From the STM images of quasicrystal surfaces to the chemistry of the bulk-terminations

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Abstract. The model $\mathscr{M}(\mathscr{T}^{*(2F)})$ of icosahedral quasicrystals of an F-phase is obtained through the decoration of the icosahedral tiling $\mathscr{T}^{*(2F)}$ by the the icosahedral atomic configurations in shape of the Bergman and the Mackay polyhedra [1, 2]. The model $\mathscr{M}(\mathscr{T}^{*(2F)})$ is based on the diffraction results of the Boudard model [3] and to the Katz-Gratias model [4], see also [5]. The same model of atomic positions describes $Al_{70}Pd_{21}Mn_9$ and $Al_{62}Cu_{25.5}Fe_{12.5}$ [6]. In the model we study the bulk terminations generalising the Bravais' rule valid in crystals to the variant of the Bravais' rule in quasicrystals. Among other conclusions, concerning the relation of the fivefild termination to the clusters in the model, the information from the STM (scanning tunnelling microscopy) simulations of the images on the surface provides us with some hints important for the chemistry of the bulk-terminations as well.

Fivefold surfaces and corresponding bulk terminations

The most stable clean surfaces of icosahedral Al-Pd-Mn (i-AlPdMn) and of icosahedral Al-Cu-Fe (i-AlCuFe), which are the fivefold followed by the twofold surfaces [7], are *terrace-stepped* [8]. The fivefold surfaces (orthogonal to the fivefold symmetry axis) present sequences of flat terraces with characteristic terrace step heights $m = 4.08$ Å and $l = 6.60$ Å, see Fig. 1. On the twofold terrace-like surfaces of i-AlPdMn the common heights are circa 6.3 Å and 10.2 Å.

According to the Bravais rule, which is generally valid for crystals, the most stable surfaces are the densest atomic planes in the bulk. In [9] we observed that 2.52 Å thick atomic layers of (equal) maximum density appear in correct sequences as terrace-like sequences of the surfaces. This *thick* layer that contains four planes with spacings q_1-plane, 0.48 Å, b_1-plane, 1.56 Å, b_2-plane, 0.48 Å, q_2-plane is a candidate for a fivefold termination. (The labels q and b mark the atomic positions belonging to different translational classes with respect to the D_6 lattice in the 6-dimensional space. See Refs [2, 10].) For the bundle we define an effective (averaged) *planar* density of internally contained thin layers[1]/planes

$$\rho_{5f}(z_\perp) = (\rho_{q_1}(z_\perp) + \rho_{b_1}(z_\perp))/2 + (\rho_{q_2}(z_\perp) + \rho_{b_2}(z_\perp))/2. \tag{1}$$

[1] Under a *thin layer* we consider a layer of 2-3 planes of stacked atoms, on a distance significantly smaller than 0.86 Å. Such a layer we treat as a single plane.

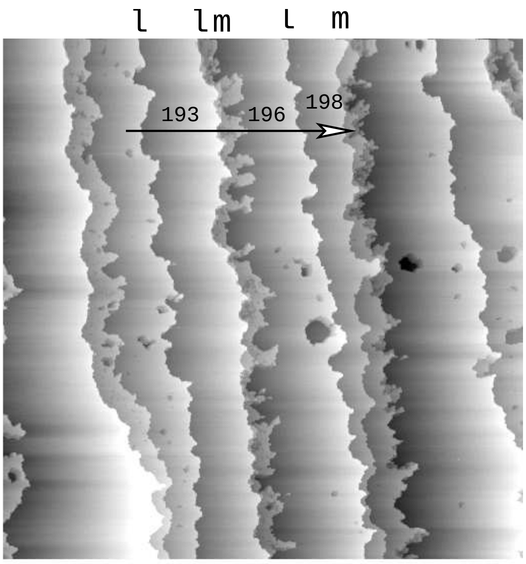

FIGURE 1. An STM image of a fivefold surface, size 1750 $\times$ 1750 nm^2, of i-AlPdMn, done by J. Ledieu. A Fibonacci sequence of the step heights (circa) $m = 4.08$ Å and $l = 6.60$ Å was measured on the surface. The marked subsequence of steps l, l, m, l, m from left - right, downwards, corresponds to a subsequence of the (q,b,b,q)-terminations in $\mathscr{M}(\mathscr{T}^{*(2F)})$ from Fig. 2 (*right*). Numbers 193, 196 and 198 label the tiling fivefold planes in the model.

