

# Ab initio energetics of transition metal ordering in decagonal Al–Co–Cu

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## Abstract

We perform ab initio total energy calculations for approximants to a model of decagonal Al–Co–Cu. These calculations support previously proposed chemical ordering of Co and Cu atoms along tile edges. Preferred arrow orientations are identified and shown to obey a subset of the single-arrow Penrose matching rules. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Competing explanations for thermodynamic stability of quasicrystals range from *energetic stabilization* [1] utilizing matching rules such as those that force quasiperiodicity in the Penrose tiling [2], to *entropic stabilization* [3] focusing on the configurational entropy available in random tiling models [4,5]. Experimental evidence fails to unambiguously settle the matter. Theoretical insight into the problem is now possible because highly reliable structural models identify the positions and chemical identity of the majority of atoms, and ab initio calculations based upon electronic density-functional theory now yield meaningful total energies for small quasicrystal approximants.

Quasicrystal structures may be effectively described as coverings of space by shapes known as tiles, each tile being decorated in some manner by atoms. This paper explores the coupling between tile decoration and local tiling structure in decagonal Al–Co–Cu. We focus especially on the chemical ordering between Co and Cu atoms along tile edges [6]. We demonstrate that chemical ordering exists, assigning arrows along tile edges. Given the existence of arrows along tile edges, we investigate the relative energies of different arrow configurations and show these energies can be modeled by interactions between arrows. We find that the favored arrowing of tile edges sharing  $72^\circ$  vertices is consistent with a subset of the Penrose matching rules.

## 2. Model and calculational method

We recently introduced a model for decagonal Al–Co–Cu based upon tilings of space by hexagon, boat and star-shaped (HBS) tilings decorated deterministically with atoms [6]. A key feature of the model is the zigzag chains of alternating Cu and Co atoms extending along the periodic axis. Within the zigzag, Cu and Co atoms are separated by a near-neighbor distance of  $2.55 \text{ \AA}$  consisting of a  $1.52 \text{ \AA}$  separation within the quasiperiodic plane and a  $\frac{1}{2}c = 2.04 \text{ \AA}$  separation along the periodic ( $c$ ) axis. We may describe the Cu–Co chain geometry, when projected onto the quasiperiodic plane, as an ‘arrow’ pointing from the Cu atom towards the Co atom. The directions of arrows in our deterministic model are in perfect agreement with the Penrose ‘single arrow’ matching rules. It is not known if this special arrangement of arrows is favored energetically, i.e. whether there is a unique ground state exhibiting the arrowing of the Penrose tiling.

Our original model was based on mock-ternary pair potentials. In the present paper, we employ a more rigorous all-electron ab initio approach utilizing the locally self-consistent multiple scattering (LSMS) method [7] based upon density functional theory. This is an order- $N$  method that is particularly well adapted to ab initio calculations on alloy systems with complex structures. The major advantage of order- $N$  methods is their computational effort scales linearly with the number of atoms in the unit cell. We employ a muffin-tin approximation for the potential and von Barth–Hedin exchange-correlation for the local density approximation.

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The muffin-tin approximation for potentials can be dangerous when applied to the structures in which different atoms have different muffin-tin radii. This may lead to non-physical energy shifts of their semi-core levels, and invalidate the energy change of atomic swap between inequivalent sites. All atoms involved in our swap lie on geometrically equivalent tile edge sites and therefore share equal muffin-tin radii.

Because our method demands periodic boundary conditions, we must carry out our calculations for quasicrystal “approximants”, periodic crystalline structures whose complex unit cells contain fragments of the infinite quasicrystal structure. The calculations reported in this paper treat two distinct 50 atom structures containing only hexagonal tiles, two tiles per unit cell. The atomic formula for both structures is the same,  $\text{Al}_{34}\text{Co}_{10}\text{Cu}_6$ . These structures are illustrated in Fig. 1a and b. Space group and lattice constants are, respectively, symmetry  $mC$  with a cell  $23.3 \times 7.6 \times 4.09 \text{ \AA}^3$  and  $oP$  with a cell  $14.4 \times 12.3 \times 4.09 \text{ \AA}^3$ . All atoms occupy idealized positions defined by the model of Cockayne and Widom — no relaxation has been performed. The atoms are all at height  $\frac{1}{4}c$  or  $\frac{3}{4}c$  except for the cell vertex and center atoms that are at height 0.

