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Ab initio study of quasiperiodic monolayers on a fivefold *i*-AlPdMn surface

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We present a structural model for quasiperiodic monolayers formed on the fivefold surface of an icosahedral AlPdMn quasicrystal, based on *ab initio* density functional calculations. As a starting point we have investigated the relative stability of unsupported triangular, square, and quasiperiodic monolayers. The unsupported quasiperiodic monolayers are shown to be unstable upon relaxation by interatomic forces. This result indicates the important role of the adsorbate/substrate interaction for the stabilization of a quasiperiodic layer. The structural model of a monolayer adsorbed on the fivefold surface has been constructed on the basis of a mapping of the potential-energy landscape of an isolated adatom on the *i*-AlPdMn substrate. The structure of a clean fivefold *i*-AlPdMn surface is well described by a $P1$ tiling, with the vertices of the tiling located in the centers of B (Bergman) clusters and occupied by Pd atoms. The potential-energy mapping emphasizes the important role of the $P1$ skeleton for the stabilization of a quasiperiodic adlayer: adsorption at the vertices of the $P1$ tiling leads to high binding energies of $\simeq 4$ eV/atom. The midedge positions of the $P1$ tiling and Mn atoms exposed at the surface are identified as further favorable adsorption sites. Altogether this leads to a structural model of the quasiperiodic adlayer with atoms at the vertices and midedge positions of the $P1$ tiling, centered pentagonal motifs decorating the pentagonal tiles, and one additional atom in the center of the pentagonal star and of the boat tile. For this structure we calculate a surface coverage of $\simeq 0.09$ atoms/Å^2 in perfect agreement with experiment. The diffraction pattern of the adlayer exhibits (pseudo)decagonal symmetry. The structural stability of a 2/1 approximant to this model has been tested for Sn, Bi, and Sb monolayers via relaxation by the Hellmann-Feynman forces from *ab initio* density function theory calculations. The skeleton of adsorbed monolayers based on the $P1$ tiling was found to be stable, although the atomic decoration inside the tiles is partially distorted, albeit without violating the overall symmetry.

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I. INTRODUCTION

In the past 10 years significant progress has been made in the preparation and characterization of surfaces of icosahedral and decagonal quasicrystals. Surfaces of stable quasicrystals, particularly of the icosahedral AlPdMn and decagonal AlNiCo quasicrystals were studied most intensively. Low-magnification scanning tunneling microscopy (STM) images revealed that the high-symmetry fivefold and tenfold surfaces of quasicrystals exhibit a quasiperiodic or periodic sequence of flat terraces corresponding to planes of high atomic density. High-resolution STM images of single terraces of an *i*-AlPdMn surface[1,2] show quasicrystalline order at the surface and atomic scale features with local fivefold symmetry.

The interpretation of the experimental results has been based on a bulklike termination of the ideal quasicrystalline structure. Papadopolos *et al.*[3] mapped high-resolution STM images of a fivefold surface of *i*-AlPdMn onto a planar tiling derived from a geometrical model of icosahedral AlPdMn. The experimentally derived tiling of the surface matches a geometrical tiling derived from the structural model. It was found that the atomic positions on the terraces correspond exactly to cuts across the basic atomic clusters of the bulk structure, the so-called Bergman and pseudo-Mackay clusters. The characteristic structural features—dark pentagonal holes—in the STM pictures correspond to the Bergman 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. At low coverage below one monolayer, adatom clusters with fivefold symmetry were observed on fivefold[4] and tenfold surfaces.[5] To grow a quasicrystalline thin film with a long-range order turned out to be substantially more difficult. Most attempts resulted in amorphous or polycrystalline films with domains of common crystalline structures. Bolliger *et al.*[6] observed fcc textures on Al films deposited on an *i*-AlPdMn surface. Similar results were reported by Fournée *et al.*[7] who studied nucleation and growth of Ag films deposited on the *i*-AlPdMn surface. They found hexagonal islands with five different orientations, rotated by $2\pi/5$ and reflecting the fivefold symmetry of the substrate.

Other attempts led to the development of surface alloys having icosahedral or decagonal symmetry.[8,9] Shimoda *et al.*[8] observed the formation of an epitaxial Au—Al alloy film on a quasiperiodic surface of icosahedral AlPdMn. The film was not obtained on the clean surface, but an ordered Au—Al layer with icosahedral symmetry was formed in the presence of predeposited In, which acted as a surfactant. Naumović *et al.*[9] produced a stable decagonal *d*-AlPdMn film on an *i*-AlPdMn substrate. A decagonal AlPdMn film was epitaxially grown as a single domain overlayer on the fivefold surface of *i*-AlPdMn, with the tenfold axis of the overlayer parallel to the fivefold axis of substrate.

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Recently Franke *et al.*[10] prepared quasicrystalline epitaxial single-element monolayers adsorbed on the surfaces of icosahedral AlPdMn and decagonal AlNiCo quasicrystals. Elastic helium atom scattering and low-energy electron diffraction (LEED) of the deposited monolayers confirmed long-range quasicrystalline ordering in the films. A single-element monolayer film was recently prepared also by Ledieu *et al.*[11,12] They deposited an ultrathin film of Cu atoms on the fivefold *d*-AlPdMn surface.[12] The observed structure of monolayers comprises quasiperiodic arrays of atomic rows with spacings of $S=4.5$ Å and $L=7.3$ Å, whose ratio equals the golden mean τ within experimental error.

The present work is a continuation of our previous *ab initio* study of the structure, electronic properties, and the stability of a clean fivefold surface of an *i*-AlPdMn quasicrystal[13] where we have demonstrated that the surface of *i*-AlPdMn is well described by a planar $P1$ tiling with the vertices of the tiling located in the centers of the Bergman clusters. In the present work we investigate the structure and the stability of quasiperiodic monolayers adsorbed on an *i*-AlPdMn surface. Our work has been motivated mainly by the experimental work of Franke *et al.*[10] We report our results for the structure and stability of single-element quasiperiodic monolayers on the fivefold *i*-AlPdMn surface. The atomic structure of the adsorbed monolayer is not known *a priori*. On the basis of an analysis of the landscape of binding energies of a single adatom we propose a structural model for the adsorbed quasicrystalline monolayer. We obtained very good agreement of the coverage density of the monolayer with the experimentally determined value.[10] The symmetry of the clean *i*-AlPdMn surface is fivefold. However, the calculated diffraction pattern of the proposed atomic structure of the adsorbed monolayer exhibits a (pseudo)decagonal symmetry in agreement with the observed symmetry of the LEED images.[10] The origin of this decagonal symmetry is in the decagonal shape of the occupation domain in hyperspace of the $P1$ tiling forming the skeleton of the atomic structure of the monolayer.

The important question is the stability of the adsorbed monolayer. The monolayer is formed by interacting atoms. The interatomic bonding is mediated by atomic orbitals of *s*, *p*, or *d* symmetry. The valence of orbitals and their bonding hybrids lead to certain preferential orientations of bonds. Are the preferred bond lengths and angles of atoms in the monolayer compatible with quasicrystalline ordering? Although the main aim of this work is to study the structure and the stability of quasiperiodic monolayers adsorbed on a fivefold surface of *i*-AlPdMn quasicrystal, it is worthwhile to consider first the possible existence and stability of unsupported monolayers. One has to answer the question if in a single-element monolayer which is not supported by a quasicrystalline substrate, stable quasiperiodic ordering can exist. This preliminary study of unsupported single-element quasiperiodic monolayers will show us which elements can eventually favor quasiperiodic ordering and for which ones such an ordering is expected to be highly unstable. This will help us to suggest elements that are suitable not only for the present *ab initio* studies of the adsorbed monolayers, but also for experimental studies of possible epitaxial deposition of single-element quasiperiodic monolayers on surfaces of quasicrystals.

II. METHOD

The increasing computational power of present computers and the progress in the development of highly efficient computational methods makes it feasible to obtain interesting physical information from *ab initio* calculations on highly realistic but complex structural models. We have used the advanced *ab initio* method implemented in the Vienna *ab initio* simulation package VASP[14,15] to perform electronic structure calculations and structural optimizations. The theoretical background of VASP is the density functional theory within the local density approximation. The wave functions are expanded in plane waves. The Hamiltonian is based on pseudopotentials derived in framework of the projector-augmented wave (PAW) method.[15] VASP performs an iterative diagonalization of the Kohn-Sham Hamiltonian. The plane-wave basis allows us to calculate Hellmann-Feynman forces acting on the atoms. The total energy may by optimized with respect to the positions of the atoms within the cell. The calculations were performed within the the generalized-gradient approximation (GGA).[16] VASP has also been used to calculate charge distributions.

