0.086 Å. The maximum displacement is 0.14 Å found for Ru_α atoms.

In the experimentally refined $B_{11}Mg_5Ru_{13}$ structure [10], neither the atomic occupation nor the decomposition 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 can be interchanged by means of a *bowtie tile flip* [8] (see dashed lines in Fig. 1). Tile flips are examples of localized *phason* fluctuations [14] in quasicrystals, but can also occur in crystalline approximants to quasicrystals where they become discrete configurational degrees of freedom. Because the atomic decoration is not deterministic, there is no guide as to how to resolve the region covered by an HB pair into its separate tiles.

Occupancy of the partially occupied sites must be highly correlated. For example, pairs of 50% occupied Mg sites are only 0.5 Å apart. A single Mg atom should occupy one out of the two sites at any instant in time. In addition, we find the nearby partially occupied B sites are strongly correlated with the Mg position. When the B atom occupies its preferred site relative to the Mg atom, the HB pair resolves uniquely into an H tile and a B tile, each decorated as shown in Fig. 2.

Thus we believe the experiment reveals partial occupancy as a result of tile flip disorder. This disorder could be planar in nature, with the HB pairs resolved randomly within a single slab that is then stacked with perfect 3 Å periodicity along the c axis. Alternatively (and more likely, as we show below) the disorder could be truly three dimensional, with an HB pair in a given 3 Å slab possibly resolving oppositely to a BH pair in an adjacent slab, introducing a tiling flip between slabs.

H and B tiles alone can cover the infinite plane quasiperiodically. However, other tile types beyond H and B are possible (see Fig. 2). To generate the full set of tiles we use, start with an H tile and add a bowtie to generate a B tile. Adding an additional bowtie to a B tile generates either a star (S) tile or else the tile type we call E. This process can be continued indefinitely creating ever larger tiles, leading to a generalization of the set of 2-level tilings [13]. All additional tiles in this family can be created from the set of prototiles illustrated with dashed lines in Fig. 2.

For 10-fold symmetric quasiperiodic tilings, the composition is rigidly fixed by the ideal atomic decorations of the tiles. The Boat:Hexagon ratio of $\tau : 1$ (here $\tau = (\sqrt{5}+1)/2$ is the golden mean) corresponds to fractions of atomic species as $x_B = 1/\tau^2 = 0.382$, $x_{Mg} = 1/(\tau^2 + 2\tau) = 0.171$ and $x_{Ru} = \tau^2/(\tau^2 + 2\tau) = 0.447$. This ideal composition is about 0.1% richer in B and Ru than the composition of the $B_{11}Mg_5Ru_{13}$ crystal. Owing to the the intrinsic ternary nature of B-Mg-Ru, the composition cannot be adjusted 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 B-Mg-Ru it would be necessary to move to a quaternary (pseudoternary) system such as B-(Mg,Zr)-Ru.

Given our quasicrystal model we study structural stability by calculating cohesive energies in the B-Mg-Ru ternary system. Our first-principles total energy calculations employ electronic density functional theory using the plane-wave program VASP [15]. We use the GGA approximation with the VASP-supplied PAW potentials [16]. Our energy cutoff and k-point densities achieve convergence of energy to an accuracy of better than 1 meV/atom. For all structures examined we relax atomic positions and lattice parameters. We consider all known binary and ternary crystal structures [11], a large number of hypothetical structures drawn from chemically similar alloy systems, and 70 different quasicrystal approximants. Our methods are described in more detail in Ref. [1] and quantitative cohesive energy data is available on the WWW [17].

These calculations exactly reproduce the known binary phase diagrams of B-Mg and Mg-Ru in the sense that all known stable phases lie on the convex hull of energy versus compositions, and all hypothetical structures lie above the convex hull. For B-Ru, all unknown structures correctly lie above, and most known structures lie on the convex hull. However, two phases, B_3Ru_7 (presumed stable) and B_8Ru_{11} (presumed metastable) lie far above the convex hull (by 66 and 143 meV/atom, respectively). Introducing vacancies lowers 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 reproduced exactly.