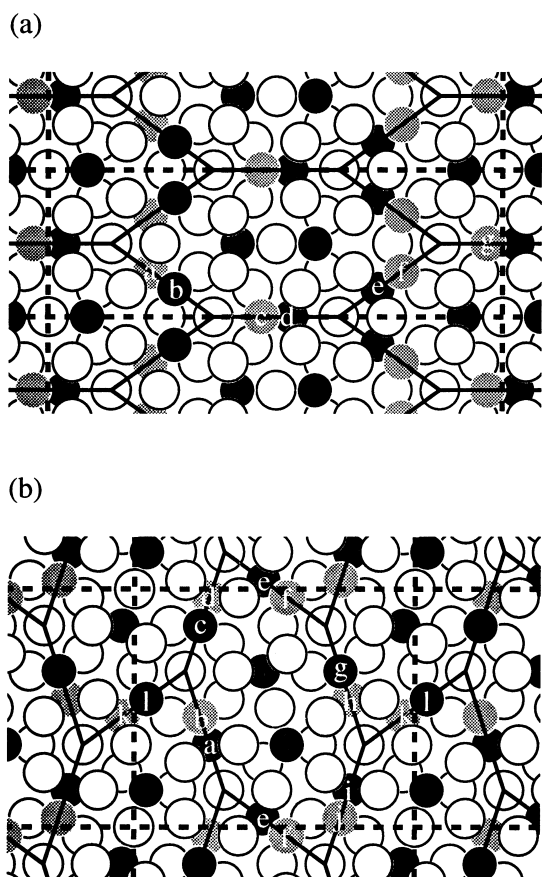


Fig. 1. (a) Monoclinic and (b) orthorhombic tilings, both utilizing orthorhombic cells as indicated with dashed lines. Open circles denote Al, black disks denote Co and gray disks denote Cu. Atoms labeled a–l are discussed in the text.

### 3. Results

We employ swaps of atoms among the labeled sites in Fig. 1 to convert directed (CoCu) bonds to pure (CoCo and CuCu) bonds and also to reverse bond directions. Because of the periodic boundary condition, the energy changes are calculated as if the swaps are performed simultaneously among all periodic images of the calculation cell. Approximate energies for truly localized swaps may be inferred: the  $a$  and  $b$  lattice constants are sufficiently large that interaction of a swap bond with its periodic images in the  $x$ – $y$  plane should be quite weak; interaction with images displaced by  $\pm c$  are quite strong because they involve nearest-neighbor atoms, but may be estimated because they create pure (CoCo and CuCu) bonds whose energies we will determine.

To present our data, we need a notation for different structures considered. Those based upon the monoclinic and orthorhombic structures depicted in Fig. 1a and b are denoted, respectively, M and O. Atomic swaps are denoted with suffixes of the form  $Sxy$ , where  $x$  and  $y$  are the labels of the sites whose atoms have been swapped. For example, MSab reverses a directed bond, and MSdg replaces the pair of horizontal directed bonds, in Fig. 1a with a pair of pure bonds. Energy differences are reported in Table 1 between pairs of structures, always subtracting the lower energy structure from the higher, resulting in positive energy changes.

