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Ab initio study of quasiperiodic Bi monolayers on a tenfold *d*-Al-Co-Ni surface

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We present an *ab initio* study of the formation of quasiperiodic Bi monolayers on the tenfold surface of a decagonal Al-Co-Ni quasicrystal. The structural model of the surface has been derived from the recently resolved structure of the *W*-(AlCoNi) approximant phase. As the bulk *W* phase can be cleaved at the flat *A* plane or the puckered *B* plane we investigate the formation and stability of the monolayers on both surfaces. The structural model of a Bi monolayer adsorbed on the tenfold surface has been constructed on the basis of a mapping of the potential-energy landscape of an isolated Bi adatom on the substrate. We found stable quasiperiodic monolayers on both surfaces. The structure of the monolayer on the *B* surface is less dense and more regular than that on the *A* surface. The surface coverages are within the experimentally determined range $\simeq 0.08 \pm 0.02$ atoms/Å^2.

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I. INTRODUCTION

Despite the complex aperiodic atomic structure of quasicrystals, their surfaces can be atomically flat. Under suitable conditions smooth surfaces with extended flat terraces can be prepared. During the past ten years significant progress has been made in the preparation and characterization of surfaces of icosahedral and decagonal quasicrystals. Surfaces of stable quasicrystals, particularly of icosahedral Al-Pd-Mn and decagonal Al-Co-Ni quasicrystals, have been studied most intensively. After the successful characterization of clean surfaces the question arises whether quasicrystalline adsorbate phases can be grown on a quasicrystalline substrate. If monoatomic thin films adsorbed on the surface of a quasicrystal adopt ordered structures reflecting the quasiperiodic structure of the substrate, an interesting example of a two-dimensional (2D) monoatomic quasiperiodic system is achieved. The adsorbate overlayers are potentially important also from a technological perspective. Surfaces of quasicrystals exhibit high hardness and good tribological properties such as low surface friction; they also show high oxidation resistance, and thin coatings propagating the quasiperiodic order may offer a way to a further improvement of surface properties.

Quasicrystalline surfaces and thin films represent a potential for creating new, unusual structural forms of matter having extraordinary physical properties. While the surfaces of ordinary crystal provide only a few inequivalent sites for the adsorption of atoms or molecules, the complex landscape of a quasicrystalline surface provides a rich variety of adsorption sites. The possibility to stabilize nanostructures on the a quasicrystalline substrate is very intriguing. Eventually, the surfaces of quasicrystals can be used as templates for "quasicrystal nanotechnology."

The adsorption of different elements on the surfaces of quasicrystals has been investigated using a variety of experimental techniques. The question whether quasicrystalline surfaces could be used as templates for quasiperiodic monolayers has been investigated. It turned out that to grow a quasicrystalline thin film with long-range order is rather difficult. Most attempts to fabricate quasicrystalline single-element films resulted in amorphous or polycrystalline films with domains of common crystalline structures. Bolliger *et al.*[1] observed fcc textures on Al films deposited on an *i*-Al-Pd-Mn surface. Cai *et al.*[2] reported Al growth on a fivefold surface of *i*-Al-Cu-Fe and came to the conclusion that Al forms in submonolayer regime pseudomorphic islands but as coverage increases three-dimensional islands are formed. Similar results were reported by Fournée *et al.*[3] on the nucleation and growth of Ag films deposited on an *i*-Al-Pd-Mn surface. They found hexagonal islands with five different orientations, rotated by $2\pi/5$ such as to reflect the fivefold symmetry of the substrate. Other attempts led to the development of surface alloys having icosahedral or decagonal symmetry.[4,5] Shimoda *et al.*[4] observed the formation of an epitaxial Au-Al alloy film on a quasiperiodic surface of icosahedral Al-Pd-Mn. The film was not produced 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.*[5] produced a stable decagonal *d*-Al-Pd-Mn film on an *i*-Al-Pd-Mn substrate. A decagonal Al-Pd-Mn film was epitaxially grown as a single-domain overlayer on the fivefold surface of *i*-Al-Pd-Mn, with the tenfold axis of the overlayer parallel to the fivefold axis of substrate.

