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Structural themes in approximant and decagonal quasicrystalline phases in Al based alloys

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ABSTRACT

The structure of two periodic phases in the Al–Pd–Mn system showing the importance of chemical ordering in the formation of decagonal quasicrystalline and approximant crystalline structures is reviewed. Different descriptions of the periodic phases in terms of clusters, dense planes and pentagonal chains of transition metals are presented. We also review a structural model for AlPdMn decagonal quasicrystals derived from the general schematic distribution of TM existing in the approximant phases. This model is discussed in relation of an unique decagonal overlapping cluster in a Penrose pentagonal tiling.

1. Introduction

Many works have been related to structural models of decagonal and icosahedral quasicrystals since their discovery by Shechtman et al. [1] and Bendersky [2]. Several of these models were derived from closely related crystalline structures [3–5] as for instance the cubic α Al–Mn–Si [6] phase (related to icosahedral quasicrystals) or the orthorhombic T-Al_3Mn [7] phase (related to decagonal quasicrystals). Main advantage of working with periodic crystals is that the structural features can precisely be described thanks to the nowadays available crystallographic tools for solving periodic structures. By example if a similar chemical order exists in the periodic phase and the related quasicrystalline phase, then its precise description in the approximant phase could be used in order to build or improve models describing the quasiperiodic structure. To illustrate these features, we will briefly review two crystalline structures closely related to decagonal quasicrystals [8–10]in the Al–Pd–Mn system. In particular we also review how, among the different descriptions presented, the one in term of pentagonal chains of transition metals [8] can be used to build a structural model for AlPdMn decagonal quasicrystal [11].

2. Approximant phases

2.1. The structure of the T-Al_3 (Mn,Pd) quasicrystalline approximant phase

The structure of the phase T-Al_3(Mn,Pd) is isomorphous with the one of the T-Al_3Mn [7] phase. It is orthorhombic, with $Al_{72.3}Pd_{3.2}Mn_{24.5}$ composition, its space group is Pnma and magnitudes of cell parameters are $a = 1.4717$ nm, $b = 1.2510$ nm and $c = 1.2594$ nm [9]. The structure is built of two layers stacked along the b axis: a flat layer F, and a puckered layer P composed of two sublayers P1 and P2. The stacking sequence of the layers is ... P' P F P P' F' P' P ... and can be deduced from the fact that F and F' are mirror planes and there is an inversion center at the origin between P and P' (F' and P' correspond to the application of the inversion center to F and P). The F, P1 and P2 layers are located at $y = 0.25$, 0.38 and 0.43 and are represented in Fig. 1(a). Pentagonal chains of transition metal (TM) atoms have been outlined. Local pentagonal symmetry can be identified around points A, B and C. A complete description of the T-Al_3Mn structure and its relation with decagonal quasicrystal, with a 1.2 nm periodicity can be found in Refs. [5,12]. In particular, columnar clusters are described around points A and B and there is an alternate stacking of small pentagons and central atoms along the b axis. These pentagons form pentagonal prisms p and antiprisms a extending along the b axis with the sequence $aapaa$ and all together with the alternating atoms cantered in A and B define four interpenetrating icosahedra with their pseudo-fivefold axis parallel to the b axis.

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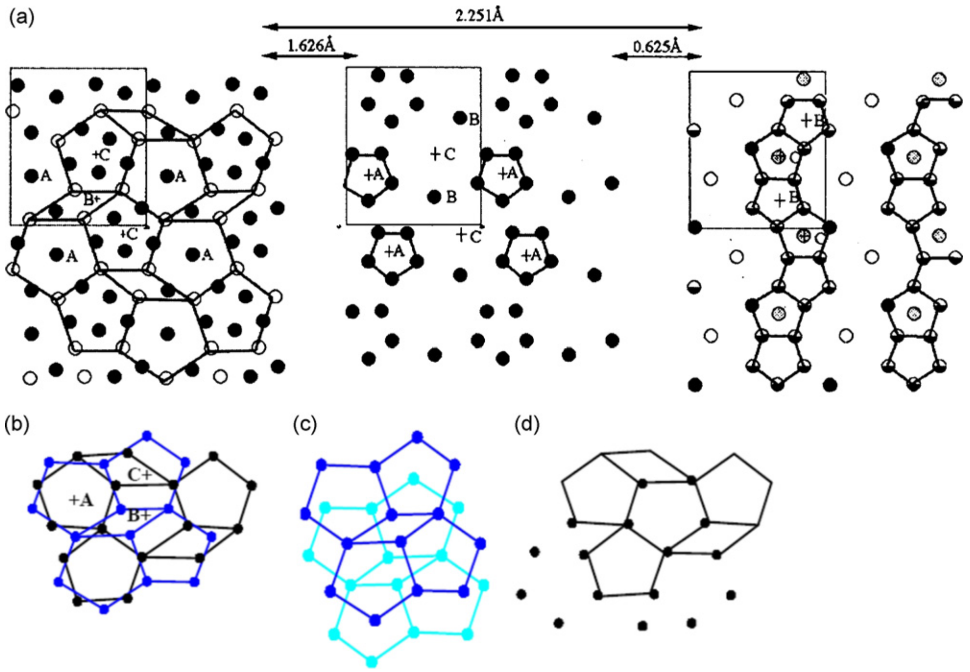