In the coding space $\mathbb{E}_\perp$, $\rho(z_\perp)$ is the smooth density graph. It has a plateau. The support of the plateau, marks the layers with equal maximum densities, the **terminations**. Each module point in the support along the fivefold symmetry axes $z_\perp$ in the coding $\mathbb{E}_\perp$ space corresponds one to one to $z_\parallel$, a position of the penetration of a fivefold symmetry axis (in observable $\mathbb{E}_\parallel$ space) into a single terminating layer. The height of the plateau defines the density of the terminations to be 0.134 Å^{-2}. But, one can bundle the dense (b,q) and (q,b) plane-like layers into a 2.52 Å bundle (b,q,q,b) as well. For the layer we define an effective density as in the case of the (q,b,b,q) layer. The height and the width of the plateau on the density graph for the bundle (q,b,b,q) are of the same size as for the bundle (b,q,q,b). The width is $\frac{2\tau}{\tau+2}$ ⑤ and encode the Fibonacci sequence of terrace heights $l = \frac{2\tau^2}{\tau+2}$⑤$=$ 6.60 Å and $L = \tau l = 10.68$ Å. But the density graph of the layer (b,q,q,b) is slightly steeper in the region which is the complement of W in τW $(\tau W/W)$ than the graph of the layer (q,b,b,q) and causes that the appearance of the terrace height 4.08 Å is less probable to appear, see Ref. [2]. For that reason we declared in Ref. [9] that the support of the plateau of the density graph in the case of the (q,b,b,q) atomic layers defines the sequence of fivefold bulk terminations.

In Fig. 2 we show the positions of the atomic layers 2.52 Å thick as candidates for the fivefold bulk terminations, relative to the positions of the layers of the 6.60 Å broad Bergman polyhedra in the model. The fivefold layers of Bergmans, 6.60 Å$= l$ broad, are marked in the figure with the l-intervals. According to Fig. 2, the most stable fivefold terminations (independent of which candidate, (q,b,b,q) or (b,q,q,b), is the

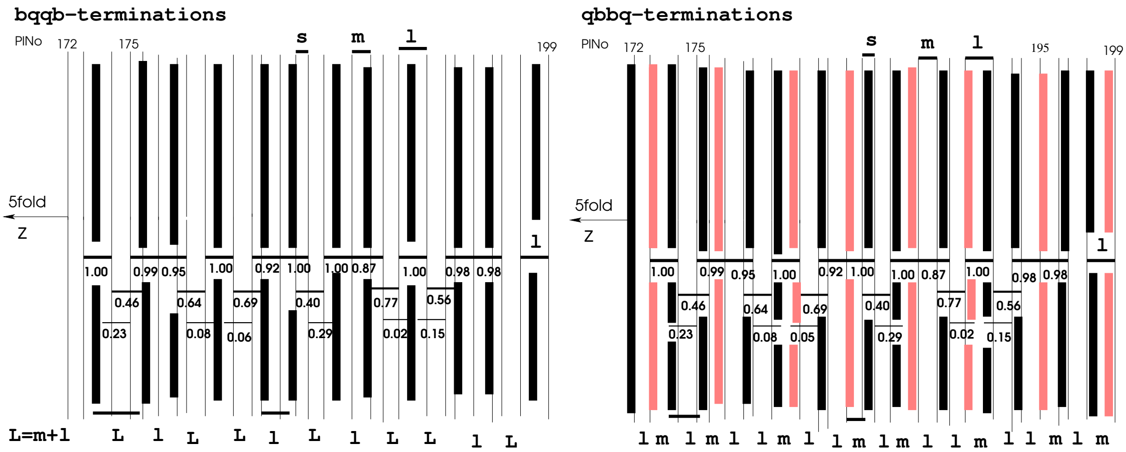

FIGURE 2. In the finite segment of $\mathscr{M}(\mathscr{T}^{*(2F)})$ thin lines mark the fivefold tiling $\mathscr{T}^{*(2F)}$ planes, labelled from 172 to 199. The distances between the tiling planes are $s = 2.52$ Å, $m = \tau s$ and $l = \tau m$, $\tau = (1+\sqrt{5})/2$. The fivefold layers of 6.60 Å broad Bergmans are marked by the l-intervals. Below each is its relative density. (*left*) The Fibonacci sequence $\{l, L = l + m\}$ of the (b,q,q,b)-terminations presented relative to the sequence of the fivefold planes of the tiling. (*right*) The Fibonacci sequence $\{m, l\}$ of the (q,b,b,q)-terminations presented relative to the sequence of the fivefold planes of the tiling. In gray (pink) are possible less dense terminations and should appear as smaller terraces on a surface (see Fig. 1).

correct fivefold termination) in the model pass through the dense layers of the Bergman polyhedra; hence these can not be energetically stable clusters. Similar argument is valid for the Mackay polyhedra. Analogous results are applicable for any icosahedral quasicrystal described with the $\mathscr{M}(\mathscr{T}^{*(2F)})$ model, in particular for i-AlCuFe [4].