III. UNSUPPORTED MONOLAYERS

The central issue is the structural stability of free-standing, unsupported monolayers. One has to distinguish between several different levels of stability. In this work we consider the local stability at zero temperature. The structure is stable if its total energy corresponds to a local minimum, each atom is in its equilibrium position with respect to the forces acting from the neighboring atoms. A stable structure can be obtained by relaxing all forces, eventually stresses in the system. Another level of stability is the stability of the system at elevated temperatures. An investigation of finite temperature stability can in principle be performed by molecular dynamics (MD) methods. However, *ab initio* MD methods are computationally much more demanding than static optimizations and, unfortunately, such investigation of our models of quasiperiodic monolayers is beyond what is possible with our present computational facilities. The highest level of the stability is the thermodynamic stability with respect to all competing phases in the phase diagram.

A. Rectangle-triangle tiling and single-component decagonal quasicrystal

At first sight, it is clear that quasiperiodic monolayers could have a certain relation to decagonal quasicrystals. Decagonal quasicrystals are quasiperiodic in a plane and periodic in the direction perpendicular to this plane. One could speculate that the building principle and bonding in a quasiperiodic monolayer is similar to that in the quasiperiodic plane of a decagonal quasicrystal. However, there is one significant point that has to be considered. All known quasicrystalline phases, decagonal or icosahedral, are multicomponent systems, typically ternary systems. The possible existence of stable one-component quasicrystals has been the subject of several studies. Smith and Ashcroft[17,18] performed extensive lattice-sum potential energy calculations for a variety of crystalline and quasicrystalline structures, using pair potentials generated by pseudopotential theory. Their conclusion was that stable one-component systems are indeed possible, albeit within a restricted range of potential parameters having no counterpart in the Periodic Table. Finite-temperature studies of one-component quasicrystals based on classical density functional theory (for atoms, not for electrons!)[19] have been performed by Carley and Ashcroft[20] and Denton and Hafner.[21] Carley and Ashcroft considered hard-sphere (HS) systems with a purely entropic free energy and concluded that HS quasicrystals are at best metastable—hence, ordinary entropy (lattice vibrations and disorder) is insufficient to stabilize quasiperiodic ordering. Denton and Hafner studied ensembles of atoms interacting via effective metallic pair potentials. Thermodynamically stable quasicrystals were predicted for potential parameters approaching the limits of stability of the crystal structures. Quasicrystalline stability is attributed to energetically favorable medium-range and long-range interactions and to vibrational stiffness.[21] The result that no single element falls into this parameter range is confirmed, but it includes the virtual-crystal parameters of known ternary quasicrystalline alloys. Hence, it is not surprising that so far no single-component quasicrystal could be prepared.

The structural models for quasicrystals considered in these exploratory studies are Penrose tilings in either a two-dimensional or a three-dimensional variant. In a simple model with a vertex decoration where atoms are placed at vertices of a two-dimensional Penrose tiling there are three nearest neighbor distances, 1.0, 1.18, and 0.62 (expressed in units of the quasilattice constant). The difference between the shortest one and the two others is too large to represent bonds between the same type of atoms. In the three-dimensional (3D) Penrose tiling there is one even shorter distance of 0.56. This explains the observation that quasicrystalline stability is observed only at electronic valences and core radii where close packing is increasingly disfavored and more open structures become competitive. Near electronic valences and core radii where close-packed structures lose mechanical stability, but where the covalent component in the bonding is not yet strong enough to stabilize directional bonding, theory predicts quasicrystalline stability. Another simple decoration of the Penrose tiling where atoms are put in the centers of the tiles even directly implicates a two-component quasicrystal with bigger atoms in the fat rhombi and smaller atoms in the skinny rhombi. Of course, the real arrangement of atoms in Penrose tiles is more complicated than in these simple models but, nevertheless, all known quasicrystals whose structure can be interpreted as a Penrose tiling are multicomponent systems.

However, the arrangement of atoms based on Penrose tilings are not the only possible quasiperiodic arrangements. Other tilings offer more favorable conditions for a single-component quasiperiodic arrangement of atoms. One such candidate is the rectangle-triangle (RT) tiling. In this tiling there are only two distances of similar lengths between the neighboring vertices, namely 1.0 and 1.18, and no short distances. The bond angles of 90, 72, and 54 deg are also acceptable bonding angles. The RT tiling can be not only a proper pattern for the structure of a quasiperiodic monolayer, but the building principle of RT tiling can even be used for the construction of a single-component decagonal quasicrystal.

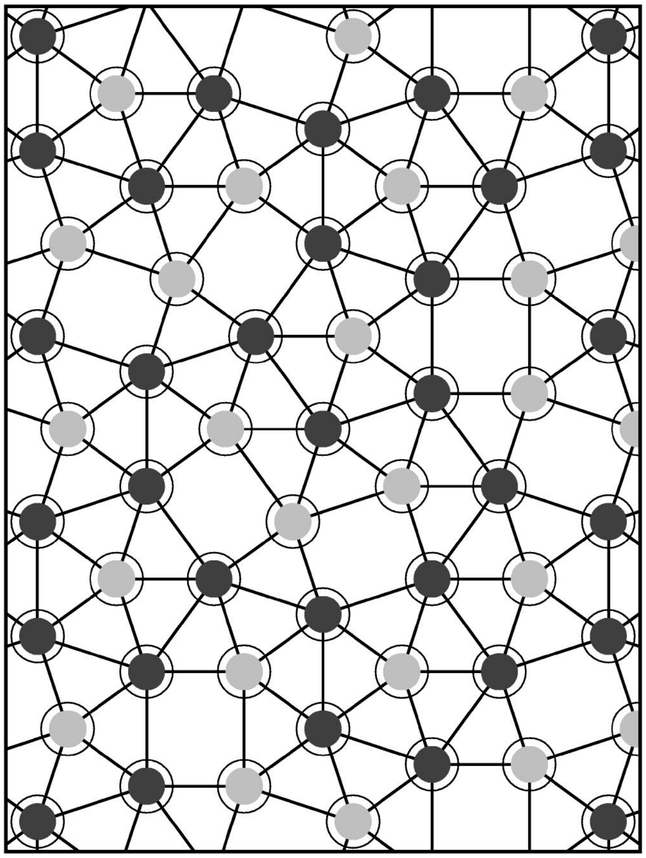

FIG. 1. Part of the quasiperiodic rectangle-triangle tiling. Atoms represented by darker circles are typically arranged in the form of pentagons centered by atoms marked as light circles. In the decagonal one-component quasicrystal, the darker atoms are shifted to $z=0.25$, the lighter atoms to $z=-0.25$, admitting a dense sphere packing, cf. text.

The single-component decagonal quasicrystal is a hypothetical monoatomic quasicrystalline system. It is based on a locally stable quasicrystalline sphere packing proposed by Cockayne and Mihalkovič.[22] The structure is based on two main principles: (i) transformation of a decagonal rectangle-triangle tiling to a sphere packing, and (ii) maximizing the density of disk packing in the decagonal tiling. A two-dimensional unit-disk packing can be achieved by centering disks of diameter 1 on a subset of vertices of the RT tiling consisting of rectangles and triangles, see Fig. 1. The planar tiling is rescaled such that the tile edge is $\sqrt{3}/2$. The RT tiling is bipartite, and it is possible to subdivide vertices into two kinds, A and B. The spheres whose centers project onto vertices of type A (B) are shifted in the direction perpendicular to the plane of the tiling by $+1/4$ $(-1/4)$, respectively. A three-dimensional decagonal structure is generated by replacing each disk in the RT tiling by a vertical column of touching spheres. Each sphere touches the spheres immediately above and below, as well as those spheres in the other layer located at an in-plane distance of $\sqrt{3}/2$ and a distance $1/2$ in the perpendicular direction. Although the spheres do not

TABLE I. Optimal lattice parameters a_{ot}, a_{os} and corresponding total energies E_{ot}, E_{os} of triangular and square monolayers, respectively. Δa_0 and ΔE_0 are differences of the corresponding values between the triangular and square lattices, $\overline{a_0}$ is an average value of a_{ot} and a_{os}.

