Tile Hamiltonians for Decagonal Phases

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Abstract

A tile Hamiltonian (TH) replaces the actual atomic interactions in a quasicrystal with effective interactions between and within tiles. We study Al-Co-Ni and Al-Co-Cu decagonal quasicrystals described as decorated Hexagon-Boat-Star (HBS) tiles using *ab-initio* methods. A dominant term in the TH counts the number of H, B and S tiles, favoring tilings of H and B only. In our model for Al-Co-Cu, chemical ordering of Cu and Co along tile edges defines tile edge arrowing. Unlike the edge arrowing of Penrose matching rules, however, the energetics for Al-Co-Cu do not force quasiperiodicity. Energetically favored structures resemble crystalline approximants to which the actual quasicrystalline compounds transform at low temperature.

Explaining thermodynamic stability is a fundamental problem in the field of quasicrystals. Competing explanations range from *energetic stabilization* utilizing matching rules such as those that force quasiperiodicity in the Penrose tiling [1], to *entropic stabilization* [2] focusing on the configurational entropy available in random tiling models [3, 4]. Experimental evidence so far has not unambiguously settled the matter, and the true situation is certainly more complex than either of the two extremes just described. With the advent of plausible atomistic quasicrystal models and advances in first-principles calculation methodology we hope further theoretical progress may be made in this area.

Our approach reported here is based on a "tiling Hamiltonian", in which a family of low energy atomistic structures is placed in 1:1 correspondence with a family of tilings of the plane. The energetics of the tiling Hamiltonian is defined in a manner that closely approximates the *ab-initio* energetics of the atomistic structures. The energetics we derive proves remeniscient of Penrose "matching rules" (which force global quasiperiodicity in minimum-energy structures) but differs in crucial aspects. Indeed, we find that our tile Hamiltonian does *not* favor quasiperiodicity. Quasiperiodicity may occur at high temperatures as a result of random tiling configurational entropy. At low temperatures energy favors transformation to crystalline phases, which is indeed often observed experimentally [5, 6, 7, 8, 9].

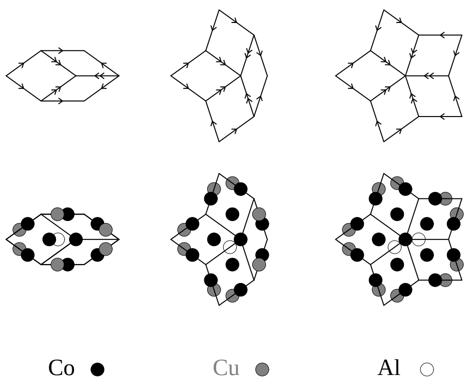

Fig. 1. (A) HBS tiles and their decompositions to Penrose tiles. (b) Atomic decorations for AlCoCu. In (b), only TM and symmetry breaking Al atoms are shown. For AlCoNi both edge sites are decorated with Ni atoms.

Penrose tiles are fat and thin rhombi (Fig 1a). Edges are assigned single- and double-arrow decorations (as shown) which must match for common edges in adjacent tiles. Perfect quasicrystals obey these rules everywhere. The double-arrow matching rule [4] causes rhombi to associate into hexagon (H), boat (B) and star (S) shapes (with relative frequency H:B:S=$\sqrt{5}\tau$:$\sqrt{5}$:1), while the single-arrow rules force quasiperiodicity in the HBS tiling. It has been shown previously [10, 11] that plausible atomistic structures of AlCoNi and AlCoCu can be described as HBS tilings decorated with atoms (Fig 1b). Hence, we may consider the Penrose rhombus double-arrow rules to be satisfied by definition of our basic HBS tiles.

In a tiling model of quasicrystals, the actual atomic interactions in the system Hamiltonian can be replaced with effective interactions between and within tiles [12]. The resulting tile Hamiltonian is a rearrangement of contributions to the actual total energy. In a simple atomic interaction picture (pair potentials for example) the relation between the actual atomic interactions and the tile Hamiltonian is straightforward. It might be difficult to find the relations between them for more complicated atomic interactions (many body potentials, or full *ab-initio* energetics, for example) but it is theoretically possible. The tile Hamiltonian includes terms which depend only on the number of tiles, and includes other terms for tile interactions. The tile Hamiltonian greatly simplifies our understanding of the relationship between structure and energy, and is a reasonable way to describe the tiling ensemble.

