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Quasicrystals / Quasicristaux

Quasicrystals and atomic clusters

Quasicristaux et amas atomiques

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ABSTRACT

Historically, two principal approaches exist to determine the quasicrystal atomic structures: one is derived directly from diffraction experiments, using cut and projection of higher dimensional space-representation techniques; the other one takes use of the similarity between so-called approximant crystalline phases, observed to co-exist with quasicrystals. The known structure of these phases is shown to be the starting point of building a quasicrystal model in terms of constitutive polyatomic clusters of icosahedral symmetry. It requires to apply inflation properties of quasiperiodicity, and decoration of elementary building tiles. One example is detailed and discussed, in terms of a two-cluster model, in the case of AlLiCu.

RÉSUMÉ

Historiquement, il existe deux approches principales pour déterminer la structure atomique d'un quasicristal : l'une découle directement, par des techniques de coupe et de projection de représentations dans des espaces de dimensionnalité supérieure à 3, des expériences de diffraction ; l'autre utilise la similarité avec des cristaux approximants qui coexistent avec les quasicristaux. Leurs structures, connues, peuvent être le point de départ de la construction de celle d'un quasicristal, en fonction d'amas polyatomiques de symétrie icosaédrique constitutifs, et en appliquant des règles d'inflation propres à la quasipériodicité, et une décoration atomique des briques élémentaires. Un exemple est donné, puis discuté, pour AlLiCu, en fonction d'un modèle à deux amas.

1. Introduction

Shechtman et al. discovered in 1984 [1] by transmission electron microscopy (TEM) examination of rapidly solidified AlMn alloys, diffraction patterns with symmetries forbidden by the usual periodicity alive in crystallography. This symmetry, observed by Shechtman et al., corresponds to icosahedral symmetry. For instance, Fig. 1 shows typical electron diffraction patterns of 2-fold, 3-fold, and 5-fold axes of icosahedral symmetry, and a corresponding bright-field image of AlMnSi quasicrystalline particles embedded in an Al matrix. Macroscopic specimens were then discovered, opening a new field of intense research in various fields: thermodynamics, physical, chemical and mechanical properties.

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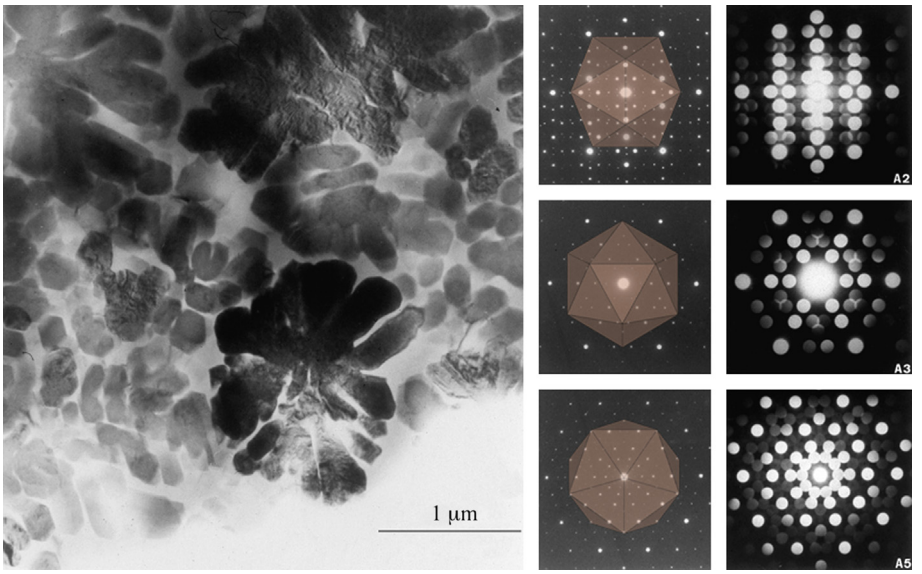

Fig. 1. (Color online.) TEM bright-field image of i-AlMnSi particles embedded in an Al matrix with 2-, 3- and 5-fold symmetry diffraction patterns displaying the "icosahedral" aperiodicity of the structure. Different icosahedral directions can be identified from the transparent calques of an icosahedron oriented along A2, A3 and A5 axes and superimposed to the diffraction patterns. Both types of diffraction patterns correspond either to a parallel or slightly convergent electron beam.

