

# Stable clusters in quasicrystals - fact or fiction?

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Without doubt, the cluster approach has been a very successful and useful tool for describing and modelling the structure of quasicrystals. The only open questions are how stable these clusters are, in what way they contribute to the stability of quasicrystals and what physical properties they have. The discussion session should focus on the open questions connected therewith and the ways to answer them.

*Keywords:* clusters; quasicrystals; discussion session

## 1. What we call clusters

Most models of quasiperiodic structures and their approximants are based on one or more characteristic structural units commonly referred to as *clusters* (Fig. 1) [1-7]. Depending on the context the term *cluster* may denote a *structure motif* (purely geometrical pattern), a *structural building block* or *unit* (perhaps with some physical justification), a *quasi-unit cell* (stable entity in the meaning given by Jeong & Steinhardt [8]) or a *complex coordination polyhedron* (with some chemical stability). Frequently, clusters are seen as electronically stabilized entities. According to the *jellium model* [9], clusters can be considered a kind of soft superatoms. In case of strong covalent intra-cluster bonds they may even have a significant mechanical stability [10].

[Insert figure 1 about here]

The nanometre-sized particles obtained, for instance, by laser ablation and investigated in mass spectrometers, are called *free (bare, naked) clusters* [11,12]. If a *bare cluster* sits on a surface [13] or in a matrix [14] it is called a *supported cluster*. One gets *embedded clusters* if the matrix is formed by organic ligands, like in metal-organic compounds [15,16]. There, the clusters correspond to a polyhedral arrangement of up to more than one hundred metal atoms. In all these cases it is clearly defined by the character of chemical bonding which atom belongs to a cluster and which one does not.

## Examples

<i>structure motif:</i>	C <sub>4</sub> -tetrahedra in the diamond structure (just geometrical visualization);
<i>structural building unit:</i>	SiO <sub>4</sub> -tetrahedra in silicate structures (rather stable entities existing in differently connected ways and also in isolated form, <i>e.g.</i> SiO <sub>4</sub> <sup>4-</sup> -complexions in nesosilicates);
<i>coordination polyhedron:</i>	NaCl <sub>6</sub> -octahedra in the sodium chloride structure (just geometrical visualization);
<i>covering cluster:</i>	A structural unit is a <i>covering cluster</i> if a quasiperiodic structure can be completely covered by overlapping copies of it (see, for instance, [2]).
<i>quasi-unit cell:</i>	Columnar <i>covering clusters</i> (Gummelt decagons) in decagonal Al-Co-Ni [8];
<i>free cluster:</i>	Ni-Al clusters up to 55 atoms [17]; fcc NaI clusters [11];
<i>supported cluster:</i>	nanoparticles of Au on SiO <sub>2</sub> [18];
<i>embedded cluster:</i>	Icosahedral Tl <sub>13</sub> <sup>10-</sup> -cluster in Na <sub>4</sub> K <sub>6</sub> Tl <sub>13</sub> (electronically stabilized) [19]; pentagonal bipyramidal Ga <sub>7</sub> -cluster in [Li(thf) <sub>4</sub> ][{(Me <sub>3</sub> Si) <sub>3</sub> Si} <sub>4</sub> {(m <sub>2</sub> -Me <sub>3</sub> Si) <sub>3</sub> SiGa} <sub>2</sub> Ga <sub>7</sub> ], [20];
<i>molecular cluster:</i>	Fullerenes and nanotubes.

## 2. Why we should define what we mean by clusters

Cluster-based structures may have very interesting physical properties provided that clusters and matrix behave differently with respect to electrons [21,22], phonons [23], propagation of defects (dislocations, cracks) [24], diffusion etc. Structures of this type can be considered as a kind of *single-phase nanocomposites* with components (atoms, clusters and matrix) interacting on different scales. On one hand, there is a discrete distribution of atoms, the anisotropy of the crystal structure. On the other hand, the distribution of clusters and the contrast to the matrix can be considered somehow in terms of a continuum theory.

