Ternary model of an Al-Cu-Co decagonal quasicrystal

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We propose a structural model for decagonal Al-Cu-Co quasicrystals based upon existing experimental diffraction data supplemented by total energy calculations. Exploiting the observation that Cu substitutes for both Al and Co in the structure, we deduce the full Al-Cu-Co ternary structure using electronic-structure-based pair-potentials for Al-Co binary compounds. The model is a decoration of tiles related to the Penrose rhombus tiling. Strong chemical ordering between Cu and Co leads to chains of alternating Cu and Co atoms. These chains project onto tile edges, where they define arrows. At low temperatures, the interatomic potentials lead to rules fixing the relative orientation of a majority of the arrows. These rules are a subset of the Penrose rhombus matching rules.

More than a decade after the discovery of quasicrystals [1] answers are emerging to the fundamental question [2] "Where are the atoms?". X-ray and neutron diffraction experiments successfully determine the location of the majority of atoms in quasicrystals [3]. Still, important questions remain. Quasicrystal structure refinements based on a finite number of diffraction peaks exhibit split atoms and atoms whose chemical identity can not be determined [4,5]. Species determination is especially difficult for compounds such as Al-Cu-Co that contain elements near each other in a row of the periodic table, since their x-ray form factors are nearly equal. Furthermore, chemical disorder and partial occupancy is not well described. For example, a partially occupied site of high atomic number may mimic a fully occupied site of low atomic number. The atomicity condition is insufficient to resolve these issues; additional methods are required to investigate quasicrystal structure in greater detail.

We have developed techniques to supplement experimental diffraction data with total energy considerations to resolve the above difficulties [6,7]. Here, we apply these techniques to create a model of the decagonal quasicrystal phase of Al-Cu-Co [8]. This phase exhibits quasiperiodic atomic layers stacked with a net 4 Å periodicity in the perpendicular direction. We focus on this compound because its stable quasicrystalline phase has been well studied by diffraction, but experimental information suffers difficulties of the type described above. Furthermore, the existence of electronic-structure-based pair-potentials for Al-Co alloys [9] allow total energy calculations to discriminate among candidate structures. We deduce the ternary alloy structure using only Al-Co binary potentials.

After we review the current experimental knowledge of Al-Cu-Co decagonal phases, we discuss our computational method and then our results. Our results include an ideal hyperspace model and a corresponding real space structure. We describe the real space structure from two perspectives: linked clusters and space-filling tilings. We show that chemical ordering between Cu and Co enforces a subset of the Penrose matching rules.

The temperature- and composition-dependent phase diagram of Al-Cu-Co alloys is well studied experimentally [10]. While the full composition range of thermodynamic stability of the decagonal phase shifts and widens as temperature increases, the principal domain of phase stability surrounds a straight line in the composition plane

$$Al_{73.5-0.5x}Cu_xCo_{26.5-0.5x}, \tag{1}$$

for $12 < x < 24$. Notice that Cu substitutes in roughly equal proportions for Al and Co in this compound.

Close to $x = 0$ there exists a monoclinic structure, $(Al,Cu)_{13}Co_4$, for which the ternary structure is known up to $x = 0.06$ [11]. This structure contains decagonal motifs, but has somewhat different local structure compared with decagonal Al-Cu-Co, including an 8 Å stacking periodicity. Cu preferentially substitutes for Al in this monoclinic structure, while Cu preferentially substitutes for Co in the CsCl structure of AlCo [12].

The structure of decagonal Al-Cu-Co has been well investigated by x-ray diffraction by Steurer and Kuo [4]. They analyze the structure through the hyperspace crystallographic method applicable to any perfectly quasiperiodic structure [13]. Assuming that the real-space atomic positions may be represented as intersections of physical space with a fictitious five-dimensional crystal, mathematical transformations of the diffraction intensities reveal the cell parameters and decoration of the five-dimensional unit cell. The unit cell is the product of an A_4 lattice [14] of lattice parameter $\sqrt{5}\, a_0 = 3.368$ Å with a Z_1 lattice of lattice parameter $c = 4.148$ Å. The structure obtained from the intersection with physical space possess a screw axis parallel to the periodic direction. The space group is $10_5/mmc$.