Element	a_{ot} (Å)	a_{os} (Å)	Δa_0 (Å)	$\overline{a_0}$ (Å)	E_{ot} (eV)	E_{os} (eV)	ΔE_0 (eV)
Al	2.69	2.64	0.05	2.66	−3.037	−2.771	−0.266
Pd	2.63	2.54	0.09	2.59	−4.157	−3.866	−0.291
Mn	2.28	2.12	0.16	2.20	−6.967	−7.043	0.076
Cu	2.43	2.35	0.08	2.39	−3.036	−2.729	−0.307
Ag	2.79	2.71	0.08	2.75	−2.248	−2.034	−0.214
Au	2.75	2.67	0.08	2.71	−2.926	−2.633	−0.293
Ga	2.75	2.62	0.13	2.68	−2.488	−2.429	−0.059
In	3.16	2.99	0.17	3.08	−2.152	−2.094	−0.058
Tl	3.30	3.11	0.19	3.20	−1.903	−1.852	−0.051
Ge	2.77	2.58	0.19	2.68	−3.775	−3.811	0.036
Sn	3.16	2.96	0.20	3.06	−3.323	−3.304	−0.019
Pb	3.30	3.12	0.18	3.21	−3.113	−2.990	−0.123
As	2.75	2.58	0.17	2.66	−3.898	−4.111	0.213
Sb	3.14	2.95	0.18	3.04	−3.472	−3.602	0.130
Bi	3.29	3.12	0.17	3.21	−3.313	−3.338	0.025

touch other spheres in the same layer, the in-plane distance of neighboring spheres is only 1.018. The decagonal structure based on a rectangle-triangle tiling maximizes the packing fraction.[23,24] The achieved packing fraction of $\eta=0.6953$ should be compared to the packing fraction $\eta_{fcc}=0.7405$ of close packed structures (fcc or hcp) and to the packing fraction $\eta_{bcc}=0.6801$ of a body-centered-cubic arrangement. The resulting structure is stable in the sense that each sphere is fixed by its neighbors. *Ab initio* density functional theory (DFT) calculations on low-order approximants to decagonal Al (see Ref. 25) have demonstrated that the decagonal structure is metastable, but higher in energy by 60–70 meV/atom than fcc Al.

The RT tiling thus is a good framework for the construction of quasiperiodic monolayers. The building principle of the single-component decagonal quasicrystal can also serve for the construction of bilayers or multilayers. However, if the spheres are replaced by real atoms the directional character of interatomic bonding can significantly affect the stability of the system. A good probe for revealing the directional character of the interatomic bonding in a monolayer is a comparison of the total energies for triangular and square lattices.

B. Triangular versus square monolayers

We have performed an extensive study of a relative stability of the triangular versus square monolayers for many elements of the Periodic Table. For both lattices the size of the lattice parameter a was varied in a certain range around the value corresponding to the minimum of the total energy. The difference between the minima of the total energies shows the degree of preference for a particular lattice. The results are collected in Table. I. The table includes the optimal lattice parameters, total energies, and their differences for all noble metals and for the main group elements from columns IIIb to Vb.

In a quasiperiodic arrangement based on the RT tiling both triangular and rectangular configurations of atoms are present. One can quite naturally expect that elements that have a large structural energy difference ΔE_0 between triangular and square monolayers will not be suitable for a quasiperiodic arrangement. The arrangement of the atoms in the quasiperiodic monolayer with large ΔE_0 has a tendency to collapse to either a triangular or a square arrangement. From Table I it is therefore clear that Al, Pd, Cu, Ag, and Au will prefer the densest triangular arrangement, as for these elements this structure is preferred by more than 0.2 eV/atom.

Most of elements listed in Table I prefer a triangular lattice. A notable exception are the elements from group V: As, Sb, and Bi. Figure 2 presents the total energies of the square and triangular lattices and the differences in the equilibrium bond lengths for As, Sn, and Bi monolayers. These elements favor a square arrangement of atoms in a monolayer. The physical origin of this preference is in a specific character of the interatomic bonding. In these elements the s states have very low energies and they are separated from the p band. The bonding thus has a pure p character. The preferred rectangular arrangement of atoms results from the rectangular orientation of the p orbitals participating in the bonding.

The smallest difference between the triangular and square monolayers is observed for Sn ($\Delta E_0=-0.019$ eV/atom) and Bi ($\Delta E_0=0.025$ eV/atom). Figure 2 illustrates the near degeneracy of the total energies of the square and triangular lattices in the case of the Bi monolayer. Small values of this difference are calculated also for Ge

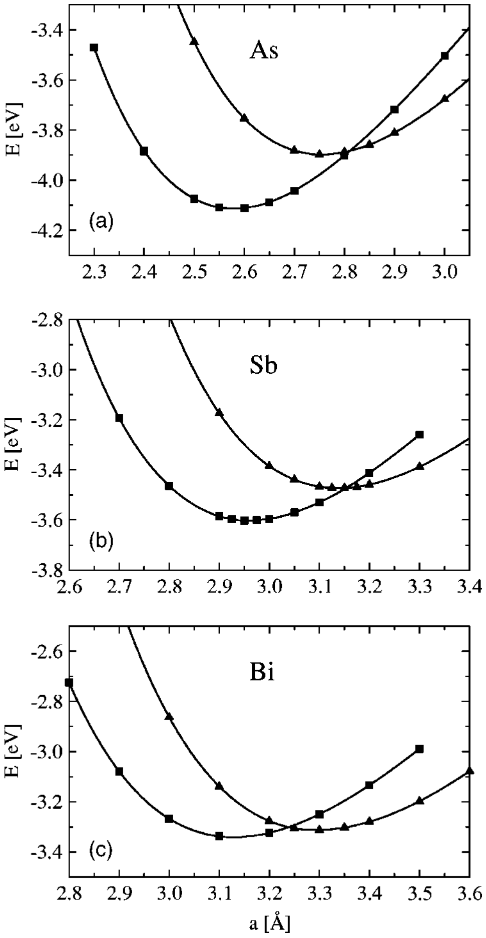

FIG. 2. Total energy of unsupported triangular and square monolayers as a function of the lattice parameter a. The curves for triangular and rectangular lattices are marked by triangles and square, respectively. The panels show the results for monolayers consisting of As (a), Sb (b), and Bi (c) atoms.

($\Delta E_0 = 0.036$ eV/atom) and all elements of group III: Ga, In, Tl ($\Delta E_0 = -0.051$ to -0.059 eV/atom). These elements are thus good candidates for a quasiperiodic arrangement in a monolayer.

C. Unsupported quasiperiodic monolayers and multilayers

One can expect that monolayers composed of atoms that have no strong preference for either a triangular or a rectangular arrangement could perhaps be stable in the quasiperiodic RT tiling. We have performed several studies of the stability of quasiperiodic planar monolayers composed of Sn or Bi atoms. Sn atoms have a very small preference for the triangular arrangement, Bi atoms have a weak preference for the rectangular arrangement. We put the atoms in the vertices of the RT tiling (see Fig. 1) and searched for an optimal size of the elementary cell. Then the coordinates of atoms were relaxed by the interatomic forces. Unfortunately, none of our attempts was successful. The arrangement of atoms after the relaxation was amorphouslike. The planar symmetry was broken, the atoms moved out of the original planar arrangement. A similar amorphouslike result was obtained also for a constrained relaxation with fixed z coordinates of the atoms.

The single-component decagonal quasicrystal consists of periodically repeated quasiperiodic bilayers. It is therefore relevant to investigate a possible stability of unsupported quasiperiodic bilayers. Unfortunately, neither Sn nor Bi bilayers were found to be stable. We attempted to stabilize them by increasing the surface density of atoms. Although at reduced size of the elementary cell they exhibited somewhat higher stability, nevertheless, long relaxation runs always led to amorphouslike structures.

Both unsupported quasiperiodic monolayers and bilayers based on the RT tiling are thus mechanically unstable. On the other hand the single-component decagonal quasicrystal composed of periodically repeated bilayers is mechanically stable. We tested the stability of this quasicrystal for Sn, Bi, and some other elements. The decagonal quasicrystal has been proven to be metastable even for Al.[25] Here we mean stability at zero temperature, i.e., stability against relaxation of coordinates with the interatomic forces. The unsupported quasiperiodic bilayers are unstable, but their periodic stacking leads to a stable structure. One can therefore expect that quasiperiodic films of a thickness larger than a certain critical thickness could eventually be stable. Although such a theoretical study is feasible, experimentally it would be difficult to prepare such a quasiperiodic film. The theoretical calculations show that the single-component decagonal quasicrystals appear to be significantly less stable than the corresponding crystalline phases. Sn crystallizes in the diamond (cF8) structure. The single-component approximant to the decagonal quasicrystal consisting of 47 atoms per unit cell is thermodynamically less stable by 0.064 eV/atom. For Bi the stable phase is a rhombohedral hR2 phase. The quasicrystalline approximant is higher in energy by 0.156 eV/atom.