Fig. 1. (a) Flat (F) and puckered (P1 and P2) layers (from left to right) of the T-Al_3(Mn,Pd) structure. Circles represent Mn (blue), Al (black), mixed Al/Mn (black and white) sites and Pd (gray) atoms. Distances between layers are indicated in Å. Pentagonal chains formed by TM atoms are outlined in the F layer. (b) Superimposed TM (blue) and Al (black) pentagonal chains in the F layer. (c) Superimposed TM pentagonal chains in F (blue) and F' (cyan) layers. (d) Superimposed Al pentagonal chains in F (black line, corresponding dots have not been included for a most clear representation) and F' (black dots) layers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The chemical order in T-Al_3(Mn,Pd) (Fig. 1(a) has been described with respect to that of the T-Al_3Mn phase [9]. T-Al_3(Mn,Pd) appears more ordered and reveals the importance of pentagonal chains of TM as outlined in Fig. 1(a) and (b) in the F layer. In particular Pd ordering has been related to the Ni ordering in R-$Al_{60}Mn_{11}Ni_4$[13]. Equivalent description can be considered for both structures were the Mn atoms in the F layer belong to pentagonal chains [8] as for T-Al_3(Mn,Pd) and T-Al_3Mn phases and the Ni and Pd atoms occupy equivalent positions. This special position for Ni and Pd atoms could be responsible for the stabilizing mechanism of the R-(Al–Mn) phase (metastable phase reported by Li and Kuo [14]) leading respectively to a Ni-stabilized phase, the R-$Al_{60}Mn_{11}Ni_4$, and to an isomorphous Pd-stabilized phase, the R-(Al–Pd–Mn) which appears as a stable phase in the (Al–Pd–Mn) ternary system [15].

2.2. The structure of the ξ' phase

The Al_3Pd orthorhombic structure [16] was considered as an approximant of a metastable decagonal quasicrystal with a 1.6 nm periodicity observed in the Al–Pd system [17]. Such a phase was also observed as forming a ternary orthorhombic compound ξ' in the Al–Pd–Mn ternary system. The structure of the phase ξ' [8] is orthorhombic, with $Al_{73.5}Pd_{22.4}Mn_{4.1}$ composition, its space group is Pnma and magnitudes of cell parameters are $a_{\xi'} = 2.389$ nm, $b_{\xi'} = 1.656$ nm and $c_{\xi'} = 1.256$ nm.

2.2.1. Description of the structure: layer structure

Fig. 2 shows the projection of the unit cell viewed along its *c* axis. Four different layers can be identified at $y = 0$, 0.12, 0.16 and 0.25. The other layers in the unit cell can be deduced from space group symmetries. The stacking of these layers along the *b* axis leads to a 1.6 nm periodicity. The layers at 0, 0.16 and 0.25 are flat whereas the layer at 0.12 is puckered.

Fig. 2 represents the arrangement of atoms in each layer. Local pentagonal symmetry has been outlined around points A, B and C (vertices of flattened hexagons marked with lines).

2.2.2. Description of the structure: icosahedral clusters

Most of the transition metals (TM = Pd and Mn) are located at the vertices and at the centres (point C at layer 0 in Fig. 2) of slightly distorted icosahedra which form layers perpendicular to *b*. The adjacent icosahedra in a layer share three edges and are centered on the vertices of the flattened hexagons outlined in Fig. 2 (this feature is in agreement with electron microscopy observations that show the presence of flattened hexagons as salient features of the structure [18]). In between layers the icosahedra share vertices and are related by a mirror symmetry. In addition, there is an icosidodecahedron of Al around each central atom (Al atoms with pentagonal symmetry distribution outlined around the point C of Fig. 2 top) that form with the TM atoms the external shell of a Mackay icosahedron [19] represented in the bottom left part of the figure.

