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QUASI-CRYSTAL AND CRYSTAL IN AlMn AND AlMnSi. MODEL STRUCTURE OF THE ICOSAHEDRAL PHASE

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Résumé - Il existe une grande similarité entre la phase cubique a dans AlMnSi et la phase icosaédrique i-AlMnSi ou AlMn. Une étude par microscopie électronique en transmission (T.E.M.) d'un ruban hypetrempe où les deux phases coexistent, établit clairement leurs relations. On montre que les deux structures peuvent être décrites à partir d'unités de bases communes -un double icosaèdre Al-Mn- connectées en orientation parallèle suivant leurs axes d'ordre 3 par des liaisons Mn octaédriques. Une connection déterministe des icosaédres dans la phase i est cohérente avec un pavage Penrose à 3 dimensions. Un squelette i de grandes dimensions est construit par ordinateur, où la décoration du pavage par les icosaédres, satisfaisant à des contraintes stériques, est résolue par un algorithme de théorie des graphes. Des projections du modèle sur des plans normaux à des axes de symétrie et les diagrammes de diffraction calculés, après comparaison avec des résultats T.E.M. haute résolution et de diffraction, indiquent qu'il contient l'essentiel de la structure de la phase i dans ces alliages.

Abstract - There is a close similarity between the cubic a-phase in AlMnSi and the icosahedral phase i-AlMnSi or AlMn. A transmission electron microscopy (T.E.M.) study of a melt-spun ribbon where the two phases coexist, establishes clearly their relationships. It is shown that both structures can be described with common basic unit -a double Al-Mn icosahedra- connected in parallel orientation along their 3-fold axes by octahedral Mn bonds. A deterministic connection of the icosahedra in the i-phase appears to be consistent with a 3 dim-Penrose tiling. A large size i-skeleton is then computer generated, where the decoration by icosahedra of the tiling, prescribed by steric constraints, is solved by a graph theory algorithm. Projections of the model on planes perpendicular to symmetry axes and calculated diffraction patterns, once compared with high resolution T.E.M. and diffraction data, indicate that it contains the main point of the i-phase structure in these alloys.

I - INTRODUCTION

One expects the physical properties of quasi-crystals, of which only little is known today, to rely for long wave length excitations on their long range orientational order or translational quasi-periodicity, and for short wave length ones on their local atomic arrangements.

Soon after the discovery of the icosahedral phase (i-phase) in Al-Mn by Shechtman et al. /1/, the long range problem was solved by the very elegant and powerful technique of cut and projection of periodic 6-dimensional hyperlattices /2/ /3/ /4/, leading to a 3 dim.-generalization of the Penrose tiling (3 DPT). The agreement of the Fourier transform of such a quasilattice with experimental electron diffraction data was sufficiently good to assign a second order role to the local atomic order.

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However significant intensity variations observed in diffraction experiments with varying scattering lengths (X rays /6/, neutrons /7/, see also this conference) evidenced the existence of an atomic ordering on the quasi-lattice sites.

Solve the local order is equivalent to decorate with atoms the prolate and oblate rhombohedral tiles of the quasi-lattice, with a special difficulty inherent to the matching rules constraining the tiling: it is not obvious that an unique pair of elementary tiles can be defined. On the other hand it is clear that the decoration is easier to perform in the 3 dim-space, in order to reap advantage from the elementary rules of chemistry; a further climb of the atoms in the 6 dim-hyperspace for simpler Fourier transform calculations is possible.

It also appears simpler and with a physical ground to decorate the 3 DPT by polyatomic clusters which preserve its icosahedral symmetry elements: icosahedron, dodecahedron, rhombic triacontahedron... The size of the units implies to start with a basic bare tiling of convenient size (fixed by the edge length $a_R$ of the rhombohedral tiles). The analysis of the resulting modelling, in a further step, may be done in terms of atoms locations, and consider, whether or not a deflated atomic tiling exists.

A natural choice of the dressing clusters can be addressed to crystalline phases, where there are known to exist but packed periodically. On the basis of the intrinsic stability of the clusters, the difference between crystals and quasi-crystals is then related to their connectivity (coordination number, bond length) and its long range propagation (periodic; aperiodic but deterministic; at random). To that respect, liquid, amorphous, quasicrystalline and crystalline states may enter into a single filiation, where the formation kinetics is suspected to play an important role.

