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Marian Krajci, Juergen Hafner. Ab-initio study of a quasiperiodic Bi monolayer on a fivefold i- AlPdMn surface. *Philosophical Magazine*, 2006, 86 (06-08), pp.825-830. 10.1080/14786430500256334 . hal-00513576

HAL Id: hal-00513576

<https://hal.science/hal-00513576>

Submitted on 1 Sep 2010

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**Ab-initio study of a quasiperiodic Bi monolayer on a fivefold
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Journal:	<i>Philosophical Magazine & Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-05-May-0146.R2
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	20-Jun-2005
Complete List of Authors:	Krajci, Marian; Slovak Academy of Sciences, Institute of Physics; University of Vienna, Center for Computational Materials Science Hafner, Juergen; University of Vienna, Institute of Material Physics and Center for Computational Materials Science
Keywords:	surfaces, quasicrystals, density-functional methods, adsorption, ab initio
Keywords (user supplied):	AIPdMn, Bi



Ab-initio study of a quasiperiodic Bi monolayer on a fivefold i-AIPdMn surface

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The structure and stability of a quasiperiodic Bi monolayer formed on a five-fold surface of an icosahedral AIPdMn 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-AIPdMn. This leads to a structural model of the quasiperiodic adlayer with atoms at the vertices and mid-edge positions of the P1-tiling. The internal decoration of the tiles is enforced by the decoration of the circumference of the tiles.

Keywords: quasicrystals; surfaces; ab-initio; AIPdMn; Bi

Introduction

The structure of the i-AIPdMn quasicrystal can be interpreted in terms of pseudo-Mackay and Bergman-type clusters[1, 2]. Instead of using the term pseudo-Mackay or Bergman-type we shall, in agreement with Gratias et al.[3], call the clusters the *M* and *B* clusters. The *B* cluster has a Pd atom in the centre. The *M* clusters are centred by Mn atoms. The first atomic shell of the *M* cluster is very irregular. Seven or eight atoms occupy vertices of a small dodecahedron, but their spatial arrangement around the central Mn atom is irregular with respect to icosahedral symmetry. The interpretation of the STM images of the i-AIPdMn surface has been based on a bulk-like termination of the ideal quasicrystalline structure. Papadopolos et al.[4] mapped high-resolution STM images of a fivefold surface of i-AIPdMn onto a planar tiling, denoted as P1, derived from a geometrical model of icosahedral AIPdMn. It was found that e.g. the characteristic structural features - dark pentagonal holes - in the STM pictures correspond to the *B* clusters in the bulk layers.

After the successful characterization of clean surfaces the question arises whether quasicrystalline adsorbate phases can be grown on a quasicrystalline surface. To grow a quasicrystalline thin film with a long-range order turned out to be difficult[5, 6, 7]. Most attempts resulted in amorphous or polycrystalline films with domains of common crystalline structures. Recently Franke et al.[8] prepared quasicrystalline epitaxial single-element monolayers adsorbed on the surfaces of icosahedral AIPdMn and decagonal AlNiCo quasicrystals. Elastic helium atom scattering and LEED of the deposited monolayers confirmed long-range quasicrystalline ordering in the films. From the experiments the detailed atomic structure of the adsorbed monolayer is difficult to determine. A structural modeling and ab-initio methods can provide this missing information. In this paper we report our results for the structure and stability of a single-element quasiperiodic monolayer on the fivefold i-AIPdMn surface. On the basis of an analysis of the landscape of binding energies of a single Bi adatom we propose a structural model for the adsorbed quasicrystalline Bi monolayer.

Fivefold surface of i-AIPdMn

The structural models of the bulk i-AIPdMn approximants are based on cut-and projection method with triacontahedral acceptance domains according to the Katz-Gratias-Boudard (KGB) model[1, 9]. A five-fold surface is prepared by cleaving the bulk structure along a plane perpendicular to a five-fold axis such that a layer with a high atomic density is exposed at the surface. The position of the plane bounding the quasicrystal should correspond to a plane of high atomic density[10]. The pseudogaps in the atomic density between high-density planes are natural cleavage planes of the quasicrystal[10]. The distances between the atomic density minima form a Fibonacci-like sequence. As a model of a surface of the AIPdMn quasicrystal we have chosen the surface that corresponds to one of the most frequently reported terminations of i-AIPdMn perpendicular to a five-fold axis. In the notation of Papadopolos et al.[4] it is equivalent to the R termination. The structural model derived from the 2/1 approximant includes 205 atoms. The computational cell has an orthorhombic shape. In addition to the slab of atoms it includes a 6 Å thick vacuum layer[12]. The charge density distribution and the interatomic forces have been calculated using the Vienna ab-initio simulation package VASP[13].

