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Classification, based on energetics, of ideal icosahedral clusters, and building blocks of icosahedral quasicrystals and approximant crystals

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Abstract. We have classified, by their energy, compact finite clusters of icosahedral symmetry, composed of a single atom type, constituted by at most ten layers, and centered at an empty or occupied site with coordination number 12. The clusters are formed by adding one by one the best possible icosahedral layers in the surface potential minima and by relaxing numerically the cluster at each step. Polyatomic clusters are also considered. The energy is calculated from two-body pair potentials depending only upon the distance. Comparison is made between (1) the succession of layers inside these ideal icosahedral clusters, (2) the layers constituting the real clusters present in $m\overline{3}5$ -approximant crystals and (3) the icosahedral local order in icosahedral quasicrystals as deduced from the 'experimental' atomic surfaces. After revisiting many $m\overline{3}5$ -approximant crystals, we propose a characterization and a classification of local icosahedral order in crystallized matter and icosahedral quasicrystals.

1. Introduction

It is now known that the icosahedral local order in icosahedral quasicrystals and some $m\bar{3}5$ -approximant crystals in a given system is fundamentally the same, up to very small deformations [1,2]. In the i-phase, the diffraction process is dominated (1) by the diffraction properties of the different pseudoicosahedral clusters of atoms formed locally (pseudoinflation rules, pseudoicosahedral invariance, etc.), and (2) by the quasiperiodic way these pseudoicosahedral clusters assemble and interpenetrate [3] to provide long range orientational order, and the diffraction properties of quasiperiodicity [4]. The quasiperiodic distribution of the clusters is dictated by the structure of the possible icosahedral clusters which can be formed in a definite system, where cluster centers cannot be at any atomic site [5]. In ref. [6], Henley has classified the various icosahedral phases by classes, but his classifica-

tion is essentially done by systems, and in fact, by the types of icosahedral local order the systems 'can offer'. It is therefore relevant to determine the different possible types of icosahedral local order which can occur in a system, that is, the different possible icosahedral atomic configurations of clusters of lowest energy which can be formed and are stable with a small number of atom types, by (1) starting to obtain ideal clusters, and (2) comparing with pseudoicosahedral clusters in binary i-phases and approximant crystals.

After recalling Henley's classification [6], we investigate ideal icosahedral atomic clusters, then propose a realistic classification of real pseudoicosahedral clusters as they occur in approximant crystals, and finally discuss the possible building blocks for both approximant crystals and i-phases.

2. Icosahedral order in icosahedral quasicrystals: Henley's classes

For icosahedral quasicrystals, the situation seems a priori simpler than in approximant crys-

tals, since there exists only *one way* to define the action of the icosahedral group in reciprocal space, which amounts to having only *one* orientational family of pseudoicosahedral clusters in real space [7,8]; the presence of quasiperiodicity in the i-phase eliminates the possibility of several coexisting orientational families of pseudoicosahedral clusters, families which, on the contrary, generally coexist in the case of approximant crystals (see below and, for instance, ref. [8] for the Ti-TM system). In ref. [6], Henley has reported i-phases and approximant crystals, in various sys-

tems, and cluster packing geometries with small-sized (i.e. limited to a few layers) clusters as follows:

- the Al-TM class, where TM is a transition metal and Al in substitution by other elements: $Pm\bar{3}5$ type: i-AlMn, i-AlMnSi, i-AlGeMn, i-AlCr, i-AlCrSi, i-AlV, ...; $Fm\bar{3}5$ type: i-Al-FeCu, i-AlPdMn, i-AlCuOs, i-AlCuRu, ...;
- the AlMgZn class: i-AlLiCu, i-AlMgZn, i-Al-LiZn, i-AlAgMg, ... (i-GaMgZn);
- the Ti-TM class: i-TiMn, i-TiCo, i-TiFe, ...;
- the i-PdUSi class.

Fig. 1. Succession of icosahedral layers in two energetically favourable monatomic clusters: (a) sequence 1, starting by a Mackay icosahedron, (b) sequence 4 starting by a Bergmann unit. The center is occupied or not by an atom (the other sequences are not represented for lack of space).