Are Penrose single-arrow matching rules enforced by energetics of real materials? For a simple model [11] of $Al_{70}Co_9Ni_{21}$ in which both edge sites are occupied by Ni atoms there is no source of symmetry-breaking at short length scales able to define an orientation of the tile edges. The energetics of structures based on HBS tiles decorated in this manner depends primarily on the numbers of H, B and S tiles. As seen in Fig. 2, certain phason flips convert an HS pair into a BB pair (or vice-versa). Pair-potential-based total energy calculations of these two structures [11, 15] reveal that structure (a) containing the BB pair is lower in energy than (b) containing the HS pair by 0.2 eV. The physical origin of this energy difference lies in the number of 72° vertices, which drops by 1 in the transition HS $\rightarrow$ BB. At a 72° vertex transition metal pairs are close neighbors, causing a reduction in the number of energetically favorable [16] aluminum-transition metal near neighbor interactions.

Hence we may express the tile Hamiltonian as

$$H = E_s N_s \tag{1}$$

where N_s is the number of star tiles present, and the coefficient $E_s = 0.2$ eV. To fully model decagonal AlCoNi (indeed any decagonal phase) we should add into the Hamiltonian (eq. (1)) terms representing phason stacking disorder. Unfortunately, at this time the magnitude (and even the sign) of this term is unknown [15]. Additional corrections relating to the number of 144° vertices are small relative to the term shown [11, 15]. Hence we focus our attention on the two-dimensional behavior defined by Hamiltonian (eq. (1)).

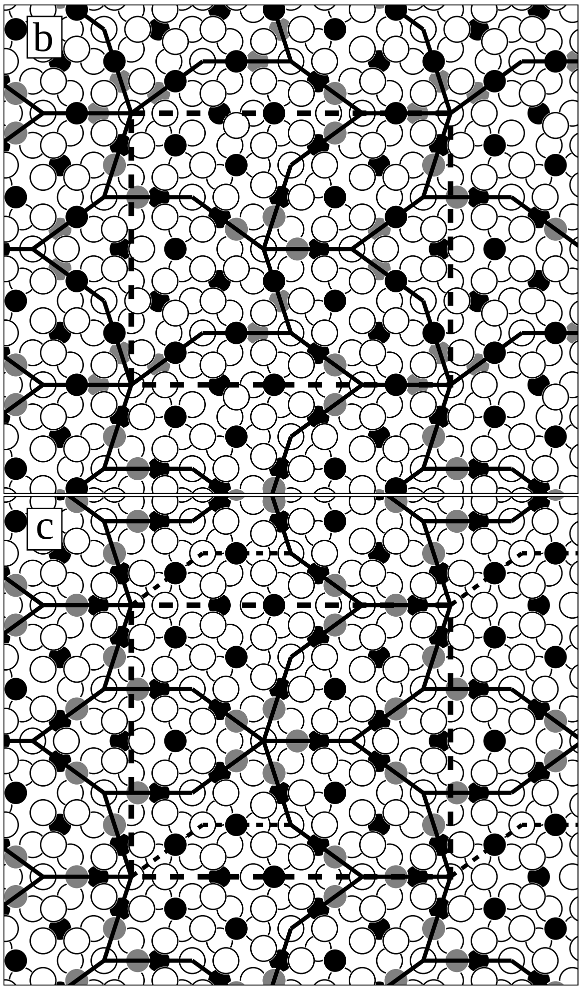

Fig. 2. Space can be tiled in many ways using HBS tiles. Both these approximants contain equal numbers of each atom type. Structures in (a) and (b) differ by the phason flip outlined in (b) with a dashed line, which converts two B tiles into and H and an S.