Success in the formation of ordered quasiperiodic overlayers consisting of a single element has been achieved only recently. Franke *et al.*[6] prepared quasicrystalline epitaxial single-element monolayers adsorbed on the surfaces of icosahedral Al-Pd-Mn and decagonal Al-Ni-Co quasicrystals. Elastic helium atom scattering and low-energy electron diffraction (LEED) on the monolayers confirmed the long-range quasicrystalline ordering in the films. A single-element monolayer was recently prepared also by Ledieu *et al.*[7,8] They deposited an ultrathin film of Cu atoms on a fivefold *i*-Al-Pd-Mn surface.[7] The observed structure of the monolayers consists of 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. Recently Sharma *et al.*[9] observed polymorphic growth of Sn monolayers on the fivefold surface of *i*-AlCu-Fe, at elevated temperatures. High-resolution scanning tunneling microscopy (STM) images reveal that Sn grows polymorphically and exhibits a quasicrystalline structure. Very recently Fournée *et al.*[10] reported growth of Bi nanostructures on a fivefold surface of icosahedral Al-Cu-Fe. The thin Bi film was investigated by STM and reflection high-energy electron diffraction (RHEED). At elevated temperatures (250 °C) they observed the formation of a pseudomorphic layer. At submonolayer coverage, they found islands with a density varying from terrace to terrace, suggesting that nucleation of Bi islands occurs at specific quasilattice sites having a density that is also terrace specific. At room-temperature deposition, they observed the formation of crystalline Bi islands with five different orientations (fivefold twinning).

The question whether quasicrystalline adsorbate phases and ultrathin films can be stabilized by a quasicrystalline substrate thus remains open. The formation of quasiperiodic monolayers obviously depends on details of the interatomic interactions between the atoms in the adsorbate and on the adsorbate-substrate interaction as well. In our previous *ab initio* work[11] we attempted to shed light on some of these aspects by *ab initio* calculations. First we theoretically investigated the possible existence of unsupported quasiperiodic monolayers. We performed an extensive study of the relative stability of triangular and square monolayers for many elements of the periodic table. A possible quasiperiodic arrangement consists of both triangular and rectangular configurations of atoms (triangle-rectangle tiling). One can expect that elements with a large structural energy difference between triangular and square monolayers will not be suitable for a quasiperiodic arrangement. We found that the best candidates for the formation of stable quasiperiodic monolayers are Bi and Sn. However, a relaxation of the unsupported quasiperiodic monolayers by *ab initio*–calculated forces showed that they are mechanically unstable. Although we obtained this negative result only for the rectangle-triangle tiling, we assume that this result has a more general validity. The existence of a stable unsupported quasiperiodic single-element monolayer seems to be unlikely. This finding emphasizes the important role of the adsorbate-substrate interaction for the stabilization of a quasiperiodic layer. In our recent work[11] we also investigated the formation of Sn, Bi, and Sb monolayers on a fivefold surface of an icosahedral Al-Pd-Mn quasicrystal. 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. Our work[12] on the structure and stability of a clean *i*-Al-Pd-Mn surface has demonstrated that the surface structure is well described by a *P*1 tiling, with the vertices of the tiling located in the centers of Bergman clusters. The potential-energy mapping emphasizes the important role of the *P*1 skeleton for the stabilization of a quasiperiodic adlayer with strong adsorption at the vertices and midedge positions. The decoration of the interior of the tiles undergoes considerable surface-induced relaxations. The regularity of the internal decoration of the tiles is enforced by the decoration of the circumference of the tiles.

In the present work we study the formation of quasiperiodic Bi monolayers on the tenfold surface of *d*-Al-Co-Ni quasicrystals. A structural model of the surface has been derived from the recently resolved structure of the *W*-(AlCoNi) approximant phase.[13] The bulk quasicrystal can be cleaved at the flat *A* plane or at the puckered *B* plane. We investigate the formation of a monolayer on the surface for both possible bulk terminations. We restrict our study to Bi monolayers only. As already noted above Bi and Sn are good candidates for the formation of quasiperiodically ordered overlayers. This is not only the conclusion of our theoretical study[11] but also an experimental observation; both elements form well-ordered structures on most metals and semiconductors.[6]

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. The stability of the monolayers has been tested via relaxation by forces from *ab initio* density-functional (DFT) calculations.

II. METHOD

We have used the advanced *ab initio* method implemented in the Vienna *ab initio* simulation package VASP (Refs. 14 and 15) to perform the total-energy calculations and structural relaxations. The theoretical background of VASP is density-functional theory within the local-density approximation. The wave functions are expanded in plane waves. The Hamiltonian is based on pseudopotentials derived in the 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 generalized-gradient approximation (GGA).[16] VASP has also been used to calculate charge distributions.

III. MONOLAYERS ADSORBED ON THE TENFOLD *d*-Al-Co-Ni SURFACE

Franke *et al.*[6] studied quasicrystalline epitaxial single-element monolayers adsorbed on the surfaces of icosahedral *i*-Al-Pd-Mn and decagonal *d*-Al-Co-Ni quasicrystals. Single-element quasicrystalline monolayers are prepared by deposition of Sb and Bi on the fivefold surface of icosahedral $Al_{71.5}Pd_{21}Mn_{8.5}$ 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. Dominant Bragg peaks are formed at the bulk-derived positions of the clean surfaces. The work of Franke *et al.*[6] motivated us to study these systems using *ab initio* density-functional methods. In our previous work[11] we studied the formation of single-element quasiperiodic monolayers on the fivefold surface of *i*-Al-Pd-Mn. In the present work we extend our study to monolayers on the tenfold surface of a *d*-Al-Co-Ni quasicrystal.