These phases may coexist with decagonal phases, having common symmetry axes. The pseudoicosahedral clusters, having a chemical disorder or not [9], when slightly flattened along the tenfold axis, now become pseudocyclic or pseudodihedral units in the d-phase.

The primitive character of i-AlMnSi, i-AlCr, ... phases corresponds to one icosahedral environment type. On the contrary, fcc icosahedral structures like i-AlFeCu, i-AlCuRu are compatible with the existence of at least two local icosahedral environments, the second one being either a chemical variation of the first one (i-AlPdMn, [10]) or different (i-AlFeCu, [11]).

3. Classification of ideal icosahedral building blocks

We are interested in stable clusters having exactly the icosahedral symmetry $m\bar{3}\bar{5}$ as a symmetry group, and composed of only one type of atom. Stable means that, whatever the (small) displacements we impose on the atomic sites, the cluster recovers entirely the icosahedral symmetry by numerical relaxation [18], with the same geometry as in the initial state (relative energy minimum). The energy is calculated by means of a normalized 6–12 Lennard–Jones pair potential depending only upon the distance.

The construction process for the clusters is the following:

3.1. Monoatomic clusters

Starting from a central site which could be unoccupied, we successively add icosahedral atomic-site polyhedra (one atom at each vertex). The surface potential and the configuration energy of the cluster are calculated at each step. The atoms of the added shell are positioned at the minima of the surface potential, respecting each time the icosahedral symmetry. The cluster is then relaxed, and so on up to tenth neighbors. We always start from CN 12 sites (icosahedron as first layer). For the second and third neighbors, we have only two possibilities: the sequence ico1–icosi1–ico2 (Mackay icosahedron) and the

sequence ico1–dodeca1–ico2 (Bergmann unit). For the fourth neighbors and above, the number of possibilities increases rapidly. But, at the final step (tenth neighbors), many cases can be eliminated because the configuration energy is too high or there is a too low density around some atoms in the inner shells. This elimination reduces the number of possible icosahedral clusters. The following sequences of icosahedral layers represent the succession of layers inside the more energetically favourable clusters, assumed to be surrounded by vacuum:

- 1) ico1–icosi1–ico2–hexe1–ico3–icosi2–pentakis1–hexe2–ico4 (fig. 1(a));
- 2) ico1–icosi1–ico2–dodeca1–pentakis1–ico3–trisico1–hexe1–pentakis2;
- 3) ico1–dodeca1–ico2–pentakis1–dodeca2–ico3–hexe1–icosi1–pentakis2;
- 4) ico1–dodeca1–ico2–hexe1–ico3–icosi1–pentakis1–hexe2–ico4 (fig. 1(b));
- 5) ico1–dodeca1–ico2–icosi1–hexe1–ico3–trisico1–pentakis1–hexe2.

The other cluster energies are singularly higher, and only these five sequences are relevant. The succession of radii is not given since a slight change in the eV-calibration of the potentials modifies them.

3.2. Polyatomic clusters

Atoms of different sizes are now considered. We proceed by reference to the above classification; we introduce no chemical disorder in the cluster with two or three kinds of atoms. These new atoms have a reasonable difference of size with respect to the first one (ratio of the radii between 0.75 and 1). A layer in a cluster is then monoatomic and of perfect icosahedral symmetry. With two types of atoms, some configurations are more stable than others: sequence 1 is favoured, and it is the situation encountered in the α -Al-MnSi type phases with Al and transition metals; sequence 3 enters in competition with sequence 1, is energetically less favored, and probably does not occur. Sequence 3 corresponds to the R-phase type local order but with constitutive atoms having a *large* difference of size; sequences 2 and 5 are also energetically favored and may exist in

hypothetical icosahedral or approximant crystals. Ni environments in η -Ti₂Ni and some Mn environments in μ -Al₄Mn are given by sequence 5 which is close to the α -phase type [8,12]. Therefore, among the five above sequences, only four of them remain physically reasonable. In this approach, the discriminator for the classification is the energy, but the energy calculations, with real atoms, are extremely complicated and should be done by ab initio methods [13]. The present construction process with Lennard-Jones potentials is just a guide which provides possible stable atomic configurations with no chemical disorder with respect to the icosahedral symmetry.

