Structural model of quasiperiodic Pb monolayer deposited on fivefold i-Al-Pd-Mn surface

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Abstract. On the basis of analysis of experimental STM images and ab-initio calculations we propose a structural model of the quasiperiodic Pb monolayer grown on the fivefold i-Al-Pd-Mn surface at a coverage close to the saturation. The skeleton of the Pb monolayer can be seen as a network of the "star-fish" (SF) clusters. The atomic structure of the monolayer is based on a decorated P1 tiling. The model can reproduce also the experimentally observed quasiperiodic τ-scaled P1 ordering (τ is the golden mean). The bright spots seen in STM images appear at Pb atoms in the centers of those SF clusters where the substrate has Al atoms at these positions.

1. Introduction

Adsorbates on quasicrystalline surfaces can potentially create novel forms of matter with interesting physico-chemical properties. Much effort has been devoted to grow single-element adlayers on quasicrystalline surfaces [1–7]. Pb is one of few elements that adopts a pseudomorphic structure when deposited on quasicrystalline substrates [5, 7]. In previous work [5] a quasiperiodic Pb monolayer on the fivefold i-Al-Pd-Mn surface has been successfully prepared and characterized by the scanning tunneling microscopy (STM) and other experimental techniques. The initial adsorption of Pb on the five-fold Al-Pd-Mn surface has been investigated both experimentally and by ab-initio calculations [7]. It was found that Pb monolayer nucleates in pentagonal islands dubbed as starfish clusters. The atomic structure of these clusters has been resolved and the calculations confirmed their structural stability. In this contribution we go a step further and propose a structural model of the whole monolayer.

The atomic arrangement in an adlayer is a result of a complex interplay between the structure of the support, the adatom/substrate interactions, and the lateral interaction between adatoms in the adlayer. Understanding the structure of the substrate is a prerequisite for understanding the structure of the adlayer. STM studies of the clean five-fold Al-Pd-Mn surface in images with atomic resolution have identified two characteristic motifs, the pentagonal "dark stars" (DS) [8, 9] and the "white flower" (WF) [10, 11]. WF motif has been assigned to truncated pseudo-Mackay clusters which are, together with Bergman clusters, the constituting elements of the bulk icosahedral structure. This assignment has been confirmed by detailed simulations
of the STM contrast based on ab-initio density-functional calculations [12]. These simulations also showed that DS corresponds to a surface vacancy originating from the irregular atomic arrangement around the low-coordinated Mn atoms in the center of the pseudo-Mackay clusters.

The quasiperiodic arrangement of the atoms at the surface can be described by a planar tiling. The choice of this tiling is, however, not unique. One possible choice relating to the cluster structure of the bulk quasicrystal is a P1 tiling [13] consisting of regular pentagons, pentagonal stars, boats and thin golden rhombi. The positions of centers of the Bergman clusters projected to the surface plane coincide with the vertices of the P1 tiling, the centers of the pentagonal tiles correspond to the positions of the pseudo-Mackay clusters. Other choice of the quasiperiodic tiling is a decagonal DHBS tiling which naturally describes ordering of atoms in the top surface plane. This choice will be discussed more in detail in Sec. 3.

2. Experimental STM studies
The growth of a Pb monolayer on the fivefold surface of the Al-Pd-Mn quasicrystal has been investigated in detail in previous studies [5,7]. At the early stages of the deposition, Pb adatoms diffuse across terraces and form nano-sized islands. Because of their protruding “arms” and their overall pentagonal shape, these clusters were dubbed “starfish” (SF). These clusters exhibit a similar size and orientation across successive terraces independently of the deposition flux used. These observations suggest an heterogeneous nucleation, hence a preferred nucleation site. The local atomic arrangements around single Pb atoms (i.e. at the first stage of the SF nucleation) and around completed SF motifs have been investigated on several atomically resolved STM images. It appears that these pentagonal islands are located on equatorially truncated pseudo-Mackay cluster surrounded by five truncated Bergman clusters, i.e. on top of WF motifs. This conclusion is supported by additional measurements of the SF-to-SF distances across terraces [7].