2.2.3. Chemical order

Most of the Pd atoms are located on a flat sub-layer ($y = 0.12$) of the puckered layer and in the layer at $y = 0.25$ (see Fig. 2). Some of them present Pd/Al substitutional disorder. Mn atoms occupy special positions in the sub-layer at $y = 0.08$ and in the layer at $y = 0$. Al atoms present a large amount of fully occupied sites and a minor proportion with partial occupancy factor. In particular in the layer $y = 0$, only 3 sites have partial occupancy factor. These Al atoms lie by pair at the edge of the hexagons drawn in Fig. 2 and correspond to interpenetrating Al icosidodecahedra surrounding point C (see the two adjacent decagonal wheels in plain and dashed lines at layer 0 in Fig. 2). In the puckered layer at $y = 0.12$, all the Al sites have partial occupancy factors. Most of them lye inside the TM pentagons centered around point C[1].

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[1] It is interesting to remark that in $Al_{13}Co_4$ structure, 3 of the 5 atoms lying in the inside of TM pentagons also have partial occupancy factor [20].

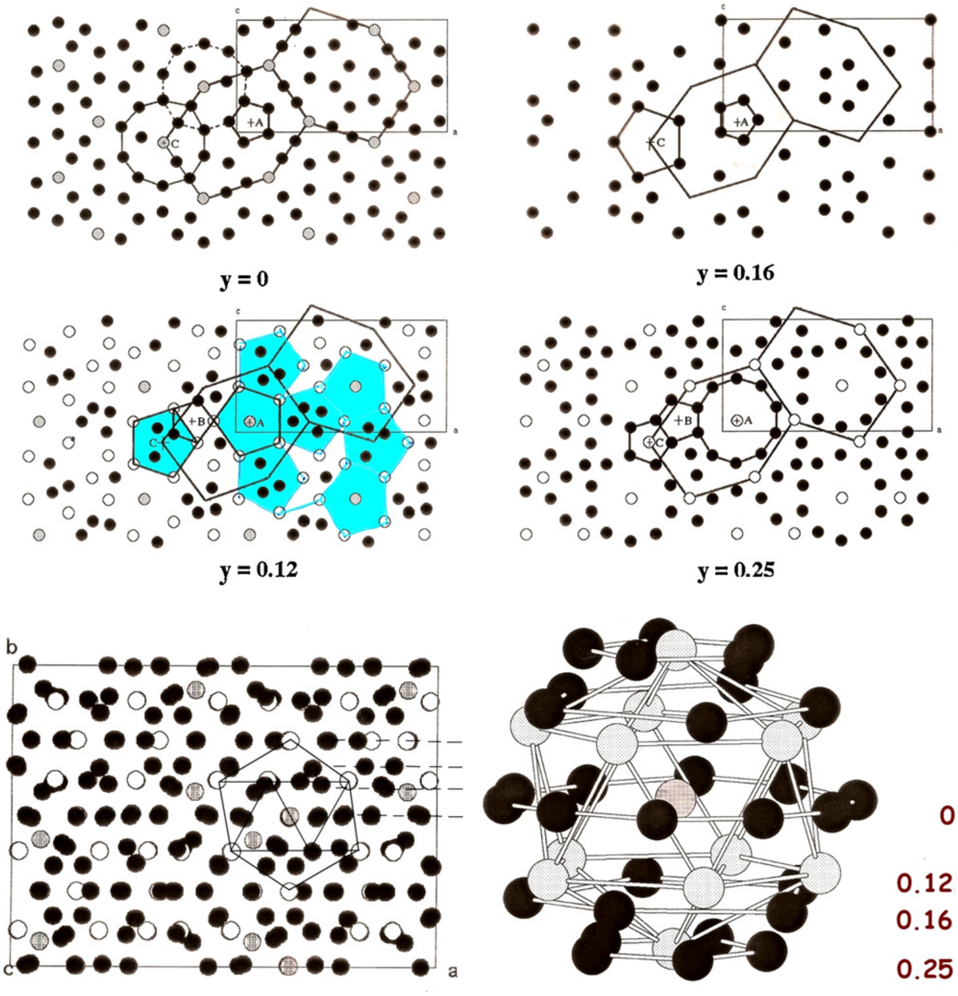

Fig. 2. Top panel: the four different layers for the ξ' phase. Local pentagonal symmetry around points A, B and C (vertices of the squashed hexagons). Open (Pd), gray (Mn) and black (Al) circles represent atoms. Bottom panel left: projection of the unit cell viewed along its *c* axis. The different layers are identified with dashed lines. Bottom panel right: Mackay type icosahedron. Figures in the right make the correspondence with the layers.