IV. MONOLAYERS ADSORBED ON A FIVEFOLD I-ALPDMN SURFACE

The unsupported quasiperiodic single-element monolayers based on the RT tiling have been found to be unstable. Although we obtained this negative result only for one kind of the quasiperiodic tiling, we assume that this result has a more general validity. The existence of a stable unsupported quasiperiodic single-element monolayer thus seems to be unlikely. It is therefore interesting to investigate whether a quasiperiodic ordering in a monolayer can be stabilized when it is supported by a quasicrystalline substrate. This question has already been tested experimentally. Franke *et al.*[10] studied quasicrystalline epitaxial single-element monolayers adsorbed on the surfaces of icosahedral *i*-AlPdMn and decagonal *d*-AlNiCo quasicrystals. Single-element quasicrystalline monolayers are prepared by deposition of Sb and Bi on the fivefold surface of icosahedral $Al_{7.15}Pd_{21}Mn_{8.5}$ and the tenfold surface of decagonal $Al_{71.8}Ni_{14.8}Co_{13.4}$. The quasicrystalline ordering in the epitaxial films has been verified by elastic helium atom scattering and LEED. Bragg peaks are formed at the bulk-derived positions of the clean surfaces. The work of Franke *et al.*[10] motivated us to study these systems with *ab initio* methods. In this work we restrict our study to monolayers on the fivefold surface of an *i*-AlPdMn quasicrystal.

A. Clean fivefold surface of *i*-AlPdMn

The structure and stability of a clean fivefold surface of *i*-AlPdMn were investigated in detail in our previous paper.[13] We prepared a set of rational approximants to the quasicrystalline structure. For bulk *i*-AlPdMn our approximants are based on cut-and projection models with triacontahedral acceptance domains according to the Katz-Gratias-Boudard (KGB) model.[26–29] A fivefold surface is prepared by cleaving the bulk structure along a plane perpendicular to a fivefold axis such that a layer with a high atomic density is exposed at the surface. The choice of the cleavage plane is discussed in our previous paper.[13]

The *i*-AlPdMn quasicrystal is a *F*-type quasicrystal. Its structure can be interpreted in terms of pseudo-Mackay and Bergman-type clusters.[27,30–33] Pseudo-Mackay and Bergman-type clusters are not independent structural units, as they are mutually interpenetrating. It is relevant to note that the "Mackay" and "Bergman" clusters in *i*-AlPdMn are a little different from those encountered in various complex intermetallic crystalline structures. Instead of using the term pseudo-Mackay or pseudo-Bergman we shall, in agreement with Gratias *et al.*,[34] call the clusters the *M* and *B* clusters. Each bc site of the hyperspace structure of *i*-AlPdMn is a center of a *B* cluster. The *B* cluster has a Pd atom in the center. The *M* clusters are centered 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. Thus, the *B* clusters can be more conveniently used as guidelines for identifying the mean structural features and discussing physical properties of the *i*-AlPdMn quasicrystal. In particular, the heights of the terraces observed in STM images of *i*-AlPdMn surfaces match the distances between layers characterized by a high density of *B* clusters and their distribution pattern. A complete *B* cluster consists of 33 atoms. The cleavage plane representing the bulk termination dissects the *B* clusters. In the truncated cluster 6 atoms are missing. The truncated *B* cluster exposes at the surface a characteristic pentagon of Pd atoms with an edge length of 4.80 Å, together with a smaller Al pentagon whose edge measures 2.96 Å. As the central Pd atom is below the surface plane, at the surface a shallow hole is seen in the center of the *B* cluster.

Figure 3(a) shows the atomic structure of the surface of the 2/1 model derived from the KGB model of bulk *i*-AlPdMn. The surface is covered by a periodic approximant of a quasiperiodic *P*1 tiling.[3] The edge of the *P*1 tiling measures 7.76 Å. The tiling in the figure consists of four different tiles—of a regular pentagon, a boat, and of thin and thick golden rhombuses. A general quasiperiodic *P*1 tiling consists of four species of tiles. In addition to a regular pentagon, a boat, and a thin rhombus a pentagonal star can occur. The thick golden rhombus that we observe in the 2/1 approximant does not appear in the quasiperiodic *P*1 tiling. The appearance of this motif in the 2/1 approximant is a consequence of the phason strain leading to the formation of a periodic pattern. The two edge-sharing thin rhombi also represent a violation of the matching rules belonging to this phason defect. The *P*1 tiling is a planar tiling which can be

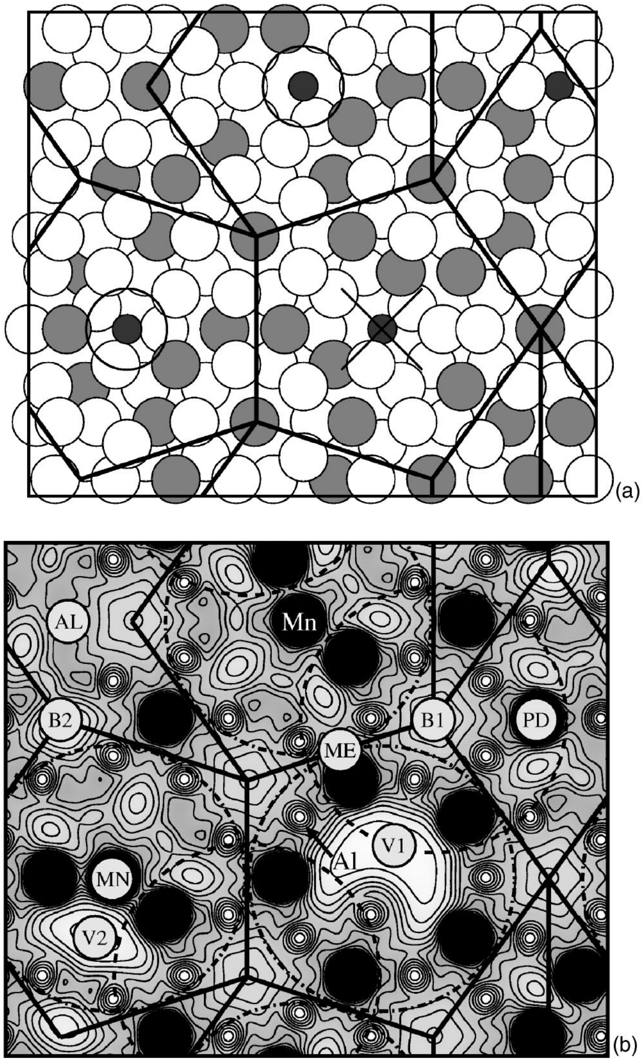

FIG. 3. The atomic structure of the clean fivefold surface of *i*-AlPdMn as represented by the 2/1 approximant (a). The surface is covered by part of a *P*1 tiling. The tiling consists of a regular pentagon, a boat, and a thin and a thick golden rhombus. The pentagons may be classified as top and bottom, as marked by circles and crosses, respectively. The quasiperiodic *P*1 tiling contains in addition a star which does not appear in the the 2/1 approximant. The positions of atoms are displayed by circles: Al—open circles, Pd—shaded circles, Mn—small solid circles. The part (b) shows the electronic charge density distribution in the surface plane of the same model. The contour plot presents the valence charge density distribution in a plane intersecting the top atomic layer, cf. text. The *B* clusters are marked by dashed circles, the *M* clusters by dot-dashed circles. The transition metal atoms in the plane create a high charge density—black circles. The Mn atoms are marked explicitly, the remaining black circles are the Pd atoms. The positions of the Al atoms can be recognized as small circular islands of local density minima; one Al atom near the center of figure is marked explicitely. For the discussion of the energy landscape several special sites on the surface are marked: *B*1, *B*2—positions in the centers of complete or incomplete *B* clusters respectively, ME—position at the midedge of the *P*1 tiling, AL, PD, MN—positions on top of Al, Pd, and Mn atoms, respectively, *V*1, *V*2—positions inside the surface vacancies.

obtained by projection from a hyperspace. The acceptance (occupation) domain of the $P1$ tiling is a decagon. The decagonal acceptance domains of the tiling correspond to the maximal cross sections of the triacontahedra defining the three-dimensional structure of the bulk quasicrystal.

