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High-Resolution Electron Microscopy Image Simulations on the R-Al₅CuLi₃ Icosahedral Approximant Phase

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Abstract

The study of crystalline approximant structures is an important way to understand the local order in quasicrystalline phases. We compare here high-resolution electron microscopy (HREM) image simulations of the cubic approximant phase $R\text{-Al}_5\text{CuLi}_3$ with experimental HREM images of the icosahedral Al_6CuLi_3 phase. Local two-dimensional (2D) arrangements such as Penrose tiles of different scales and projections of icosahedral clusters (triacontahedra) are found to be common to both phases, confirming the close similarity of their short- and medium-range order. The shape and decoration of three-dimensional (3D) tiles is suggested from their 2D projection. A 2D and 3D inflation rule, comparable with that expected in the icosahedral phase is demonstrated in the approximant phase.

§ 1. INTRODUCTION

Several methods have been performed in order to determine the structure of the quasicrystalline phase. Direct methods (experimental) allow the high-dimensional periodic structure of these phases to be obtained directly from X-ray or neutron diffraction data and the analysis of high-dimensional Patterson function. This class of methods, however, needs sufficiently large monoquasicrystalline samples with few defects. It has been applied to icosahedral phases (i-phases) and decagonal phases (d-phases): (Al-Mn-Si) (Janot, de Boissieu, Dubois and Pannetier 1989, de Boissieu, Janot and Dubois 1990), i-(Al-Fe-Cu) (Cornier-Quiquandon *et al.* 1991), i-(Al-Pd-Mn) (Boudard *et al.* 1991), d-Al-Cu-Co (Steurer and Kuo 1990) and d-(Al-Co-Ni).

For other phases, indirect methods are used. This class of methods builds quasicrystalline structures with the help of the local order found in closely related crystalline phases called approximants. Indeed, several diffraction, extended X-ray absorption fine-structure and electron-energy-loss spectroscopy experiments have shown the close resemblance between the local orders of quasicrystalline and associated approximant phases. In the case of i-phases, the structural study of the local order of approximant phases had provided evidence for complete, or partial, fairly large icosahedral atomic clusters. These clusters are used as fundamental building blocks for the construction of quasicrystalline phase structures. The quasicrystal structure is obtained in different ways.

- (1) One can stack randomly these blocks which are oriented in the same way. This is the 'icosahedral glass' model formerly proposed by Shechtman and Blech (1985) and Stephens and Goldman (1986) and modified by Robertson and Moss (1991).

- (2) One can decorate either a perfect three-dimensional (3D) Penrose tiling (quasicrystalline models) or a random tiling (entropic model). The decoration of the Penrose tiles is either 'atomic', suggested by the decomposition of the approximant crystal in tiles (Henley and Elser 1986, Yamamoto and Hiraga 1988), or 'molecular', where the tiles are decorated by icosahedral clusters found in the approximant phase structure (Audier and Guyot 1988). The random-tiling model was first suggested by Elser (1985) and developed by Strandburg, Tang and Jaric (1989) and Widom, Deng and Henley (1989).
- (3) One can construct a high-dimensional crystal decorated with atomic surfaces chosen in a way to obtain, by an irrational cut, a 3D quasicrystal structure with a local order which is the closest possible to that of the approximant phase. This is the method used by several workers (Cahn, Gratias and Mozer 1988, Duneau and Oguey 1989, Qiu and Jaric 1989, Yamamoto, Kato, Shibuya and Takeuchi 1990).

Indirect methods have been widely used to describe i-phases such as i-(Al-Mn-Si) (Guyot and Audier 1985, Audier and Guyot 1986), i-(Al-Li-Cu) (Audier and Guyot 1988), i-(Ti-Ni) (Tamura, François, Loiseau and Verger-Gaugry 1991), i-(Mg-Al-Zn) (Henley and Elser 1986) i-(Al-Mg-Cu) (Sakurai, Tanaka, Watanabe and Nanao 1990) and 2D quasicrystalline phases with decagonal, octagonal and dodecagonal symmetries. They are the only possible method for some metastable phases obtained in too low quantities (i-(Ti-Ni) for instance) or with many defects.