2.3. Comparison with other related phases: a general 2D description in terms of packing of pentagons

The particular distribution of TM in the F layer is a general feature which is found in several structures as for example:

- the T-Al_3TM and R-Al_4TM phases [13–15];
- the ξ' and ξ phases [15,8];
- the Al_3Co [21] and $Al_{13}Fe_4$ type structure [22].

The structural features corresponding to the distribution of TM can be described by 2 dimensional tilings using linear chains of pentagons. The elementary part of the chains (see Fig. 3) is made of two adjacent pentagons one up and one down sharing an edge (these pentagons can be different and thus one of it was marked with circle). These pentagonal chains or its basic pentagonal units (pentagons centered at points A and C) corresponding to location of TM atoms have been outlined in Figs. 1 and 2. Fig. 3 a–f shows different ways of linking the chains (extending from left to right corresponding to Al_3Mn, Al_4TM, ξ', ξ, Al_3Co and $Al_{13}Fe_4$ phases. The different unit cells resulting from the periodic tilings are outlined and several relations between cell parameters can be explained (e.g. both ξ' and Al_3Mn c cell parameters are nearly the same (c ξ'=1.2339 nm and cAl_3Mn = 1.251 nm) as shown in Figs. 3a and 3c along the horizontal direction). We have drawn two different flattened hexagons (one for figs. 3(a and b) and another for Fig. 3(c and d) that lead to a description in terms of two types of tilings with hexagons. For Al_3Mn and ξ' tilings, the hexagons are in quincunx (Fig. 3(a and c) whereas they are in a parallel way for Al_4TM and ξ tilings (Fig. 3(b and d). As can be seen from the shadowed circles there is a major difference arising from the different space groups (Pnma for quincunx tilings and Cmcm for parallel ones): there is an additional mirror in the hexagons of the parallel tilings. Al_3Co (space group Pmn21) and $Al_{13}Fe_4$ (monoclinic space group C2/m) type structures can be related to 2D tilings similar to those corresponding to Al_3Mn and Al_4TM phases but with different decorations of pentagons (breaking of the pseudo mirror symmetry, compare Fig. 3a to Fig. 3e and Fig. 3b to Fig. 3f). In these structures two orientations of the chains with respect to the vertical direction of Fig. 3 are possible. This fact leads to a different linking between the chains.

3. Relation with decagonal quasicrystals

The decagonal phases present in the Al–Pd–Mn system with 1.6 nm periodicity [23,17] can be related to the ξ' and the ξ phase and those with 1.2 nm periodicity [24,23,5] can be related to the R-Al_4(Mn,Pd) and T-Al_3(Mn,Pd) phases. We will focus on the schematic distribution in terms of pentagons described previously which represent the distribution of TM atoms (and Al for the particular case of T-Al_3(Mn,Pd)) in one layer (see Figs. 1 and 3) and will