Upon further deposition in the sub-monolayer coverage regime, the largest distinguishable pentagonal features can be understood as a set of SF clusters. Similarly, the skeleton of the complete Pb monolayer can be seen as a self-assembled network of the SF clusters. As the size of the SF cluster can be characterized by a pentagon with the edge of the P1 tiling (7.76 Å), it is then possible to assume that the atomic structure of the monolayer is a decorated P1 tiling. However, the quasiperiodic structure of the Pb monolayer as observed by STM is characterized by a \( \tau \)P1 tiling, which is the P1 tiling with the edge \( \tau \) inflated compared to the structure of the substrate, \( \tau = 1.6018 \ldots \) is the golden mean. Hence, the atomic decorations of the \( \tau \)P1 and P1 tilings are still to be determined. An inspection of the STM images also reveals a rather large degree of structural disorder in the monolayer (see Fig. 1). Although a part of the disorder could
have a thermal origin, a significant contribution should come from an imperfect match between
the local structures of the substrate and the adlayer.

3. Modeling of the structure of Pb monolayer based on ab-initio DFT calculations
The theoretical modeling of the structure of the Pb monolayer is based on density-functional
theory (DFT). We have used the Vienna Ab-initio simulation Package VASP [14, 15] to perform
ab-initio electronic structure calculations, structural optimizations and simulation of the STM
images. More details of the method can be found in our previous papers [7, 16, 17]. A model of
the surface has been derived from the Katz-Gratias-Boudard model [18, 19] of bulk i-Al-Pd-Mn.
The atomic structure of the fivefold surface is derived from the structure of an icosahedral
approximant by cleaving at a plane perpendicular to one of the fivefold axes. Details of
construction of models of the bulk and the surface can be found in our previous papers [12,17,19].

Fig. 2 is the atomic structure of the top atomic plane of the five-fold Al-Pd-Mn surface. The
quasiperiodic arrangement of atoms in this plane can be most naturally
described by a decagonal DHBS tiling (black). The centers of the
decagonal tiles occupied either by Mn (closed circles) or Al (open
circles) atoms coincide with the
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Our previous studies [7] of initial Pb adsorption have been performed on a slab model of the
fivefold surface derived from the 2/1 approximant to the quasicrystalline Al-Pd-Mn structure.
However, the 2/1 approximant is too small for modeling a quasiperiodic ordering at the scale of the \( \tau \text{P1} \) tiling. In the present study we use a model of the surface derived from the 3/2-approximant. The model has a shape of a slab with size of 32.86 \( \text{Å} \times 38.63 \text{Å} \) and thickness of 4.2 \( \text{Å} \). Although this small thickness (5 atomic planes only) is not sufficient to achieve converged binding energies for the adsorbants for simulation of STM images (i.e. reproducing the charge density distribution several \( \text{Å} \) above the surface) it was found to be thick enough. Positions of all atoms in the slab, except the atoms in two bottom atomic planes were relaxed together with the positions of the adsorbed atoms. Neighboring images of the slab are separated by a 14 \( \text{Å} \) thick vacuum layer. The computational cell has an orthorhombic shape, it contains 350 atoms of the substrate plus up to 106 atoms of the adsorbed monolayer.

The geometry of one SF cluster can be characterized by a pentagon of the P1 tiling. The P1 tiling consists of two types of pentagons differing in orientation. We distinguish them as pentagons pointing “up” and “down”. We shall denote them as uP and dP tiles, respectively. The orientation of the SF cluster corresponds the uP pentagon. The uP tiles are concentric with the D tiles of the DHBS tiling. Some of the dP pentagons correspond to the surface vacancies. The surface vacancies act as trap sites binding ad-atoms very strongly. We assume that these sites are occupied in very early stages of the deposition. Simulation of STM images have shown that a single Pb atom bound inside the surface vacancy does not give any special contrast. Above the central Pb atom filling the vacancy the dP tiles can accommodate 5 Pb atoms forming a regular pentagon. This pentagon can adopt one of two possible orientations discussed below. The decoration of other tiles is to a large extent enforced by the decoration of the pentagonal tiles.

We have considered many possible configurations of adsorbed Pb atoms. The stability of the adsorbed Pb layer was probed by performing a conjugate-gradient relaxation of the structure of the adlayer/substrate complex under the action of the Hellmann-Feynman forces. Because of the limited extent of this paper we present a result for one configuration only representing a structure of a densely packed Pb monolayer with the coverage of 0.083 atoms/\( \text{Å}^2 \) (\( \Theta \approx 0.63 \)). We note that the experimentally measured coverage of 1 ML at the full saturation is \( \approx 0.09 \) atoms/\( \text{Å}^2 \).