An accurate knowledge of the local order of approximant phases is therefore very useful for the determination of the structure of quasicrystalline phases. In this paper, we are concerned with the well known approximant-i-phase couple R-Al₅CuLi₃-i-Al₆CuLi₃. Our purpose is to achieve a 3D correspondence between some fundamental building blocks seen in high-resolution electron microscopy (HREM) image simulations of the R-phase and to compare them with those encountered in the HREM images of the i-phase. A pseudo-inflation rule comparable with that reported for the α -AlMnSi phase (Tamura and Verger-Gaugry 1992), is demonstrated in the R-Al₅CuLi₃ structure and is investigated using the HREM images.

For the R-phase, we have first generated slices of crystal oriented along a pseudo-fivefold axis as 'supercell' files. The HREM images are then computed by a multislice method, using Stadelmann's (1987) image simulation software. This was done for different thicknesses, different defocuses and for an accelerating voltage of 400 kV. At the Scherzer defocus and for a thickness of 4.6 nm, the white dots correspond to low-potential areas whereas dark regions are high-potential areas. Several contrast inversions happen when the defocus varies.

This paper is divided into three parts. First, in § 2, we briefly recall the description of the R-phase in terms of pseudo-icosahedral symmetry. In § 3, we see how the inflation rule and the different clusters defined in § 2 on HREM image simulations are visualized and compare them with the i-phase. Section 4 is devoted to HREM image motifs which are shown to be common to both phases and we try to achieve a connection between the two-dimensional (2D) motifs visible on HREM images and 3D structural motifs in the R-phase.

§ 2. DESCRIPTION IN TERMS OF PSEUDO-ICOSAHEDRAL ORDER OF THE R-PHASE STRUCTURE

R-Al₅CuLi₃ is a b.c.c. crystalline phase (space group, Im $\bar{3}$; $a = 1.3914$ nm) with 160 atoms per unit cell (Audier *et al.* 1988). The unoccupied origin and body-centred sites are surrounded by successive atomic shells with almost icosahedral symmetry: a small

Al, Cu icosahedron ($r=0.2518$ nm), a Li pentagonal dodecahedron ($r=0.4532$ nm) and a second Al, Cu icosahedron ($r=0.5049$ nm). The set of the two last shells forms the small triacontahedron. The next shells are an Al, Cu pentakis-dodecahedron called a 'soccer ball' ($r=0.6686$ nm), a second Li dodecahedron ($r=0.7505$ nm) and a Li icosahedron ($r=0.8123$ nm). The two last shells form the large triacontahedron. This second triacontahedron is nearly τ times larger than the first triacontahedron (τ designates the golden mean).

The R-phase is described as a b.c.c. stacking of large triacontahedra. The connections between atomic pseudo-icosahedral clusters of adjacent sites are as follows: 'soccer balls' share a hexagonal face and large triacontahedra an oblate Ammann rhombohedron along the $[111]$ directions. They also share respectively an edge and rhombic face along the $[100]$ directions (fig. 1).

Pseudo-icosahedral shells are all oriented in the same way defining one pseudo-icosahedral orientation as follows: $[0, -1, \tau]$ are pseudo-fivefold directions, $[1, 1, 1]$ and $[1, 0, \tau^2]$ are pseudo-threefold directions and $[1, 0, 0]$ and $[1, \tau, \tau^2]$ are pseudo-twofold directions. Cluster connections are then along pseudo-twofold and pseudo-threefold directions.

Above, we have ended the list of the successive atomic shells at the second triacontahedron. This is sufficient to describe the entire R-phase structure as a stacking of pseudo-icosahedral clusters, but this list is not exhaustive and larger shells were in evidence. Figure 2(a) shows a projection of a slice of the R-phase along a pseudo-fivefold axis. We have represented the first, the second, the third and the fourth

Fig. 1

The cubic approximant phase $R\text{-Al}_5\text{CuLi}_3$ is described as a body-centred stacking of clusters formed by a small Al, Cu icosahedron, a Li pentagonal dodecahedron, a second Al, Cu icosahedron (the two last polyhedra form the small triacontahedron), an Al, Cu soccer-ball and a Li large triacontahedron.