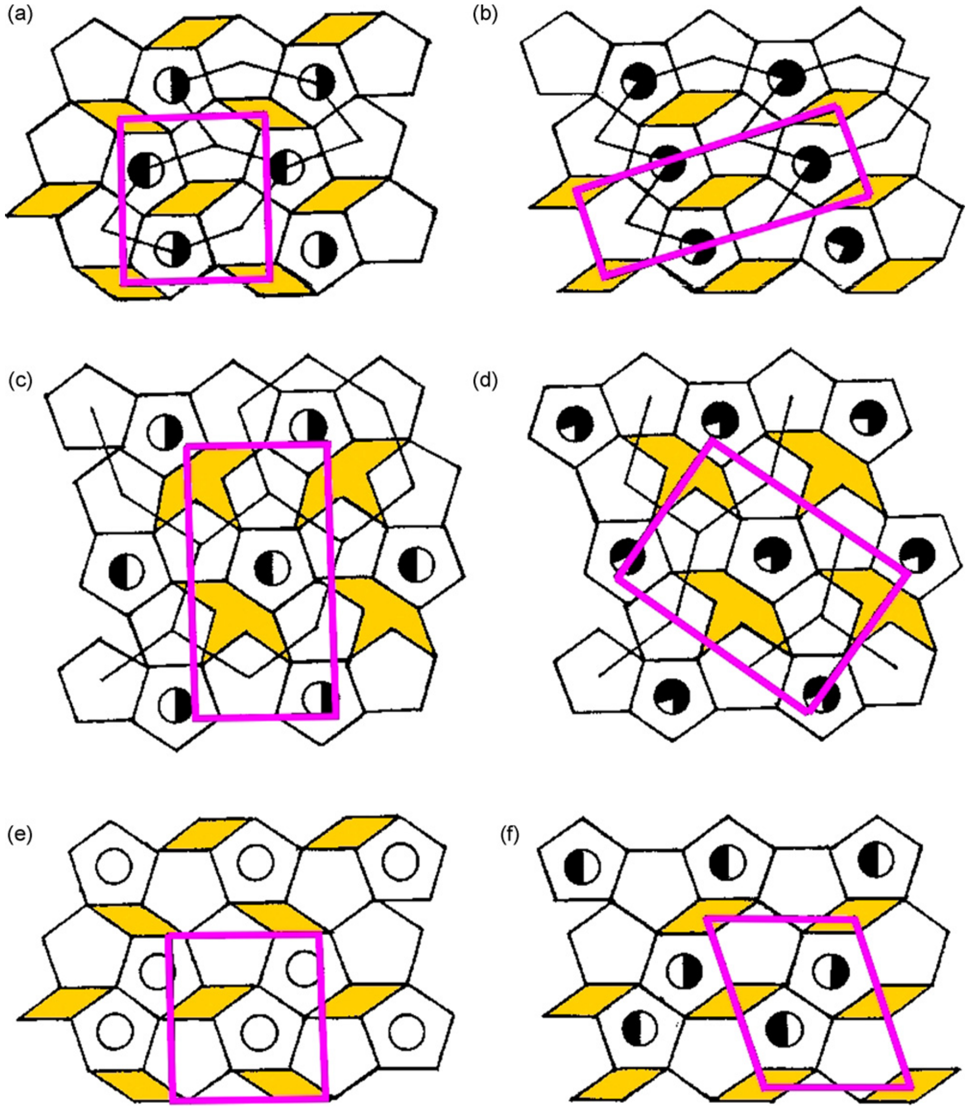

Fig. 3. Different periodic arrangement of pentagonal chains corresponding to (a) T-Al_3TM, (b) R-Al_4TM, (c) ξ', (d) ξ, (e) Al_3Co, and (f) $Al_{13}Co_4$ ($Al_{13}Fe_4$). Shadowing of the circles evidence the symmetry operations corresponding to the different space groups. The different unit cells are outlined.

review the relation proposed with decagonal quasicrystals by considering a pentagonal Penrose tiling (PPT) [11]. This tiling is build by three tiles: pentagons, losange and boat that can also be identified in Fig. 3. Thus considering the TM atoms distributed on sites of a PPT could be a suitable extension from the periodic to the quasiperiodic structures. The edge length of the pentagons is about 0.47 nm.

In Ref. [11], when considering the relation between the T-Al_3(Mn,Pd) phase and the decagonal quasicrystal with 1.2 nm periodicity we found illustrative to consider, as proposed in [25], the tiling represented in Fig. 4. This 2-dimensional quasiperiodic tiling has been obtained by the cut algorithm considering a 5-Dimensional periodic image (for details see for example [25]). Left bottom part of Fig. 4 represents the rhombic icosahedron located at Zperp=0 which generates the tiling in Fig. 4. The different sections containing the points in the perpendicular space (i.e. the atomic surfaces if one works with a 4-Dimensional periodic image) represented on the Fig. 4 can be labeled according to their different values of the coordinate Zperp. By example atomic surface labeled 0 corresponds to the largest section of the rhombic icosahedron at Zperp=0 and have a decagonal shape. We also include in Fig. 4 the case corresponding to the standard Penrose tiling (in this case a vertex of the rhombic icosahedron is located at Zperp=0 and the corresponding atomic surface shrinks to a single point. The pentagonal shaped atomic surfaces corresponding to the tiling are labeled 1, 2, 3 and 4 and the center of the rhombic icosahedron lye between surfaces 2 and 3).

The tiling described above provides us with three subset of points lying on PPTs represented in Fig. 5 and corresponding to the inner decagons drawn in the atomic surfaces labeled 1, 0 and −1 in Fig. 4. Indeed most of the vertices to be consider are distributed on a PPT build by three tiles: pentagons, losange and boat. By example only a small fraction of the vertices corresponding to the atomic surface 1 (resp. −1) (see Fig. 5) does not belong to a PPT. Indeed the atomic surface 1 (resp. −1) can be slightly modified into a decagonal shape (see Fig. 4) which generates the PPT labeled 1 (resp. −1) shown in Fig. 5. The PPT labeled 0 corresponds to the inner decagonal region drawn in the large decagonal section labeled 0 in Fig. 4.