Initially, we followed a part of this procedure, by trial and error, borrowing icosahedral units and bonds of the crystalline cubic $\alpha$-phase in AlMnSi or AlFeSi. Introducing a simple breaking of periodicity in the connection of the icosahedra, we proposed a realistic structure of the $i$-phase in AlMn /7/. Independently, the development of the cut and projection technique led Elser and Henley /8,9/ to a similar result, after describing the cubic crystal through a 6 dim-strip of rational slope, approximant of the golden number $\phi = (1 + \sqrt{5})/2$.

In the present work, we give a more complete structural approach of the $i$-phase. We first introduce the cubic $\alpha$-phase, as observed during the crystallization of a melt-spun AlFeSi glass. We show next, in a melt-spun AlMnSi ribbon where $\alpha$ and $i$-phase coexist, the close relations between crystal and quasicrystal. The relevance to use the icosahedral units of the $\alpha$ phase to build the $i$-phase is outlined. Finally a quasicrystal is computer generated with a size close to the correlation length experimentally determined in AlMn - $\sim 20$ nm - /5/. The decoration of the 3 DPT is solved by a graph algorithm, and beyond the basic icosahedron various larger atomic units are also tested. Projections of the model on planes perpendicular to symmetry axes and Fourier transforms are compared with high resolution electron microscopy and diffraction data.

II - THE $\alpha$-PHASE

The cubic $\alpha$ phase has first a strong similarity with the $i$-phase in its as grown dendritic morphology: in Fig. 1a), a $\alpha$ crystal has been formed after heating a melt-spun Al$_7$Fe$_{13}$Si$_7$ glass /10/, whereas in Fig.1b), the quasi-crystals are as spun from a melt Al$_6$Mn. A comparison of their respective stoichiometry, as determined by X-EDS analysis in a scanning transmission electron microscope (STEM) /10,11/ is also instructive: Al$_8$Fe$_2$Si for $\alpha$, Al$_4$Mn for $i$, i.e. the ratio of transition metal to aluminium atoms has a common value of 20 %. Finally a strong correlation in electron diffraction patterns was noticed /7,12/, somewhat detailed later in the study of an as spun Al$_{74.8}$Mn$_{20.9}$Si$_{5.8}$ ribbon, where $i$-and $\alpha$-phases are found to coexist, announces a relationship between the structures of the two phases.
The α or i-phases are formed by a first order transformation: from the amorphous state for α, Fig. 1a) - a rejection of pure Al (white parts) at the periphery of the crystal is clearly evidenced, from the liquid state for i, Fig. 1b) - the i-phase Al₄Mn is embedded in a f.c.c. matrix, which is a supersaturated solid solution of Mn in Al /11/.

The structure of the α phase, established by Cooper and Robinson /13/ and Cooper /14/, is cubic, either Pm3 in AlMnSi or Im3 in AlFeSi, with a unit cell parameter a₃ = 12.68 Å and a₄ = 12.56 Å respectively. The structure, schematically drawn in Fig. 2, consists in a packing of double icosahedra (an Al icosahedron, with a vacant center, surrounded by a parallel double sized Mn icosahedron). The Mn icosahedra are connected along the <111> directions through four of their 3-fold axes; the face-to-face connections forms a Mn octahedral bond, of length a₃/3 = 10.98 Å in
α-AlMnSi, which maintains the icosahedra in the same orientation. Inside this skeleton, the Al icosahedra are connected through <111> chains of three bonding Al octahedra, whereas others Al atoms cap the Mn icosahedral vertices. It is interesting to note that the vacancy in transition metal at the center of the Al icosahedron is also discarded in the i-phase from Mössbauer data /15/.

III - RELATIONSHIPS BETWEEN α- AND i-PHASE IN Al_{74.2%Mn_{20}Si_{5.8}}

It is now known that a small addition of Si stabilizes the i-phase and confers it a higher quasi-crystalline perfection as compared with the i-phase in AlMn /16/. Furthermore, a small proportion of α-phase, which coexists with the i-phase in the ribbons, confirms (see also /17/) the tight structural connection that we initially suggested when the two phases were separately formed /7/.

Fig. 3a) is a bright field micrograph of the tip of a dendrite where islands of i-phase coexist with the α-phase. Convenient tilts around [010]α and [101]α allow to establish the orientation relationships between the two phases (simply summarized in Fig. 3g), where the icosahedron -which 2, 3 and 5 fold axes are those of the i-phase-, is inscribed in the α cube, namely: [100]α// [A2]i, [111]α// [A3]i, [201]α// [A1]i, ([502]α or [1305]α at 9° or 13° from [A3]i), [100]α// [A5]i ([305]α or [508]α at 75° or 28° from [A5]i).

