Structure Model of the Al-Cu-Co Decagonal Quasicrystal

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A structure model for the decagonal quasicrystals AlCuCo and AlNiCo is proposed. The model agrees with available experimental data, i.e., with three-dimensional and five-dimensional Patterson analysis of x-ray-diffraction data and with direct-space atomic patterns found by high-resolution electron microscopy. The model allows for a dualistic description. It can be viewed both as a set of specifically decorated overlapping decagonal clusters and as a cutting and projecting of only two simple "atomic surfaces."

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Among the numerous experimentally discovered decagonal quasicrystals, two alloys, $Al_{65}Cu_{20}Co_{15}$ and $Al_{70}Ni_{15}Co_{15}$, have attracted the most attention. They deserve this attention because of their outstanding properties: Up to cm-sized single crystals can be grown from melt, and they are thermodynamically stable and exhibit extremely sharp diffraction peaks (the coherence length is about 2000 Å) [1-7]. Moreover, the quality of the diffraction pattern improves upon annealing [3,4]. A decagonal quasicrystal has a layered structure, with every layer being a two-dimensional quasicrystal. The stacking of layers along the tenfold axis is usually presumed to be periodic. Although there are certain doubts regarding the stacking periodicity [8], this question will not be addressed below, and the structure will be considered periodic with a period c of approximately 4.5 Å [1-7]. The doubling of this period reported in *some* samples [1,6,7] is not taken into account.

The determination of the atomic structure of quasicrystals is not trivial, as standard crystallographic methods cannot be used straightforwardly because of the lack of periodicity. There are two general experimental approaches based on two theoretical perceptions of what quasicrystals are. One views a quasicrystal as a section of definite "atomic surfaces" in five-dimensional (5D) space, the coordinates of *individual* atoms being given by the cut method [9]. The atomic surfaces of a particular quasicrystal can be determined by measuring diffraction intensities, calculating the Patterson function (electron-density autocorrelation function), and deconvolving the Patterson function numerically. This method, previously used to treat icosahedral quasicrystals [10], has been recently applied to decagonal ones [5,6]. The other, competing, approach is based on the tiling and decoration concept [11], which views a quasicrystal as being built from two elementary cells, or tiles, which fill the space quasiperiodically. The 5D space is used within this approach to refer to the coordinates of the *tile vertices*, not individual atoms. Inside the tiles atoms are placed in positions that provide reasonable local packing. The two approaches are not mixed and are sometimes considered incompatible, which causes a sort of dispute between adherents of the two methods. Neither of the two approaches works perfectly. Direct determination of atomic surfaces by Patterson analysis relies on numerical structure refinement and gives only *approximations* of the atomic surfaces, which, after being cut and projected, often yield unrealistic local environments in physical space. On the other hand, whereas any tiling model can be viewed as a cut-and-project one, the number of atomic surfaces is, in general, equal to the number of atoms in the tiles. In all known cases [5,6,10] the Patterson analysis shows only two or three very simple atomic surfaces. At a first glance, this rules out the elaborate tiling models with many atoms in each tile which are usually introduced to achieve reasonable packing. One of the aims of this Letter is to present a structure which can be obtained by *both* cut-and-project *and* tiling-and-decoration methods, after certain restrictions are imposed on both of them. The model obtained in this way appears to be a good model of AlCuCo and AlNiCo. It agrees with experimental data: the results of 5D and 3D Patterson analysis of single-crystal x-ray-diffraction data [6,7] and the direct-space atomic patterns found by high-resolution electron microscopy (HREM) [3].