The question is whether or not quasicrystals are typical representatives of such a material class and whether or not their formation, stability and properties can be explained employing a cluster-based approach.

### 3. How do clusters in quasicrystals look like

Often, quasicrystal structures are modelled based on clusters derived from approximant structures (Fig. 1). On a first glance this seems to work quite well. Under the constraints of crystal chemistry (packing density, bonding, stoichiometry), however, the fundamental clusters (Mackay icosahedron, pseudo-Mackay icosahedron, Bergman cluster,...) are not sufficient to cover all atoms in a quasicrystal structure. A certain amount of disorder either in glue atoms or in the clusters seems to be unavoidable [25]. Duneau & Gratias [26] even conclude 'that a unique decorated covering cluster is unlikely to be found in real quasicrystals'.

Anyway, given one or several clusters have been identified, the task will be to find those structural units that are physically different (based on a different type of chemical bonding) from their surrounding if any. Metallic bonding is a collective phenomenon resulting from interactions of atoms inside and outside a cluster. Significant differences in intra- and inter-cluster bonding may be restricted to those cases where strong covalent bonding contributions exist.

#### *Example Al-Mn-Pd*

From the 2/1-approximant a 9(12)-shell cluster with 20.21 Å diameter was derived [27], which was used in the structural description of the icosahedral phase [28]. Taking a closer look at this cluster (Fig. 2) one finds that it consists of fully occupied shells and of disordered/distorted or partially occupied shells breaking the icosahedral symmetry. The pentagon-dodecahedral Al-shell (2a) is fully occupied with rather long Al-Al distances of 2.947-3.015 Å. The icosahedral shells (1) and (2b) are separated by 1.573 Å only and the 24 sites can be occupied by 12 Pd atoms only. The 60 split sites of the third shell can be occupied by 30 atoms only, etc.

[Insert figure 2 about here]

At high temperature, there can be a high mobility of the atoms between the split positions. Consequently, it will be really difficult to define the 'stable part' of this cluster, which looks like a kind of 'roller bearing'.

Not everything what geometrically looks like a cluster needs to be a cluster in a physical sense. An example for that is shown in Fig. 3. Around any Al atom an infinite number of cluster shells (coordination polyhedra) can be identified. However, this is just a purely geometrical construction without any particular physical meaning since this just fcc aluminium.

[Insert figure 3 about here]

#### 4. Geometrical versus physically stable cluster

There are some indications that stable clusters (*i.e.* stabilized by covalent bonding, for instance) are much smaller than the features seen on electron microscopic images. One example has been discussed above. The stable part of the Al-Mn-Pd cluster may just end at shell 2 resulting in a cluster diameter of 8-9 Å. A rather small cluster has also been identified in a thorough theoretical analysis of possible atomic clusters in *F*-type quasicrystals [26]. The 8.12 Å diameter 33-atom B-cluster (centred icosahedron + dodecahedron) results as the best choice for a well ordered quasicrystal such as Al-Cu-Fe. Larger clusters automatically introduce disorder. However, since only 78.83% of the total number of sites is covered by the B-clusters, additional partially disordered clusters (M, M') are needed to fill the gaps.

According to a charge density study [22], indications of covalent bonding in the first two shells of the Mackay cluster in  $\alpha$ -Al(Mn,Re)Si corroborate the possible larger stability of very small clusters. Important is, of course, whether the centre of the innermost icosahedral cluster is empty or filled. According to Kimura [29], empty Al<sub>12</sub>-cluster shells (*e.g.* in Mackay clusters) have a covalent bonding nature while the centred Al<sub>13</sub>-ones (*e.g.* in Mg-Al-Zn quasicrystals) are metallic. Typical for Al<sub>12</sub>-clusters are very short nearest neighbour distances below 2.55 Å (in fcc Al  $\approx$ 2.86 Å), which are indicative of strong bonding. In Al<sub>6</sub> clusters, the atomic distances can even reach 2.435 Å [13].

Clusters forming in undercooled liquids [30], certainly have a kind of stability as well as free clusters with a magic number of atoms (electrons).