We also note (not indicated in the Fig. 3) that the more intense spots are in nearly coincidence: [035]α and [100001]i, [532]α or [0006]α and [110001]i, [031]α and [110001]i, using for the i-phase reflexions the 6 icosahedral indices of Bancel et al. /5/.

High resolution imaging in axial illumination along [100]α// [A2]i and [503]α// [A5]i are shown in Fig. 4, where orientation relationship and degree of coherency can be directly appreciated. In Fig. 4b), two 36° rotated α variants, αI and αII, seem to be issued from the i-phase. Using the α phase as a standard it is then possible to calibrate the i-phase quasi-lattice constant, as discussed in next section.

IV - MODEL STRUCTURE OF THE i-PHASE IN AlMn AND AlMnSi

IV-1 - Principle:

A logical idea to model the i-phase structure is to pack icosahedra maintaining the same orientation in order to propagate at long range their orientational order. A packing vertex-to-vertex or edge-to-edge, as initially proposed by Shechtman and Stojech /13/, see also /19/, suffers from a rotation freedom around the connection, which makes the rule somewhat "ad hoc". At the opposite the face-to-face connection as in the first cousin α-phase, is rigid.

Applying this 3-fold axis connection, we first built by hands /7/ /11/ a double icosahedra skeleton according to the following rules: for steric constraints no octahedral bonds on adjacent icosahedron faces are allowed; the first-neighbours coordination number must be lower than 8, which insures the translational periodicity of the α-phase; the distance between first-neighbouring icosahedra along a 3-fold axis may be slightly at variance from this in the α-phase. A local icosahedral symmetry of the model was obtained, which comparison of atoms projections with high resolution micrographs, and of dense atomic plane spacings with diffraction data /5/ was satisfactory /12/.

The results of §.III, in terms of the diffraction indexation /12/, allow to determine the size ai of the Mn icosahedron edge in the i-phase:

i/ within the precision of the diffraction pattern of Fig. 3b), the (005) reflection lies at half-distance of (11010)j and (110000)j, from which we deduce ai = 2/5 a = 5.07 Å.

ii/ the i-fringes of Fig. 4a), pependicular to the 3-fold axis, correspond to (110001)j; their spacing, ai (φ + 1)/2√5, as measured from the directly imaged cubic cell a, is equal to 3.66 Å; then ai = 5.10 Å.
Fig. 3 - Transmission electron micrograph of coexisting α- and i-phases in a melt-spun Al74.2Mn20Si5.8 (a), and related diffraction patterns after convenient tilt angles, (b) to (f) - see text for details - (g) summarizes the orientation relationships. The weak spots of the pattern - (e) are formed by double diffraction by the i-phase of the α diffracted beams: due to the aperiodicity of the i-phase, this effect gives rise to rows of spots.
Fig. 4a)-High resolution of the \( \alpha \)- and \( i \)-phase in the overlap region:

\[ [100]_{\alpha} // [A2]_{i} \]

This estimation is in good agreement with the Cooper and Robinson measurements in the \( \alpha \) phase where \( a_{\alpha} = a_{i} \times (2.493 \pm 0.009) \). We conclude that \( \alpha \) and \( i \)-phases in \( \text{AlMnSi} \) are two different packings of the same Mn icosahedron. The distance icosahedron center-Mn vertex is \( \approx 4.85 \) \( \text{\AA} \).

IV-2 - Computer modelling:

The local analysis of this skeleton showed that it was consistent with 3 DPT rhombohedral tiles, of edge length \( a_{R} = a_{i} \phi^{2} / \phi + \frac{\sqrt{3}}{2} /12/ \), shown in Fig. 5. Four of the eight vertices of both tiles are occupied by a double icosahedron, on the opposite vertices of the rhombic faces; whereas the oblate rhombohedron is always empty, two types of prolate ones are distinguished: one which contains one icosahedron on its large diagonal, in the ratio \( 1: \phi \) from the occupied vertex to the vacant one (Fig. 5), the other being empty. The opposite faces of these rhombohedra are not equivalent, which precludes their translational periodic packing.

On this basis, an extended skeleton has been computer generated, decorating the tiles of a 3 DPT built by the cut and projection method /2/, with icosahedra accor-
Fig. 4b) - High resolution of the α and i-phase in the overlap region: [503]_α // [A5]_i.