Clusters on fivefold bulk terminations

We compare the highly resolved STM images of clean surfaces of i-AlPdMn, with STM simulations on the model $\mathscr{M}(\mathscr{T}^{*(2F)})$. In the STM simulations we consider the same topographic contrast for all atomic positions regardless of their chemical nature. Hence, if slightly scaled, these images present STM simulations of *any* compound described with the model of atomic positions $\mathscr{M}(\mathscr{T}^{*(2F)})$. The STM simulations are based on a simplified atomic charge model [11], in which a spherical shape of the valence charge density is assumed for the atoms. Under the assumption that the recently published Ref. [12] is correctly reformulating the quantum chemistry, follows that all the atoms have indeed the spherical symmetry, and the “simplified atomic charge model” from Ref. [11] becomes the real atomic charge model.

We performed the STM simulations of a fivefold surface on candidates for the bulk-terminating layers, (b,q,q,b)-layer and on a (q,b,b,q)-layer [2, 13]. On the STM image one notices two characteristic fivefold symmetric configurations, a “white flower” (wF) and a “dark star” (dS), see Ref. [10]. The “white flowers”, and in particular the “dark stars”, are evidently better reproduced on the (q,b,b,q)-layers; compare (*left*) and (*right*) images to the (*middle*) image in Fig. 3. Hence, we have discovered a confirmation that

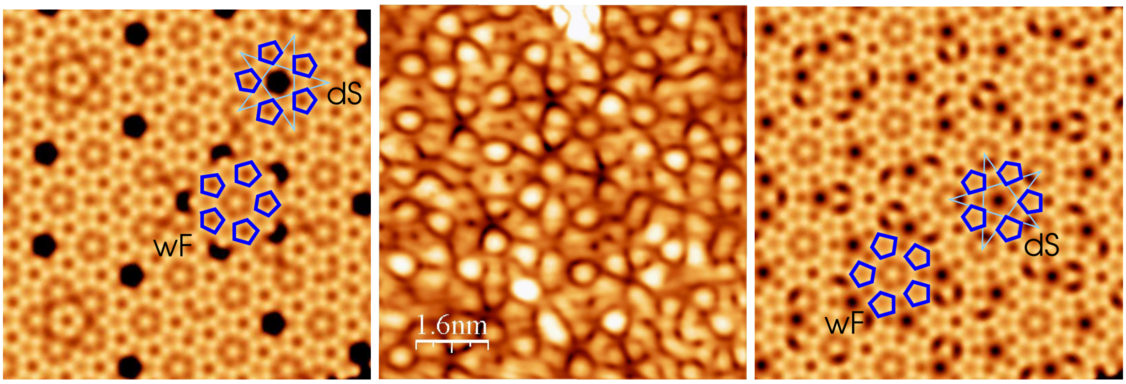

FIGURE 3. STM simulations of a fivefold surface on candidates for the bulk-terminating layers (*left*) on a (b,q,q,b)-layer (*right*) on a (q,b,b,q)-layer. (*middle*) An STM image of the real fivefold clean surface of i-AlPdMn. Each of 3 images is 80×80 Å^2. The candidates for the observed *fivefold symmetric* local configurations, "white flower" (wF) and the "dark star" (dS) are marked on simulations. The wF and the dS are not marked on the STM image, but can be easily recognised. Whereas dS appears on (b,q,q,b)-layers as a dark pentagon, it looks indeed like a dark pentagonal star on (q,b,b,q), hence terminating layer. The same local configurations were observed on the STM images of the fivefold surface of i-AlCuFe as well.

the maximum dense fivefold (q,b,b,q)-layers are the fivefold bulk terminations in the model $\mathscr{M}(\mathscr{T}^{*(2F)})$. From the model independent investigations [14] we know that the top q-plane in the terminating layer must be rich in Al atoms, but it is not the case in the model. Hence, the conclusion contradicts the chemistry of the model $\mathscr{M}(\mathscr{T}^{*(2F)})$, adopted from the Boudard model. By i-AlCuFe, contradicts the Katz-Gratias model.

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