

Universal structure unit for AlLiCu, AlMnSi, and AlFeCu quasicrystals

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It is suggested that the structure of icosahedral quasicrystals is the result of dodecahedral arrangement of closest atoms observed in the AlLiCu, AlMnSi, and AlFeCu alloys. New cubic approximants of icosahedral quasicrystals are found. Unconventional projection scheme for construction of quasicrystals and their crystal approximants is discussed.

After a remarkable progress in the understanding of general principles of quasicrystalline structures,^{1,2} one of the basic questions seems to be still unresolved: what is the *local* arrangement of atoms which leads to the *global* noncrystalline symmetry of quasicrystals (icosahedral, decagonal, octagonal, etc.)? Earlier it was widely believed that icosahedral symmetry of quasicrystals is a result of icosahedral local arrangement of twelve atoms around a central atom; however, x-ray and neutron diffraction studies show that in real alloys only a minority of the atoms has the icosahedral coordination; moreover, the center of the icosahedron may be empty. Therefore, more sophisticated structure units are considered (like the orthorhombic triacontahedron for AlLiCu and the Mackay icosahedron for AlMnSi), which include about fifty (or even more) atoms. However, why these units are stable and how they are growing is not clear yet.

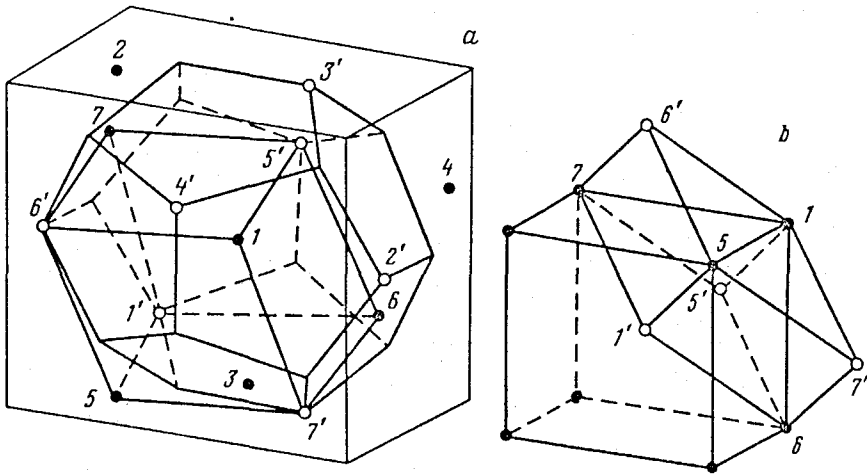


FIG. 1. The relationship between atomic arrangements in $\langle 2/1 \rangle$ (a) and $\langle 1/1 \rangle$ (b) cubic approximants. In (a), atom 1 is at the cube center, whereas all other atoms are on the cube faces. The ratio of lattice constant is τ , but the rhombohedra, drawn at both figures and marked by numbers, are equal.

In the present paper, we propose another local arrangement for the basic structure motif in icosahedral quasicrystals. We assume that most of the atoms have the closest neighbors at the vertices of dodecahedra, and it is shown that such motif may be found in the crystal approximants of AlMnSi and AlLiCu quasicrystals; the latest available experimental data³ give evidence for the same arrangement in AlFeCu quasicrystals. In this approach the positions with icosahedral coordinations arise as the places of frustration, where the dodecahedral arrangement leads to contradiction; therefore, it is not surprising that those positions may be empty.

It is convenient to start with the consideration of the structure units in the crystal approximants;⁴ the reason is that in the approximants only those positions can survive which are the most favorable energetically. The analysis of the numerous experimental data shows^{5,6} that at least four cubic approximants have been observed in the AlMnSi alloys: $\langle 2/1 \rangle$ (MnSi structure), $\langle 5/3 \rangle$ (α -AlMnSi), $\langle 13/8 \rangle$, and $\langle 34/21 \rangle$ with the lattice constants 4.6 Å, 12.6 Å, 33.1 Å, and 86.6 Å, respectively. The cubic approximant is labeled by two Fibonacci numbers, $\langle F_{n+1}/F_n \rangle$, if the most intense pseudofivefold reflections in this crystal have the Miller indices $\{F_{n+1}, 0, F_n\}$. The ratio of the lattice constants α_{n+1} and α_n of two succeeding approximants, $\langle F_{n+2}/F_{n+1} \rangle$ and $\langle F_{n+1}/F_n \rangle$, is close to the golden mean τ [$\tau = (1 + \sqrt{5})/2 = 1.618034\dots$]. To avoid confusion, it should be noted that there is another labeling scheme,⁴ in which α -AlMnSi crystal is labeled $\langle 1/1 \rangle$, but in this case we have the unnatural notation $\langle 0/-1 \rangle$ for the MnSi crystal.

