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BEYOND THE ICOSAHERAL GLASS MODEL, THE INTERPENETRATING PSEUDO - ICOSAHERAL CLUSTERS (IPIC) MODEL.

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ABSTRACT. We analyze the diffraction properties of infinite "formal" quasiperiodic, resp. periodic, packings of atoms in 3 dimensional Euclidian space that are considered as quasiperiodic, resp. periodic, distributions of identically oriented pseudo - icosahedral clusters which all have a finite spatial extension and interpenetrate. Restoring the icosahedral local order in the formalism leads to count atomic sites several times, when taken into account from the center of one cluster or another. Scattering functions are treated in perturbation over site multiplicity and icosahedral symmetry. The periodic case corresponds to approximant crystals, while the quasiperiodic one to icosahedral quasicrystals: the rank of the $\mathbb{Z}$ - module generated by the centers of clusters is then 3, resp. m , with $m > 3$. A periodization of the quasicrystal can be performed in $\mathbb{R}^m$. Pseudo - inflation rules arise from the geometry of an average cluster. This formalism is new and provides a "continuous link" between classical crystallography and quasi-crystallography.

1. INTRODUCTION

Icosahedral quasicrystals are now classified into four main classes (Henley, 1990 [1]): 1) the Al-TM class, where TM is one or several transition metals, such as i-AlMn or i-AlCuFe, 2) the AlMgZn class, such as i-AlLiCu or i-GaZnCu, 3) the PdUSi class with i-Pd₅₈Si₂₁U₂₁ [2], 4) the Ti-TM class, such as TiCo, TiMn [3 - 6]. On the other hand, many of these i-phases have known approximant crystals, such as α -AlMnSi, β -AlMnSi or μ -AlMn for i-AlMnSi [7 - 9]. The discriminator of the classification is the geometry of the icosahedral cluster (or its equivalent in terms of atomic surface in the hyperspace approach) as in the "nearest" approximant crystal or as determined by a Patterson analysis from qc single crystals; it is limited to a few icosahedral shells, defined up to small deformations: the sequences of sites polyhedra, from the center, are either ico - icosi - ico (Double Mackay Icosahedron, case 1) or ico - dodeca - ico (Bergman unit, cases 2 and 4) with

centers which are empty (cases 1 and 2) or occupied (cases 1 and 4). Case 3) is somewhat different because of steric effects [8] (as usual, ico, icosi, dodeca stand for icosahedron, icosidodecahedron, dodecahedron respectively).

One possible key for modelling the i - phase consists in guessing new linkages between the atomic icosahedral clusters that we can observe in the approximant crystals in the same system, and which then give rise to quasiperiodic assemblies of atoms with only one common orientation for the icosahedral clusters: we call such an infinite collection of identically oriented clusters an orientational family in the following. However, it is a fact that approximant crystals possess in general several orientational families, as it was shown for instance by Tamura et al [5, 6, 9] for β - AlMnSi (with two families) and the isomorphous crystalline compounds η - Ti₂-TM

(space group Fd $\bar{3}$ m) where TM = Ni, Fe, Co, Mn, Cr. In this latter case, eight orientational families do exist in real space for which, because of icosahedral extinctions due to superimposition effects on the reciprocal lattice, only four of them appear in reciprocal space. By this, we mean that four pseudo - icosahedral clusters of intense peaks (centered at the central spot) can be observed, for which some Bragg peaks (vertices) are common to several clusters. Duality relations (by Fourier transform) between the orientational families in real space and the pseudo - icosahedral clusters of intense peaks in reciprocal space are totally satisfied [3, 5]. These clusters are centered at the TM(e) atomic sites. Of course, any investigation of reciprocal space (by any diffraction experiment) leads to sectioning such a 3 dimensional information, and we observe merely "rugous" sections of pseudo - icosahedral polyhedra, where all the spots to be considered for reasons of symmetry lie in a planar section having a certain (small) thickness.

Besides such examples of approximant crystals where several orientational families coexist, but where clusters are limited to a few layers [6, 9], we have the example of the α - AlMnSi phase (space group Pm $\bar{3}$) for which there is only one orientational family of pseudo - icosahedral clusters, but where the icosahedral shells extend over very large distances [9, 10], up to 4 nm and more, much larger than the lattice parameter, $a = 1.268$ nm, and therefore which interpenetrate a lot.

The purpose of this note is to report on some recent model of interpenetrating pseudo - icosahedral clusters (we call it "IPIC model") in a periodic context, that is to say approximant crystals, and in an aperiodic one, ie icosahedral quasicrystals (Verger - Gaugry et al., 1991 [11, 12]). Here, for simplicity's sake, only one orientational family is assumed to exist and pseudo - icosahedral clusters are all bounded in size.