Figure 3(a) demonstrates that most vertices of the $P1$ tiling coincide with the positions of the Pd atoms in the centers of the truncated B clusters. On the other hand, the pentagonal tiles are located at the positions of the M clusters centered by the Mn atoms. Figure 3(b) represents the charge density distribution in the plane of the top atomic layer. The top layer is occupied only by Al atoms and a few $(\approx 2\%)$ Mn atoms.[35–37] 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 Mn atom in the center of the pentagonal star is also located in this subsurface layer. 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/Å^2. This value is in very good agreement with the experimental value of 0.136 atoms/Å^2 reported by Gierer *et al.*.[35]

Figure 3(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 AlPdMn surface.[3,38–40] 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. However, 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. In a regular Mackay cluster the first atomic shell consists of 12 atoms forming a small icosahedron. In the M cluster in *i*-AlPdMn the central Mn atom has a lower coordination of 7–8 atoms,[29] as confirmed by extended x-ray absorption fine structure (EXAFS) experiments.[41] These atoms are distributed on the sites of a small dodecahedron, leaving other sites vacant such that their spatial arrangement breaks the local icosahedral symmetry. The vacancies exist also in the idealized structure. The existence of "vacancies" (or rather less dense regions) in the structure of bulk *i*-AlPdMn has been confirmed experimentally by Sato *et al.*[42] The surface vacancies and their behavior under thermodynamic treatment have been studied experimentally by Ebert *et al.*[43]

The positions of the pentagonal tiles correspond to the positions of the M clusters. The centers of the M clusters are projected onto the centers of the pentagonal tiles. 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 M clusters. According to this vertical position of the centers of M clusters 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 inside the slab (see Ref. 13 for more details). We note that any two neighboring pentagons that share one edge have always opposite orientations. In Fig. 3 the central Mn atoms in the bottom pentagons are near the bottom of the slab chosen to represent the surface and therefore they do not contribute to the surface charge density. This contributes to the formation of the pronounced charge density minima associated with the surface vacancies. On the other hand, in the top pentagons the central Mn atoms in the top atomic layer (together with Al atoms) are well seen in the surface charge density distribution. Figure 3(b) also shows that not only the internal arrangement of the pentagons is irregular, but also the thin rhombuses have irregular decorations. It is possible to conclude that the quasiperiodic order at the surface is represented by the $P1$ tiling, but on the other hand internal decoration of the tiles is rather irregular. The irregularities are also well seen in the high-resolution STM images of the pentagonal AlPdMn surfaces.[1,3] We emphasize that these irregularities exist in the model with idealized positions of atoms and therefore are not a consequence of the relaxation of the atomic positions or of a possible surface reconstruction.

In our previous work[13] we also attempted to answer the question whether the idealized structural model for the surface is sufficiently stable to serve as a useful model for a real surface. Structural optimizations have been performed for the $2/1$ approximant. The results of a careful structural optimization show that the positions of the transition-metal atoms are very stable. The skeleton of the $P1$ tiling fixed by the positions of the Pd atoms remains almost unchanged. On the other hand, the arrangement of the Al atoms decorating the tiles undergoes certain modifications at the surface. In particular, the Al atoms around the centers of the pseudo-Mackay clusters are subject to quite substantial displacements from their idealized positions. The effect of these relaxations is to flatten the charge-density minima associated with the surface vacancies.

B. Stable positions for adsorbed atoms

A clean five-fold surface of *i*-AlPdMn has a quite complex structure. The surface is considerably corrugated. At first sight it is not clear what could be the structure of an adsorbed quasiperiodic monolayer. 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 atom bound to specific sites on the surface. We calculated the binding energy of adsorbed Sn and Bi atoms. A systematic repetition of this procedure for selected points on the surface makes it possible to identify the most stable positions for the adsorbed atoms. The results of this study for several special positions of adatoms defined in Fig. 3(b) are listed in Table II. Below we discuss the binding energies for a Bi atom only. The discussion of the energetic landscape seen by a Sn atom leads to the same conclusions.

It is not surprising that the largest binding energies were found for the sites inside the surface vacancies. The vacancy

TABLE II. The binding energies E_b and vertical positions h of Sn and Bi adatoms at specific sites on the i-AlPdMn fivefold surface.

Description of site	Notation	E_b(Sn) (eV)	E_b(Bi) (eV)	h(Sn) (Å)	h(Bi) (Å)
Vertex of $P1$ (center of B cluster)	$B1$	−4.173	−4.369	1.61	1.68
Vertex of $P1$ (center of incomplete B cluster)	$B2$	−4.070	−4.323	1.82	1.83
Midedge position of $P1$	ME	−3.399	−3.925	2.18	2.20
Vacancy $V1$ (bigger)	$V1$	−4.657	−4.604	0.34	0.44
Vacancy $V2$ (smaller)	$V2$	−4.816	−4.954	0.99	1.22
Top of Al	AL	−2.632	−2.860	2.26	2.53
Top of Pd	PD	−3.353	−3.430	2.59	2.34
Top of Mn	MN	−4.073	−4.575	2.22	2.24

denoted as $V1$ in Fig. 3(b) is so big that it can almost completely adsorb a Bi adatom. The surface plane is defined by the positions of the centers of atoms of the most top atomic plane. The height above the surface plane of a Bi atom adsorbed on the $V1$ site is 0.44 Å, i.e., only 14% of its diameter. On the other hand, the vacancy denoted as $V2$, although in Fig. 3(b) it appears to be smaller than the vacancy $V1$, binds the adatom more strongly. As it was already noted, the surface vacancies result from the irregularities of the environment of the low-coordinated central Mn atom. The vacancies can appear in both types of the pentagonal sites—top ($V2$) and bottom ($V1$). Their shape and occurrence is irregular. For this reason we assume that although they bind isolated adatoms very strongly, the vacancies will not systematically contribute to the formation of a regular quasiperiodic monolayer. If occupied by additional atom or not, they will contribute to the corrugation of the surface on which a regular monolayer is placed. The sites on the top of Mn atoms exhibit the second largest binding energies. The centers of top pentagons are thus stable sites with binding energies of −4.58 eV. However, the number of such sites at the surface is very small, only ≈2% and therefore their role in the formation of a quasiperiodic monolayer is limited. The most abundant element on the surface is aluminum. The Al sites are regularly distributed on the surface, the nearest distances between the Al sites of 2.29 Å are well compatible with the size of Sn atoms and with a certain relaxation these sites could accommodate also Bi atoms. Moreover, the experimentally observed coverage density of the monolayer of 0.09 ± 0.02 atoms/Å^2 roughly coincides with the surface density of Al atoms (0.10 atoms/Å^2). It is therefore tempting to relate the atomic positions in a possible quasiperiodic monolayer with the positions of the Al atoms. However, a calculation shows that the binding energy of Bi(Sn) adatoms on the Al sites of −2.86(−2.63) eV is the lowest of all considered sites. A quasiperiodic monolayer consisting of adatoms placed on top of Al atoms would thus receive only a modest stabilization from the binding to the substrate. This expectation was also confirmed by our calculations. We attempted to stabilize such structure with additional atoms placed inside the decagonal rings of Al atoms surrounding the central Mn atom in the top pentagons. This model of a quasiperiodic monolayer was amorphised during relaxation.

Neither will Pd atoms that are 0.48 Å below the surface plane stabilize a quasiperiodic monolayer. A Bi adatom on top of a Pd atom has an intermediate binding energy of −3.43 eV, see Table II. However, we found that significantly more stable are the positions at the vertices of the $P1$ tiling. These vertices are the centers of the B clusters. The binding energies of Bi adatoms inside the complete or incomplete B clusters are −4.37 and −4.32 eV, respectively. These sites are quasiperiodically distributed on the surface and therefore their occupation by an adatom would already form a stable quasiperiodic monolayer of low coverage. Other stable positions that are systematically distributed at the surface are the midedge positions of the $P1$ tiling. These sites are very close to a triangle of two Al and one Pd atom. An adatom is thus supported by this triangular configuration of atoms. The binding energy of Bi at this site is −3.92 eV, i.e., it is 0.5 eV more stable site than at the position on top of a Pd atom alone and about 1 eV more stable than at the Al site. From these results we concluded that the sites at the vertices and the midedge positions of the $P1$ tiling are the framework of a possible stable quasiperiodic monolayer on top of five-fold i-AlPdMn surface.

