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Ab-initio study of a quasiperiodic Na monolayer on a fivefold
i-AlPdMn surface

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The structure and stability of a quasiperiodic Na monolayer formed on a five-fold surface of an icosahedral AlPdMn quasicrystal have been investigated using ab-initio density-functional methods. The structural model of the adsorbed monolayer has been constructed on the basis of a mapping of the potential-energy landscape of an isolated adatom on the fivefold surface of i-AlPdMn. Na atoms adsorbed on the surface arranged to a highly regular quasiperiodic monolayer. The quasiperiodic ordering can be described by a tiling of decagons, hexagons, boats and pentagonal stars (DHBS). The coverage density of the adsorbed monolayer is 0.067 atoms/Å².

Keywords: quasicrystals; surfaces; ab-initio; AlPdMn; Na; monolayers;

Introduction

Very recently Shukla et al. [1] have reported an X-ray photoelectron spectroscopy (XPS) study of Na and K adlayers on the fivefold surface of an icosahedral Al-Pd-Mn quasicrystal. Below one monolayer coverage a formation of a dispersed phase is reported. From the variation of the adlayer and substrate core-level intensities with coverage they conclude an layer-by-layer growth. Although the structures of the adsorbate phases have not yet been experimentally determined the possible existence of quasiperiodically ordered alkali metal overlayers adsorbed on the surface of a quasicrystal is highly interesting from at least two viewpoints. First, alkali metal adsorption on metal surfaces has been an interest of surface science for many years [2, 3] due to important technological applications of alkali covered surfaces (increased electron emission rates in cathodes, enhanced oxidation, promotion of heterogenous catalysis) but also due to the fundamental scientific interest. Chemically "simple" alkali metal atoms with one s-electron form very complex structures [3] on "simple" metal surfaces such as e.g. Al(111). A second reason for the investigation of the possible existence of quasiperiodic alkali metal adlayers is the fact that real quasiperiodic structures are multicomponent phases and therefore the existence of a single-element quasiperiodic structure is highly interesting.

Adsorbate thin films and monolayers grown on quasicrystalline surfaces have been already investigated experimentally by several groups [4, 5, 6, 7]. To grow a thin film with a quasiperiodic long-range order turned out to be difficult [4, 6]. Most attempts resulted in amorphous or polycrystalline films with domains of common crystalline structures, but successful attempts have been also reported [5, 7]. The detailed atomic structure of adsorbed monolayers is difficult to determine using experimental methods only. Structural modeling and ab-initio methods can provide the missing information. In our recent studies [8] we investigated the structure of the clean five-fold surface of icosahedral Al-Pd-Mn and the formation of quasiperiodic Bi and Sn monolayers on this surface [9]. A similar study has been performed for the surface of decagonal

Figure 1: Left: (a) The atomic structure of the surface of the 3/2-approximant to i-AlPdMn. Positions of the atoms: Al - open circles, Pd - shaded circles, Mn - closed circles. The surface is covered by a periodic approximant of a quasiperiodic P1 tiling. The pentagonal tiles have two orientations "top" marked by circles and "bottom" marked by crosses. Right: (b) The electronic charge density distribution of a surface model derived from the 2/1 approximant. The contour plot presents the valence charge density distribution in a plane intersecting the top atomic layer. The transition metal atoms in the plane create a high charge density - black circles. The positions of the Al atoms can be recognized as small circular islands of local density minima; one Al atom near the centre of figure is marked explicitly. The large charge depressions inside the pentagonal tiles correspond to surface vacancies. The B clusters are marked by dashed circles, the M clusters by dot-dashed circles. The labeled sites are discussed in the text.

Al-Co-Ni [10, 11]. In this paper we present our results for the structure and stability of quasiperiodic alkali-metal monolayer on the five-fold surface of i-Al-Pd-Mn. On the basis of an analysis of the landscape of binding energies of a single alkali adatom we propose a structural model for the adsorbed monolayer. The stability of the adsorbed structure has been tested via relaxation by forces from ab-initio density-functional calculations. Because of limited length of this contribution we restrict the presentation to study to the formation of Na monolayers. The results of our studies of the stability of monolayers and multilayers of Na and other alkali metals will be published elsewhere.

Fivefold surface of i-AlPdMn

The structure of the i-AlPdMn quasicrystal can be interpreted in terms of pseudo-Mackay and Bergman-type clusters [12, 13, 14]. Instead of using the term pseudo-Mackay or Bergman-type we shall, in agreement with Gratias et al. [15], call the clusters the *M* and *B* clusters. The construction of the structural model of the five-fold i-Al-Pd-Mn surface surface has been described in detail in our previous work [8]. The structural model of the surface derived from the 3/2 approximant includes 357 atoms. The computational cell has an orthorhombic shape. In addition to the slab of atoms it includes a 10 Å thick vacuum layer [9]. The charge density distribution and the interatomic forces have been calculated using the Vienna ab-initio simulation

package VASP [16].

