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 AlCoCu. 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.

Keywords: Decagonal Quasicrystal, AlCoCu, ab-initio

1. Introduction

A fundamental question in the field of quasicrystals is the origin of thermodynamic stability of these non-periodic structures. Competing explanations 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]. Experimental evidence fails to unambiguously settle the matter, and the true situation is certainly more complex than either of the two extremes just described. Considerable progress has been made in two areas that, together, pave the way for additional theoretical insight on the problem. First, highly reliable structural models identify the positions and chemical identity of the majority of atoms in a variety of decagonal and icosahedral phases. Second, 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. The preferred positions and chemical identities of atoms within a tile may be coupled to the environment in which the tile sits. Conversely, the environment is influenced by the presence of the tile and its atomic decoration. This paper explores the coupling between tile decoration and local tiling structure in decagonal AlCoCu. We focus especially on the chemical ordering between Co and Cu atoms along tile edges [5]. 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° vertices is consistent with a subset of the Penrose matching rules.

2. Model and calculational method

We recently introduced a model for decagonal Al-CoCu based upon tilings of space by hexagon, boat and star-shaped tiles (HBS tilings) decorated deterministically with atoms [5]. 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 Å consisting of a 1.52 Å separation within the quasiperiodic plane and a $c/2$=2.04 Å 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 is in perfect agreement with the Penrose 'single arrow' matching rules [6]. It is not known if this special arrangement of arrows is favored energetically. If there were a unique ground state exhibiting the arrowing of the Penrose tiling, then it is conceivable that quasiperiodicity in this model would be forced energetically.

Our original model was based on mock-ternary pair potentials. Pair potentials provide only an approximation to the true total energy because they neglect many-body interactions that might be important, especially for transition metal atoms with two or more transition metal neighbors as indeed occur along tile edges. Here we consider Cu as a transition metal atom due to the proximity of its d-orbits to the Fermi level. An added uncertainty in our previous calculations involved our treatment of the Cu interactions. In the absence of genuine Cu potentials we treated Cu as a 50%-50% mixture of Al and Co.

In the present paper we employ a more rigorous all-electron ab-initio approach utilizing the Locally Self-consistent Multiple Scattering [7] (LSMS) method 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. Each processor in a parallel supercomputer treats the electron scattering problem for an individual atom, including multiple scattering effects associated with neighboring atoms within a "local interaction zone". Local charge density and one-electron potentials are iterated until self-consistency is achieved. Each self-consistent iteration takes approximately 1 minute on a Cray-T3E system, regardless of the number of atoms in the structure under consideration. Typically 50-100 iterations are required to achieve convergence for a 50 atom structure starting from pure elementary potentials.

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. Under this condition, energy change calculated by LSMS are comparable to those calculated by VASP [8, 9], an electronic structure calculation package using a plane wave pseudopotential method.