Monte Carlo simulations show that S tiles are infrequent at T = 1000K and completely absent in the lowest energy structures, which are random HB tilings with relative frequency H:B=1:τ. A typical structure is illustrated in Fig. 3a.

The situation for AlCoCu is more complicated than for AlCoNi, due to the chemical alternation of Co/Cu pairs on tile edges. Cockayne and Widom [10] suggested that tile edges could be assigned arrow direction based on their Co/Cu decorations (Fig.1b). The physical origin of Co/Cu chemical ordering rests on the status of Cu as a Noble Metal with completely filled d orbitals, unlike normal transition metals such

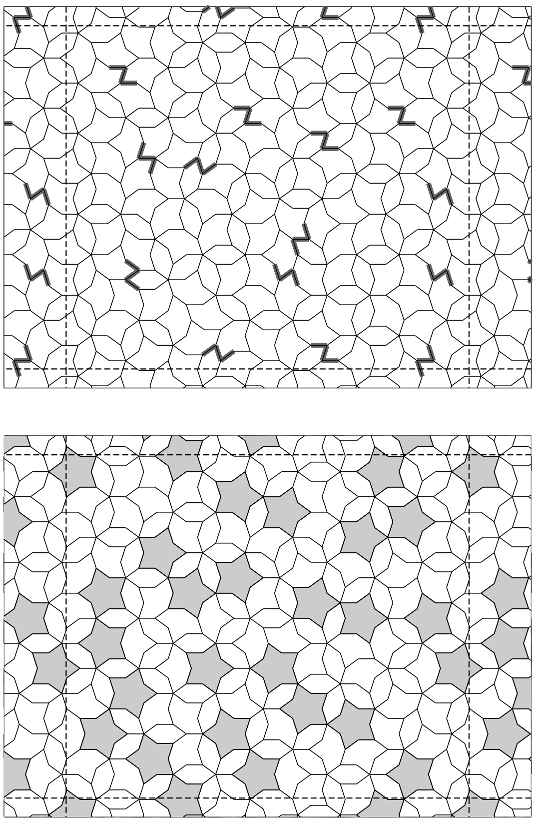

Fig. 3. Typical low temperature configurations. (a) Tile Hamiltonian (eq. (1)), or (eq. (2)) with $E_s > 2E_{zz}$. Wide gray bonds identify "zig-zag" structures. (b) Tile Hamiltonian (eq. (2)) with $E_s < 2E_{zz}$. Star tiles are shaded gray for emphasis.

as Co. Energetically, it turns out to be highly favorable for Co/Cu pairs to orient such that the Co atoms are further removed from 72° vertices than Cu atoms.

For consistency with Penrose matching rules, we thus define the arrow to point from Cu towards Co. When the HBS tiles are decorated consistently with the Penrose matching rules, all arrows point outwards from 72° vertices, minimizing the energy associated with chemical ordering of Co/Cu. However other tilings (such as the random HB tiling illustrated in Fig. 3a) contain "zig-zag" structures. The middle of the three bonds in a zig-zag can never be oriented to point outwards from each of its 72° vertices, leading to a minimum energy cost for each zig-zag, E_{zz}. Hence we define our tile Hamiltonian

$$H = E_s N_s + E_{zz} N_{zz} \tag{2}$$

where N_{zz} is the number of zig-zags present, while the coefficients $E_s = 0.2$ eV and $E_{zz} = 0.12$ eV have been derived from full *ab-initio* calculations [13]. Eq. (2) is actually a simplification of the full tile Hamiltonian [13, 14] which captures accurately the energetics of the lowest energy structures. Although we assign the energy cost to the zig-zag shape, its origin is the frustration of the central bond orientation, and not a feature of the shape itself.

We have found a few special approximants containing neither stars nor zig-zags. The simplest of these approximants (and the largest phason strain) covers space by translation of a single boat tile (see tiling B1 in Ref. [13]). The next larger of these approximants (but the smaller phason strain) covers space with "lightbulb" objects (see Fig. 4a) consisting of two boats and a hexagon. Other star- and zig-zag-free structures have been found that are basically superstructures of the lightbulb tiling.