A. Clean tenfold surface of *d*-Al-Co-Ni

The structure, the electronic structure, and the stability of a clean tenfold surface of *d*-Al-Co-Ni were investigated in detail in our previous paper.[18] In comparison with icosahedral quasicrystals the structure of decagonal quasicrystals with only two-dimensional quasiperiodicity seems to be more easily accessible to intuitive interpretations. Despite this fact, so far no satisfactory, generally accepted model of decagonal Al-Co-Ni quasicrystals exists. Recently, significant progress in the structural modeling has been promoted by the discovery of the *W* approximant in the Al-Co-Ni system. The atomic structure of this phase has been resolved by Sugiyama *et al.*[13] using x-ray diffraction. The structure of the *W*-(AlCoNi) phase is closely related to that of the decagonal Al-Co-Ni quasicrystal. It provides information on the fundamental atomic arrangement for the columnar clusters observed commonly in Al-Co-Ni decagonal quasicrystals. A 5D hyperspace model of the quasicrystalline structure derived from the *W* approximant has been proposed by Deloudi *et al.*[17] As at present the *W*-(AlCoNi) phase is the only approximant to the decagonal quasicrystal with experimentally determined atomic positions, it was natural to base our model of the bulk *d*-Al-Co-Ni quasicrystal on the *W*-(AlCoNi) phase.

As x-ray diffraction does not provide the information necessary for distinguishing the two transition-metal (TM) atoms Ni and Co, the structural model of Sugiyama *et al.*[13] for the *W* phase is in fact a model for an Al-*M* approximant. Mihalkovič and Widom[19] successfully determined the chemical occupation of the transition-metal sites and optimized the occupancies of the mixed Al-*M* sites as well. The structure of the *W* approximant was refined by optimizing the total energy under the constraint of a fixed overall content of the three species Al, Ni, and Co. The resulting composition of our approximant to *d*-Al-Co-Ni is $Al_{70.78}Co_{14.61}Ni_{14.61}$. This composition is close to the composition $Al_{71.8}Ni_{14.8}Co_{13.4}$ of the decagonal quasicrystal used for the surface studies reported in Ref. 6.

The space group of the *W* phase is *Cm* (No. 8). It has approximately an orthorhombic shape with the lattice parameters $a=39.67$ Å, $b=23.39$ Å, and $c=8.16$ Å. The *W* phase thus belongs to the decagonal approximant phase with 8 Å periodicity along the decagonal axis. The structure of the *W* phase can be described in terms of alternating flat (A) and puckered (B) atomic layers perpendicular to the *c* axis. The structure of the flat *A* layer at $z=0$ corresponds to that at $z=0.5$ (A') which is shifted by a half period along the *a* axis. The puckered layers at $z=0.25$ and $z=0.75$ are related to each other by mirror planes at $z=0$ and $z=0.5$. The structure of the *W* approximant can be thus described as a $ABA'B$ stacking of atomic planes along the *c* axis. The orthorhombic elementary cell consists of 534 atoms.

A structural model of a quasicrystalline surface of *d*-Al-Co-Ni is obtained from the *W*-(AlCoNi) approximant by cleaving it at a proper plane. The structural model of the *W* approximant naturally offers two possible termination planes. The bulk approximant can be cleaved at the flat *A* plane or at the puckered *B* plane. In the present work we shall consider both possible terminations.

The size of the model with 534 atoms is already too big for the *ab initio* calculations. For our adsorption studies we used instead the model with a full thickness of 8 Å, a smaller model consisting only two atomic layers *AB* and half the number of atoms. The adatoms are adsorbed on the *A* or *B* surface of a slab model of 4 Å thickness. In addition to the slab of atoms the computational cell includes a 6-Å-thick vacuum layer. The atoms in the slab are fixed at their bulk-relaxed positions. In our previous work[18] we investigated the relaxation and possible reconstruction of the *d*-Al-Co-Ni surface and concluded that atoms at the surface essentially remain at their bulk positions. We also did not observe any significant contraction of the interlayer spacing between the first two surface layers. The 4 Å thickness of the slab representing the surface is sufficient to support an adsorbed monolayer. The same thickness we used also in the case of our previous study of quasiperiodic monolayers on the fivefold surface of *i*-Al-Pd-Mn.[11] We have found that when the thickness of the slab representing the surface increased from 4.08 Å (M model) to 6.60 Å (MS model) the calculated binding energies of selected adatoms changed by ≈0.02 eV only. This value is substantially smaller than the characteristic differences in binding energies between inequivalent adsorption sites that range from 0.5 to 1.5 eV.