Fig. 2

Pseudo-inflation and inflation rules in the approximant and the i -phases in the Al-Cu-Li system respectively. (a) Projection of the R-phase structure along a pseudo-fivefold axis. A pseudo-self-similarity property in the ratio of the golden mean can be defined around origin and body-centred sites. The four triacontahedra are slightly distorted in the actual 3D structure and are complete except for the third triacontahedron where eight vertices out of 32 are unoccupied. (The large atoms are Li, and the small atoms are Al). (b) HREM image simulation of the R-phase for a sample of thickness 4.6 nm at the Scherzer defocus and along a pseudo-fivefold axis. The pseudo-self-similarity property is locally apparent around projections of body-centred and origin sites but is slightly distorted. (c) Experimental HREM image of the $i\text{-Al}_6\text{CuLi}_3$ phase along a fivefold axis. The thickness of the sample is less than 5 nm. The defocus is near the Scherzer value (Hirabayashi *et al.* 1989). The self-similarity property is intrinsic to the quasicrystalline phase structure.

triacontahedra, which follow a pseudo-inflation rule in the ratio of the golden mean. The third triacontahedron is indeed almost τ times larger than the second, and the size of the fourth follows a similar relation to the third, and so on. This 2D self-similarity property is quite remarkable. We have shown that at least the third and the fourth triacontahedra actually exist in the 3D structure. The third is incomplete (eight vertices out of 32 are missing). The mean radii are respectively, 1.2220 nm for the Al incomplete dodecahedron and 1.3144 nm for the Li icosahedron. The fourth triacontahedron is complete and the mean radii are respectively, 1.9473 nm for the Li dodecahedron and 2.1561 nm for the Al icosahedron. These triacontahedra are only slightly distorted. This

shows that the pseudo-icosahedral feature of the approximant phase is not limited to the first neighbours but propagates as far as 2 nm around the central site in spite of the necessary perturbing effect of the periodicity. Approximant phases such as $R\text{-Al}_5\text{CuLi}_3$ and $\alpha\text{-AlMnSi}$ are therefore more 'approximant' than expected because of this pseudo-similarity property which is thought to be rather a characteristic of the so-called quasicrystalline phases.

§ 3. SHAPE OF ICOSAHEDRAL CLUSTERS ON HREM IMAGES

Figure 2(b) is a HREM image simulation of the R-phase for a sample of thickness 4.6 nm at the Scherzer defocus. The beam direction is $[0, -1, \tau]$. The image sides are parallel to $[1, 0, 0]$ and $[0, \tau, 1]$ directions. Figure 2(c) is an experimental HREM image of the $i\text{-Al}_6\text{CuLi}_3$ icosahedral phase taken by Hirabayashi, Hiraga, Shindo and Williams (1989). The sample is assumed by the workers to be less than 5 nm thick and near the Scherzer defocus. We notice a strong similarity in the local environment between the two phases and several motifs (such as pentagons, 2D Penrose tiles, projections of prolate and oblate Ammann rhombohedra of different sizes, and projections of triacontahedra of different sizes) are common to both phases.

In this section we are concerned by the representation of the icosahedral clusters described in § 2, for both the approximant and the i-phase on the HREM images. In the R-phase simulation, the small triacontahedra appear as rings of ten white dots with an inner non-homogeneous ring. These rings appear periodically along the $[1, 0, 0]$ direction and quasiperiodically along the $[0, \tau, 1]$ direction. They are complete or tangled with other rings. These rings are similar in shape and in size to those appearing stacked aperiodically on the i-phase micrograph. The second triacontahedron appears as a ring of black holes surrounded by three white dots. For the i-phase (fig. 2(c)), we have represented the successive triacontahedra projection in the geometrical sequence in the ratio of the golden mean which is characteristic of the self-similarity property of the quasicrystal. As for the approximant phase, this property which is apparent in the simple projection of the structure (fig. 2(a)) and which has been given as evidence in 3D (see § 2) is somewhat hidden by the periodicity effect in HREM. This periodicity effect becomes prominent with increasing sample thickness. We have also represented the third triacontahedron but larger triacontahedra are not clearly visible. We notice that the pseudo-self-similarity property is more apparent for different values of defocus, particularly in contrast inverted images (for instance at the defocus 70 nm).