##### ***Example decagonal Al-Co-Ni***

It has been very tempting to use a large ( $\approx$ 20 Å or even  $\approx$  32 Å diameter) *covering cluster* (Gummelt decagon, *quasi-unit cell* approach) for the explanation of structure and stability of decagonal quasicrystals [2,31,32]. However, there is an ongoing discussion about the structure and even the symmetry of this basic cluster of decagonal Al-Co-Ni (see [33] and references therein). Intrinsic disorder complicates the structure analysis, particularly, since only averaged structures have been studied so far.

Taking into account the studies on free Ni-Al [18] or transition metal clusters [12] as well as the structure of the approximants in the system Al-Co-Ni, the 'stable clusters' seem to be the pentagonal-bipyramidal ones. The  $\approx$ 20 Å clusters, consequently, consist of small stabler subclusters (*e.g.*, *S* and *P* subclusters [34]). Most Al atoms are just glue atoms with a rather high mobility. In a Monte Carlo simulation even some 40 % of all Al atoms have been found rather delocalized [35].

## 5. How stable are clusters in quasicrystals

There are some observations that have been interpreted as proof for the existence of clusters in quasicrystals with a rather high mechanical stability:

- cleavage and annealing experiments on icosahedral Al-Mn-Pd [10,36-39] and decagonal Al-Co-Ni [40];
- molecular-dynamics-based modelling of crack and dislocation propagation in simple quasiperiodic model structures [24,41-43].

A cleavage surface results from crack propagation, which avoids cutting strong bonds. Consequently, the cleavage surface should be parallel to the network of strongest bonds. This is also true for equilibrium surfaces, which usually are parallel to net planes of atoms, connected by the strongest bonds (annealed surfaces obtained after the usual surface preparation procedures always are atomically flat). The low-energy planes in icosahedral Al-Mn-Pd have been studied by Yang et al. [44].

Since surface atoms always have incomplete coordination, the energy-weighted surface has to be a minimum. This minimum-energy surface does not necessarily need to be flat. If there are strong covalent bonds only within the cluster shells and not perpendicular to them, a kind of 'cobblestone' surface could be energetically more favourable. However, if the hollows would be filled by glue atoms (i.e. the matrix between the clusters), the energy balance of the flattened surface would turn even better. The energy costs for moving glue atoms has been shown to be one order of magnitude smaller than that for cluster atoms [45].

If even after annealing the 'cobblestone' surface is maintained, there are obviously no mobile glue atoms. This means, the chemical bonding does not differ very much between atoms belonging to different cluster shells or to glue atoms.

An analysis of gas-phase clusters made from laser-vaporized icosahedral Al-Pd-Mn did not identify any clusters occurring in the bulk structure [46].

If one looks at the distribution of strong bonds (short nearest neighbour distances) in the 2/1-approximant of icosahedral Al-Mn-Pd, one would expect a very puckered cleavage plane indeed (Fig. 4). However, the crystal is expected to break along the strongest bond chains, which seem not to be along the shells of the geometrical clusters known.

An *ab initio* study of the five-fold surface of a 3/2-approximant of icosahedral Al-Mn-Pd revealed even after relaxation a flat surface cutting through the Bergman and pseudo-Mackay (M) clusters [47]. A high mobility of Al atoms in the M clusters was observed. It is remarkable that the metallic character of the electronic structure is enhanced at the surface.

[Insert figure 4 about here]

### ***Effective cluster radius***

The effective size of a cluster may depend on the kind of property considered. We may identify rather large clusters for geometrical repetition units (structural building blocks) [32]. Medium sized clusters may be relevant to electronic [21,22] or vibrational properties [23]. A particular mechanical stability against crack propagation [41-43] or dislocation motion [24] due to strong bonds may be restricted to the smallest clusters.

## **6. What is to be done**

- define the term cluster geometrically, chemically and physically;
- describe its structure and properties in quasicrystals;
- describe its role for the formation and stabilization of quasicrystals;
- identify key experiments and theoretical calculations that must be performed to answer the open questions concerning clusters in quasicrystals.