C. Adsorbed monolayer

On the basis of the results from previous sections we propose a model for the structure of a monolayer with a quasiperiodic ordering. First we occupy the most stable regular positions, i.e., the vertices and the midedge positions of the $P1$ tiling. Figure 4 shows the surface charge density of a 3/2 approximant with the energetically favorable positions for adsorbed atoms marked by circles. Franke *et al.*[10] reported a coverage for a Bi monolayer on i-AlPdMn of 0.09 ± 0.02 atoms/Å^2. Occupation of the stable sites only would lead to a coverage of 0.045 atoms/Å^2, i.e., only the half value of the experimentally observed coverage. On the other hand, Fig. 4 also shows that there is plenty of space inside the $P1$ tiles for additional adsorbed atoms. The decoration of the interior of the tiles follows quite naturally from the decoration of the vertices and the midedge positions, i.e., by the decoration of the circumference of the tiles. The decoration depends on the size of an adsorbed atom. First we shall discuss a decoration with atoms measuring 3.0 Å in diameter. Table I shows that this choice would correspond, e.g., to Sn atoms (the average between optimal lattice constants for the triangular and square tilings is 3.06 Å) or Sb (3.04 Å). Bi atoms (3.21 Å) are somewhat larger, but as will

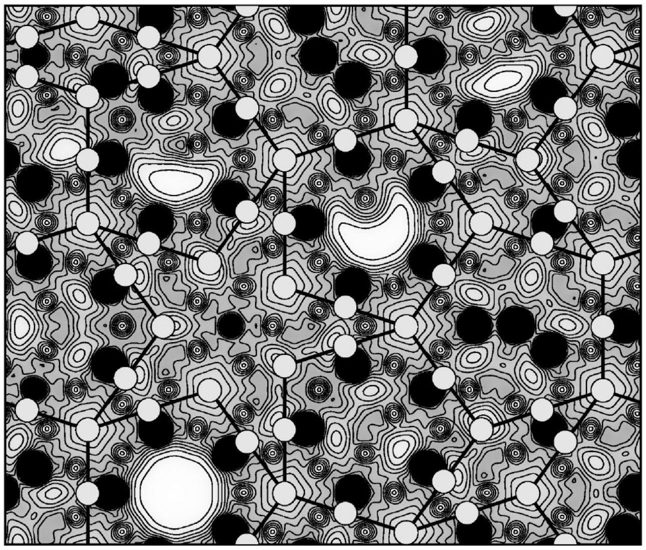

FIG. 4. The surface charge density of a 3/2 approximant with indicated stable positions for adsorbed atoms. The analysis of binding energies for specific sites shows that atoms adsorbed at the vertex positions or the midedge positions of the *P*1 tiling exhibit enhanced stability. These sites are quasiperiodically distributed.

be shown later the decoration with Bi atoms will not differ too much from the decoration with Sn or Sb atoms.

Inside the thin rhombus there is no space for an additional atom. The thick rhombus (this tile occurs in the 2/1 approximant only) has space for just one additional atom put into the center of the rhombus. The center of the pentagonal star is occupied by a Mn atom. This is a stable position for an adatom. If one puts one adatom on top of the central Mn atom, there is no additional space for other atoms. Similarly, if the center of the boat tile is occupied by one atom there is no space for additional atoms. Inside the pentagonal tiles there is space for several atoms. The centers of the top pentagons are occupied by Mn atoms. As the Mn atoms are also very stable binding sites for adsorbate atoms it is natural to put additional adatoms there. The space between the central adatom and the adatoms at the circumference of the pentagon is just large enough for five atoms forming a pentagon smaller by a factor 0.5 than the pentagonal tile. Although the bottom pentagons do not systematically have stable sites in their centers, inside these pentagonal tiles there is also space for just six atoms. These can be be most naturally arranged in the same way as in the top pentagons, i.e., as a central atom plus a small pentagon. With a proper size of atoms this regular decoration is enforced by the decoration of the circumference of the tile. This enforcement of the regular pentagonal ordering by high surface density of packing of the adatoms is similar to the enforcement of hexagonal ordering of spheres by their dense packing on a plane.

Figure 5 shows the atomic structure of a monolayer adsorbed on the surface of a 5/3 approximant resulting from the previous analysis. The surface density is very satisfactory. Its value is 0.09 atoms/Å^2, i.e., just in the center of interval of experimentally determined coverage density of Bi atoms. Adsorbed atoms are distributed on the surface quite evenly with some exceptions. In the tiles with sharp angles of 36 deg (thin rhombus, boat, and star) there is a rather short distance of 2.41 Å between two neighboring midedge positions. One can expect that these short distances will increase upon relaxation. For bigger atoms there is also a possibility to replace this pair of atoms by a single atom located on the long diagonal. If atoms are a bit smaller than the considered size of 3.0 Å, there will be a space for an additional three atoms inside the boat tile and five atoms inside the pentagonal star. On the other hand, for smaller atoms one cannot expect that the decoration of the vertices and midedge positions will also enforce a regular pentagonal decoration inside the pentagonal tiles.

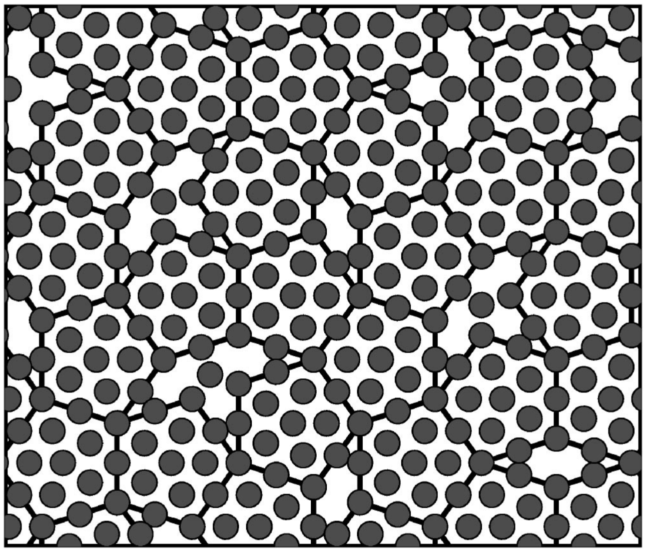

FIG. 5. The atomic structure of a monolayer adsorbed on a surface of the 5/3 approximant. The surface density is 0.09 atoms/Å^2, i.e., just in the center of interval of experimentally determined coverage density of Bi atoms (See Ref. 10). The regular arrangement of atoms inside the tiles is enforced by the atoms at stable positions at the vertices and midedge positions of the *P*1 tiling.

If one compares the decoration of the pentagonal tiles by the atoms in the surface layer and by the atoms adsorbed at the surface it is clear that the ideal structure of the adsorbed monolayer has a higher symmetry than the underlying fivefold surface of *i*-AlPdMn. Figure 6 shows the diffraction pattern of the monolayer calculated for the 5/3 approximant. It exhibits a pseudodecagonal symmetry. This fact is interesting as a nearly decagonal symmetry was observed also in the LEED images of the adsorbed Bi and Sb monolayers on the five-fold *i*-AlPdMn surface.[10] It is relevant to note that the LEED image of the clean surface exhibits only fivefold symmetry. The origin of the decagonal symmetry is in the decagonal symmetry of the acceptance domain in hyperspace (the acceptance domain has a shape of a single decagon) of the *P*1 tiling that propagates the long-range quasiperiodic ordering in the monolayer.

The remaining important point is to verify the stability of the position of atoms in the monolayer. We have performed this study for a monolayer adsorbed on the surface of the 2/1 approximant. We have considered three chemical compositions: Sn, Bi, and Sb.

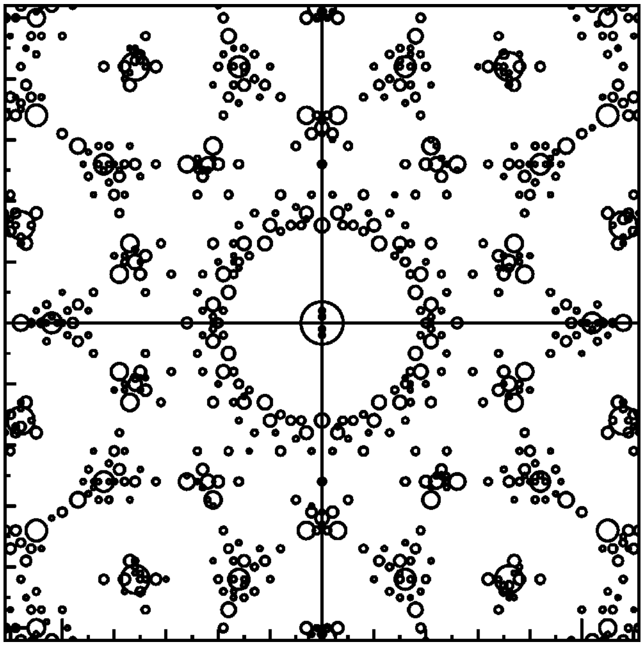

FIG. 6. A diffraction pattern of the adsorbed quasiperiodic monolayer on the 5/3 approximant. It exhibits a (pseudo)decagonal symmetry.