[Insert figure 1 about here]

Fig. 1(a) shows the atomic structure of the surface of the 2/1-model derived from the KGB model of bulk i-AIPdMn. The surface is covered by a periodic approximant of a quasiperiodic P1 tiling[4]. The edge of the P1 tiling measures 7.76 Å. The P1 tiling is a planar tiling which can be obtained by projection from a hyper-space. The acceptance (occupation) domain of the P1 tiling is a decagon. The decagonal acceptance domains of the tiling corresponds to the maximal cross-sections of the triacontahedra defining the three-dimensional structure of the bulk quasicrystal. Most of vertices of the P1 tiling coincide with the positions of the Pd atoms in the centres of the truncated *B* clusters. On the other hand the pentagonal tiles are located at the positions of the *M* clusters centred by the Mn atoms. The *B* and *M* clusters are mutually interpenetrating. An outer part of a *B* cluster is shared with a *M* cluster and vice versa. This overlap of the clusters leads to a conflict between their building principles and chemical decorations, eventually causing a substitutional defect or incompleteness of one of the clusters. The top atomic layer of the surface is occupied only by Al atoms and a few ($\approx 2\%$) Mn atoms[11, 10, 15]. The ideal surface consists of two closely spaced atomic layers separated by a vertical distance of only 0.48 Å. The figure shows that the Pd atoms from the next 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 2/1-approximant is $n_s=0.134$ atoms/Å². This value is in very good agreement with the experimental value of 0.136 atoms/Å² reported by Gierer et al.[11].

Fig. 1(b) shows the electron density in the surface layer. 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. These charge density minima form the pentagonal holes observed in the high-resolution STM images of the AIPdMn surface[16, 17]. The Pd atoms in the centres 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

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8 charge density minima inside some of the pentagonal tiles. These charge depletions
9 correspond to surface vacancies. These vacancies are the consequence of the irregular
10 structure of the first atomic shell surrounding the Mn atoms in the centre of the M
11 clusters. Fig. 1 shows that the quasiperiodic order at the surface is represented by the
12 P1 tiling, but on the other hand internal decoration of the tiles is rather irregular. The
13 irregularities are also well seen in the high-resolution STM images of the pentagonal
14 AIPdMn surfaces[4].

15 16 **Bi monolayer adsorbed on fivefold i-AIPdMn surface**

17
18 A quasiperiodic ordering in a monolayer can be stabilized when it is supported by
19 a quasicrystalline substrate. Franke et al.[8] studied quasicrystalline epitaxial single-
20 element monolayers adsorbed on the surfaces of icosahedral i-AIPdMn and decagonal
21 d-AlNiCo quasicrystals. Single-element quasicrystalline monolayers are prepared by
22 deposition of Sb and Bi on the 5-fold surface of icosahedral $\text{Al}_{71.5}\text{Pd}_{21}\text{Mn}_{8.5}$ and the
23 10-fold surface of decagonal $\text{Al}_{71.8}\text{Ni}_{14.8}\text{Co}_{13.4}$. The work of Franke et al.[8] motivated
24 us to study these systems with ab-initio methods. In this paper we restrict our report
25 to a Bi monolayer on the fivefold surface of an i-AIPdMn quasicrystal.