A structural model of the Pb monolayer adsorbed on the surface at the coverage of 0.083 atoms/\( \text{Å}^2 \) is presented in Fig. 3. One can observe that Pb atoms occupy vertices and mid-positions of the edges of the P1 tiling. The mid-edge positions of acute angles of the tiles cannot be occupied simultaneously. Although a Pb atom could occupy a bridge position between these mid-edge sites (more accurately - a vertex position of the DHBS tiling), in most cases it prefers one of the mid-edge sites in a close contact with other Pb atoms decorating interiors of the pentagons. Obviously, the lateral Pb-Pb interaction is stronger than the Pb-substrate interaction. This is the reason why the P1 tiling is more appropriate for describing the quasiperiodic structure of the monolayer than the DHBS tiling.

The internal decoration of the uP tiles corresponds to the SF clusters. At high coverage Pb atoms are adsorbed also at the hollow sites in the centers of the SF clusters. To obtain high packing it was necessary to decorate the dP tiles with Pb pentagons with the opposite orientation compared to those inside the uP pentagons. This orientation allows us to insert additional Pb atoms in mid-edge positions between two neighboring uP and dP pentagons. At a lower coverage an opposite orientation of the Pb pentagon inside the dP tile is also possible. In dependence on the coverage the pentagonal decoration of the dP tile can thus adopt either orientations.

Fig. 4 shows that in the STM image bright spots appear in the centers of some uP pentagons. The explanation of the appearance of the bright spots in STM images, see also Fig. 1, can be found in the structure of the substrate. At the clean surface in the centers of the D tiles (Fig. 2) or concentric uP tiles either a Mn or Al atom can occur. The bright spots appear in those uP tiles
that have Al atoms at these positions. The uP tiles centered in the substrate by Mn sites give only weak contrast. The central Al atom is less strongly bonded to the neighboring Al atoms in the substrate than the Mn atom. After the structural relaxation of the adlayer/substrate complex while the central Mn atoms remain approximately in the surface plane the central Al atoms are lifted ≈0.6 Å above the surface plane pushing correspondingly up also the Pb atoms above. The distance between two neighboring bright spots is just the edge of the τP1 tiling. The bright spots can thus form vertices of the τP1 tiling as it has been experimentally observed, see Fig. 3 in [5]. The bright spots seen in STM images can also have an origin in defects. The regular decoration in some tiles can be substantially distorted. In Fig. 3 the regular pentagonal decoration of the dP tile at upper right corner of the figure was rearranged and one Pb atom was pushed up. A bright spot originating in an irregular arrangement of atoms in the monolayer can appear at any position. However, the observed defect formation can have also another interpretation. What is a decoration defect from the viewpoint of one tiling can be a regular site in another tiling. The formation of the defect observed in Fig. 4 can be interpreted as a reordering of the quasiperiodic arrangement of atoms expressed by the P1 tiling to another quasiperiodic arrangement at a larger scale described by the τP1 tiling. A similar reordering we observed also in alkali metals quasiperiodic monolayers [17] where the P1 quasiperiodic ordering was transformed to the DHBS ordering.

4. Conclusion
We have studied the structure of the quasiperiodic Pb monolayers grown on the fivefold i-Al-Pd-Mn surface. We have constructed structural models of the monolayer at a coverage close to the saturation. The skeleton of the Pb monolayer can be seen as a network of the SF clusters. The atomic structure of the monolayer is a decorated P1 tiling. The structural models reproduce also the quasiperiodic τP1 ordering observed also in the experimental STM images. The bright spots in the STM images appear in the centers of the uP (or D) tiles where the substrate has
Al atoms at these positions. The bright spots can originate also from irregular arrangements of atoms in the monolayer.

Acknowledgments
We acknowledge the European Network of Excellence on Complex Metallic Alloys (CMA) contract NMP3-CT-2005-500145 and the Agence Nationale de la Recherche, reference ANR-07-Blan-0270, are acknowledged for their financial support. The work has been supported by the Austrian Ministry for Education, Science and Art through the Center for Computational Materials Science. M. K. thanks also for support from the Grant Agency for Science of Slovakia (No. 2/5096/25) and from the Slovak Research and Development Agency (Grant No. APVV-0413-06, CEX-Nanosmart).

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