1. Sn monolayer

In this section we test the stability of the quasiperiodic ordering in the monolayer against relaxation by the interatomic forces. Figure 7 shows the charge density distribution in the adsorbed Sn monolayer on the surface of 2/1 approximant before (a) and after relaxation (b). In the relaxed model the quasiperiodic ordering is essentially conserved although significant displacements of atoms from their ideal positions are obvious. In agreement with the expected stability of the vertex sites of the *P*1 tiling the Sn atoms at these sites exhibit only minimal shifts from the ideal positions. Slightly larger displacements are observed for the midedge positions. The short nearest-neighbor distances of 2.41 Å at the sharp angles of the tiles are relaxed successfully, but as a consequence one or both atoms from midedge positions move a little into the wide-angle tiles, the pentagons, and the fat rhombus. The arrangement of Sn atoms inside the pentagonal tiles undergoes substantial modification. In the pentagon at the left side of Fig. 7(b) one of the Sn atoms almost disappears in the surface vacancy located below this atom [cf. Fig. 3(b)]. The remaining Sn atoms keep the pentagonal configuration with one additional atom in the center. In the remaining pentagonal tiles at the right side and in the upper part of Fig. 7(b) the pentagonal configuration of atoms inside the tile can still be well recognized. In the fat rhombus the central Sn atom has been attracted from its central position by the underlying Pd atom located a little off the center.

In the ideal configuration the interatomic distances are larger than optimal bonding distance between atoms (see Table I). In the relaxed monolayer one therefore observes grouping of atoms, particularly inside the *P*1 tiles. It is remarkable, that the atoms in the vertices of the tiling are rather isolated; they are only weakly bonded to the surrounding atoms in the monolayer.

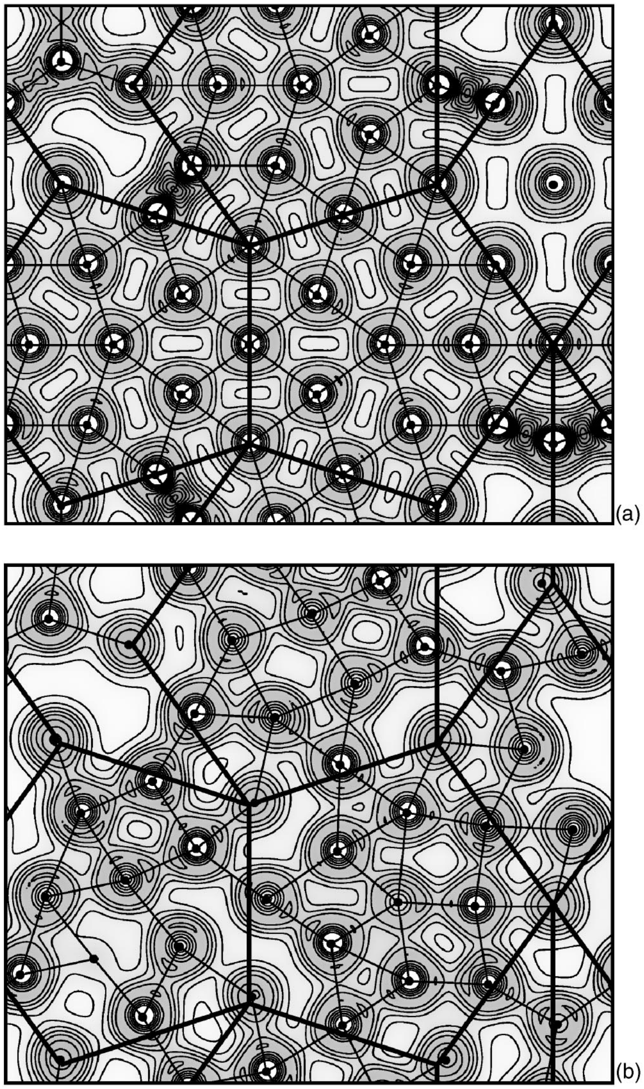

FIG. 7. The charge density distribution in an adsorbed Sn monolayer on the surface of 2/1 approximant before (a) and after relaxation (b). In the relaxed model the quasiperiodic ordering is essentially conserved although significant displacements of atoms from their ideal positions are obvious. In agreement with the expected stability of the vertex sites of the *P*1 tiling (represented by thick lines) the Sn atoms at these sites exhibit only minimal shifts from the ideal positions. In the pentagon at left side of the one of Sn atoms partially disappeared in the surface vacancy located below this atom. The quasiperiodic structure of the monolayer is decomposed to a polygonal network (thin lines), cf. text.

It is interesting to compare the average coordination number of Sn atoms in the adsorbed quasiperiodic monolayer with the coordination numbers of the Sn atoms in unsupported periodic monolayers studied in Sec. III. The atoms in the triangular lattice have six neighbors, the coordination number of the square lattice is 4. For a quasiperiodic monolayer one would expect a value between these two numbers. In Fig. 7 the quasiperiodic structure of the monolayer is decomposed to a polygonal network. The prevailing polygons in the network are triangles and tetragons. The neighboring atoms in the monolayer are defined by a geometrical distance smaller than certain cutoff radius r_c. From the analysis of the

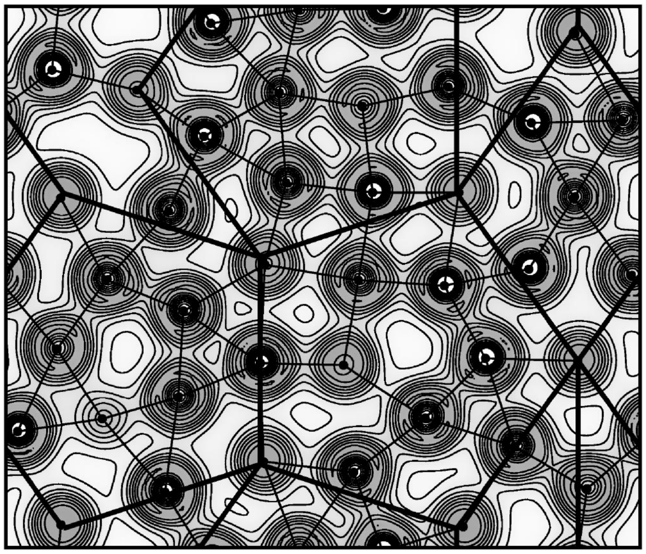

FIG. 8. The charge density distribution in an adsorbed Bi monolayer on the surface of 2/1 approximant after relaxation, cf. Fig. 7.

pair distribution function we have found that the cutoff radius separating the first and second nearest neighbors is equal to $r_c = 3.6$ Å. The average coordination number $Z(\mathrm{Sn})$ of Sn atoms in the ideal, nonrelaxed monolayer is 3.1. After relaxation $Z(\mathrm{Sn}) = 3.2$. This increased number reflects a clustering of atoms in the relaxed structure and formation of some additional bonds, e.g., between the central atom inside the fat rhombus and the neighboring atoms. The calculated average coordination numbers of atoms in the adsorbed monolayers are significantly lower than those in the unsupported monolayers. These low numbers result from the fact that the adsorbed atoms have already some bonds with the substrate atoms. This is particularly well illustrated by the atoms in the vertices of the *P*1 tiling. The average coordination number of these atoms is only 1.7. The atoms in the vertices of the *P*1 tiling are strongly bonded to the substrate and exhibit only little tendency to the formation of bonds with neighboring atoms in the monolayer.

2. Bi monolayer

From the study of unsupported monolayers we learn that Bi atoms prefer an average nearest-neighbor distance of 3.21 Å, see Table I. This size leads to a very dense packing of Bi atoms inside the pentagonal tiles and to significant lateral stress. During the relaxation some of the atoms jumped up to positions above the monolayer. Therefore we modified the ideal decoration by skipping the central atom inside the pentagonal tiles. This would lead to a somewhat lower coverage of 0.085 atoms/Å^2, still within the experimentally determined range of (0.090 ± 0.02) atoms/Å^2. The distribution of Bi atoms in the adsorbed monolayer is again displayed in the form of the charge density distribution in the monolayer, see Fig. 8. The resulting picture of atomic displacements is similar as for the previous case of a Sn monolayer. A greater difference is seen only in the pentagonal tile in the upper half of the figure. The pentagonal decoration inside the tile collapsed. The pentagonal configuration of Bi atoms without the stabilizing central atom was destroyed. Such a collapse is not surprising as the pentagonal configuration of Bi has no intrinsic stability originating from the interatomic bonding. The local irregularity of the surface supporting the pentagonal configuration is also not favorable to the conservation of the initial regular pentagonal arrangement of atoms. On the other hand, it is remarkable that the regular configuration of the atoms was conserved in the right pentagonal tile in Fig. 8 despite the surface vacancy below the Bi atoms. We have found that the lateral forces that can cause the collapse of the pentagonal configuration are quite small.