Cluster packing description.—There are two plane layers per vertical period in the proposed structure. Each has only fivefold symmetry, but the layer at $z=c/2$ is rotated by 36° with respect to the layer at $z=0$ revealing overall decagonal symmetry. The atomic structure in the x-y plane can be presented by two methods, whose equivalence has been established analytically. The first, a modified tiling-and-decoration method, is formulated as follows. Our structure is built from *one* building block, a decagonal cluster (Fig. 1). The particular atomic decoration of the cluster coincides 90% with the decoration inferred by Hiraga, Sun, and Lincoln from the HREM images [3]. The same cluster was also obtained by 3D Patterson analysis [7]. However, it is not enough to determine cluster decoration: One must find out how clusters are assembled together. Since *tiling* of the plane by decagons is impossible, a *covering* of the plane is introduced. Two clusters are allowed to overlap, but only the two overlappings shown in Fig. 1 are permitted. Note

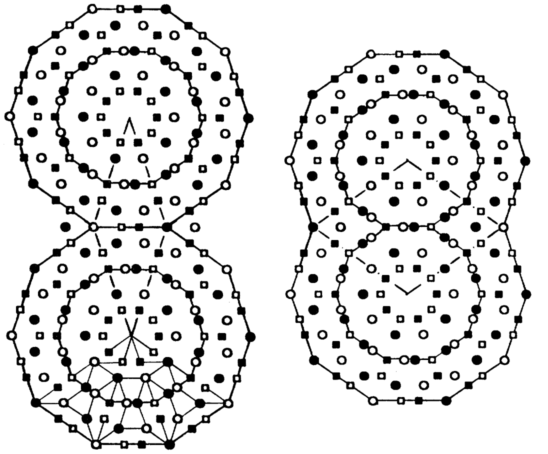

FIG. 1. Two allowed overlappings of decagonal clusters and corresponding tiles. A portion of the decagonal network hosting the atoms is shown. Circles, Al; squares, transition metal; open symbols, $z=0$; solid symbols, $z=c/2$ layer.

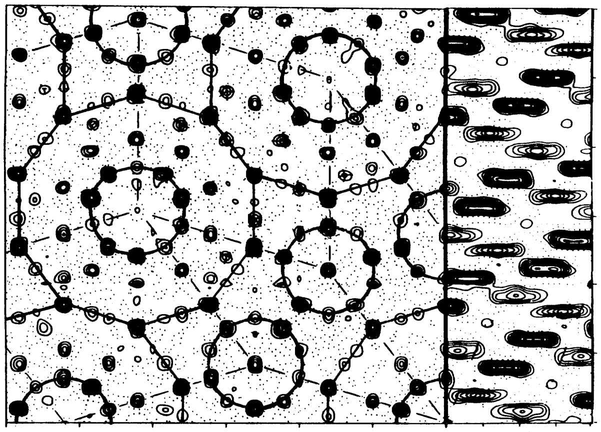

FIG. 2. Atoms in the decagonal plane as obtained from 5D Patterson analysis [6]. The right-hand panel is a section of atomic surfaces by a plane spanned by one parallel and one perpendicular basis vector.

that no atomic displacements are introduced when clusters intersect, nor are "glue" atoms [11] used.

Consider a covering of the plane by decagons such that if any two clusters intersect then the intersection is one of the two allowed ones (multiple intersections are not excluded). First, one has to prove that such a covering is possible. This has been done in [12] by proving that any such covering is equivalent to a *binary tiling*. A binary tiling (Fig. 2) is a tiling by two Penrose rhombi such that in every vertex all angles are either all even or all odd (the angles $2\pi/5$ and $4\pi/5$ are called even; $\pi/5$ and $3\pi/5$ are odd) [13]. This restriction has a physical basis: An even and an odd angle cannot meet in one vertex, because atomic decorations of their interiors are different and cannot be matched. The basic building blocks, decagonal clusters of 10.3 Å radius, are centered at odd vertices, whereas even vertices are corners of decagons (Fig. 1). Strictly speaking, the cluster has decagonal shape but only pentagonal symmetry; in particular, its corners are of two types ("colors"). When one goes around the cluster (i.e., an odd vertex) the colors of the decagon's corners (i.e., even vertices) alternate (Fig. 1). This leads to a "colored" binary tiling, with all odd vertices being equivalent and there being two inequivalent types of even vertices, which alternate as described above. The self-consistency of this alternation rule, not obvious from the definition, has been demonstrated in [12]. The structure can also be viewed as built from smaller decagons (of τ^{-1} radius) centered at odd vertices and from eleven-atom ringlike clusters of τ^{-3} radius centered at even vertices (do not confuse them with ten-atom rings inside decagons centered at odd vertices, Figs. 1 and 2). All the small decagons are oriented the same way, including coloring, whereas the colors of eleven-atom rings alternate. To transform the latter cluster from a "white" to a "black" state, one has to apply a screw axis transformation (36° rotation plus half-a-period vertical shift).