4. Real icosahedral local order in $m\bar{3}5$ -approximant crystals

The approximant crystals prototypes are: 1) the α -phase type: ico1(Al)-icosi1(Al)-ico2(TM)-hexe1(Al)-ico3(Al)-icosi2(Al, TM)-pentakis1(Al, TM)-incomplete hexe2(Al), and incomplete trisico1(Al)-ico4(Al). Other larger polyhedra can be defined: an arithmetic sequence of 17 icosahedra, a geometric sequence of 10 icosidodecahedra (inflated by the golden mean), etc. [3,12]. The body centered site is surrounded by a similar environment but hexe1 is somewhat distorted whereas ico3 is replaced by an incomplete dodecahedron. The α -phase structure is a CsCl type stacking of Mackay icosahedra (54 atoms) at body centered sites, and a larger cluster defined by the above sequence truncated at ico3 (126 atoms), at the origin sites; 2) the R -phase type: ico1(Al)-dodeca1(Li)-ico2(Al)-pentakis1(Al)-dodeca2(Li)-ico3(Li)-incomplete icosi1(Al)-hexe1(Al, Li)-... at body centered sites and origin sites. The structure is described by a bcc stacking of the cluster obtained by truncating the above sequence at the ico3. To emphasize size effects, we have, for the building block: ico1(MA)-dodeca1(LA)-ico2(MA)-pentakis1(LA, MA)-dodeca2(LA)-ico3(LA), where LA means large sized atom (Li, Mg,...) and MA middle sized atom (Al, Zn,...). It is a fact that a strong interpenetration of the big clusters actually occurs in both phases.

From investigations on many approximant crystals having local atomic configurations exhibiting almost the icosahedral symmetry and for which this symmetry spreads far inside the crystal from certain centers (which are occupied or empty sites), we propose the following classification scheme; the approximant crystals are characterized by:

- the *number* of pseudoicosahedral clusters (counted by their center) per unit cell of the Bravais lattice;
- the *cluster type*, which is, starting from their centers, chosen from the above sequences 1 to 5 (section 3), and is either of Mackay type: ico1-icosi1-ico2-..., or of Bergmann type: ico1-dodeca1-ico2-...;
- the number of *icosahedral orientations* in the whole family of clusters; one orientational family is constituted by only one type of cluster of the same orientation. (It is the number of non $m\bar{3}5$ -equivalent ways the action of the icosahedral group can be coherently defined in the basis of the Bravais lattice [7]);
- the degree of *interpenetration* of the clusters [3];

where the cluster type is specified by:

- the *occupation or not* of the center of the cluster by an atom;
- the *succession* of the average radii of the (pseudoicosahedral) layers;
- the *spatial extent* of the cluster in the approximant crystal;
- the *deformation*, global and by layer, with respect to a perfect icosahedral cluster optimally positioned in the orientational family of the cluster [7,14];
- the *degree of completeness* of the pseudoicosahedral layers, and the layer from which empty sites begin to appear;
- the *types of atoms* in the layers;
- the *chemical disorder* of the cluster with respect to the icosahedral symmetry, which is measured, on a complete layer, by the proportion of different atoms (where we assume that the action of the icosahedral group is transitive), while a cluster without any chemical disorder corresponds to the situation where each layer exhibits only one type of atoms;

- the existence, inside and outside the cluster, of *arithmetic* integral sequences (the n th layer is n times farther than the first one) and of *geometric* sequences (the $(n+1)$ th one is t^n times farther than the first one, where t is a real number > 1) of homothetic concentric layers (homothety is exact, ‘up to small deformations’).