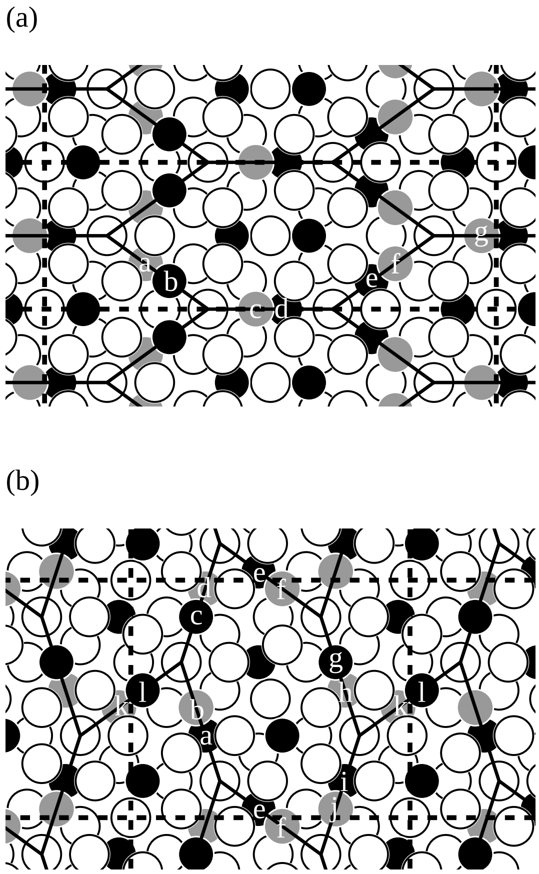

Fig. 1. (a) Monoclinic and (b) orthorhombic tilings, both utilizing orthorhombic cells as indicated with dashed lines. Open circles denote Al, Black disks denote Co and gray disks denote Cu. Atoms labeled a-l are discussed in the text.

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, $Al_{34}Co_{10}Cu_6$. These structures are illustrated in figure 1a and b. Space group and lattice constants are, respectively, symmetry mC with a cell $23.3 \times 7.6 \times 4.09$ Å^3 and oP with a cell $14.4 \times 12.3 \times 4.09$ Å^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 $c/4$ or $3c/4$ except for the cell vertex and center atoms that are at height 0.

3. Results

We employ swaps of atoms among the labeled sites in figure 1 to convert directed (CoCu) bonds to pure (CoCo and CuCu) bonds and also to reverse bond directions. All energy changes are reported "per cell". Because of the periodic boundary condition, the energy changes are calculated as if the swaps are preformed 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 figures 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 figure 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.

Table 1. Energy differences among structures. Units eV/cell.

Comparison	Energy	Comparison	Energy
MSdg-M	0.168	OSab-O	0.130
MSabScd-MSab	0.011	OSgh-O	0.099
M-MSabScd	0.029	OSabSgh-O	0.230

From our total energy calculations for the structures M and MSdg we determine the energy difference MSdg-M=0.168 eV/cell. Apparently there is a substantial energetic preference, 0.168 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 eV at T=1000K, 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, 4 directed bonds are lost and 4 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 0.168eV/2=0.084eV 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 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 [10] 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, for example. Double the unit cell of the monoclinic structure along the c axis, and compare the energy of the structure MSdgM (MSdg placed above the the structure M) with the energy of the structure MM (M placed above itself). Counting near-neighbor transition metal bonds we find 4 directed bonds are replaced with 4 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 figure 1a because the bonds involved in this particular swap do not participate in any 72° vertices, allowing a clean separation of the energy associated with chemical ordering from the energies associated with arrow patterns at 72° vertices. There should be some energy associated with 144° 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° 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 figure 1b the arrow rules are satisfied (arrows point outwards) at two vertices (efij 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 figure 1b.

Our numerical results supports this claim. By reversing bonds we may vary the numbers of inwards, mixed and outwards vertices. for example, interchanging atoms a and b converts the 72° 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° 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° vertex and also interactions within 144° vertices. We can isolate certain linear combinations of 72° and 144° interactions. Comparing MSabScd with MSab isolates the combination (2*mixed-in-out=0.011 eV/cell) of 144° vertex interactions without any contribution from 72° vertex inteactions. In contrast, comparing M with MSabScd isolates the combination (2*mixed-in-out=-0.029 eV/cell) of 72° interactions without any contribution from 144° vertices. It seems that the 72° interactions are indeed stronger than the 144° interactions, roughly by a factor of 3. Unfortunately, even comparing all possible edge arrowing patterns in figures 1a and b it is impossible to determine individually all 72° and 144° 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 AlCoCu chemical ordering along tile edges is favored and that the directionality of these bonds at 72° 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=1000K. 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° 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 hexagon, boat and star 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 figure 1, we found the main interaction among edge arrows occurred at 72° and 144° 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 figure 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 AlCoCu decagonal quasicrystals. Interactions among arrow directions at 72° 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 [11]. Furthermore, we expect significant interactions associated with 144° 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.

5. Acknowledgments

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