We resolved the partial occupancy of $B_{11}Mg_5Ru_{13}$ in many different ways to find the lowest energy. It turns out that introduction of tile flips between adjacent slabs is favored, lowering the total energy by 8.4 meV/atom. The lowest energy structure is obtained by arranging two boat and two hexagon tiles in a single slab as shown in Fig. 1 (we call this optimal tiling $\mathcal{O}$), then stacking a second slab above that differs by the tile flips outlined by dashed lines. The resulting tiling, which we denote $\mathcal{O}'$, is equivalent to the starting tiling, but reflected and translated. The optimal structure thus exhibits a 6 Å periodicity perpendicular to the tiling plane, an alternating sequence of $\mathcal{O}$ and $\mathcal{O}'$ with space group Pnma. We assign this structure Pearson symbol oP116.

Other tilings exist within the same lattice parameters. Indeed, a different arrangement of two boat and two hexagon tiles in a single slab, alternating with a partner to yield 6 Å periodicity and space group Pnma as before, has energy just 0.3 meV/atom above the $\mathcal{O}\mathcal{O}'$ structure. We denote this structure as $\mathcal{Q}\mathcal{Q}'$, where $\mathcal{Q}$ differs from $\mathcal{O}$ by just one bowtie flip.

Starting from ideally decorated tiles we find significant atomic relaxation in the tiling flip regions. In particular, the Mg atom displaces by over 1 Å towards the bowtie center (see Fig. 1, bottom). Adjacent Ru_α atoms relax towards the now-vacant vertex. The Ru layers become slightly non-flat. Our relaxed positions are all within 0.05 Å of the experimentally determined atomic positions for $B_{11}Mg_5Ru_{13}$.

Our calculated cohesive energies show that the known ternary structures are highly stable (enthalpies of formation are around 350 meV/atom). However, a great many hypothetical approximant structures lie quite close to the convex hull, starting about 2.5 meV/atom above. In other words, we find a cluster of many distinct but very nearly degenerate structures in the vicinity of the ideal quasicrystal composition.

To understand why experiments find a disordered 3 Å-periodic structure for $B_{11}Mg_5Ru_{13}$, while our calculations find an ordered 6 Å-periodic minimum energy state, we carry out transfer matrix calculations. These model the temperature dependence of the thermodynamic ensemble of structures that differ by tiling flips. First we construct all 2-D tilings α that fit within a given periodic boundary condition in the xy-plane. Each tiling describes a slab of B-Mg-Ru with height 3 Å along the z axis, decorated as in Fig. 2. Then we consider combinations $\alpha\beta$ in which slab β is placed above slab α along the z axis, for a total height of 6 Å. We only consider combinations which differ by disjoint localized tile flips, so the tilings match on all vertices neighboring the flipped vertex. Specifically, these are the four vertices forming the outside corners of the "bowtie" that flips. For each combination $\alpha\beta$, we calculate the relaxed total energy $U_{\alpha\beta}$.

We may think of $U_{\alpha\beta}$ as comprising: the energy of slab α; the energy of slab β; twice the interaction energy of slab α with β. This factor of 2 arises from the periodic boundary condition along the z axis. Within this energy model, the total energy for a stack of n layers $(\alpha_1\alpha_2\alpha_3\dots,\alpha_n)$ with periodic boundary conditions of height $n \times 3$ Å, becomes $E_{\alpha_1\alpha_2} + E_{\alpha_2\alpha_3} + \cdots + E_{\alpha_n\alpha_1}$, where $E_{\alpha\beta} = \frac{1}{2}U_{\alpha\beta}$. This approximation neglects interactions of second- and further-neighbor slabs.