Three symmetry-independent atomic surfaces (see Fig. 1) decorate the unit cell deduced from experiment. Atomic surfaces concentrate electron density in bounded, nearly flat, regions oriented perpendicularly to real space. The positions and multiplicities of the atomic surfaces in the unit hypercell are given in Ref. [4]. The distribution of chemical species is not precisely known, but it is believed that atomic surfaces 1 and 3 contain mostly aluminum, and atomic surface 1 is empty near its center. Atomic surface 2 contains transition metals (Co and Cu) near the center and Al around the edges.

We refine the atomic structure using a fixed-site Monte Carlo simulation [7]. A set of ideal atomic positions is defined by the experimentally determined atomic surfaces. Our Monte Carlo simulation treats a lattice gas of atoms occupying a subset of these ideal sites. Because the sizes and shapes of atomic surfaces are not precisely determined experimentally, and indeed the occupation probabilities may fall off smoothly near the atomic surface edges, we deliberately oversize the atomic surfaces (see dashed lines in Fig. 1). This way we include all experimentally plausible atomic positions, and also can investigate the energetics of atomic positions shown experimentally to be vacant. In addition to the oversized atomic surfaces, we include additional "averaged" sites described in more detail below.

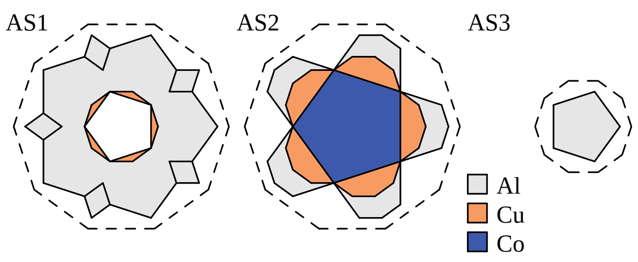

FIG. 1. Atomic surfaces. Dashed lines show outlines of oversized atomic surfaces used to generate site list. Colored regions show deterministic model that agrees well with simulation results. Gray, orange and blue denote, respectively, Al, Cu and Co atoms.

We cannot directly perform a Monte Carlo simulation of the Al-Cu-Co ternary alloy because interatomic potentials for this compound are not known at the present time. However, given that Cu substitutes equally for both Al and Co over a range of Cu content (eq. 1), we can identify likely Cu sites by using the *opposite* substitution, replacing Cu in the simulations with a ficticious species M (for mixed) that behaves as a mixture of Al and Co.

Because the axis of the domain of stability of the decagonal phase is along 0.5 Cu + 0.5 Al → Cu, we define interaction potentials of M atoms with other atoms of chemical species X = Al, M or Co as follows:

$$V_{\mathrm{MX}}(r) = 0.5 V_{\mathrm{AlX}}(r) + 0.5 V_{\mathrm{CoX}}(r). \quad (2)$$

Note that each potential $V_{\mathrm{MX}}(r)$ in eq. 2, including $V_{\mathrm{MM}}(r)$, can be expressed in terms of binary Al-Co interactions. As a test of these potentials, we investigated chemical ordering in monoclinic $(\mathrm{Al,Cu})_{13}\mathrm{Co}_4$. We confirm the finding of Freiburg and Grushko [11] that Cu (actually M in our simulation) preferentially substitutes for Al in three particular flat layer sites at 6 atomic % Cu.

Justification for the hypothesis that Cu occupies M sites lies in the status of Cu as a noble metal at the end of the 3d transition series. Its interactions with other atoms partially resemble interactions of transition metals because of the proximity of the d-orbitals to the Fermi surface. Quantitatively, however, the interactions may be dominated by its nearly free s-electrons because the d-orbitals are almost filled. Cu is thus an appropriate element to place at positions that are not reserved strictly for a transition metal (Co) or a simple metal (Al) [16]. However, total energies calculated for this mock-ternary cannot be quantitatively related to total energies for the true Al-Cu-Co ternary.

With these atomic interactions and oversized atomic surfaces, we calculate ideal atomic positions in orthorhombic approximant unit cells up to the 5/7 approximant with lattice constants of $60.4 \times 83.2 \times 4.1$ Å^3. This cell contains 2784 ideal sites plus 864 averaged sites, among which we must place approximately 1450 atoms. Because the quasicrystal phase exists over a range of composition, a deterministic structure at a given composition represents just one among infinitely many reasonable alternatives. Small changes in stoichiometry lead to small changes in simulated atomic surface occupation. We choose to examine a precise number of atoms and composition that permits a relatively simple deterministic tile decoration. One such choice is composition $\mathrm{Al}_{64.8}\mathrm{Cu}_{15.6}\mathrm{Co}_{19.6}$ with atomic volume 14.22 Å^3/atom. This composition lies inside the experimentally determined composition range, and the atomic volume compares well with the experimental value 14.3 Å^3/atom [4].