A local reshuffling move responsible for phasons is a standard binary-tiling flip [13]. Combined with the specific tile decoration (Fig. 1), it prescribes certain finite but moderate (a couple of angstroms) jumps of individual atoms (the details will be presented elsewhere).

Two features make the present model distinct from a general tiling-and-decoration model. First, binary tiling emerges as a consequence of rules for cluster overlapping and the decoration of the Penrose tiles is deduced from the cluster decoration. Second, all atoms sit on a decagonal network, i.e., every two atoms can be connected by a path made of intervals of length a having ten decagonal orientations ($a=2.44$ Å, whereas the cluster radius is $\tau^3 a=10.33$ Å). The scheme also demonstrates that imposing reasonable rules of overlapping inevitably leads to a 5D description.

Before mapping the present tiling description to the cut representation one should realize that there are infinitely many binary configurations and all of them are different from conventional Penrose tilings. When all of the tile configurations are ascribed equal statistical weights, one obtains random binary tiling [13]. When the binary tiling is viewed as a projection from 5D space with some acceptance domain with sharp boundaries, the binary tiling is called "ideal." There are some different choices of the acceptance domains; below, one choice will be made: The domain consists of three "pancakes," a decagon [14], and two 5-stars, which are shown in Fig. 3 as subdivisions of the whole polygons. The choice between random and ideal versions is equivalent to the choice between energy and entropy as a factor stabilizing quasicrystals [2-5,14,15]. The latter dispute is still unsettled and the present model cannot help to resolve it: The model may

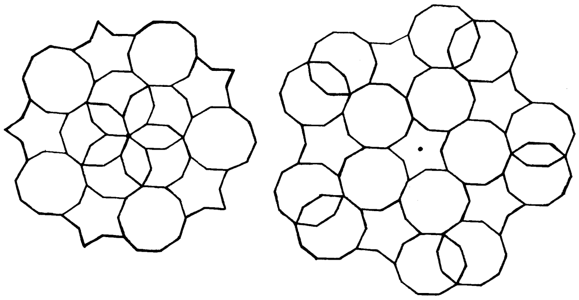

FIG. 3. Atomic surfaces of "ideal" structure (no phason disorder). Left, transition metal; right, Al. Decomposition to smaller polygons classifies local environments.

exist in both frameworks. However, the translation to the cut language is easier with the ideal binary tiling.

Cut-and-project description.—To describe the same structure in a cut formalism one has to lift the coordinates of the individual atoms up to 5D space. If the decoration of the Penrose rhombi were to be of a general type, the lifting would create dozens of atomic surfaces. However, straightforward analytic calculations show that in the present model the atomic surfaces merge together, forming only two larger atomic surfaces (Fig. 3). Thus, the second, equivalent, cut-and-project description is as follows: Coordinates of all the *individual* atoms can be obtained by cutting four atomic surfaces. Two of them, shown in Fig. 3, give the $z=0$ layer. One surface, occupied by Al, is centered at $-\mathbf{B}$, where $\mathbf{B}=(1,1,1,1,1)/5$; the other surface, occupied by transition (T) metal (Cu and Co, or Ni and Co, which are mixed randomly), is centered at $+2\mathbf{B}$. The $z=c/2$ layer is given by the same surfaces as in Fig. 3, but rotated by 36° and centered at $+\mathbf{B}$ (Al) and $-2\mathbf{B}$ (T). Subdivisions of the atomic surfaces in Fig. 3 reflect different atomic environments (the details will be presented elsewhere). The atomic surfaces are not of a general form: They are flat, have complicated boundaries (which were never tried in Patterson analyses), and are centered at special points of the 5D unit cell. The latter fact was noticed in virtually all experimental Patterson-analysis works, which might mean that tiling and cut duality holds for icosahedral and other quasicrystals. Note that the shapes in Fig. 3 have been obtained from exact geometric considerations, not from computer-assisted refinement of experimental data, as in [5] and [6].