26
27 Very helpful in the search for the structure of the adlayer is a mapping of the energetic
28 landscape of the surface, searching for the most stable positions of adsorbed atoms.
29 As a probe we have chosen a single atom bound to specific sites on the surface. We
30 calculated the binding energy of adsorbed Bi atoms. A systematic repetition of this
31 procedure for selected points on the surface makes it possible to identify the most
32 stable positions for the adsorbed atoms. It is not surprising that the largest binding
33 energies of $\simeq -4.90$ eV were found for the sites inside the surface vacancies. As it was
34 already noted, the surface vacancies result from the irregularities of the environment
35 of the low-coordinated central Mn atom. Their shape and occurrence is irregular
36 and therefore they will not systematically contribute to the formation of a regular
37 quasiperiodic monolayer. The sites on the top of Mn atoms exhibit the second largest
38 binding energies of -4.58 eV. The number of such sites at the surface is very small
39 and therefore their role in the formation of a quasiperiodic monolayer is limited. The
40 most abundant element on the surface is aluminum. However, a calculation shows
41 that the binding energy of Bi adatoms on the Al sites of -2.86 eV is the lowest of all
42 considered sites. A quasiperiodic monolayer consisting of adatoms placed on top of Al
43 atoms amorphised during relaxation. Neither will Pd atoms that are 0.48 Å below the
44 surface plane stabilize a quasiperiodic monolayer. A Bi adatom on top of a Pd atom
45 has an intermediate binding energy of -3.43 eV. We found that significantly more
46 stable are the positions at the centres of the B clusters. The binding energies of Bi
47 adatoms inside the complete or incomplete B clusters are -4.37 eV and -4.32 eV,
48 respectively. These sites are quasiperiodically distributed on the surface and therefore
49 their occupation by an adatom would already form a stable quasiperiodic monolayer
50 of low coverage. Other stable positions are the mid-edge positions of the P1 tiling.
51 The binding energy of Bi at these sites are -3.92 eV. From these results we concluded
52 that the sites at the vertices and the mid-edge positions of the P1 tiling are the
53 framework of a possible stable quasiperiodic monolayer on top of 5-fold i-AIPdMn
54 surface. The decoration of the interior of the tiles follows quite naturally from the
55 decoration of the vertices and the mid-edge positions, i.e. by the decoration of the
56 circumference of the tiles. The decoration depends on the size of an adsorbed atom.
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8 With a proper size of atoms a regular decoration is enforced by the decoration of
9 the circumference of the tile. Fig. 2(a) shows the ideal distribution of atoms in the
10 monolayer. If the centres of the pentagonal tiles are occupied the coverage density
11 is $0.09 \text{ atoms}/\text{\AA}^2$, exactly in the centre of the experimentally determined range of
12 $(0.09 \pm 0.02) \text{ atoms}/\text{\AA}^2$. Bi atoms prefer an average nearest-neighbor distance of $\simeq 3.2$
13 \AA . This size leads to a very dense packing of Bi atoms inside the pentagonal tiles
14 and to significant lateral stress. During the relaxation some of the atoms jumped
15 up to positions above the monolayer. Therefore we skip the central atom inside the
16 pentagonal tiles. This would lead to a somewhat lower coverage of $0.085 \text{ atoms}/\text{\AA}^2$,
17 still within the experimentally determined range. The ideal structure of the adsorbed
18 monolayer has a higher, decagonal symmetry than the underlying 5-fold surface of
19 i-AIPdMn.

20 [Insert figure 2 about here]

21
22 We tested the stability of the quasiperiodic ordering in the monolayer against relaxation
23 by the interatomic forces. Fig. 2(b) shows the charge density distribution in the
24 adsorbed Bi monolayer on the surface of 2/1 after relaxation. In the relaxed model
25 the quasiperiodic ordering is essentially conserved although significant displacements of
26 atoms from their ideal positions are obvious. In agreement with the expected stability
27 of the vertex sites of the P1 tiling the Bi atoms at these sites exhibit only minimal
28 shifts from the ideal positions. Slightly larger displacements are observed for the mid-
29 edge positions. The arrangement of Bi atoms inside the pentagonal tiles undergoes
30 substantial modification. The observed deviations of the relaxed atomic positions from
31 the ideal ones are not surprising: (i) the distortion of the regular pentagonal motifs
32 inside the pentagonal tiles reflect the irregularity of the substrate, which has the
33 origin in the irregular first atomic shell of the M cluster, (ii) significant deviations of
34 atomic positions from their ideal ones are commonly observed also in bulk icosahedral
35 quasicrystals where no such irregular atomic configurations exist. Our calculations
36 were performed at zero temperature. From the analysis of the rather flat energetic
37 landscape it is clear that higher temperature could be favorable for increasing the
38 quality of the quasiperiodic ordering. At higher temperatures the atoms located on
39 the irregular part of surface of i-AIPdMn inside the P1 tiles can assume more symmetric
40 average positions.