Applying the simulation method described above we deduce a structural model for decagonal Al-Cu-Co. The proposed model is close in energy to a true ground state of the Al-M-Co mock-ternary. Model atomic surfaces that match our simulation results and produce an especially simple ideal quasiperiodic structure are shown in Fig. 1, using colors to identify differing atomic species. The shapes and sizes of the atomic surfaces are similar to those deduced by Steurer and Kuo. One difference is the partitioning of the transition metal region of atomic surface 2 into separate regions of Cu and Co. A Cu shell surrounds the central Co shell in atomic surface 2. Also, our model includes some Cu regions inside atomic surface

1 surrounding its empty center. Our model for Cu/Co ordering differs from that proposed by Burkov [17,18].

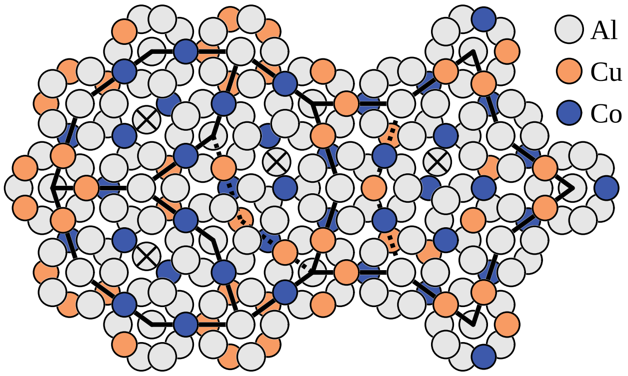

FIG. 2. Tiling decoration model for Al-Cu-Co based on Monte Carlo simulations. All atoms shown are at $z = 0.25$ or $z = 0.75$ except for those on tile vertices and those marked by an X.

The structure is based on columnar clusters containing 11 atoms per 4 Å repeat distance. Pentagons of alternating orientation are located every 2 Å along the clusters. Pentagons with 4 or more Al atoms (Al-rich) alternate with pentagons with 2 or fewer Al atoms (Al-poor). Additional Al atoms in Fig. 2, are located along the axis of the cluster, either 0.97 Å above or below the planes of the Al-rich pentagons.

Columnar clusters centered on axes 6.4 Å apart link together. The cluster pentagons all have the same orientation within a given atomic layer, respecting the 5-fold rotational symmetry of each layer. However, the Al-rich pentagon in a given layer of one cluster is linked to the Al-poor pentagons in the same layer of its neighboring clusters. The two layers are thus chemically equivalent, leading to the 10_5 screw axis.

The centers of these clusters define vertices of tiles. Three tiles are observed, shaped like the hexagon, boat and star shown in Fig. 3 and also outlined in Fig. 2. When two clusters link, bonds form between neighboring Cu and Co atoms from each cluster. One cluster contributes Co atoms in its Al-poor atomic layers to the bonds; the other cluster contributes Cu atoms in its Al-poor atomic layers. This leads to an alternation of Cu and Co atoms along a zigzag chain extending along the c axis, lying in the plane spanned by this axis and the Co-Cu bonds. Projected views of these zigzag chains lie on each tile edge in Fig. 3. The energetics of the mock-ternary model favor this ordering by 100 meV per 4 Å layer over the mean energy of Cu-only and Co-only chains. Similar chains of alternating Cu and Co atoms are found [11] in monoclinic $(Al,Cu)_{13}Co_4$, which is comprised of hexagon-shaped tiles.

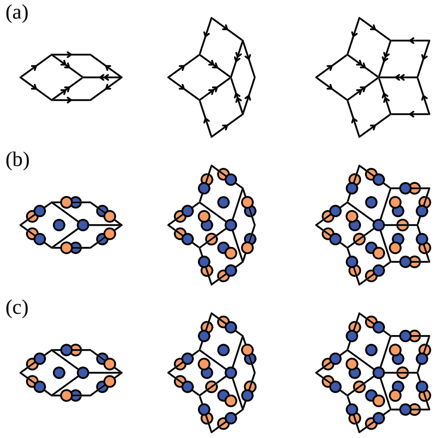

FIG. 3. Relationship between Penrose tiles and current model. (a) Penrose tiles and matching rules. (b) Cu and Co atoms in Penrose tile decorations. (c) Cu and Co positions that minimize intratile energies.