Fig. 1(a) shows the atomic structure of the surface of the 3/2-model derived from the model of bulk i-Al-Pd-Mn. The surface is covered by a periodic approximant of a quasiperiodic P1 tiling [17]. The edge of the P1 tiling measures 7.76 Å. The tiling in the figure consists of several different tiles - of a regular pentagon, a pentagonal star, a boat and of thin and thick golden rhombuses. The centers of the pentagonal tiles are chosen to correspond to the positions of the *M* clusters. In the P1 tiling the pentagonal tiles adopt two different orientations. The orientation of the pentagonal tiles is related to the vertical position of the Mn atoms centering the *M* clusters. According to this vertical position we designate the pentagonal tiles as "top" and "bottom". In the top pentagon the center of the *M* cluster is at the top surface of the slab chosen to represent the surface. In the bottom pentagon the center of the *M* cluster is at a position deeper (2.56 Å) inside the slab (see Ref. [8] for more details). Any neighboring pentagons that share one edge have always opposite orientations. Most of the vertices of the P1 tiling coincide with the centers of truncated *B* clusters. The top atomic layer of the surface is occupied only by Al atoms and a few ($\approx 2\%$) Mn atoms [18, 19]. The ideal surface consists of two closely spaced atomic layers separated by a vertical distance of only 0.48 Å [20, 21]. The Pd atoms from the layer located 0.48 Å below the top layer also contribute to the surface charge density. The corrugated surface is thus composed of the atoms from the two top-most layers. The total surface atomic density of the model derived from the 3/2-approximant is $n_s = 0.132 \text{ atoms}/\text{\AA}^2$ [8]. This value is in very good agreement with the experimental value of $0.136 \text{ atoms}/\text{\AA}^2$ reported by Gierer et al. [18].

Fig. 1(b) shows the electron density in the surface layer of a smaller 2/1-approximant. The charge density minima at the vertices of the P1 tiling occupied by Pd atoms are surrounded by a complete or incomplete pentagon of Al atoms. The Pd atoms in the centers of the truncated *B* clusters are located deeper below the surface and their electrons do not contribute substantially to the surface charge density. The most striking features of the surface charge density distribution are large charge density minima inside some of the pentagonal tiles. These charge depletions correspond to surface vacancies. These vacancies are the consequence of the irregular structure of the first atomic shell surrounding the Mn atoms in the center of the *M* clusters. The quasiperiodic order at the surface is represented by the P1 tiling, but on the other hand the internal decoration of the tiles is rather irregular. In our previous work [22] we have demonstrated a good agreement of the scanning tunneling microscopy (STM) images calculated on the basis of our structural model with experimental images. It was found that both characteristic structural features of the experimental STM images - white flowers (WF) and dark stars (DS) in the STM pictures correspond to the *M* clusters in the bulk layers. A WF is formed by a central *M* cluster surrounded by five *B* clusters. The surface plane dissects the *M* cluster in the center, at its equatorial position. DS's originate from surface vacancies that exist inside some *M* clusters. While WF's coincide with the position of the "top" pentagons, DS's are related to the "bottom" pentagons of the P1 tiling.

Na monolayer adsorbed on five-fold i-Al-Pd-Mn surface

A quasiperiodic ordering in a monolayer can be stabilized when it is supported by a quasicrystalline substrate [8]. Very helpful in the search for the structure of the adlayer

is a mapping of the energetic landscape of the surface, searching for the most stable positions of adsorbed atoms. As a probe we have chosen a single Na atom bound to specific sites on the surface. We calculated the binding energy of adsorbed Na atoms. It is not possible to systematically scan the whole surface and investigate all possible sites. Fortunately, the local pentagonal symmetry of the various structural motifs at the surface allows to reduce the number of investigated sites. The selected sites are defined in Fig. 1(b). As the approximate local pentagonal symmetry does not guarantee that the binding energies on the symmetry-equivalent sites all are the same for each symmetry-equivalent sites we have chosen two representatives for each type of symmetry-equivalent sites to demonstrate energy differences between them. It is not surprising that the largest binding energies of -1.93 eV and -1.63 eV were found for the sites inside the surface vacancies denoted as VC1 and VC2. The surface vacancies result from the irregularities of the environment of the low-coordinated central Mn atom. Their shape and occurrence is irregular and therefore they will not systematically contribute to the formation of a regular quasiperiodic monolayer. The sites on the top of Pd atoms, PD1 and PD2, exhibit the second largest binding energies of -1.46 eV and -1.57 eV, respectively. It is interesting that comparably large binding energies are found also for two other types of symmetry-inequivalent sites. At the sites BC1 and BC2 located at the vertices of the P1 tiling we found binding energies of -1.40 eV and -1.53 eV, respectively, and the charge density minima denoted as CM1 and CM2 exhibit the binding energies of -1.45 eV and -1.50 eV, respectively. On the other hand, much lower binding energies were observed on top of Al and Mn sites. For the sites AL1 and AL2 we calculated the binding energies of -1.17 eV and -1.08 eV, respectively. For manganese atoms MN1 and MN2 we found binding energies of -1.28 eV and -1.15 eV, respectively. For simplicity, the binding energies of other sites are not discussed here.