A first basic question was obviously to try to understand their atomic structure, able to produce such diffraction patterns of non-crystallographic point group, $I_h(m\bar{3}5)$ or $I(235)$ [2]. Historically, two approaches were quickly explored: 1) to build a "quasicrystallographic" strategy specific to these icosahedral "quasicrystals" (called first "cut and projection" and later "atomic surfaces determination"), living in a higher-dimension space (6D for the icosahedral phase), where the quasiperiodicity transforms in periodicity and restores therefore the usual tools of crystallography [3,4]; 2) to take advantage of some direct observations by electron microscopy, where quasicrystals co-exist, after casting, with large unit cell crystals. These last were called later "approximants" of icosahedral quasicrystals in the sense that their periodic structure are approximations of the quasiperiodic one. The larger their unit cell size, the better the approximation. Moreover, such approximants exhibit crystallographic orientation relationships with quasicrystals [5,6]. We followed in 1985 the last way, and propose a first atomic model in the case of AlMn icosahedral phase [7]. It is briefly illustrated here in the case of AlLiCu.

2. Approximant bcc crystals and structural icosahedral clusters

TEM observations of crystallographic orientation relationships between the i-AlLiCu icosahedral phase and the cubic approximant R-AlLiCu are shown in Fig. 2. These relationships, deduced from the set of electron diffraction patterns corresponding to selected area on i- and R-AlLiCu interfaces, are very simple: three orthogonal 2-fold axes A2 of the i-phase are parallel to ⟨100⟩ axes of the cubic R-phase. There are also four 3-fold axes A3 of i-phase parallel to ⟨111⟩ axes; the six other A3 axes are parallel to $\langle 1\tau^2 0\rangle$ axes (where τ is the golden mean). The six 5-fold axes A5 of the i-phase are parallel to $\langle 1\tau 0\rangle$ axes of the cubic R-phase.

The crystallographic work of the Pauling school on the atomic structure of complex phases, as Frank–Kaspers, sigma and other Laves phases, gave the key of the problem of understanding the relation between the two structures. Some of these phases, co-existing with i-phases, were shown to contain polyatomic arrangements with i-symmetry, the so-called "i-clusters", as shown in Fig. 3 [8,9]. They are composed of several concentric i-subshells (icosahedron, dodecahedron, icosi-dodecahedron, triacontahedron, truncated icosahedron or "soccer ball"), whose vertices are occupied by the atoms, as indicated in Fig. 3. MacKay and Bergman clusters contain each 54 and 137 sites. Their sizes exceed the nanometer.

These clusters are packed periodically in the bcc phases, with first neighbors along the ⟨111⟩ directions [7,10].

3. Clusters and quasicrystals: a filiation

According to the previous experimental observations, our strategy was to keep the same clusters as in the cubic approximants and aggregate them with minor distortions, in order to build atomic models of quasicrystals. Clusters are packed in parallel orientation, and with a quasiperiodic long-range order respecting the decoration of an underlying inflated 3D-Penrose or Ammann tiling. The procedure has been given in detail in Refs. [12,6,13]. One example of such a simulated "MacKay" quasicrystal is shown in projection parallel to a 5-fold axis in Fig. 4 [5,11]. We develop below the more complex approach for the AlLiCu alloy.