The chemical species corresponding to the three PPTs can be inferred from the T-Al_3(Mn,Pd) phase. Two PPTs have to be consider in the F (resp. F') layer of a decagonal quasicrystal:

- the schematic distribution in terms of pentagons of TM atoms (see Fig. 1(a–c) can be extrapolated to a quasiperiodic structure by considering a PPT.

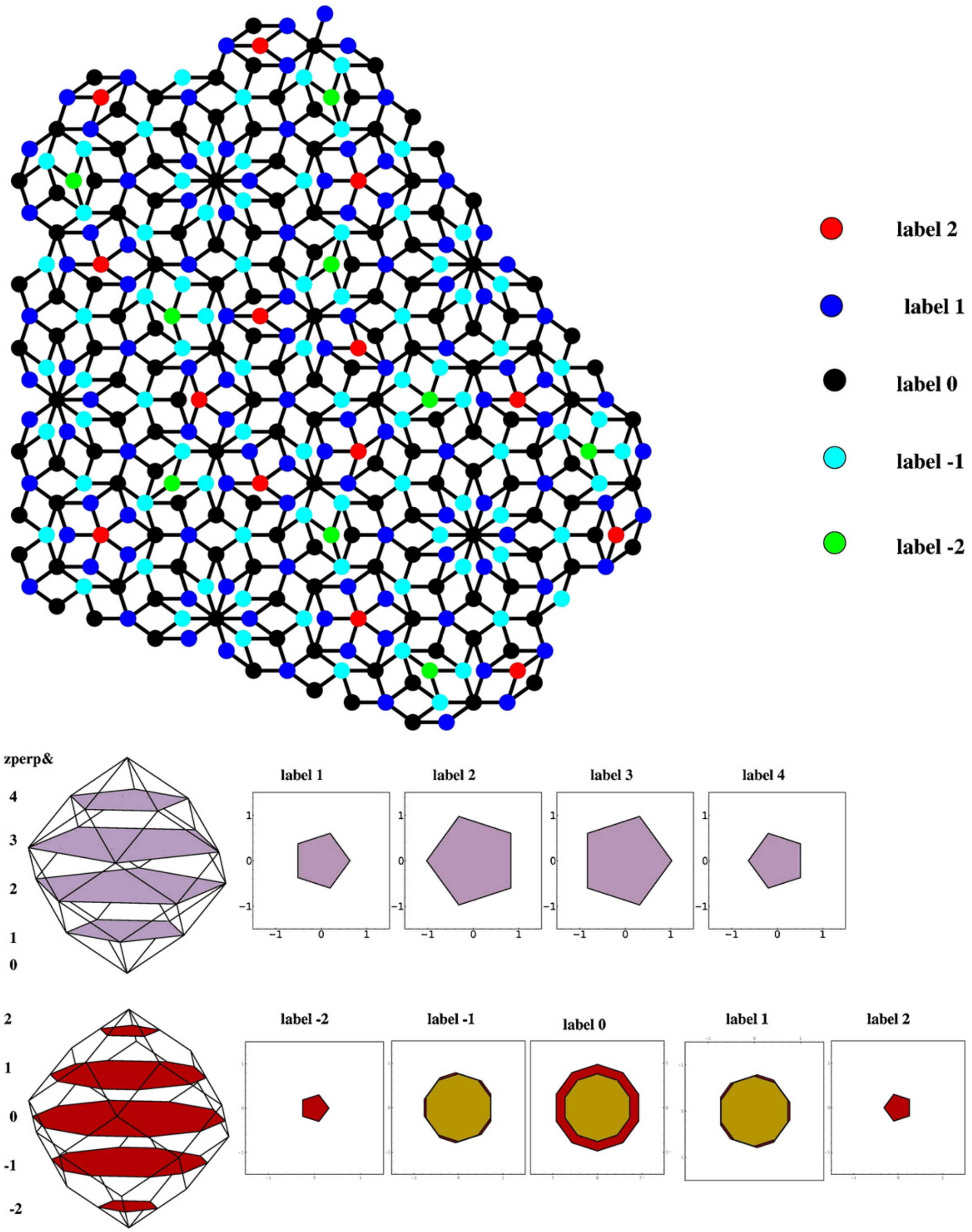

Fig. 4. Top panel: Penrose tiling generated by the rhombic icosahedron located at Zperp = 0. The colors of the vertices correspond to the different section of the rhombic icosahedron described in the bottom panel. Bottom panel: rhombic icosahedron corresponding to the standard Penrose tiling (top) and rhombic icosahedron located at Zperp = 0 (bottom) which generates the tiling on the top part of the figure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

- the schematic distribution in terms of pentagons of Al atoms (see Fig. 1(a–d) can be extrapolated to a quasiperiodic structure by considering another PPT[2].