Arrows on Penrose rhombus tiles (shown in Fig. 3a) force quasiperiodic ordering. When all double arrow edges of the Penrose tiling are removed, one obtains a set of three tiles, the hexagon, boat and star tiles of our model, whose single arrow matching rules force a quasicrystal. Interestingly, the alternating chains of Cu and Co atoms of our tiling model can be mapped onto arrows located on the tile edges. As shown in Fig. 3(b), first the chains are projected into the xy plane, leading to a Cu and a Co atom on the tile edge, then a single arrow is drawn from the projected Cu position toward the projected Co position.

Although the tile decoration model presented here respects matching rules, we do not claim that the present mock-ternary interactions force these matching rules nor that they lead to a quasicrystalline ground state. To investigate this topic further, we took each tile and held all atoms fixed except for those on the tile edges. We then determined the chain orientations that minimized the intratile energies. The corresponding arrows are shown in Fig. 3(c). There are two arrow orientations that disagree with those of the Penrose tiling, one each in the hexagon and boat. When these arrows are reversed to agree with those in the Penrose tiles, the energy increases by only about 10 meV/tile/4 Å. Any other arrow reversal raises the energy by at least 70 meV/tile/4 Å.

Intertile interactions, not included in the calculations leading to Fig. 3(c), complicate the energetics. For example, frustration of the arrowing illustrated in Fig. 3(c) occurs in boat-star pairs like the one shown in Fig. 2. The ground state of the boat-star segment is the one shown, with all the arrows identical to the Penrose tiling matching rule arrows. Similarly, the relative orientation of the edge arrows on the hexagon tile is context dependent in the simulations. It is impossible for the arrows on every tile in an approximant to agree with those of the Penrose tiling; we find in our simulations that the disagreements occur most frequently in the hexagons.

There are additional tile interior atoms not belonging to clusters. The interior Co positions shown are highly stable in the simulations. Interior Cu and Al positions are more variable. Interior atoms marked by an X are located at $z = 0$ or $z = 0.5$. These are the so-called averaged sites. We introduce them because some pairs of ideal aluminum sites (those associated with the rhombic regions near the edges of atomic surface AS1 in figure /refasurf.eps) are separated in real space by only 2.27 Å. These pairs are never simultaneously occupied, but rather they share a single aluminum atom. Often it is energetically favorable for this atom to sit at the symmetric averaged site midway between the two ideal sites. This site is an 2.82 Å from the nearest occupied Al, a separation commonly observed in Al-Co alloys, and energetically reasonable.

In our simulation, these averaged positions are highly stable for Al atoms in the hexagonal tiles. In the boat and star tiles, some of the ideal AS1 sites remain occupied, without displacement to the averaged sites. These Al atoms are 2.44 Å from the nearest occupied Al site. This separation, and all other smallest interatomic spacings in our model, are comparable to spacings observed in $(Al,Cu)_{13}Co_4$.

Note that, as drawn in the model, there are interior Cu-Co chains in the boat and star tiles. These can define new tile edges (shown with dashed lines in Fig. 2) to form interior subtiles shaped like bowties. The bowtie is the region involved in the smallest tiling flip changing one HBS tiling to another. The star-boat pair in Fig. 2 can be reversed by the exchange of a single column of Al atoms with a column of Cu atoms located 2.44 Å away, along with small displacements of 4 other columns of Al atoms. The hexagon-boat pair can be reversed in the same way.

Many features of the simulated Al-Cu-Co structure exhibit fluctuations down to very low temperature ($<$ 100K). These features include: (1) the positions of some tile interior Cu atoms and (2) the z coordinates of cluster axis and tile interior atoms located off-plane. Additionally, a full simulation should allow for relaxation of atoms from our fixed sites. The fine details of the ground state are likely to depend on the interatomic potentials used. In particular, the energetics of tile edge arrows, with their implications for the origin of quasicrystalline stability, whether energetic or entropic, will require very accurate interatomic potentials. Genuine ternary pair-potentials for Al-Cu-Co may be obtained from first-principles electronic-structure calculations. [19]

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