Let us consider the MnSi $\langle 2/1 \rangle$ approximant with the space group $P2_13$; its unit cell contains eight atoms in $4a$ sites x, x, x at the threefold axes: four Mn and four Si. In crystallographic books it is referred to as a $B20$ or FeSi-type structure and is found in many alloys: AlMnSi, CoGeSi, GeRu, HfSn, and others.⁷ In the idealized structure of

this approximant (Fig. 1a), $x_A = 1/(4\tau)$ for A atoms (filled circles) and $x_B = 1 - x_A$ for B atoms (open circles).

This structure is a periodic system of interpenetrating dodecahedra: each A atom is surrounded by seven B atoms positioned at seven vertices of an ideal dodecahedron and vice versa. Therefore, the A - B bonds are directed along the threefold $\langle 111 \rangle$ direction and pseudo-threefold $\langle 01\tau^2 \rangle$ direction. Next, the atomic shell contains six atoms of the same species as the central atom; the A - A and B - B atoms are parallel to the pseudo-twofold $\langle 1\tau\tau^2 \rangle$ directions. The closest A - B distances are equal to $\sqrt{3}/(2\tau)$, whereas the closest A - A (or B - B) distances are slightly longer (τ^{-1}); thus there is a rather compact cluster with threefold symmetry, where the central atom is surrounded by 13 atoms. Further atomic shells are distorted by the periodicity and they should be analyzed in higher approximants.

Aside from the higher-order approximants, let us consider the relationship between the MnSi crystal and the lower-order approximant $\langle 1/1 \rangle$. The latter is a cubic crystal (Fig. 1b) with a $Pm3m$ space group known as $B2$ - or CsCl-type structure; its lattice constant a_1 is τ times smaller than a_2 ; if $A = B$, it is a conventional bcc crystal with $Im3m$ symmetry. It is interesting that many alloys are known in both modifications, shown in Fig. 1, with nearly the same density (AlPd, AlPt, FeSi, OsSi, etc.). The relationship between the two structures becomes evident if we compare the rhombohedra drawn at both figures: those rhombohedra are equal, but they have a different orientation relative to the cubic axes. In other words, we can say that inside the lower-order $\langle 1/1 \rangle$ approximant there is a piece of the $\langle 2/1 \rangle$ approximant (eight atoms, a complete unit cell!).

Such relationship is a general property of approximants. For instance, in the one-dimensional case, the structure of the $\langle F_{n+1}/F_n \rangle$ approximant contains the unit cell of the $\langle F_{n+2}/F_{n+1} \rangle$ approximant and even the unit cell of the $\langle F_{n+3}/F_{n+2} \rangle$ approximant. This gives us a way to construct higher-order approximants from the lower ones and to obtain a quasicrystal as a limit of this process. Fortunately, this procedure applies in the three-dimensional case too, but it is not a trivial job to find a larger unit cell inside another atomic structure, because the symmetry axes may have different orientations, as we can see in Fig. 1. Nevertheless, a direct computer search shows that the next Fibonacci approximant, $\langle 3/2 \rangle$, can be found inside the idealized MnSi structure (details of this procedure will be published elsewhere). The cubic axes of the approximant are directed parallel to the pseudo-twofold directions $\langle 1\tau\tau^2 \rangle$ in MnSi and the unit cell is τ times larger than that of MnSi. The space group of this approximant is $Pa3$, with 32 atoms per unit cell: eight A atoms in the $8c$ sites x,x,x and 24 B atoms in the general $24d$ sites x,y,z , where the calculated values of atomic coordinates are the following:

$$x_A = 1/(4\tau^2), (x_B, y_B, z_B) = (\sqrt{5}, 1, \tau^3)/(4\tau^2). \quad (1)$$

As in MnSi, the closest neighbors of each atom occupy vertices of dodecahedra: seven around each A atom and only six around each B atom. The interesting feature is the occurrence of eight holes in the x,x,x sites ($x = \tau/4$) with *icosahedral* coordination. If we try to continue the dodecahedral arrangement inside these holes, a new atomic site will appear too close to one of the old sites. Therefore, such holes may be considered as

TABLE I. Atomic sites in the cubic approximants of different order.