One can expect that depending on the density of the adsorbed adatoms different surface structures are formed. The subject of our interest is the arrangement of atoms in a monolayer close to the saturation coverage. The most important factor limiting the atomic density of the adlayer is the size of the adatoms. The size of Na atoms estimated from the interatomic distances in bulk bcc Na is 3.66 Å. A similar value of $d_{Na-Na}=3.70$ Å was observed for interatomic distances in the (4×4) phase on Al(111) at densities close to saturation [3]. First we put Na atoms into the surface vacancies. However, because of their deep vertical positions they are not considered as a part of the adsorbed monolayer. Considering the size of adatoms and their binding energies we proposed a geometrical model for a quasiperiodic Na monolayer as shown in Fig. 2(a). As the vertices of the P1 tiling are among the most stable sites we assumed that the P1 tiling, similarly as for Bi and Sn monolayers [9], forms the framework of the quasiperiodic structure of the monolayer. The number and arrangement of atoms inside the tiles depends on the size of adatoms. For instance, inside the pentagonal tiles there is space for just five Na atoms. Within the "bottom" pentagons, The Na atoms are placed on-top of the strongly binding Pd atoms, within the "top" pentagons Na atoms are placed at symmetry-equivalent sites corresponding to the charge density minima. Additional Na atoms are placed into sites binding to Pd atoms located within the arms of the pentagonal star and within rhombic tiles. The coverage density of the proposed structure of adsorbed monolayer is 0.067 atoms/Å².

We tested the stability of the quasiperiodic ordering in the monolayer against relaxation under the action of the interatomic forces derived from ab-initio calculation. Fig.

Figure 2: Left: (a) A proposed ideal structure of a Na monolayer adsorbed on the i-Al-Pd-Mn surface. Closed circles represent positions of Na adatoms. The ordering in the monolayer reflects the quasiperiodic ordering of the substrate expressed by the P1 tiling. Right: (b) The charge density distribution in an adsorbed Na monolayer on the surface. In the relaxed model the adatoms re-arranged in a highly regular quasiperiodic structure different from the initial structure. The quasiperiodic ordering in the relaxed structure is represented by a DHBS tiling consisting of decagons, squashed hexagons, boat-shaped tiles and pentagonal stars.

2(b) shows the atomic positions and the charge density distribution in the adsorbed Na monolayer on the surface of $3/2$ after relaxation. The most interesting result is that the atoms in the monolayer adopt positions of a highly regular quasiperiodic structure. It is surprising that adatoms re-arranged in a quasiperiodic pattern different from the initial structure with idealized positions shown in Fig. 2(a). As expected Na atoms in the vertices of the P1 tiling remained in their original positions. Five atoms arranged on a pentagon decorating in the initial idealized structure the interior of the "top" pentagonal tiles form a pentagon with the same orientation also in the relaxed structure, but the size of this pentagon is somewhat reduced. A substantial rearrangement of atoms is observed inside the "bottom" pentagonal tiles and the pentagonal star of the P1 tiling. Here the rearrangement of atoms goes across the boundaries of the tiles. The quasiperiodic ordering in the relaxed structure is represented by a DHBS tiling consisting of decagons (D), squashed hexagons (H), boat-shaped tiles (B) and pentagonal stars (S). In comparison with the previously studied Bi and Sn monolayers on the i-Al-Pd-Mn surface [9] and Bi monolayers on d-Al-Co-Ni surface [11] the quasiperiodic arrangement of Na atoms on the i-Al-Pd-Mn surface exhibits a substantially higher regularity. The comparison with a Bi monolayer on the five-fold i-Al-Pd-Mn surface is particularly interesting. Because of the smaller size of Bi atoms this monolayer has, as experimentally observed, a higher atomic density of $0.09 \text{ atoms}/\text{\AA}^2$. The quasiperiodic arrangement of Bi atoms in the relaxed monolayer is also described by a P1 tiling, albeit in addition to the vertices of the tiling, mid-edge positions are also stable sites occupied by Bi atoms. The pentagonal tiles are also occupied by five Bi atoms. The five Bi atoms on the "top" pentagonal tiles preserve the regular pentagonal shape while the regular arrangement of five Bi atoms decorating "bottom" pentagonal tiles in most cases collapses. The behavior of the Bi atoms is

in this point similar to the Na atoms. However, because of the stable vertex and mid-edge positions the rearrangement of Bi atoms in the "bottom" pentagonal tiles does not go across the boundaries of the P1 tiles and the quasiperiodic ordering remains defined by the P1 tiling. To look at the differences in the structure of Bi and Na monolayers on the five-fold i-AlPdMn surface more closely we performed a relaxation of a Bi monolayer with the same coverage density and initial idealized positions as for a Na monolayer. Bi atoms did not form the regular DHBS tiling, their quasiperiodic ordering remains more appropriately described by the P1 tiling.