From our total energy calculations, for the structures M and MSdg we determine the energy difference  $\text{MSdg} - \text{M} = 0.168 \text{ eV/cell}$ . Apparently there is a substantial energetic preference,  $0.168 \text{ eV/cell}$ , for directed bonds as opposed to pure bonds. To gauge the strength of this preference, we consider dimensionless energy units by dividing the strength of a preference in eV by  $k_B T = 0.0862 \text{ eV}$  at  $T = 1000 \text{ K}$ , a typical temperature at which quasicrystals form and are clearly equilibrium phases. We must take care of the number of bonds involved in each swap, recognizing the periodic boundary conditions. For example, in the swap MSdg, four directed bonds are lost and four pure bonds created. Thus, the energy change for swapping one pure CoCo and one pure CuCu bond with a pair of directed CoCu bonds is  $\frac{1}{2}0.168 \text{ eV} = 0.084 \text{ eV}$  and the dimensionless energy change is  $0.102 \text{ eV}/k_B T = 0.97$ .

When interpreting energy differences in terms of bond strength, we must recognize assumptions underlying the interpretation. Of particular importance are the spatial range

Table 1  
Energy differences (eV/cell) among structures.

Comparison	Energy
MSdg – M	0.168
MSabScd – Msab	0.011
M – MSabScd	0.029
Osab – O	0.130
Osgb – O	0.099
OSabSgb – O	0.230

and many-body nature of interatomic interactions. Attributing the energy difference between structures to the presence or absence of certain bonds implies a degree of spatial localization of the interatomic interactions. Pair potentials used to model interatomic interactions in similar compounds [8,9] exhibit long-ranged decaying oscillations that are especially strong between transition metal atoms. Many-body interactions, also, are especially strong when one transition metal atom has multiple transition metal near-neighbors. Consequently, the bond strength calculated here applies rigorously only to the case where entire zigzags of alternating Co and Cu are replaced with entire zigzags of pure Co and pure Cu.

Presumably the energetics of certain other bonding configurations will be consistent in sign and rough magnitude with the calculation given above. Consider stacking disorder, e.g., double the unit cell of the monoclinic structure along the  $c$  axis, and compare the energy of the structure MSdgM (MSdg placed above the structure M) with the energy of the structure MM (M placed above itself). Counting near-neighbor transition metal bonds, we find four directed bonds are replaced with four pure bonds in MSdgM compared with MM. It seems likely that the energy difference MSdgM – MM will be positive and similar in magnitude, but not *exactly* equal, to MSdg – M.

We extracted the energy for replacing directed bonds with pure bonds using the monoclinic structure in Fig. 1a because the bonds involved in this particular swap do not participate in any  $72^\circ$  vertices, allowing a clean separation of the energy associated with chemical ordering from the energies associated with arrow patterns at  $72^\circ$  vertices. There should be some energy associated with  $144^\circ$  vertices, and some even longer-ranged interactions with tile edges that do not share a vertex in common with the edges involved in the swap. We presume that these interactions are weak compared with the 0.168 eV energy found for this swap. Our later discussion confirms this.

Now, we evaluate the energetics of edge arrowing patterns at  $72^\circ$  vertices. We denote a vertex as outward, mixed or inward according to whether both arrows point in the outward direction, one is out and the other in, or both point inwards. The Penrose rules demand arrows point outwards, but periodic boundary conditions force at least two matching rule violations. In Fig. 1b, the arrow rules are satisfied (arrows point outwards) at two vertices (efj and ghkl) but violated (arrows are mixed) at (abkl) and (cdef). We believe this arrowing pattern represents the lowest possible energy for the tiling of Fig. 1b.

Our numerical results support this claim. By reversing bonds, we may vary the numbers of inwards, mixed and outwards vertices, e.g., interchanging atoms a and b converts the  $72^\circ$  vertex (abkl) from mixed to inwards. Such a swap raises the total energy by 0.130 eV/cell. Similarly interchange of atoms g and h converts the  $72^\circ$  vertex (ghkl) from outwards to mixed. Such a swap raises the total energy by 0.099 eV/cell.