Defining the transfer matrix elements $R_{\alpha\beta} = \exp(-E_{\alpha\beta}/k_BT)$, the partition function for a stack of n layers is $Z = \mathrm{tr}\ R^n$. In the limit of many layers, the free energy per layer $f = -k_BT\log\rho$, with ρ the largest eigenvalue of R. Other thermodynamic quantities such as internal energy U, entropy S and heat capacity C are given by temperature derivatives of f.

The broad peak in Fig. 3 illustrates the heat capacity per atom for the ensemble of structures that match the lattice parameters of $B_{11}Mg_5Ru_{13}$ in the xy plane. At low temperature the structure is locked into the minimum energy configuration $\mathcal{O}\mathcal{O}'$. It has a vertical periodicity of 6 Å because tiles flip back and forth with perfect regularity. A small peak around T=500K indicates the onset of the alternate $\mathcal{Q}\mathcal{Q}'$ structure. The heat capacity peaks around the annealing temperature T_a and well below our guess at a likely melting temperature $T_m \approx$1750K. We also plot the entropy multiplied by temperature, a measure of the free energy reduction due to tiling fluctuations. At the annealing temperature TS is around 2.6 meV/atom. At the same temperature, these fluctuations increase the internal energy U by around 1.3 meV/atom.

From the eigenvector of the transfer matrix we determine that about 69% of the slabs α occurring in equilibrium are of the optimal type $\alpha = \mathcal{O}$ or $\mathcal{O}'$. Starting from a slab of type $\mathcal{O}$, the next slab above is of type $\mathcal{O}'$ with probability around 75%. This leads to a persistence length for the 6 Å periodic $\mathcal{O}\mathcal{O}'$ sequence of 12 slabs, or 36 Å. As a result, there will be no Bragg peak associated with 6 Å periodicity, but there should be pronounced diffuse scattering.

Does the broad peak in Fig. 3 indicate a genuine phase transition? With finite extent in the xy plane, our transfer matrix describes an effectively one-dimensional system that is incapable of a genuine phase transition. A phase transition might exist in the thermodynamic limit of infinite extent in the xy plane. This cannot be done using ab-initio methods, which are already strained by the demands of the 116 atom double slabs of the $\mathcal{O}\mathcal{O}'$ model. Instead, we approximated the energetics using

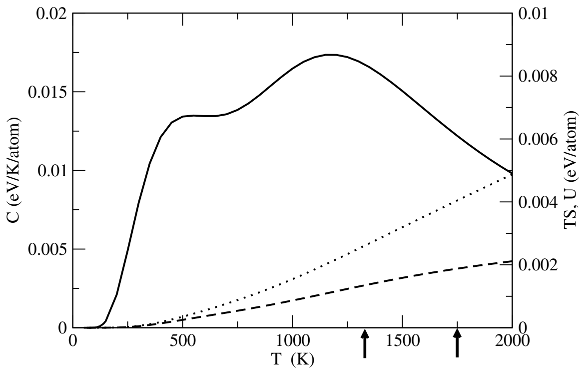

FIG. 3: Thermodynamic properties of $B_{11}Mg_5Ru_{13}$ calculated from transfer matrix for an infinite stack of single unit cells. Left axis, heat capacity C (solid). Right axis, $T * S$ (dotted), U (dashed). Arrows mark annealing temperature T_a and estimated melting temperature T_m.

a crude "tile Hamiltonian" [18, 19] that enforces tiling constraints and assigns an energy preference for tiling flips between adjacent slabs. We evaluate the tile Hamiltonian energies for supercells of the basic $B_{11}Mg_5Ru_{13}$ structure and find that the heat capacity peak narrows and diverges as system size grows. The existence of a genuine phase transition seems clear, although we do not know its temperature very accurately owing to our crude tile Hamiltonian approximation.