In Fig. 1(b) the positions of the atoms at the surface can be well recognized from the presented valence charge density distribution in the surface layer. The strong corrugation of the electron density at the surface facilitates an atomically resolved imaging by STM. In the case of a Na adlayer the situation is different. The dark circles in Fig. 2(b) correspond to the core charge density of the Na atoms. The valence charge density distribution is almost uniform and does not allow to identify the positions of the adatoms. The same holds also for an STM image of the adsorbed monolayer. The calculated STM signal provides hardly any information about the positions of the adatoms. On the other hand we have observed that the positions of the decagonal rings of Na atoms in the adsorbed monolayer (D-tiles of the DHBS tiling) coincide with the WF motifs seen in the STM images of clean i-Al-Pd-Mn surface.

Discussion

The 5-fold surface of i-AlPdMn is Al-rich. A comparison of the saturation coverage of alkali atoms adsorbed on the 5-fold i-AlPdMn surface with the alkali saturation coverage on Al(111) is therefore most interesting. The coverage of alkali adsorbates is usually expressed by the parameter Θ defined as the ratio of the number of alkali atoms to the number of substrate atoms in the first substrate layer. The atomic density of the Al(111) surface is $0.141/\text{\AA}^2$. This value is almost the same as the value of the atomic density of $0.136/\text{\AA}^2$ reported [8, 18, 21] for the 5-fold i-AlPdMn surface. It is therefore meaningful to compare the alkali coverages by a direct comparison of Θ defined independently for both surfaces. The adsorbed alkali metal atoms on Al(111) are known to form complex phases [3]. At higher temperatures Na atoms can be intermixed with the substrate atoms. For instance in the structure denoted as $(\sqrt{3} \times \sqrt{3})R30^\circ$ Na atoms substitute Al sites in Al(111) lattice positions. It is a structure in which one out of three surface Al atoms is removed and the vacancies are filled with Na atoms. The formation of such a substitutional phase is mediated by temperature activated interdiffusion processes. This structure is observed at room temperature and coexists with other surface structures over a wide range of coverages. At temperatures below 100 K no temperature activated processes can be expected. At low temperatures Na atoms adsorbed on Al(111) form several distinct phases at submonolayer coverage. For the comparison of the adsorbate structures formed on the 5-fold i-AlPdMn and Al(111) surfaces the most significant structure formed on the Al(111) surface is the phase denoted as (4×4) . This coverage corresponds to a higher-order commensurate structure in which there are 9 adatoms per (4×4) surface cell [3]. Na atoms in this structure form a pseudo-hexagonal close-packed layer. The phase appears at a coverage about $\Theta=0.42$ and remains stable up to the monolayer saturation coverage of about $\Theta=0.56$. The coverage of the quasiperiodic Na monolayer

on i-AIPdMn correspond to $\Theta=0.50$ and is thus in middle of the range of coverages observed for the (4×4) structure on Al(111).

Our ab-initio calculations investigate the structural stability of adsorbate structures at zero temperature. Simulations of processes at higher temperatures are possible but computationally prohibitively expensive. The formation of the substitutional adsorbate phase on Al(111) surface raises the question whether a similar intermixing of Na atoms and the atoms of the quasicrystalline i-AIPdMn substrate is possible. The substitution processes are thermally activated, our calculation corresponds to zero temperature. Therefore this question cannot be definitely answered on the basis of the present results. However, from our previous study [8] of the stability the i-AIPdMn surface we can expect intermixing of Na and Al atoms to occur at the surface vacancies originating from the irregular structure of the first atomic shell surrounding the Mn atoms in the center of the M clusters. For the other regions of the i-AIPdMn surface there are reasons to believe that Na atoms do not substitute atoms in the substrate even at elevated temperatures: (i) Most Al atoms in the i-AIPdMn surface are bonded to transition metal atoms in and below the surface layer. (ii) Na atoms preferably occupy charge density minima. Na atoms thus already occupy hollow sites with similar Al environments as in the substitutional $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase without necessity to replace an Al atom from the substrate. (iii) The mobility of Na atoms on the surface is limited by their preferable bonding with Pd atoms.

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