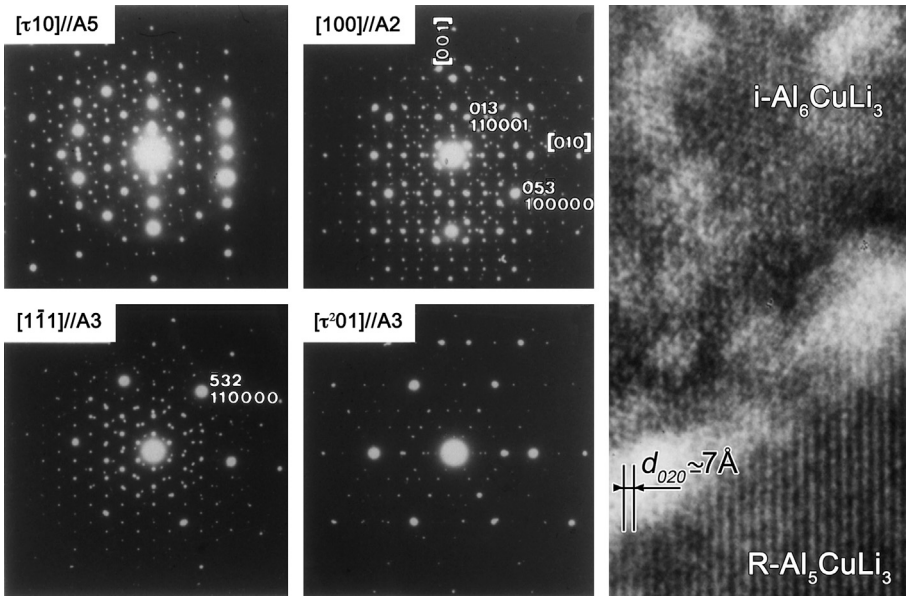

Fig. 2. TEM observations of the icosahedral phase i-Al_6CuLi_3, coexisting with a bcc cubic approximant phase R-Al_5CuLi_3; the high-resolution TEM image shows an interface between both phases oriented along zone axes $[\tau^2, 0, 1_R] \parallel A3_i$.

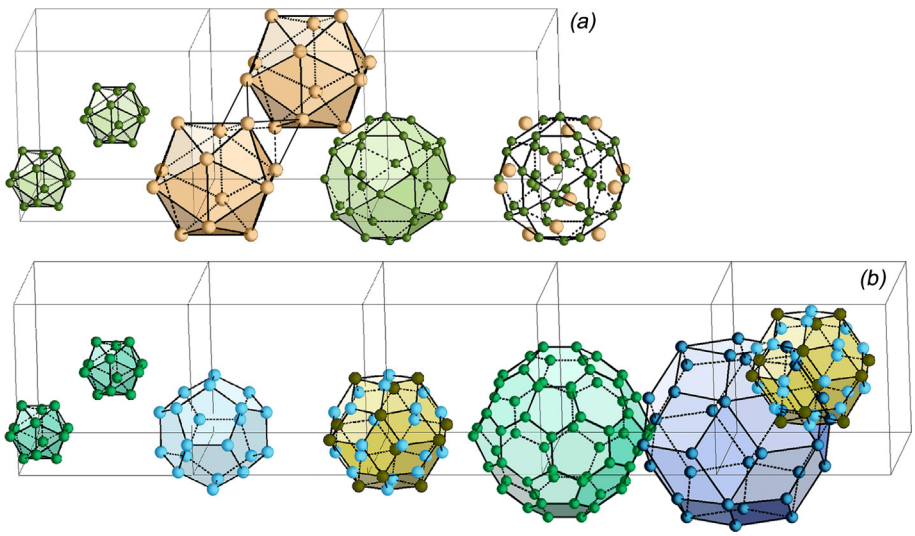

Fig. 3. (Color online.) (a) "MacKay" and (b) "Bergman" clusters, defined in α-AlMnSi [8,7], and R-AlMgZn or R-AlLiCu [9,10] cubic phases. These clusters contain each 54 atoms (MacKay) and 137 atoms (Bergman).