2. SOME REMARKS ON THE DIFFRACTION PROCESS FROM "IPIC" IN APPROXIMANT CRYSTALS

The two main building blocks for cases 1) and 2) are the Double Mackay Icosahedron and the Bergman Unit, respectively constituted with 54 atoms and 44 atoms. Few researchers have investigated the external layers of these clusters [13] in approximant crystals (by this, we mean up to 20 or more layers) since there is a tacit agreement to consider that it is not of special

interest to do so, one reason coming from the use of the decoration procedures of tiles (prolate and oblate elementary tiles, or more complicated tiles [14]) in quasiperiodic tilings, which actually utilize only a few shells of these icosahedral clusters and which force the study of the connections between the atomic units (matching rules and vertex-, edge-, face- packings [15]); another reason arises from the difficulty of making simple models of quasicrystals with interpenetrating pseudo - icosahedral clusters, where sites are belonging at the same time to several layers of several IPIC. This difficulty is a problem of conception and of handling on a computer since it is necessary to avoid different types of atoms at the same site (problem of coloration unambiguity).

However, assume now that a crystal of given space group and position parameters is composed of a finite number of pseudo - icosahedral clusters which spread over large distances and interpenetrate inside the unit cell and therefore everywhere, by periodicity (an accurate axiomatization of a G - approximant crystal, with G, a non -crystallographic point group, is given in [11]). An incident plane wave will "see" independently each pseudo - icosahedral cluster, in its totality, and will give rise to a diffracting contribution. Each cluster of the orientational family contributes equally in the global response to the incident wave, by the principle of superposition, provided that the atoms in the intersected regions are counted with their multiplicities and that a phase is introduced due to the relative positioning of the clusters centers, in the structure factor of the crystal [10, 11].

The notion of interpenetration is not classical in crystallography since the easiest way to build a crystal consists in reproducing a motif at each node of a lattice. Here, we voluntarily aim at investigating the consequences of complex overlaps of motives when some parts of them follow the icosahedral symmetry and can be coherently defined (propagation of the icosahedral symmetry) over many motives around the central one, and therefore everywhere by periodicity. In this sense, an approximant crystal is more than a "crystallographically defined" crystal since it contains extra informations on highly symmetric (empty or occupied) sites as centers of pseudo - icosahedral clusters and the spatial extents of these clusters around them. This information has to be found by hand or on the computer [12], but it is clear that classical crystallography cannot provide it.

As an example, let us consider the α - AlMnSi phase. Table 2 and Figure 2 in [10], reported from [9], show that a description of the structure in terms of icosahedral atomic units which do not overlap, necessarily implies that the real clusters, as they "exist" as diffracting entities (some icosahedral shells have an occupation rate less than unity) are drastically truncated at a suitable distance from the origin and the body - centered site. Though a Patterson analysis of this approximant crystal takes into consideration the full information in reciprocal space from the IPIC diffraction properties, we retain in the reconstructions of the structure in terms of icosahedral units only a small part of the icosahedral clusters, truncating them, trying to avoid interpenetration. This attitude seems somewhat contradictory to us and, of course, this remark will take its full meaning in the context of quasiperiodic packings of atoms constituted with IPIC, - quasicrystals -, where we do not know a priori the exact extent of the icosahedral local order.

3. IPIC MODEL

For convenience, many models of i - phase propose atomic configurations for which the icosahedral symmetry is locally exactly satisfied within the icosahedral clusters [8, 16]. However, in approximant crystals, we have already observed and analyzed some deviations (angular deviations, radial displacements and absence of atoms at some sites on some icosahedral shells in clusters (Verger - Gaugry, Tamura and Barbier, [12, 17]) with respect to the perfect icosahedral symmetry in the atomic configurations: so-called pseudo - icosahedral clusters. The angular and radial corrections are small for "good" approximants and may vary within a larger extent for other approximant crystals [6]. Similarly, it is totally reasonable to think that small deformations of the perfect icosahedral clusters also occur in the i - phase but these deformations are mainly different and quasiperiodically defined by comparison with the case of the approximant crystal. For instance, some icosahedral phases such as in the Ti-TM system should generate pseudo - icosahedral clusters with fairly large deformations: indeed, in c - Ti_2Ni , the first icosahedral shell around $Ni(e)$ atoms is constituted with two types of atoms (9 Ti and 3 Ni) conferring a "chemical and topological (size effects) disorder" for the action of the icosahedral group, and similarly for the subsequent shells.

In this framework, we have tried to understand how the quasiperiodic distribution of pseudo - icosahedral clusters and their associated perfectly icosahedral clusters [17] intervenes in the diffraction process. For this, we define a " $m\bar{3}5$ - cluster" to be a finite set of points in R^3 which is $m\bar{3}5$ - invariant around a fixed center, center which belongs to this set or not. Let us denote it by $X(n)$, with the notations of [11], where n is the number of icosahedral layers in the cluster. When $m\bar{3}5$ acts transitively on one shell, the number of sites in this shell is: with zero degree of freedom, 12 (ico), 20 (dodeca), 30 (icosi), then, with one degree of freedom in each case, 60 (3 possibilities: pentakis, hexe, trisico), then, 120 (general case), with two degrees of freedom. The color of a point of the cluster is the type of atom placed at this point and we consider as usual an atomic site as a couple (point, color). Let us denote by $\delta(X(n))$ a slight deformation of the colored perfectly icosahedral cluster, given by a collection of displacements, one for each site. A "formal" quasicrystal fqc , to name it, is merely a state of matter with no hole and no overlap of atoms and for which a compatibility exists between such deformed clusters, where atoms may belong simultaneously to different layers of several clusters.