The atomic positions in Fig. 2 have been obtained by Steurer and Kuo [6] by numerical 5D Patterson analysis of x-ray data. Their work had been published before Hiraga, Sun, and Lincoln's clusters were announced [3]. For this reason the authors of [6] did not use the knowledge of cluster geometry in their work; they determined atomic surfaces ("pancakes") in 5D space by direct numerical refinement. The atoms of Fig. 2 were obtained by cutting and projecting these experimentally determined pancakes. The lines showing the decagonal clusters and binary tiling have been added to the original figure of Ref. [6] by the author of the present paper. The agreement of Fig. 2 with the cluster representation is fairly good but not perfect. This can be attributed to the approximate character of the atomic surfaces in [6]: The authors restricted themselves to decagonal pancakes and conventional Penrose tiling, whereas real pancakes might have a more intricate shape, such as in Fig. 3, and the tiling is binary. Furthermore, the pancakes in Fig. 3 correspond to the ideal binary tiling. If the real quasicrystal is stabilized by entropy or, at least, contains a substantial amount of phason disorder, the boundaries of the atomic surfaces would not be as sharp as in Fig. 3. One more reason for a certain misfit between the theory and the experiment is the fact that the structure described above is a sort of ideal, stoichiometric structure; the real one may differ by elastic deformations, chemical disorder or, contrarily, ordering of Ni, Co, or Cu, deviation from stoichiometry, doubling or tripling of the unit cell along the tenfold axis, some puckeredness of the layers, etc. Nevertheless, one can easily see in Fig. 2 exactly the proposed decagonal clusters, and, moreover, the clusters overlap according to the rules shown in Fig. 1. The diffraction intensities calculated for the model agree with the measured ones [6] with an R factor of 16%. This accuracy has been achieved without any serious refinement: Only simple uniform phonon Debye-Waller factors were introduced.

General properties of the proposed structure.—(1) The space group is $P10_5/mmc$ (centrosymmetric), as verified by characteristic extinctions in both observed and calculated diffraction spectra [16]. (2) Kalugin's homology indices are (1,1), i.e., the number density in a decagonal layer is expressed via the basis reciprocal-lattice vector Q_{10000} as

$$n=\sqrt{5}\sin(\pi/5)(Q_{10000}/2\pi)^2(N_1+\tau N_2),$$

where N_1 and N_2, the homology indices, are both equal to 1. The latter fact means that from the homological point of view the atomic surfaces in Fig. 3 are rather simple [17]. (3) The calculated density of 4.53 g/cm^3 agrees well with the measured density of AlCuCo of 4.5 ± 0.05 g/cm^3 [6]. (4) The calculated stoichiometric composition is about $\mathrm{Al}_{60}T_{40}$; experimental data range from 62% to 68% Al. Note that real material might be off stoichiometry. (5) The interatomic distances are not shorter than 2.44 Å, which is acceptable for an Al-T bond. The volume per atom is about 13.9 Å^3, showing sufficiently dense packing; there are no big holes except for cylindric wells positioned at odd vertices. However, this is an experimental fact: Both HREM [3] and x-ray [6,7] data show that cluster centers are vacant.

Comparing the present model with the experimental data on $\mathrm{Al}_{70}\mathrm{Ni}_{15}\mathrm{Co}_{15}$ is obscured by the disagreement between the data of Refs. [5] and [18]. The model agrees with [18] with approximately the same accuracy as for AlCuCo (above). However, Ref. [5] reports not only a set of x-ray intensities different from that of [6] but even the space group *P*10/*mmm*. This might mean the existence of another decagonal phase in AlNiCo which is not described by the present model.

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