4. The Al_6CuLi_3 i-quasicrystal

The modeling procedure is basically the same, using the Bergman-type clusters. But the densification of the structure, in terms of preserved cluster entities, requires more than a single cluster. A two-cluster description approach has been proposed to model the structure of i-AlLiCu [13], involving the whole Bergman cluster and its reduced inner triacontahedron, in a τ ratio composed of its three first shells (Fig. 5(a)). These large and small triacontahedra aggregation, occurring through face and vertex connections (i.e. along 3-fold and 2-fold axes in the R-AlLiCu cubic phase), and respecting the constraint of satisfying local matching rules, has been described in detail in [6]. Two examples of possible dense triacontahedra aggregates are shown: a large triacontahedron is vertex-connected to 20 small triacontahedra, and a large triacontahedron face-connected with 30 small triacontahedra. In this case, the small triacontahedra are face-connected, a connection type that does not exist in the cubic approximant.

The long-range quasiperiodic order is ensured again by the clusters decoration of a τ^3 inflated underlying 3D-Penrose i-lattice (Fig. 5(b)). The Fourier transform of the model performed in the 6D-space [14] and experimental diffraction data

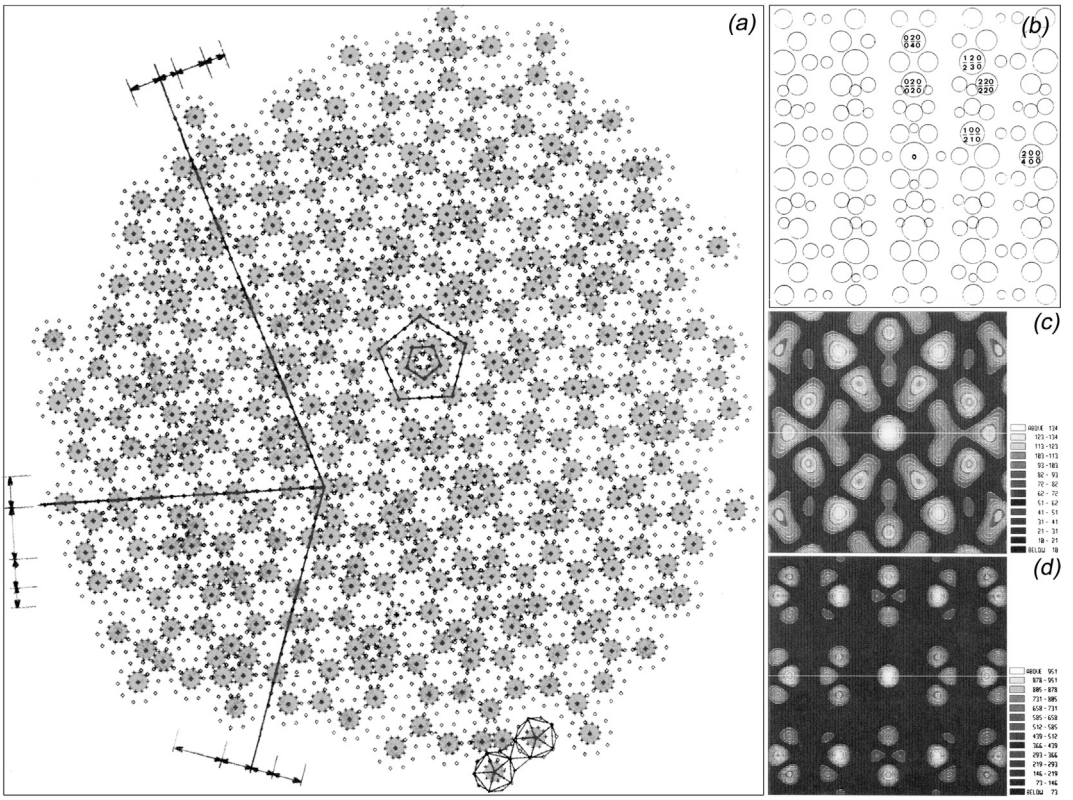

Fig. 4. (a) Projection along a 5-fold axis of a "MacKay" cluster i-quasicrystal. Two different kinds of atoms, Al and Mn, are shown (the crosses stand for Al, the circles stand for Mn; the last icosidodecahedral Al shell is not shown, for the sake of clarity). One notes the alignment of the atoms by projection on straight lines separated by scaled intervals (by τ, the golden mean), as observed on high-resolution TEM images (see Fig. 6, for instance). (b) Fourier Transform of the "MacKay" cluster i-quasicrystal cut perpendicularly to a 2-fold axis and (c, d) iso-intensity maps of the structure factor of a single icosahedron and of a single triacontahedron in a 2-fold orientation [11].

obtained by four-circle diffractometry performed on millimetric single i-crystals [6] with X-rays and neutrons, are in a reasonable agreement (reliability factors of 0.16 and 0.13, respectively).