We define a formal fqc as an infinite assembly of atoms in R^3 , by the following local conditions: 1) (homogeneity condition) there exists an enumerable infinite collection of centers of clusters, empty or occupied, called $CC = \{s_1, s_2, \dots\}$, such that $0 < r_0 < \|s_i - s_j\| < R_0$, $i \neq j$, for some real numbers r_0 and R_0 , 2) (orientational compatibility) there exists a common $N \geq 1$ such that $\cap_i [X_i(n_i) - s_i]$ is a non - empty $m\bar{3}5$ - cluster $X(N)$ (coloration is not imposed for $X(N)$), 3) (covering) each atom in the assembly fqc belongs at least to one deformed colored cluster $\delta_i(X_i(n_i))$, centered at s_i , for a certain i . Let us denote by m the rank of the Z - module generated by CC .

To obtain interesting expressions of the structure factor, as a series, of the fqc assembly, we define and study the following scattering function [18]: for any $q \in E^*$ (= reciprocal space of $E = \mathbb{R}^3$),

$$H(q, \gamma_1, \gamma_2, \gamma_3) = \sum_k \sum_j (K + \gamma_1 z_j) (\Lambda + \gamma_2 \lambda_j)^{-1} \exp[2i\pi q \cdot (x_j + \gamma_3(\delta_k(x_j) - x_j))] \quad (1)$$

with $\gamma_1, \gamma_2, \gamma_3$ in the interval $[0 ; 1]$, where the first sum is taken over the infinite collection of $m\bar{3}5$ - clusters, counted by their centers, where j runs over all the atomic sites of the k -th deformed $m\bar{3}5$ - cluster $\delta_k(X_k(n_k))$; where K is the average atomic scattering factor, z_j the atomic scattering factor excess for the j th site, Λ is the average site multiplicity (average over all the atomic sites), λ_j the site multiplicity excess for the j th site, $S(q)$ is the structure factor at q of the perfect icosahedral unit $X(N)$ (optimally positioned $m\bar{3}5$ - invariant cluster) which is the perfect icosahedral unit the closest to the distribution of slightly deformed $m\bar{3}5$ - atomic clusters (in the sense of an appropriate least squares method [17]). We obtain the following $m\bar{3}5$ - invariant expression for the intensities, at a scattering vector q in reciprocal space:

$$I(q) = (K\Lambda^{-1}T S(q))^2 + \text{linear and quadratic terms} + \dots \quad (2)$$

The function T is a transparency function associated to the collection of centers CC , and its periodization in m - dimensional Euclidian space. T may take infinite values, but since we are mainly interested in models for which the intensities all form convergent series, whatever q is in E^* , T takes special forms associated to some integrable functions in $\mathbb{R}^{m-3}$. It is the analogue of the real - internal spaces matricial correspondances in the theory of phasons [19, 20]. Due to the lack of space, it is out of reach to justify such expressions here and we refer the reader to [11, 17, 18]. The other linear and quadratic terms give the couplings between deformations (topological disorder), icosahedral symmetry, chemical order (atomic number excess), and geometrical factors linked to interpenetration.

Since no particular hypothesis is made on the geometry of $X(N)$, this study shows that, at the first - order with the general above assumptions, the diffracting properties of an average perfectly icosahedral cluster, whatever it is, but finite, control the diffracting properties of the fqc. This cluster $X(N)$ remains of fundamental importance, with the possible successions of arithmetic and geometric sequences of icosahedral shells it may contain, which have their own specific diffracting properties [9]. The question of asking why such assemblies of atoms lead to intense Bragg peaks of small widths can be answered by saying that the width is roughly a decreasing

function of the size of the object $X(N)$ in real space, by well - known properties of the Fourier Transform. Physically, this means that the peak width is, in this approach, a measure of the spatial extent of the icosahedral order in the quasicrystal. Similarly, pseudo - inflation rules in diffraction patterns then arise from those given by $X(N)$, as well as the asymmetry of intense Bragg peaks which seems to be an intrinsic character of a limited icosahedral local order [18]. The function T in eq. (2) acts on the diffraction pattern of $X(N)$ as a modulating function able to annihilate some peaks and provide "m - dimensional lattice" icosahedral extinctions.

This model is easily generalized to formal quasicrystals for which the clusters are not all finite, but such that the average cluster $X(N)$ has a convergent structure factor. This formalism is also well - adapted to describe approximant crystals [10 - 12] : there T has to be replaced by the quantity t , which is the number of clusters per unit cell of the Bravais lattice of the crystal; and the local conditions 1) to 4) of icosahedral interpenetrating clustering have slightly to be changed to have the crystallographic description of the atomic sites of the crystal true.

We have not investigated the problems of packings of icosahedral units as such, as in the icosahedral glass model [15], but the way the diffraction process can be treated when matter is obeying some local rules in a periodic case or a quasiperiodic one. This model takes into account the diffracting properties of the icosahedral glass model.

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