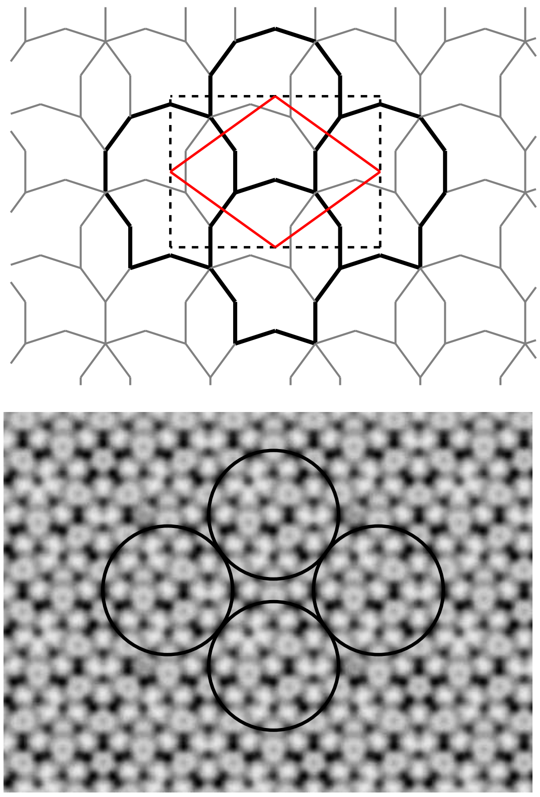

Fig. 4. zig-zag- and star-free "lightbulb tiling" structure. (a) Tiling has orthorhombic cell with lattice constants 23.1 Å × 31.8 Å (dashed lines) containing inscribed 72° rhombus with 20 Å edge length. (b) Model HREM structure image [18] showing 20 Å ring contrasts at vertices of 72° rhombus.

For large quasicrystal approximants of low phason strain it appears impossible to simultaneously eliminate both stars and zig-zags. Were we to start with a phason strain-free random HB tiling, containing N tiles (N/τ^2 tiles of type H and $N\tau$ tiles of type B), a series of tile flips could segregate the tiles into a zig-zag-free lightbulb tiling adjoining a pure H tiling. Counting up the tile numbers, we see that the lightbulb tiling contains N/τ^2 type B tiles and hence

$N/2\tau^2$ type H tiles. This leaves $(1/\tau - 1/2\tau^2)N$ extra H tiles remaining to form a pure H tiling which contains 1 zig-zag per H tile. Accordingly, we conjecture $(1/\tau - 1/2\tau^2)N$ is the minimum number of zig-zags possible in an HB tiling of N tiles at composition H_1B_τ. The number of S tiles present in an ideal HBS tiling of N tiles total works out to $(2/\tau - 1/\tau^2)N$, just twice the apparent minimum number of zig-zags. Indeed, we believe this may be the minimal allowed value of $N_s + 2N_{zz}$ in zero phason strain tilings. If this were true, then the density of stars in a zero phason strain Penrose tiling is the minimum possible density of stars in any zig-zag-free tiling.

The lightbulb tiling illustrated in Fig. 4a exhibits a unit cell of a 72° rhombus with an edge length of $2(\cos\frac{\pi}{10} + \cos\frac{3\pi}{10})L \approx 20$ Å where $L = 6.4$ Å is the edge length of the HBS tiling for AlCoCu. Such a crystal structure appears when decagonal $Al_{65}Co_{20}Cu_{15}$ is annealed at low temperatures. It is seen in HREM as a rhombic lattice of ring contrasts identified as 20 Å clusters. HREM images of the atomic structure associated with our lightbulb tiling (when decorated with atoms as in Fig. 2) contain nearly complete ring contrasts. Fig 4b illustrates a simple model high-resolution structure image [18] obtained by superposing Gaussian functions at each atomic position with weight proportional to the atomic number (to do a better job of HREM modeling we should incorporate chemical and phason stacking disorder in our structure model and perform dynamical diffraction analysis of the electron microscope imaging). Dark spots correspond to atomic columns and white to empty channels. This type of image should resemble HREM images from a thin sample near the Scherzer defocus. Fig. 4 bears a qualitative resemblence to the HREM patterns of low-temperature $Al_{65}Co_{20}Cu_{15}$ in Ref. [6]. Thus it may be that our tiling Hamiltonian gives an indication of the structure of the low temperature phase, and explains its appearance as driven by the need to eliminate star tiles and zig-zags.