One have also to consider two conditions which are fulfilled by the T-Al_3(Mn,Pd) structure:

- the layers F and F' stack in a particular way (e.g. the TM (resp. Al) pentagons overlap in a particular way represented in Fig. 1d (resp. Fig. 1e) (this condition can be consider as two conditions one for Al and another for TM PPTs));
- there is a relative position of the Al and TM PPTs in the layer F (resp. F') (see Fig. 1c).

In the present case these two conditions are fulfilled by assigning Al chemical specie to the inner decagonal region (hereafter 'inner decagonal' atomic surfaces) drawn in Fig. 4 of the section

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[2] Note that Al pentagonal chains are not present for other periodic structures as by example for Al_3Co.

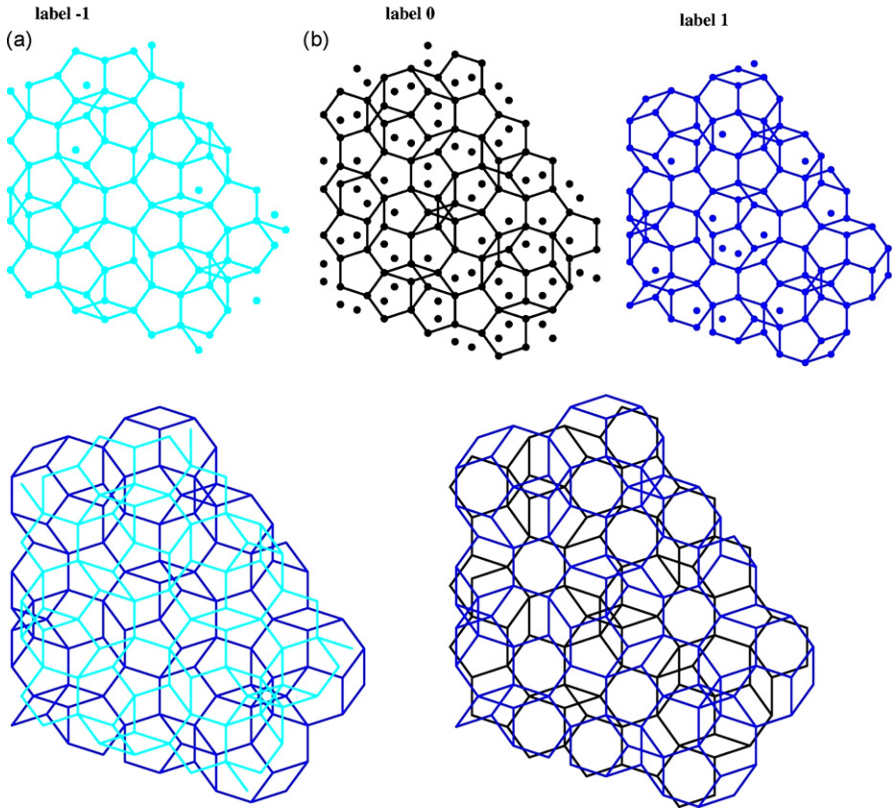

Fig. 5. Top panel: subset of points of Fig. 4 corresponding to the atomic surface labeled −1, 0 and 1. Most of the points lye on a PPT corresponding to the inner decagonal regions drawn in Fig. 4. Bottom panel: relative distribution of Al and TM PPTs in the F and F' layers of a model for decagonal quasicrystal are represented in (a) and (b). (a) Superimposed TM pentagonal chains in F (blue) and F' (cyan) layers (compare local arrangement with Fig. 1(c). (b) Superimposed TM (blue) and Al (black) pentagonal chains in the F layer (compare local arrangement with Fig. 1(b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