Fig. 5 - Icosahedra decoration of the prolate (a) and oblate (b) rhombohedral tiles.
Fig. 6 - Projections of the icosahedra skeleton on planes perpendicular to a 2-fold axis, a), and a 5-fold axis, b). \( \phi = \text{Mn atom. } + = \text{Al atom.} \) In a), the prolate rhombohedron, of edge length \( A_R \), decorated by 5 icosahedra, has been represented.
Fig. 7 - High resolution micrograph of (AlMnSi)$_i$ taken along a 5-fold axis, with a resolution lower than 6 Å. An icosahedra skeleton, of edge length $a_1 \phi^4 = 34.95$ Å, superimposes exactly on the micrograph (see text).
 ding to the rules previously described. The skeleton contains 1095 icosahedra, i.e. 26230 atoms. Its size is about 20 nm., close to the correlation length in the i-phase AlMn /5/. Various additionnal decorations of the skeleton have been attempted (§ IV-3).

The two-steps algorithm used to build the model is given in Appendix.

IV-3 - Analysis of the computer simulation:

To visualize the structure, the projections of the icosahedra skeleton on planes normal to the icosahedra symmetry axes have been made. Examples are given in Fig. 6. As emphasized in /7/ and /12/, these projections show that the atoms lie in planes parallel to the projection axis, distributed periodically or quasi-periodically—in the sense of Levine and Steinhardt /20/, i.e. with incommensurate intervals—perpendicularly to the 5, 3 or 2 fold-axis lying in the projection planes. The alignments are at best seen looking the figures at glancing angle. Fig. 7 is a medium resolution micrograph of the i-phase taken with an incident beam parallel to a 5 fold-axis with an objective aperture which cuts the resolution below ~ 6 Å. The agreement with a projected skeleton inflated of φ^4 with respect to this described in § IV-2, is indeed striking.

On the other hand, the icosahedra skeleton is evidently a loose structure, of stoichiometry Al-Mn, and although the average icosahedra coordination number, near 5.5, is higher than the value 3.4 obtained by Stern et al. (this conference) for a random packing, others atoms Al and Mn must be added in order to achieve the correct stoichiometry ( AlMn ) and density, 3.7, which is close to the α phase density (see Audier and Guyot, this conference).

To that respect, two attempts have been made:

i/ the addition of 30 Al atoms in the middle of each icosahedron edge, defining the 54-atom Mackay icosahedron, as proposed by Elser and Henley /8/. But if the stoichiometry is almost correct (Al_{42}Mn_{12}), the density is still too small.

ii/ the surrounding of each icosahedron by a triacontahedron, which sites can be occupied by either Mn or Al atoms. Fig. 8 shows such a structure, with only Mn atoms at the vertices of the triacontahedra. It can be seen that two adjacent triacontahedra either share a face, or overlap, which makes tricky the estimation of the density.

The respective merits of the models are now examined with respect to their Fourier transforms. Cuts of this Fourier transform by planes perpendicular to a 2 fold and a 5 fold-axes are shown in Fig. 9 for the icosahedra skeleton (a), the Mackay icosahedra (b), and icosahedra-Mn triacontahedra (c). The scattering lengths have been taken without scattering angle variation (f_{Mn}/f_{Al} = 1.77, for the simulation of the either electron or X-rays diffraction). These patterns appear similar to the observed electron diffraction patterns, with however certain differences for each of them; for example the intensity ratio I(100000)/I(110000) is lower than unity for the icosahedra and triacontahedra models, whereas it is larger than unity for the Mackay icosahedra and the experimental patterns. Calculations of neutron diffraction (f_{Mn}/f_{Al} = -1.11) have also been made, leading to reflection intensity variations in qualitative agreement with the results of Dubois et al. /6/.

However, even if the essential features of the diffraction patterns (symmetry, sequence of peaks and scaling along the symmetry axes) are conveniently reproduced by the models, a complete comparison of the intensities with experiments, without positionning all the atoms is premature. And again, stoichiometry and density must remove any Fourier space degeneracy. This is long well known from modelling the amorphous state...

Finally we stress the difference between our model, which is a 3 DPT decorated by icosahedra, and an elementary 3 DPT decorated by atoms. After decorating the 3 DPT of edge length a_R, smaller tiles of edge length a_R = A a^{-2}, decorated by atoms, may be considered as described in /12/. But the vertices of this a_R tiling do not form a
twice deflated 3 DPT for a simple reason: the overall self-similarity ratio of a 3 DPT is basically $\phi^{-3}$, /2/, /3/, /21/.

Furthermore, depending on which way the diffraction patterns are indexed, different values of $a_r = A_r \phi^{-2}$ are obtained in i-AlMn: either 4.85 Å, from /12/ which is related to a Hendricks-Teller analysis of the structure /22/, or 4.6 Å, according to Elser /3/.