In fact, a systematic feature of icosahedral local order in approximant crystals associated to *i*-phases is that the first layers are positioned as in Mackay type clusters (ico1–icosi1–ico2, α -Al-MnSi phase type) or in Bergmann type clusters (ico1–dodeca1–ico2, R-AlLiCu phase type), with or without an atom at the center. No other possibility was observed and this result is coherent with the classification of ideal clusters in section 3. The local environment of the α -phase type until ico3 is perfectly recognizable around Cr sites (= cluster centers) in θ -Al₄₅Cr₇ associated with *i*-AlCr, around Mn sites in hexagonal β -Al₉Mn₃Si associated with *i*-AlMnSi, around some Mn sites in hexagonal μ -Al₄Mn associated with *i*-AlMn, around some V atoms in cubic α -Al₁₀V, monoclinic α' -Al₄₅V₇ and hexagonal β -Al₂₃V₄, associated with *i*-AlV, around Fe atoms in hexagonal α' -AlFeSi and cubic α -AlFeSi. Some phases which have no icosahedral short range order nevertheless have regions of the α -phase type environment: the monoclinic θ -Al₁₃Fe₄ phase associated with *i*-AlFeCu and *d*-AlFe, thus appearing as a link between *i*- and *d*-phases [9], the orthorhombic σ -Al₄Mn and α -Al₂₃CuFe₄, respectively, associated with *i*-AlMn and *i*-AlFeCu.

As for the *R*-phase type local environment, it exists in the isostructural T-(Al, Zn)₄₉Mg₃₂, Al₆CuMg₄ and Al₆ZnLi₃ phases, respectively, associated with *i*-AlZnMg, *i*-AlCuMg and *i*-AlZnLi.

In *c*-Ti₂TM, around Ti(c) and TM(e) atoms, we have a (Bergmann) sequence, resp. truncated at the 6th and 4th neighbors, of type 5, with a strong chemical disorder already on the first layer, respectively: 3 Ni for 9 Ti, 6 Ni for 6 Ti, and therefore large deformations. Still more deformed, the UPdSi phase enters into the case of phases where icosahedral local order is formed from atoms of very different sizes, and too few

results are now known on such occurrences to compare usefully to the *i*-UPdSi class local order.

5. Comments

When no chemical disorder happens in clusters, all the layers correspond to crystallographic orbits in an n D Euclidean hyperspace ($n = 6$ currently), and this correspondence outlines the importance of models of *i*-phases given by sphere fibrations [15] and an n D space group. When holes appear in clusters in some layers, this means that a local zero curvature at these layers (in 3D space) is not suitable for obtaining the *i*-phase from the n D crystal, and we have geometric frustration [16]. The present approach emphasizes the spatial extent of clusters, more than the notions of glue atoms and polyhedra (octahedra, etc.) for linking clusters which become meaningless.

The three approaches converge towards the same classification. We have obtained a limited number (4) of stable icosahedral clusters with slightly different atomic sizes. Two of them correspond to the *i*-phases related to the α -phase and to the *R*-phase. This correspondence implies that the number of icosahedral phase types is necessarily limited by the small number of possible icosahedral local orders in metallic compounds. It is not reasonable to think that several icosahedral phases of different space group types coexist with the same approximant crystal in a given system, as it was suggested in ref. [17], since given atom types seem to force unique icosahedral local atomic configurations and linkages between the clusters, therefore, a unique *i*-phase, and unique diffraction properties in quasiperiodic conditions. However, chemical and topological disorders inside clusters and in packing rules, as far as interpenetration of clusters allows to describe them in a simple way, occur, as they occur in approximant crystals.

6. Conclusion

We have derived possible ideal icosahedral clusters and have compared them with the ico-

hedral local order, as it appears in approximant crystals. Comparison is also made with a classification of icosahedral phases, based on the icosahedral local order.

Abbreviations

ico = icosahedron; dodeca = dodecahedron; icosi = icosidodecahedron; trisico = trisicosahedron; hexe = hexecontahedron; pentakis = pentakisododecahedron (soccer ball); TM = transition metal.

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