Figure 3(d) shows a projection of a slice of the R-phase crystal along a pseudo-fivefold axis. Small triacontahedra are drawn and the white dots of the HREM image are superimposed. The white dots correspond to low-potential channels or holes in the clusters.

The similar local arrangements of white dots in HREM images of the approximant and of the i-phases strongly suggest the existence of common building blocks in both phases. A natural choice of a common building block is the constitutive icosahedral cluster of the R-phase (atomic shells up to the second triacontahedron). The connection differences between these clusters in the two phases imply some local atom rearrangements in the outer shells (soccer ball and second triacontahedron). As for larger triacontahedra, the similarity between the inflation rule stated in the R-phase and that in the i-phase is only apparent from the atomic and chemical composition points of view. Indeed, the constitutive atoms inside these triacontahedra belong to a periodic packing of building blocks in the crystalline phase and to an aperiodic packing in the i-phase.

Fig. 3

Cluster motifs in HREM images. (a) The i-phases: projection of Ammann rhombohedra of different scaling ratios and pentagons can be superimposed on the image. We have drawn here only projections of a τ -inflated oblate and of a τ^2 -inflated prolate. (b) R-phase: the motifs defined above for the i-phase are recognizable in the HREM image of the R-phase. (c) 3D correspondence of 2D motifs for the R-phase. The motifs defined in (b) are projections of distorted prolate rhombohedra. The vertices of these rhombohedra are on body-centred and origin sites of the cubic structure. (d) Projection of the R-phase structure along a pseudo-fivefold direction. The motifs noticed above are drawn. We have superimposed, on the HREM image, white dots corresponding to the small triacontahedra. White dots correspond to 'holes' or low-potential areas in the structure.

§4. CLUSTER MOTIFS IN HREM IMAGES

In this section, we are concerned with the set of cluster images drawing 2D motifs which are common to the R-phase and to the i-phase. In order to make a link with 3D structural motifs of the R-phase, we select only 2D motifs which are drawn by linking projections of cluster centres (corresponding to the origin and body-centred sites). These sites appear alternatively and periodically on parallel lines perpendicular to the $[1, 0, 0]$ direction. They appear along these lines (parallel to the $[0, \tau, 1]$ direction) in the Fibonacci sequence.

Two sets of Penrose rhombi, each set including a thin and a fat rhombus, satisfy the previous condition. The small and the large rhombi are respectively arranged as the projection of an oblate and a prolate rhombohedra. The small rhombi are in the inflation ratio of τ with regard to the quasilattice constant of the i-phase ($a_R = 0.505$ nm, corresponding to the radius of the second icosahedron in the R-phase and then to the inner radius of the small triacontahedron). The large rhombi are in the inflation ratio of τ^2 .

Simple geometrical considerations (the set of clusters centres in HREM images is an irrational projection parallel to $[0, -1, \tau]$ and along $[0, \tau, 1]$ of a b.c.c. lattice) show that these rhombi are perfect 2D Penrose rhombi. The edge size of small rhombi is exactly $a/(\tau + 2)^{1/2} = 0.732$ nm. The length of the fat rhombus is $\tau a/(\tau + 2)^{1/2}$ and the width is a/τ . The length of the thin rhombus is equal to a and the width is $a/(\tau + 2)^{1/2}$. The large rhombi are exactly τ times the small rhombi. The edge size is then $\tau a/(\tau + 2)^{1/2} = 1.184$ nm. These rhombi are identical in size and in shape with those of the HREM image of the i-phase. They are represented in fig. 3(b) for the R-phase and in fig. 3(a) for the i-phase.

