

# UNIVERSAL STRUCTURE UNIT FOR $\text{AlLiCu}$ , $\text{AlMnSi}$ , AND $\text{AlFeCu}$ QUASICRYSTALS

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It is suggested to describe the structure of icosahedral quasicrystals as a result of the dodecahedral arrangement of closest atoms, really observed in the  $\text{AlLiCu}$ ,  $\text{AlMnSi}$ , and  $\text{AlFeCu}$  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 <sup>1,2</sup>, 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 rhombic triacontahedron for  $\text{AlLiCu}$  and the Mackay icosahedron for  $\text{AlMnSi}$ ), which include about fifty (or even more) atoms. However, why these units are stable and how they are growing is not clear yet.

In the present paper, we propose another local arrangement for the basic structure motif in icosahedral quasicrystals. We suppose, that most of atoms have the closest neighbours at the vertices of dodecahedra, and it is shown that such motif may be found in the crystal approximants of  $\text{AlMnSi}$  and  $\text{AlLiCu}$  quasicrystals; the latest available experimental data <sup>3</sup> give evidence for the same arrangement in  $\text{AlFeCu}$  quasicrystals too. 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 <sup>4</sup>; the reason is that in the approximants only those positions can survive which are most favorable energetically. The analysis of the numerous experimental data shows <sup>5,6</sup> that at least four cubic approximants have been observed in the  $\text{AlMnSi}$  alloys:  $\langle 2/1 \rangle$  ( $\text{MnSi}$  structure),  $\langle 5/3 \rangle$  ( $\alpha\text{-AlMnSi}$ ),  $\langle 13/8 \rangle$ , 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 labelled by two Fibonacci numbers  $\langle F_{n+1}/F_n \rangle$ , if in this crystal the most intense pseudo-fivefold reflections have the Miller indices  $\{F_{n+1}, 0, F_n\}$ . The ratio of the lattice constants  $a_{n+1}$  and  $a_n$  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  $\tau$  ( $\tau = (1 + \sqrt{5})/2 = 1.618034\dots$ ). To avoid confusion it should be noted that there is another labelling scheme <sup>4</sup> in which  $\alpha\text{-AlMnSi}$  crystal is labelled  $\langle 1/1 \rangle$  but in this case we have unnatural notation  $\langle 0/-1 \rangle$  for  $\text{MnSi}$  crystal.

Let us consider the  $\text{MnSi}$   $\langle 2/1 \rangle$  approximant with the space group  $P2_13$ ; its unit cell contains 8 atoms in  $4a$  positions  $x, x, x$  at the threefold axes: 4 Mn and 4 Si. In crystallographic books it is referred to as  $B20$  or  $\text{FeSi}$ -type structure

and is found in many alloys: AlMnSi, CoGeSi, GeRu, HfSn, and others <sup>7</sup>. In the idealized structure of this approximant (Fig.1a),  $x_A = 1/(4\tau)$  for A atoms (full circles) and  $x_B = 1 - x_A$  for B atoms (empty circles).

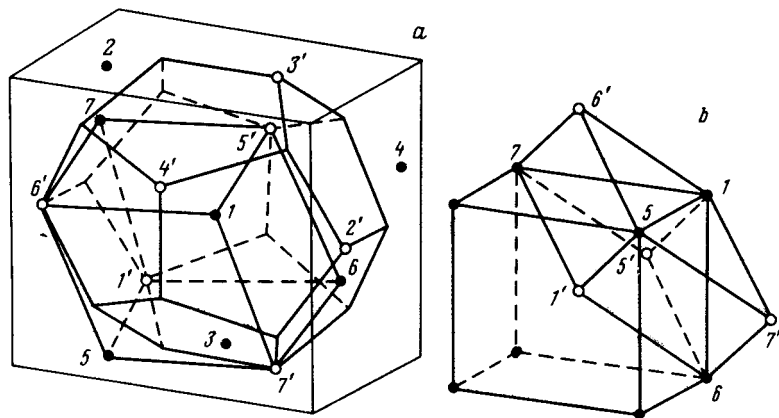


Fig.1. The relationship between atomic arrangements in  $\langle 2/1 \rangle$  (a) and  $\langle 1/1 \rangle$  (b) cubic approximants. In (a), atom 1 is at the cube center, whereas all other atoms are on the cube faces. The ratio of lattice constant is  $\tau$  but the rhombohedra, drawn at both figures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

This structure is a periodic system of interpenetrating dodecahedra: each A atom is surrounded by 7 B atoms positioned at 7 vertices of an ideal dodecahedron and *vice versa*. Therefore, the A-B bonds are directed along the threefold  $\langle 111 \rangle$  and pseudo-threefold  $\langle 01\tau^2 \rangle$  directions. Next atomic shell contains 6 atoms of the same sort as the central one; the A-A and B-B bonds 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 ( $\tau^{-1}$ ); 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.