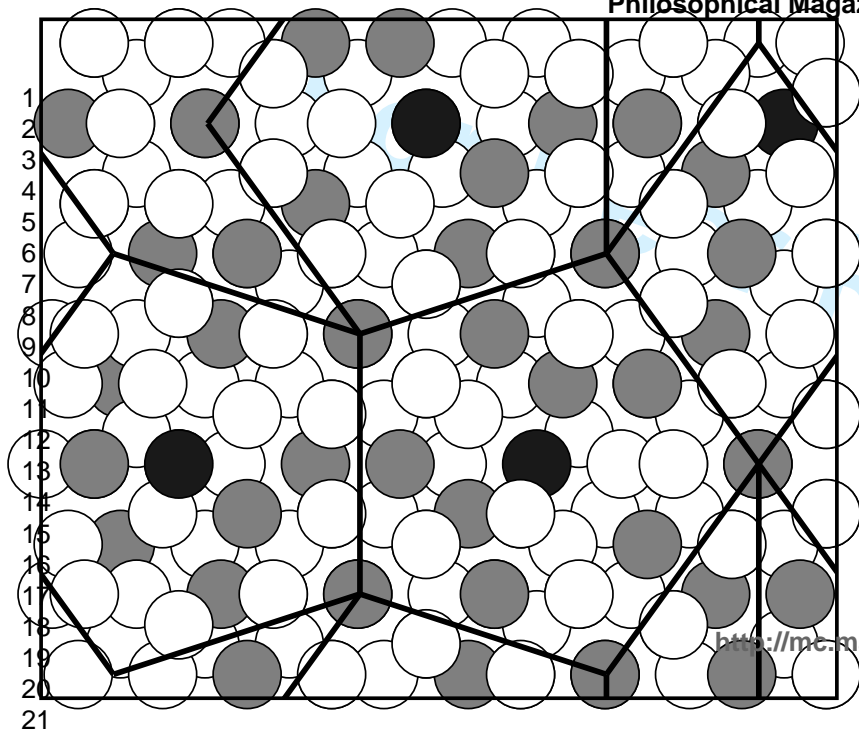
41 This work has been supported by the Austrian Ministry for Education, Science
42 and Art through the Center for Computational Materials Science (CCMS). M. K.
43 thanks also for support from from the grants No. VEGA-2/5096/25, APVT-51021102,
44 APVT-51052702, SO-51/03R80603.