On the basis of the present results, we believe that in AlMnSi, $\alpha$ and i-phases have in common the same Al-Mn double icosahedron, with the dimensions previously given. However in the $\alpha$-phase, the Mn atoms do not lie exactly at the vertices of rhombohedral tiles: they are slightly (~5.4%) displaced beyond the vertices of rhombohedra of edge length 4.6 Å, as schematically drawn in Fig. 10. So it would be in the i-phase, if one keep the same tiles. The Si atoms are in substitution on the Al sublattice.
Fig. 9 - 2 fold (left) and 5 fold (right) calculated diffraction patterns of the model. a) Al-Mn icosahedra. b) Mackay icosahedra. c) Al-Mn icosahedra + Mn triacontahedra. The area of the spots is proportional to the calculated intensity. The spot letter a holds for (100000), d for (110000), c for (111010), h for (110000)/5/.
Fig. 10 - In (AlMnSi)_a, the Mn atoms do not lie exactly on the vertices of rhombohedra. 4.6 Å prolate rhombohedron in dotted line.

APPENDIX

COMPUTER SIMULATION OF THE MODEL

The algorithm to build the computer simulation of the quasi-crystal atomic model is separated in two distinct steps:

1- Building the 3 DPT with the cut-projection method /2/.
2- Decorating this tiling with icosahedra.

1- Building the quasi-periodical tiling:

During the construction of the tiling the computer keeps two lists in memory: a list of rhombohedra and a list of rhombic faces external to the tiling. Each algorithmic step contains the following operations:

- choose a face in the list.
- compute by the projection method the new rhombohedron of the tiling on this face
- add the faces of this rhombohedron to the faces list, deleting those which are already present.

All the computations are made in the 6-dimensional space associated with the projection method. Vertices are integer sextuplets, rhombohedra are three-dimensional cubes and are represented by a 6-dimension integer point and three axes. At each step we choose the oldest face in the list, so the tiling grows compactly.

A two dimensionnal illustration with the Penrose tiling is given on the figure below. Here the "rhombohedra" are the rhombs and the "faces" are the edges.

2- Decoration of the tiling:

The Duneau-Katz 3DPT gives us a skeleton to build the net of icosahedra connected with octahedra. The tiling is decorated with the three rhombohedric motif: the oblate rhombohedron and the two prolate ones. There are two groups of icosahedra on the tiling: vertex icosahedra which stand on vertices of the tiling and internal icosahedra which are found inside some prolate rhombohedra. Note that every octahedron connects a vertex icosahedron and an internal icosahedron—two icosahedra of the same group cannot be connected.

Half the vertices are decorated with a vertex icosahedron. The rule is that no
adjacent vertices can be both decorated. If we remember that vertices are the projection of integer sextuplets and that two vertices are adjacent if they differ on one and only one coordinate by unity, we have a procedure to choose the decorated vertices. Namely, add the six integer coordinates and (without loss of generality) we decorate the vertex if this sum is even.

Finding the internal icosahedra is not as easy because there is no global rule like the coordinate sum. We have only a local exclusion rule which describes when two adjacent prolate rhombohedra cannot both have an internal icosahedron. All rhombic faces are decorated with two diagonally opposed vertex icosahedra. Let us call a face a critical face if the two icosahedra are on the long diagonal. Two prolate rhombohedra sharing a critical face cannot both contain an internal icosahedron. Since, otherwise, the icosahedron on the sharp vertex of the two rhombohedra would be connected with the two internal icosahedra. Consequently two connecting octahedra would be on two adjacent faces of the icosahedron - a configuration forbidden in the model.

The internal icosahedron problem can be restated using graph theory. Consider the graph whose vertices are the prolate rhombohedra. Two vertices are connected with an edge if the two rhombohedra share a critical face, thus they cannot both contain an
internal icosahedron. The set of prolate rhombohedra containing an internal icosahedron is a stable set of this graph (a stable set is a set of vertices of a graph containing no edges). The problem of finding a stable set with maximum cardinality is very difficult, but in our problem we can use a very simple algorithm with good results. The algorithm is called greedy algorithm because it scans the vertices adding them to the stable set whenever it is possible and never reverses on a decision. This algorithm is executed during the construction of the tiling: for each new prolate rhombohedron added to the tiling we add an internal icosahedron if the rhombohedron does not share a critical face with a rhombohedron already present in the tiling and containing an internal icosahedron.

Using this algorithm we built a model of 1000 rhombohedra and the decoration gave 1095 icosahedra, the coordinates of those icosahedra were recorded in disk files. Using this data we made all the computations: Fourier transforms, projection of the atoms, coordination numbers, ...

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