Let us now look at whether the 2D clusters motifs described above can be considered as projection of characteristic 3D motifs such as the Ammann rhombohedra (fig. 3(c)).

Because of the irrational feature of the projection, each 2D cluster centre corresponds to a unique 3D effective cluster centre. It appears that both the association of two small fat rhombi and one small thin rhombus and of one large fat rhombus and two small thin rhombi are the projection of a distorted prolate rhombohedron with two types of face. Each vertex is surrounded by the successive atomic shells (§ 1) until the second triacontahedron. Two faces are perfect rhombi with an edge length corresponding to the distance between the origin and the body-centred sites ($a3^{1/2}/2 = 1.2$ nm). The length and the width of these rhombi are respectively equal to $a3^{1/2}$ and a , so that the ratio of length to width is equal to $3^{1/2}$ instead of τ for a perfect prolate. The four other faces have two edges with origin-body-centred type of connections and two edges with origin-origin or body-centred-body-centred type of connections (distance $a = 1.3914$ nm). The ratio of the diagonals is $(11/3)^{1/2} = 1.915$ nm instead of τ . Let us recall that the connection of atomic clusters on an origin-body-centred edge is along a pseudo-threefold axis, and a pseudo-twofold axis on an origin-origin or body-centred-body-centred edge. By small slips of atomic clusters along a fivefold direction, the distorted prolate rhombohedron is changed into a perfect rhombohedron with only threefold-axis type connection along the edges and twofold-axis-type connection on the faces. These slips are conservative for the small triacontahedra but need atomic rearrangements for the larger triacontahedron and for the soccer ball. The 2D projection of this new rhombohedron is the same as that of the distorted rhombohedron. The edge length of this rhombohedron is $\tau^2 a_R$, where a_R is the quasilattice constant of the i-phase. Moreover, this rhombohedron is a part of the decorated τ^3 inflated icosahedral quasilattice proposed by Audier and Guyot (1988) in order to model the $i\text{-Al}_6\text{CuLi}_3$ phase using the R-phase local order. Indeed the connections between clusters are of the same type as those of their dodecahedral large cluster.

By using inflation-deflation rules, it is possible to define on the HREM i-phase image a smaller and a larger quasilattice with inflation of τ , τ^2 , τ^3 and so on. However, in the case of the R-phase, the τ^3 inflation leads to 2D Penrose tiles with vertices not necessarily on an origin or a body-centred site. There are no τ^3 -inflated tiles in the R-phase. In the same way, no oblate Ammann rhombohedra can be defined with τ or τ^2 inflation.

§5. CONCLUSION

In the light of this new study of HREM images of the R-phase and i-phase in the Al-Cu-Li system, a strong similarity in the local order arrangements between the two phases is noticed; the small triacontahedra of the R-phase structure appears in both phases as rings of ten white dots with an inner inhomogeneous ring. An inflation rule for the triacontahedra is evident for both phases but this rule is hidden by the periodicity effect in the R-phase for medium-range order at the Scherzer defocus. The HREM image of the R-phase along a pseudo-fivefold direction is formed of motifs (rhombi in inflation rules of τ or τ^2 with regard to the quasilattice constant of the i-phase) stacked periodically in one direction (pseudo-twofold direction) and quasi-periodically in the perpendicular direction (pseudo-fivefold axis). No rhombus in τ^3 inflation rules with vertices on a projection of cluster centre can, however, be defined. 3D correspondence of 2D motifs leads to a distorted prolate rhombohedron which, by slight displacements of the clusters long a fivefold direction, can give a perfect rhombohedron which is a part of the τ^3 -inflated quasilattice proposed by Audier *et al.* for a molecular modelling of the i-Al₆CuLi₃ phase. Starting from the close similarity between the local environments of the i-phases and approximant phases in the Al-Li-Cu system, the second step of this study is to perform HREM simulations on i-phase models. We are using two models: the first requires atomic surfaces in high-dimensional space and the second is a random-molecular decoration of a 3D Penrose tiling. Results will be published in a forthcoming paper.

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