## **7. Some open questions**

- How is the distribution of chemical bonds (length, strength, type, anisotropy) between atoms in a geometrical cluster found from structure analysis? Are the strongest bonds (shortest distances) between atoms of a shell or between atoms of different shells? Is there a difference between the bonding of different shells (decrease in bond strength from the inner to the outer shells, not every shell consists of atoms in bonding distance to each other)? How does the network of strong bonds look like for concrete examples?
- Is it possible to identify clusters clearly separated from the embedding matrix? What is the size of these clusters, how thick are the matrix parts between clusters? What is the difference between cluster and matrix in terms of chemical bonding?
- What is the role of disorder for the stability of the cluster, its properties?
- Is the existence of stable clusters a proof for energy stabilization of quasicrystals?
- What is the fingerprint of such a type of cluster? How can it be characterized?
- Is it possible to model in a first approximation the physical properties (electronic, dynamic) of quasicrystals in terms of clusters embedded in a matrix?
- Annealed quasicrystal surfaces are atomically flat and not like 'cobblestone'. What does this mean for the stability of clusters?

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### Figure captions

- Figure 1      Idealized cluster found in 2/1-approximants of icosahedral *F*-type quasicrystals.
- Figure 2      Schematic representation of the cluster at the origin in the cubic 2/1-approximant structure  $\text{Al}_{70}\text{Mn}_6\text{Pd}_{23}\text{Si}$  [27]. Each circle represents a shell or part of a double shell. The sites in the shells 1 and 3 (dashed circles) can be occupied by atoms alternating only. The shells 3, 5 and 7 (asymmetrically broadened, grey) contain up to 50% split positions.
- Figure 3      The coordination polyhedra around any Al atom in fcc aluminium. The radii of the first five coordination polyhedra have a ratio of  $1 : \sqrt{2} : \sqrt{3} : \sqrt{4} : \sqrt{5}$ .
- Figure 4      One unit cell of the cubic 2/1-approximant  $\text{Al}_{70}\text{Mn}_6\text{Pd}_{23}\text{Si}$ . The bonds between all atoms are shown, the distances of which are smaller than the sum of (a) the atomic radii, (b) the covalent radii plus 0.05 Å, (c) the covalent radii.