Could tiling disorder, whose prevalence at high temperature we have demonstrated, stabilize the quasicrystalline phase entropically [9]? To answer we must compare the entropy difference between the quasicrystal and competing crystal phases with corresponding energy differences. Substituting larger approximants for the true quasicrystal, we find the quasicrystal is high in energy by 2.5 meV/atom. The random tiling hypothesis [14] suggests the entropy of the quasicrystal is greater than that of small approximants. We already found TS of 2.6 meV/atom for the $B_{11}Mg_5Ru_{13}$ phase, but we need the entropy *difference* between that and the quasicrystal. Since we cannot directly calculate the quasicrystal entropy, we take 2.6 meV/atom as indicating the magnitude of the probable difference in TS at temperature T_a. This rises to 4.0 meV/atom at T_m.

Since both energy and entropy are of comparable magnitude, we have verified from first-principles the *feasibility* of entropic stabilization. We predict that quasicrystalline B-Mg-Ru is on the verge of stability, so effects left out of our considerations could tip the balance. A better estimate of the quasicrystal entropy could be achieved by finding an accurate tile Hamiltonian then evaluating the entropy of this model for large approximants. We should include the increase in internal energy U caused by tile fluctuations. Further, we should include atomic vibrations (phonons) which contribute their own entropy and also can be expected to modify the values of terms in the tile Hamiltonian.

In the event that further theoretical (or experimental) study shows the B-Mg-Ru decagonal phase is not stable at high temperature, moving to a quaternary system (e.g. substituting a small fraction of Mg with Sc or Zr) could stabilize it by raising the energy of competing crystal phases relative to the quasicrystal. Regardless of the stability at high temperature, we expect the ternary quasicrystal to occur metastably at low temperature, because the energy differences between crystalline and quasicrystalline structures are small, and the high entropy of the quasicrystal implies there are a large number of structures into which the system could freeze out of equilibrium. Thus, we predict the occurrence of decagonal quasicrystals in $B_{38}Mg_{17}Ru_{45}$.

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[1] M. Mihalkovič and M. Widom, sub. to Phys. Rev. B (2004), cond-mat/0405298.

[2] M. Mihalkovič and M. Widom, in *Proceedings of the MRS*, edited by E. Belin-Ferre (2004), vol. 805.

[3] W.-J. Zhu and C. L. Henley, Europhys. Lett. **51**, 133 (2000).

[4] R. Kimura, Mat. Sci. Eng. B **19**, 67 (1993).

[5] I. Boustani, A. Quandt, and P. Kramer, Europhys. Lett. **36**, 583 (1996).

[6] D. Weygand and J.-L. Verger-Gaugry, C. R. Acad. Sci. II **320**, 253 (1995).

[7] W. Steurer, T. Haibach, B. Zhang, et al., J. Phys.: Cond. Mat. **6**, 613 (1994).

[8] M. Mihalkovič et al., Phys. Rev. B **65**, 104205 (2002).

[9] M. Widom, K. J. Strandburg, and R. H. Swendsen, Phys. Rev. Lett. **58**, 706 (1987).

[10] K. Schweitzer and W. Jung, Z. Anorg. Allg. Chemie **530**, 127 (1985).

[11] P. Villars, *Pearson's Handbook, Desk Edition* (ASM International, Materials Park, Ohio, 1997).

[12] P. Gaskell, Nature **276**, 484 (1978).

[13] C. L. Henley, in *Quasicrystals*, edited by S. Takeuchi and T. Fujiwara (World Scientific, Singapore, 1998), p. 27.

[14] C. L. Henley, in *Quasicrystals: the state of the art*, edited by D. P. DiVincenzo and P. J. Steinhardt (World Scientific, Singapore, 1991), pp. 429–524.

[15] G. Kresse and J. Hafner, Phys. Rev. B **47**, RC558 (1993).

[16] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[17] M. Mihalkovič and M. Widom, web site (2004), http://alloy.phys.cmu.edu.

[18] M. Mihalkovič, W.-J. Zhu, C. L. Henley, et al., Phys. Rev. B **53**, 9021 (1996).

[19] I. Al-Lehyani and M. Widom, Phys. Rev. B **67**, 014204 (2003).