5. "In-situ" HREM cluster observations

The existence of icosahedral clusters has been demonstrated by nanometric convergent beam diffraction, showing that with an electron beam of less than 1 nm in diameter (i.e. of the size of an i-cluster), the icosahedral symmetry was clearly identified [15]. HREM imaging and image simulations of clusters in R- and i-AlLiCu phases and in a trigonal approximant and i-AlFeCu phases [16] show features corresponding to a similar local atomic order (Fig. 6) [13,16]. Therefore, such results validate the analysis of the quasicrystal structure in terms of i-clusters. Other experimental investigations exploring the local atomic order by Electron Energy Loss spectra, obtained with a nanometric electron beam and displaying similar near-edge structures of Al and Mn in i- and α-AlMnSi phases [17] as well as similar pair distribution functions determined by neutron scattering [18], act in the same directions.

6. Conclusion

This method to model the atomic structure of icosahedral quasicrystals in terms of polyatomic clusters of same symmetry has been shown to be historically the first realistic one to achieve the structure of i-AlPdMn and AlLiCu. It appeared later as very complementary to the cut and projection technique of the quasicrystals 6D-structure: it helps to make a selection among the infinite number of parameters necessary to describe in shape and position the various atomic surfaces in the perpendicular space. Inversely, the cut and projection technique is able to clarify, starting from the diffraction data, a refinement of the structure, like the atomic occupation parameters of the clusters sites, or the existence of fractional parts of clusters or Friauf polyhedra, whereas undefined "glue atoms" between clusters were first required in the cluster method.

Finally, a cluster-based classification allows a generic description of quasicrystals families, depending on their relation with cluster-type building blocks, as MacKay (i-AlPdMn) or Bergman (i-AlLiCu), or other. Lately, other clusters were discovered in cubic approximants and the binary stable CdYb i-phase (see for instance recent works reported in Ref. [19]), confirming the validity of the approach.