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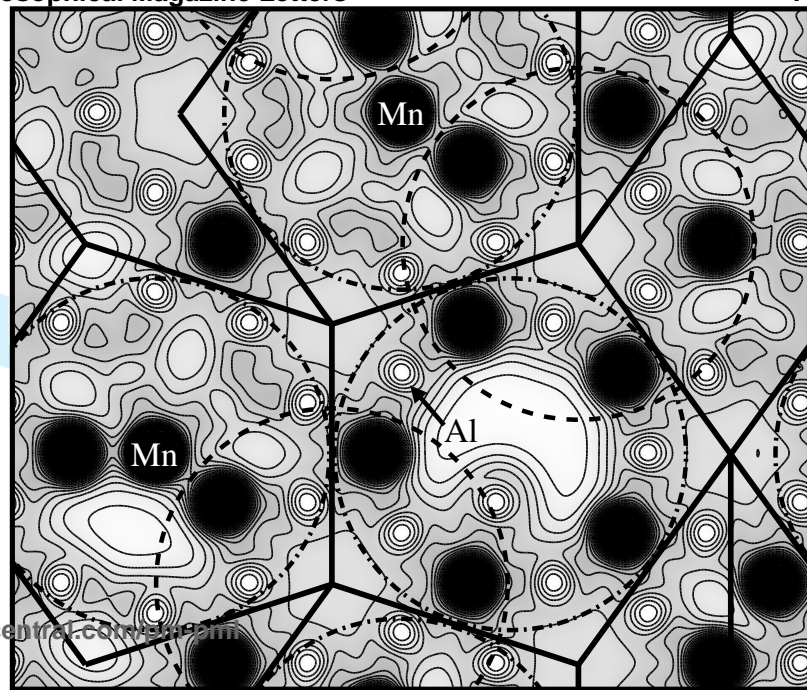
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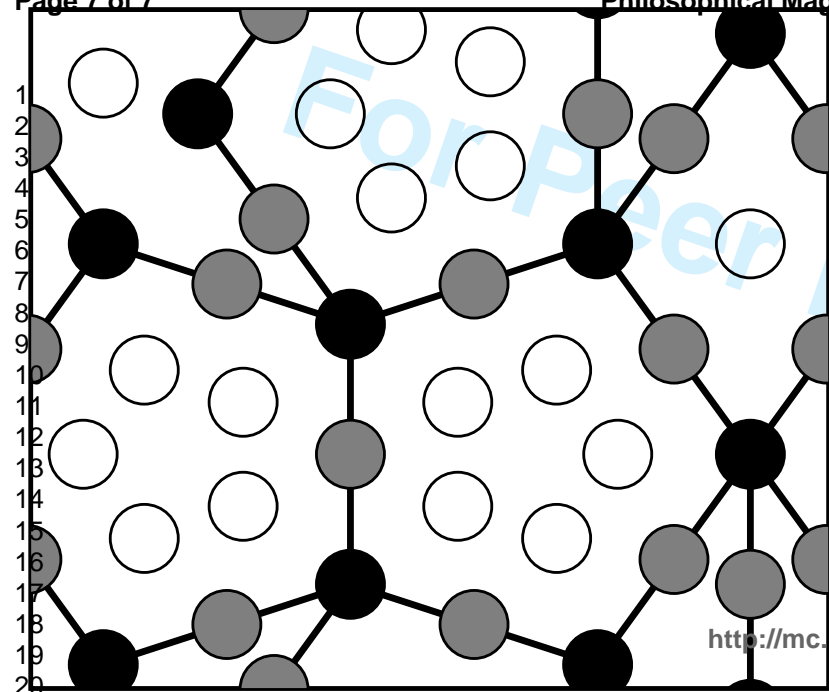
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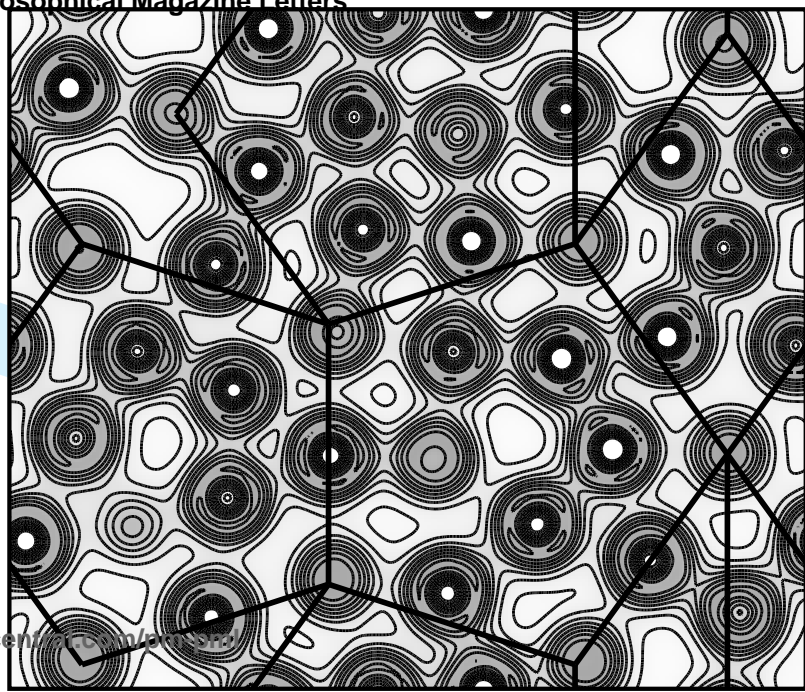
(a)



(b)



(a)



(b)