The energy changes just presented include contributions from the interaction of edge arrowing within a  $72^\circ$  vertex and also interactions within  $144^\circ$  vertices. We can isolate certain linear combinations of  $72^\circ$  and  $144^\circ$  interactions. Comparing MSabScd with MSab isolates the combination (2 mixed-in-out = 0.011 eV/cell) of  $144^\circ$  vertex interactions without any contribution from  $72^\circ$  vertex interactions. In contrast, comparing M with MSabScd isolates the combination (2 mixed-in-out = -0.029 eV/cell) of  $72^\circ$  interactions without any contribution from  $144^\circ$  vertices. It seems that the  $72^\circ$  interactions are indeed stronger than the  $144^\circ$  interactions, roughly by a factor of 3. Unfortunately, even comparing all possible edge arrowing patterns in Fig. 1a and b it is impossible to determine individually all  $72^\circ$  and  $144^\circ$  vertex interactions.

To gauge the strength of interactions among arrows that do not share a vertex in common, we compare the energy change for two simultaneous swaps with the sum of the single swap energy changes. For example, consider the interchange of atoms a and b. We find that the resulting energy change is independent of the orientation of the bond (gh) to the accuracy of our calculations (about 0.001 eV/cell). Note that the bond (gh) is located across the short axis of the hexagon from the bond (ab). The Penrose rules demand that these bonds be parallel.

#### 4. Discussion

Our conclusion, based upon these calculations, is that in the decagonal phase of Al–Co–Cu chemical ordering along tile edges is favored and that the directionality of these bonds at  $72^\circ$  vertices tends to follow the sense of the Penrose arrowing.

The energy scale associated with chemical ordering and vertex interactions is roughly comparable to  $k_B T$  at  $T = 1000$  K. At this temperature there will be an evident preference for directed bonds rather than pure bonds. Among the directed bonds, there will be an evident preference for arrowing to follow the Penrose rules at  $72^\circ$  vertices. But the energies involved are sufficiently small that a substantial minority of bonds will lack arrows, and among the tile vertices with two arrowed bonds a substantial minority will violate the Penrose rules. Monte Carlo simulations that distribute a set of atoms among a set of allowed sites, weighted according to the total energy of a given configuration, could shed considerable light on the statistics and possible phase transitions of the model.

Several additional questions must be examined before the true ground state may be identified. The HBS tile set is overcomplete, so quasiperiodicity does not fix the relative numbers of HBS tiles. Phason flips can transform hexagon–star pairs into pairs of boats. The energetics of this transformation define a “chemical potential” for the tile numbers. Currently, we do not know the energy of this phason flip.

Another consideration is the role of atomic relaxation. Holding atoms fixed on the ideal sites shown in Fig. 1, we found the main interaction among edge arrows occurred at  $72^\circ$  and  $144^\circ$  vertices. This finding is consistent with interatomic interactions that are not too long-ranged. However, elastic interactions in solids typically fall off slowly raising the possibility of energetic effects not yet accounted for in which the edge arrowing couples to the elastic strain field.

Even focusing on short-ranged effects, atomic displacement may play a role. For example, we choose to occupy the symmetric site at the center of a hexagon (see the center of the unit cell in Fig. 1b) with an Al atom. Additional, unoccupied, ideal sites lie nearby, displaced slightly from the center along the long axis of the hexagon. Possibly, the symmetry breaking of the hexagon due to the orientation of the nearby bond (ab) could force the Al atom to one of these nearby sites. This asymmetric Al position could, in turn, influence the orientation of the nearby bond (gh), creating an effective interaction between (ab) and (gh).

In conclusion, we find that chemical ordering on tile edges is strongly favored in Al–Co–Cu decagonal quasicrystals. Interactions among arrow directions at  $72^\circ$  vertices favor arrowing patterns that obey a subset of the Penrose matching rules. We note, however, that this subset of the Penrose rules is insufficient to force quasiperiodicity. Furthermore, we expect significant interactions associated with  $144^\circ$  vertices, which have no counterpart in the Penrose rules. Further calculations on larger approximants are needed to

identify this complete set of arrow interactions and identify the ground state of the model.

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