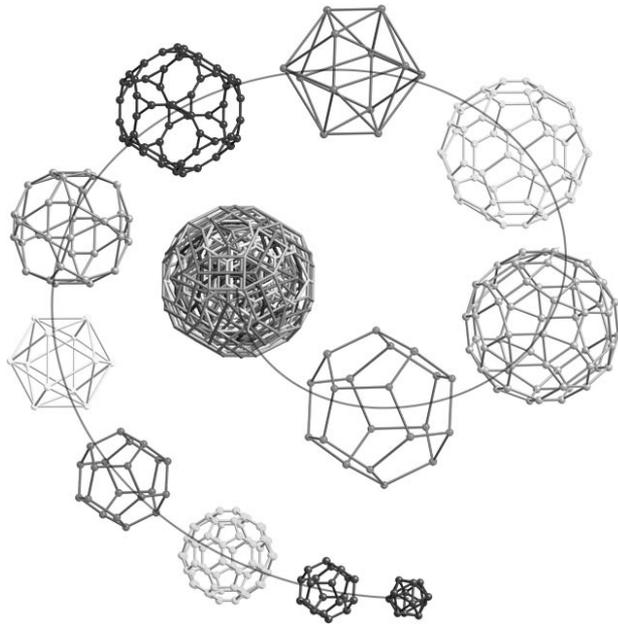


Figure 1

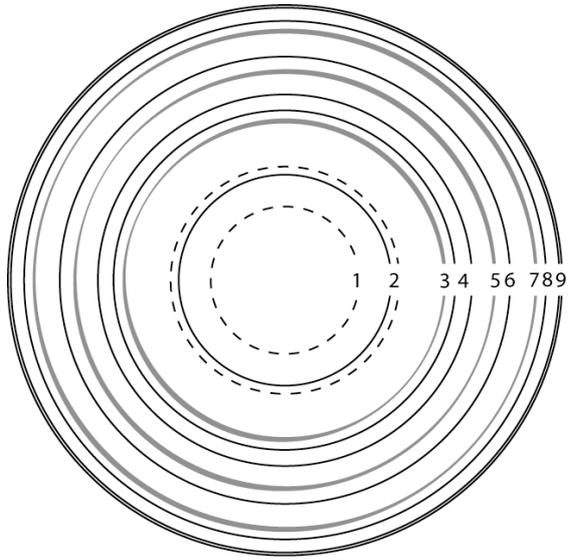


Figure 2

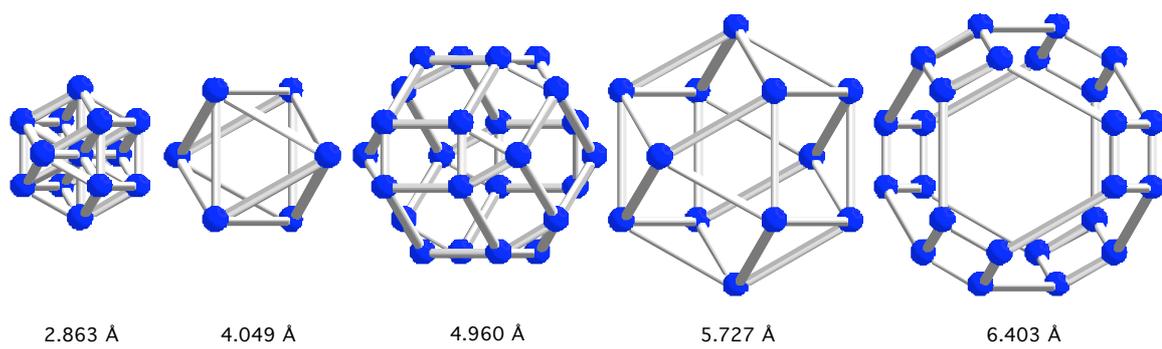


Figure 3

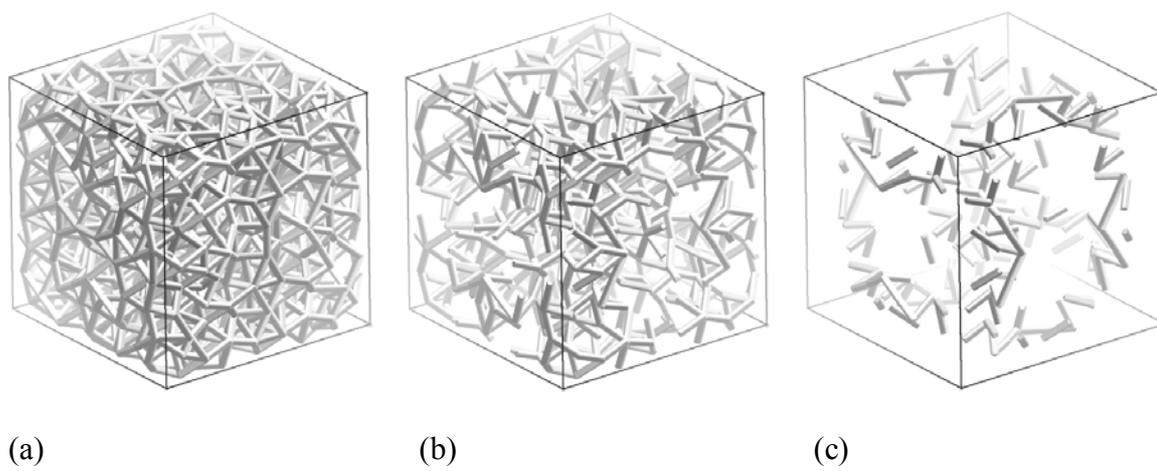


Figure 4