Before the higher-order approximants, let us consider a relationship between MnSi crystal and the lower-order approximant  $\langle 1/1 \rangle$ . The latter is a cubic crystal (Fig.1b) with  $Pm\bar{3}m$  space group known as B2 or CsCl-type structure; its lattice constant  $a_1$  is  $\tau$  times smaller than  $a_2$ ; if  $A=B$ , it is a conventional bcc crystal with  $Im\bar{3}m$  symmetry. It is interesting that many alloys are known in both modifications, shown at Fig.1, with practically the same density (AlPd, AlPt, FeSi, OsSi, and others). The relationship between the two structures becomes evident if we compare the rhombohedra drawn at both figures: those rhombohedra are equal but they have different orientation relative to 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 (8 atoms, a complete unit cell!).

Such relationship is a general property of approximants. For instance, in 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  $\tau$  times larger than that of MnSi. The space group of this approximant is Pa3 with 32 atoms per unit cell: 8 A atoms in 8c positions  $x, x, x$  and 24 B atoms in general 24d positions  $x, y, z$ , where the calculated values of atomic coordinates are the following:

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

Again, like in MnSi, the closest neighbours of each atom occupy vertices of dodecahedra: 7 around each A atom and only 6 around each B atom. The interesting feature is the occurrence of 8 holes in  $x, x, x$  positions ( $x = \tau/4$ ) with icosahedral coordination. If we try to continue the dodecahedral arrangement inside these holes, any new atomic position appears too close to one of the old positions. Therefore, such holes may be considered as the places of frustration for the dodecahedral ordering. Surprisingly, the structure of Au<sub>3</sub>NaSi 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 1), whereas Si atoms are in the holes; to my knowledge, this crystal has never been considered before as an approximant of quasicrystals.

Atomic positions in the cubic approximants of different order

Labels and examples	Coordinates of atoms in a unit cell:		6-dim. positions
	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 <sub>3</sub> NaSi	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
Al <sub>5</sub> Li <sub>3</sub> Cu	0.000,0.118,0.191	0.000,0.094,0.154	100000
Au <sub>3</sub> Na <sub>2</sub> Sn	0.000,0.309,0.118	0.000,0.305,0.117	100001
Au <sub>4</sub> Na <sub>3</sub> Si <sub>2</sub>	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

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 very popular structure exemplified by many alloys. Similarly, it may be considered as the superpositions of the dodecahedral clusters, like the one 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  $(1, \tau, 0)/(2\tau^2)$  positions (not shown in Table 1): the former is empty in Al<sub>5</sub>Li<sub>3</sub>Cu and is occupied by Au in Au<sub>3</sub>Na<sub>2</sub>Sn, whereas the latter is occupied in all known alloys, enforcing small shifts of neighbouring atoms. Perhaps because of those shifts the dodecahedral local coordination was not earlier recognized in the Al<sub>5</sub>Li<sub>3</sub>Cu approximant.

A more regular way to construct the approximants and quasicrystals is provided by the strip-projection method<sup>8</sup>. The dodecahedral arrangement of 7 atoms around the central one can be described as a projection from a 6-dimensional cubic lattice with one atom per unit cell, so that 6 basic vectors (100000), ..., (000001) give positions of the 6 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  $\lambda_n$  depends on the order  $n$  of the approximant. The 7th closest atom is a projection of (000111), whereas the next shell of 6 atoms is projected from the points like (100010), etc.. After a proper choice of a 6-dimensional acceptance domain is made, all considered approximants and  $\alpha$ -AlMnSi can be obtained. Such projection scheme is unconventional: the basic vectors (100000), ..., (000001) are projected on the *threefold* directions instead of the *fivefold*. The conventional fivefold basic vectors are the linear combinations of the threefold vectors given by equation (2), and *vice versa*. Therefore, the icosahedral symmetry of quasicrystals can be reached within both schemes. It is interesting that the holes discussed above are the projections of body-center points of the 6-dimensional lattice. Another fact worth noting is that further atomic shells around the central atom look like in the Mackay icosahedron.

Additional evidence for the dodecahedral arrangement can be found in the neutron-diffraction data: it was shown <sup>3,9</sup> that both in AlMnSi and in AlFeCu quasicrystalline alloys the closest atoms are located on the vertices of a regular dodecahedron (their maximum number was 7). In those works the dodecahedral arrangement was obtained as a result of some special decoration of 6-dimensional unit cell.

In conclusion, the dodecahedral structure unit is found to be a universal feature in quasicrystals and in their crystalline approximants. The proposed projection scheme seems to be 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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