Labels and examples	Coordinates of atoms in a unit cell:		6-dim. sites
	theoretical	experimental	
$\langle 1/1 \rangle, \text{FeSi}$	0,0,0; 0.5,0.5,0.5	0,0,0; 0.5,0.5,0.5	000111
$\langle 2/1 \rangle, \text{FeSi}$	0.845,0.845,0.845	0.846,0.846,0.846	000111
MnSi, AlPt	0.155,0.155,0.155	0.138,0.138,0.138	000000
$\langle 3/2 \rangle$	0.095,0.095,0.095	0.097,0.097,0.097	000000
Au_3NaSi	0.214,0.095,0.405	0.226,0.133,0.408	100000
$\langle 5/3 \rangle$	0.191,0.191,0.191	0.187,0.187,0.187	000000
$\text{Al}_5\text{Li}_3\text{Cu}$	0.000,0.118,0.191	0.000,0.094,0.154	100000
$\text{Au}_3\text{Na}_2\text{Sn}$	0.000,0.309,0.118	0.000,0.305,0.117	100001
$\text{Au}_4\text{Na}_3\text{Si}_2$	0.118,0.191,0.382	0.157,0.190,0.406	010000
	0.427,0.000,0.500	0.404,0.000,0.500	021010
	0.191,0.000,0.500	0.199,0.000,0.500	111000

the places of frustration for the dodecahedral ordering. Surprisingly, the structure of the Au_3NaSi crystal is found to be very close to the $\langle 3/2 \rangle$ approximant: Na and Au atoms correspond to *A* and *B* atoms, respectively (see Table I), whereas Si atoms are in the holes; to my knowledge, this crystal has never been considered before as an approximant of quasicrystals.

As the next step, the unit cell of the $\langle 5/3 \rangle$ approximant can be found inside the $\langle 3/2 \rangle$ approximant; it is a very popular structure which is exemplified by many alloys. Similarly, it may be considered as the superpositions of the dodecahedral clusters, as shown in Fig. 1a, which are centered at the $(1,1,1)/(2\tau^2)$ points. Again, there are the icosahedral holes in the 0,0,0 and the $(1,\tau,0)/(2\tau^2)$ sites (not shown in Table I): the former is empty in $\text{Al}_5\text{Li}_3\text{Cu}$ and is occupied by Au in $\text{Au}_3\text{Na}_2\text{Sn}$, whereas the latter is occupied in all known alloys, enforcing small shifts of neighboring atoms. Perhaps because of those shifts, the dodecahedral local coordination was not recognized earlier in the $\text{Al}_5\text{Li}_3\text{Cu}$ approximant.

A more regular way to construct the approximants and quasicrystals is provided by the strip-projection method.⁸ The dodecahedral arrangement of seven atoms around the central atom can be described as a projection from a six-dimensional cubic lattice with one atom per unit cell, so that six basic vectors (100000),..., (000001) give sites of the six surrounding atoms:

$$\lambda_n(\tau^2, 1, 0); \lambda_n(0, \tau^2, 1); \lambda_n(1, 0, \tau^2); \lambda_n(-\tau^2, 1, 0);$$

$$\lambda_n(0, -\tau^2, 1); \lambda_n(1, 0, -\tau^2), \quad (2)$$

where the common factor λ_n depends on the order *n* of the approximant. The seventh closest atom is a projection of (000111), whereas the next shell of six atoms is projected from the points like (100010), etc. After a proper choice of a six-dimensional acceptance domain is made, all considered approximants and $\alpha\text{-AlMnSi}$ can be obtained. Such a projection scheme is unconventional: the basic vectors (100000),...,

(000001) are projected onto the *threefold* directions, instead of the *fivefold*. The conventional fivefold basic vectors are the linear combinations of the threefold vectors given by Eqs. (2), and vice versa. Therefore, the icosahedral symmetry of quasicrystals can be reached in each scheme. It is interesting that the holes discussed above are the projections of body-center points of the six-dimensional lattice. Another fact worth noting is that additional atomic shells around the central atom look like those in the Mackay icosahedron.

Additional evidence for dodecahedral arrangement can be found in the neutron-diffraction data: It was shown^{3,9} that both in AlMnSi and AlFeCu quasicrystalline alloys, the closest atoms are located at the vertices of a regular dodecahedron (their maximum number was seven). In those studies, the dodecahedral arrangement was obtained as a result of a special decoration of a six-dimensional unit cell.

In conclusion, the dodecahedral structure unit is found to be a universal feature in quasicrystals and their crystalline approximants. The proposed projection scheme seems to be the most natural for the description of the local dodecahedral arrangement. Another advantage of our approach is that no special atomic decoration is required.

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