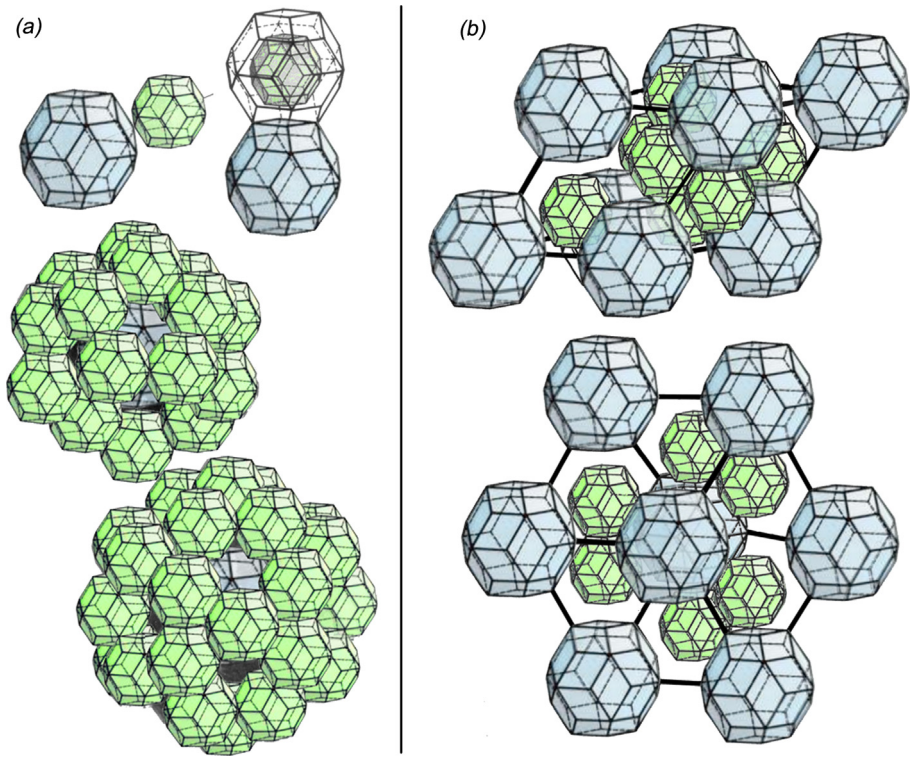

Fig. 5. (Color online.) (a) Vertex and face connections of small and large triacontahedra of the Bergman cluster. Resulting triacontahedra aggregation. (b) Small and large triacontahedra decoration of τ^3 inflated rhombohedral Penrose tiles.

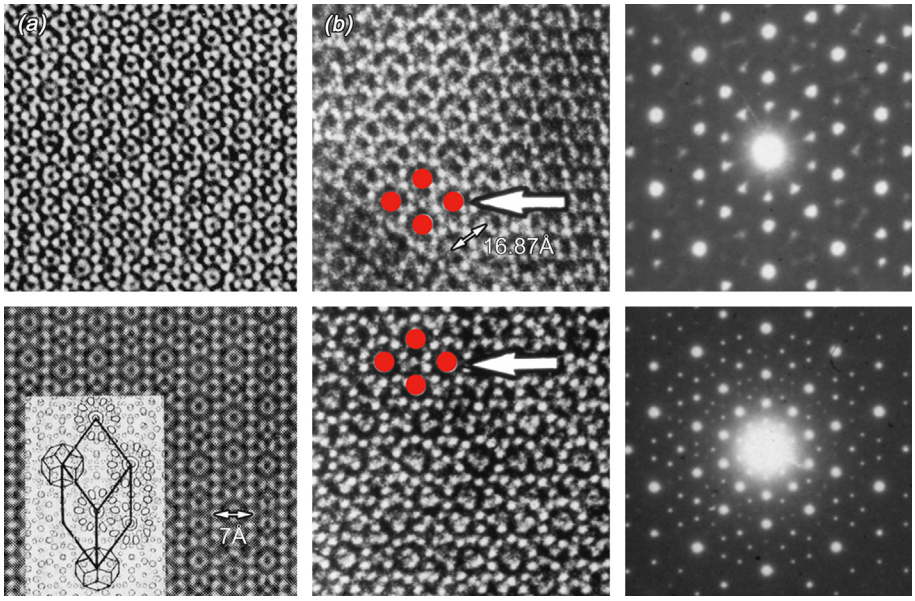

Fig. 6. (Color online.) "Cluster" HREM images within (a) i-AlLiCu and image simulation of the R-AlLiCu phases and (b) trigonal approximant and i-AlFeCu phases (with corresponding electron diffraction patterns). Note that the triangular diffraction spots in the case of the trigonal AlFeCu approximant are due to twinning.

Other characteristic quasicrystal features were predicted: cluster bonds in the i-structure are along the high-symmetry axis, their space positioning satisfies a theoretical hierarchical scaling (i.e. inflation rule in τ^3), and the atoms are located in dense planes, which may explain the classical faceting properties of the quasicrystals [20].

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