The size of the atom is an important quantity having a significant influence on the stability of the monolayer. A larger size can lead to a higher packing density which could enforce regular arrangement of atoms. However, Bi atoms are already too large for admitting a sixth stabilizing atom in the center of the pentagonal configuration inside the pentagonal tiles. On the other hand, the tiles with sharp angles have rather lose packing. It is possible to speculate that these tiles could eventually absorb the strain from the pentagonal tiles if the central sites in the pentagons are forcibly occupied. We assume that a more probable configuration would be if the the central atoms remain at a higher position in the monolayer. If one considers that the Bi atoms in the vertices are already little (≈ 0.2 Å) below the atoms inside the tile, a central atom at the higher position above the surrounding atoms would form a tip of a pentagonal pyramid consisting of 16 atoms. Such a pyramidal arrangement would manifest itself in a higher corrugation of the monolayer. Such an enhanced corrugation of Bi monolayers on the *i*-AlPdMn surface is in fact observed experimentally,[10] although not quantified in more detail. A further possibility would be to admit a disordered distribution of vacant and occupied pentagon centers, depending on the decoration of the underlying tile. The calculated average coordination number of Bi atoms in the quasiperiodic monolayer is $Z(\mathrm{Bi}) = 3.2$, i.e., comparable with that calculated for the Sn monolayer. The nearest neighbors in the monolayer are here defined by the cutoff radius $r_c = 3.7$ Å.

3. Sb monolayer

Antimony is from the same group Vb as bismuth. Sb atoms are smaller than Bi. Table I shows that Sb atoms are approximately of the same size (3.04 Å, calculated as an average between the optimal lattice constant of triangular and square monolayers) as Sn atoms (3.06 Å). Can one expect for the monolayer consisting of Sb atoms the same relaxation pattern as one observed in the case of Sn atoms? Figure 9 shows that the answer is negative. The reason is in the fact that Sb prefers by more than 0.13/atom eV a square lattice to a triangular one, whereas in Sn the triangular geometry is slightly (−0.019/atom eV) preferred. The rectangular grouping of atoms is well seen in the resulting distribution of Sb atoms in the adsorbed monolayer. The pentagonal configurations of Sb atoms inside the pentagonal tiles of the *P*1 tiling collapsed in all three tiles in Fig. 9. For the rectangular configuration the optimal lattice constant is 2.95 Å, see Table I, the Sb atoms are thus effectively

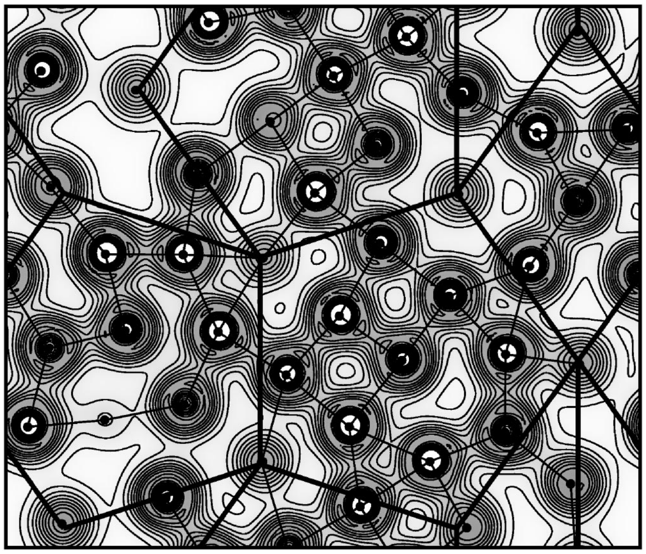

FIG. 9. The charge density distribution in an adsorbed Sb monolayer on the surface of 2/1 approximant after relaxation, cf. Fig. 7.

smaller in the preferred rectangular configuration. The packing density inside the pentagonal tiles is thus not sufficient to enforce the regular pentagonal arrangement of atoms. Nevertheless, it is necessary to note again that the lateral forces are very weak and the atoms, except those at the stable positions in vertices of the $P1$ tiling, can almost freely move on the surface.

The tendency to the rectangular bonding geometry of the Sb atoms in the monolayer is reflected also in their average coordination number $Z(\mathrm{Sb})$. Its value of 2.8 (for $r_c = 3.5$ Å) is substantially lower than that in the Sn and Bi monolayers, reflecting the increased fraction of lower coordinated sites in the polygonal network.

V. SUMMARY AND DISCUSSION

We have presented a structural model for quasiperiodic monolayers formed on the fivefold surface of an icosahedral AlPdMn quasicrystal, based on *ab initio* density functional calculations. As a starting point we have investigated the relative stability of triangular, square, and of quasiperiodic layers based on the triangle-rectangle tiling underlying the construction of a dense sphere packing with decagonal symmetry.[24,25] However, the planar triangle-rectangle tiling was found to be unstable, even for those elements (Sn, Bi) where the small structural energy difference between the square and triangular lattices suggests that a mixed quasiperiodic tiling could be stable. This finding emphasizes the important role of the adsorbate/substrate interaction for the stabilization of a quasiperiodic layer.

For this reason, our 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. Our recent work[13] on this surface has demonstrated that the surface structure is well described by a $P1$ tiling, with the vertices of the tiling located in the centers of B (Bergman) clusters. The positions of these vertices are found to be very stable upon relaxation, whereas the decoration of the interior of the tiles (which shows substantial irregularity already in a bulk-terminated configuration) undergoes considerable surface-induced relaxations. The potential-energy mapping emphasizes the important role of the $P1$ skeleton for the stabilization of a quasiperiodic adlayer: adsorption at the vertices (which are the centers of the B clusters occupied by Pd atoms) leads to binding energies of $\simeq 4$ eV/atom. Only in the surface vacancies found near the centers of some of the M (pseudo-Mackay) clusters, adatoms are more strongly bound. However, due to the large distances and irregular distribution of the surface vacancies, they cannot be expected to form the skeleton of a stable tiling. The midedge positions of the $P1$ tiling and Mn atoms exposed at the surface are identified as further favorable adsorption sites. Altogether this leads to a structural model of the quasiperiodic adlayer with atoms at the vertices and midedge positions of the $P1$ tiling, centered pentagonal motifs decorating the pentagonal tiles, and one additional atom in the center of the pentagonal star and of the boat tile. For this structure we calculate a surface coverage of $\simeq 0.09$ atoms/Å^2 in perfect agreement with experiment. The diffraction pattern of the adlayer exhibits (pseudo)decagonal symmetry, again in agreement with the experimental observation.

A 2/1 approximant to this structural model has been tested for Sn, Bi, and Sb monolayers via relaxation based on the Hellmann-Feynman forces from *ab initio* DFT calculations. For an adsorbed Sn monolayer the quasiperiodic skeleton based on the $P1$ tiling was found to be stable, although the atomic decoration inside the tiles is distorted, albeit without violating the overall symmetry. For a Bi monolayer the atomic density within the pentagonal tiles was found to be too large—the central positions have to be left vacant. Upon relaxation, the $P1$ skeleton remains fixed, but more important relaxations are observed within some of the pentagonal tiles. Eventually, a partial occupation of the pentagonal centers could improve the structural model. For an adsorbed Sb monolayer on the other hand, the density of the decorated $P1$ tiling was found to be too small, the pentagonal motifs collapsed to a nearly square local structure (which had been identified as the preferred structure for a freestanding monolayer). The preliminary study in Sec. III had shown that the unsupported quasiperiodic single-element monolayers are unstable. Single-element monolayers prefer either triangular or square arrangement of atoms in a plane.

The observed deviations of the relaxed atomic positions from the ideal ones are not surprising: (i) the distortion of the regular pentagonal motifs inside the pentagonal tiles reflect the irregularity of the substrate, which has the origin in the irregular first atomic shell of the M (pseudo-Mackay) cluster, (ii) significant deviations of atomic positions from their ideal ones are commonly observed also in bulk icosahedral quasicrystals where no such irregular atomic configurations exist.[44]

Our calculations were performed at zero temperature. From the analysis of the rather flat energetic landscape it is clear that higher temperature could be favorable for increasing the quality of the quasiperiodic ordering. At higher temperatures the atoms located on the irregular part of surface of *i*-AlPdMn inside the *P*1 tiles can assume more symmetric average positions. There should exist a certain interval of temperatures, where the strongly bound atoms at the most stable positions forming the framework of the *P*1 tiling still remain at their equilibrium positions, but the atoms less strongly bound to the *i*-AlPdMn surface inside the tiles have already sufficient energy to relax their bonding to the irregular substrate. Higher temperature can also in certain extent smear out the preference for triangular or rectangular orientational bonding within the adsorbed monolayer. This scenario is in fact observed in experiment.[10] The Bi and Sb monolayers adsorbed on the *i*-AlPdMn surface were deposited at enhanced temperatures and exhibited stability up to 750 and 400–600 °C, respectively. Quasiperiodic ordering exhibited high quality at elevated temperatures and degraded at room temperatures.[45]

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