The precise values of the coefficients E_s and E_{zz} in equations (1) and (2) can be questioned because they wre calculated with atoms placed at ideal sites. Their values will change if atomic relaxation is allowed, although we expect the general form of the tile Hamiltonians and the magnitudes and signs of the terms to be preserved. Small changes in chemical composition can lead to surprisingly large changes in the tile Hamiltonian by altering the atomic interactions specifically at those points where the unfavorable star or zig-zag energies originate. Such an effect could explain why the low temperature structure observed for $Al_{63}Co_{17.5}Cu_{17.5}Si_2$ (a 72° rhombus with a 51 Å edge length [7]) differs from that found [6] in $Al_{65}Co_{20}Cu_{15}$. In general, variation of the tile Hamiltonian parameters can lead to transitions such as that illustrated in Fig. 3.

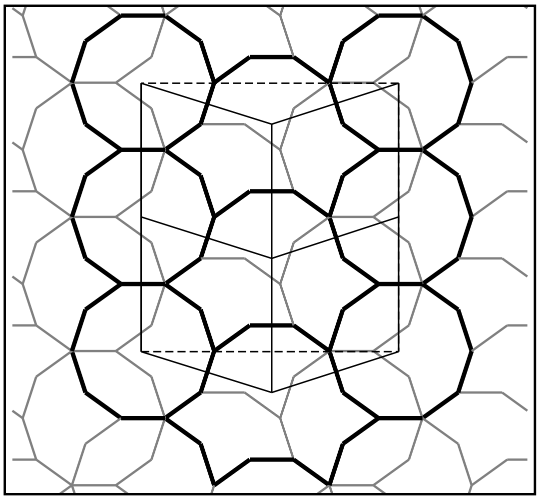

Fig. 5. Chevron tiling of 72° rhombi with 20 Å edge lengths. The rhombic unit cell of dimensions 37.6 Å × 39.7 Å matches the low temperature structure PD1 of Al-Co-Ni [9]

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A chemistry dependence is also found in the case of AlCoNi, where small changes in composition lead to a wide array of different structure types [5]. Transitions as composition (or temperature) is changed may be related to changes in the values of terms in a tile Hamiltonian. For example, a change from $Al_{70}Co_9Ni_{21}$ to $Al_{72}Co_{11}Ni_{17}$ results in CoAl pairs replacing NiNi pairs on tile edge sites at 72° vertices [11]. Consequently the energy cost of 72° vertices, and hence E_s is reduced on average. However, the Co/Al pairs carry an edge orientation (similar to Co/Cu pairs) so we need to add a zig-zag energy into the Hamiltonian (1), resulting in a new Hamiltonian like (2). Although the true low temperature phase at this composition is not certain, at a nearby composition of $Al_{71}Co_{14.5}Ni_{14.5}$ the system indeed takes on one of two structures based on tilings by 72° rhombi with 20 Å edge lengths [8, 9]. One structure, known as PD2, has the unit cell of the lightbulb tiling (Fig. 4). The other structure, known as PD1, pairs rhombi into "chevron" structures (Fig. 5) in which, again, both stars and zigzags may be avoided. Both of these structures have an 8 Å periodicity in the stacking direction, so an additional term related to phason stacking faults may need to be included in our tile Hamiltonians.

In conclusion, we show that an ensemble of low energy quasicrystal and approximant structures may be modeled using very simple tiling Hamiltonians. The tile Hamiltonians representing Al-Co-Ni and Al-Co-Cu favor crystalline structures at low temperatures but may exhibit quasicrystals in equilibrium at high temperatures. The favored low energy crystal structures resemble the transformation products actually observed in these compounds at low temperatures.

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