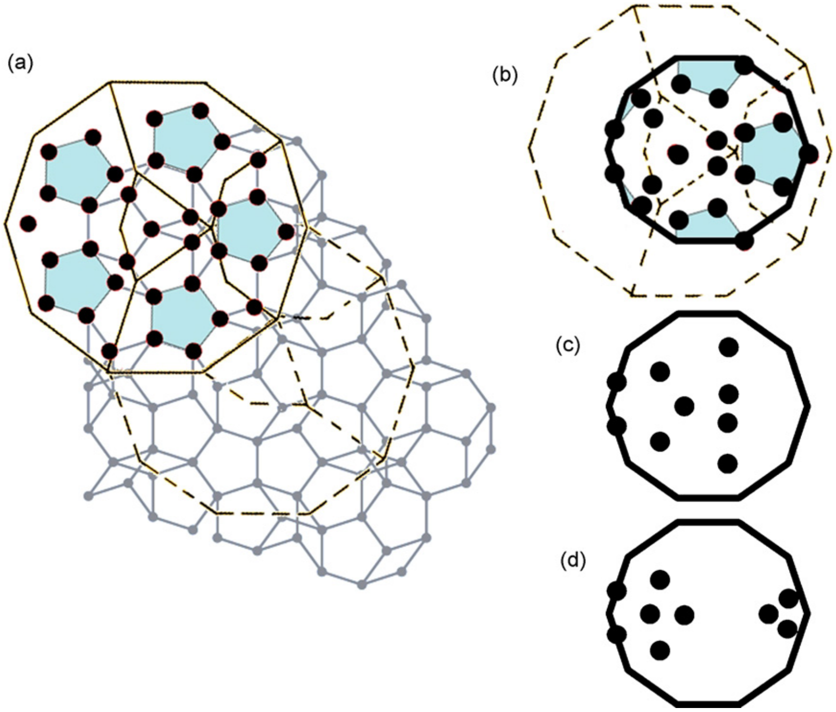

Fig. 6. (a) Two superimposed overlapping decagonal cluster are represented in dashed and plain lines on the subset of points of TM corresponding to the atomic surface labeled 1 in Fig. 5. (b) Inner region of the decagonal clsuter represented in (a). (c) TM of a layer corresponding to model available on line at http://www.physics.princeton.edu/~steinh/quasi/. (d) TM of a layer corresponding to model presented in Ref. [29].

labeled 0 and TM chemical specie to the ‘inner decagonal’ atomic surfaces in sections labeled 1 and −1. The Al and TM PPTs in the F layer are build by 0 and 1 ‘inner decagonal’ atomic surfaces while they are build in the F’ layer by 0 and −1 ‘inner decagonal’ atomic surfaces. A schematic distribution of the different PPTs and their stacking are shown in Fig. 5. The local arrangements of Al and TM atoms correspond to those represented in Fig. 1 for the T-Al_3(Mn,Pd). From the one side the ‘inner decagonal’ atomic surfaces of TM represent a well ordered skeleton which is probably present in several decagonal phases. This hypothesis is supported by the distribution of TM described previously and summarized in Fig. 3. From the other side the ‘inner decagonal’ atomic surface of Al is specific to the Al–Mn and Al–Mn–Pd decagonal quasicrystal[3].

Finally it is interesting to compare the well ordered TM skeleton to a description in term of a covering with an unique overlapping decagonal cluster [30] as the one presented in [29]. Fig. 6 shows two different examples of the unique decagonal cluster (in plain and dashed lines) corresponding to the PPT of TM building the F layer (labeled 1 in Fig. 5). The inner part of this decagonal cluster (represented in Fig. 6(b)) can be compared with the one presented in [29] corresponding to Fig. 6(d) as well as the more recent version (available online at http://www.physics.princeton.edu/∼steinh/quasi/) and represented in Fig. 6(c). The more recent version in Fig. 6(c) appears to have some similarities to the one represented in Fig. 6(b) though only 9 TM are present (nearly the half). Solutions proposed in (c) and (d) do not generate PPT of TM.

4. Conclusions

The schematic distribution of TM in periodic structures have been discussed in relation with structural models for decagonal quasicrystals. The hypothesis of considering the TM atoms to be distributed on vertices of a PPT appears as a suitable extension from the periodic to the quasiperiodic structures. This well ordered TM skeleton is probably present in several decagonal phases. For the Al–Mn(Pd) decagonal quasicrystal we can consider an additional PPT corresponding to some Al sites. By considering the structural features of the T-Al_3(Mn,Pd) phase the two PPTs can be identified as different subsets of vertices of a parent tiling. The distribution of TM in the F layer can alternatively be described with an unique decagonal overlapping cluster.

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[3] A complete description of the model which qualitatively compare with models available in the literature (Refs. [26,27] for Al–Mn decagonal quasicrystals and Refs. [24,28] for Al–Pd–Mn decagonal quasicrystals) can be found in Ref. [11].