The quasiperiodic ordering of atoms at the surface can be visualized by covering the surface by a planar tiling. The choice of the tiling is not completely unambiguous; various kinds of tilings are compatible with the ordering. We have chosen a tiling that suitably represents a network of transition-metal atoms in the surface plane. For the TM-rich *A* surface the vertices of a tiling consisting of pentagons (edge length 4.68 Å), thin rhombi, and boats are located at the TM sites; for the Al-rich surface a τ-scaled pentagonal tiling (edge length 7.58 Å) represents the network of TM atoms in the surface plane (for details see Ref. 18).

Figure 1 displays the valence charge density distribution at both surfaces, terminated by *A* and *B* planes and superposed with the tilings describing the surface structure (see Ref. 18 for details). The position of the TM atoms is characterized by high valence charge densities. At the position of the Al atoms one observes weak local valence charge density minima. Because of the different content of TM atoms in both termination planes, the overall view of both surfaces is quite different. A closer inspection of the charge density shows a significant variation of the charge density between atoms at both surfaces. It is remarkable that in terms of the variation of the local electron density the roughness of the flat *A* surface is comparable to that of the puckered *B* surface. Particularly deep are the charge density minima inside the small pentagonal tiles of the *A* surface. Inside the pentagons formed by five TM atoms one observes from one to five additional atoms. The charge density minima are the most pronounced if one or two atoms are located inside the pentagons only, but a clear charge density minimum is formed even in the case where five atoms fill the pentagon.

On the *B* surface the internal decoration of the large TM pentagons is regular. One can here also observe various charge density minima between the atoms. As we shall see in the next Section III B the surface charge density minima are important as binding sites for adsorbate atoms.

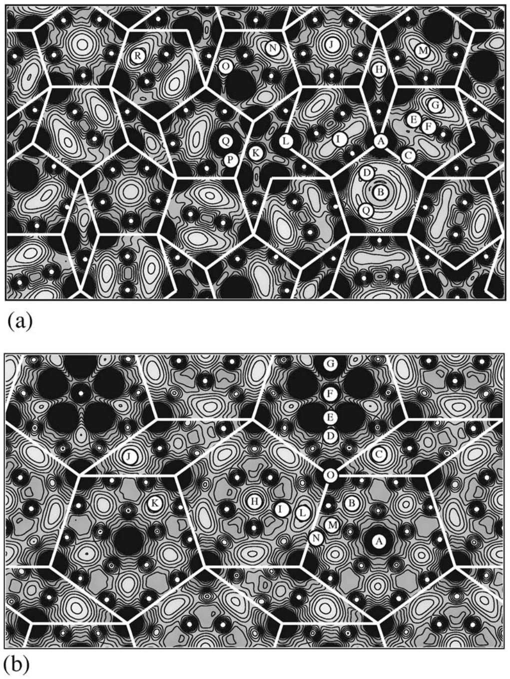

FIG. 1. Valence charge density distribution at surfaces *A* (a) and *B* (b) of the *W* approximant to *d*-Al-Co-Ni. For the discussion of the potential-energy landscape of adatoms several special sites on the surface are marked. The binding energies of Bi atoms at these sites are listed in Table I. The position of transition-metal (TM) atoms is characterized by high valence charge densities -black circles [e.g., labeled as *A* and *L* in (a)]. The positions of the Al atoms can be recognized as small circular islands of local density minima [e.g., labeled as *C* and *E* in (a) or *I* and *N* in (b)]. The tilings represent networks of the transition-metal (TM) atoms in the surface planes. Because of the different content of TM atoms, the tilings are different in both planes. The *A* plane is more TM rich. The edge length of the tiling superposed on the *A* plane is 4.68 Å, the edge of tiles in the *B* plane is 7.58 Å.

TABLE I. The binding energies E_b and vertical positions h of Bi adatoms at specific sites on the *A* and *B* surfaces of *W*-(AlCoNi) approximant. The table is ordered in descending binding energies. The labels refer to those marked in Fig. 1.

Description of site	Label	E_b [eV]	h [Å]
Surface *A*			
Charge density minimum inside a pentagon	*R*	−5.14	1.85
Charge density minimum inside a pentagon	*N*	−4.98	1.86
Charge density minimum inside a pentagon	*D*	−4.95	1.95
Charge density minimum inside a pentagon	*G*	−4.87	1.84
Position between two TM atoms	*P*	−4.86	2.15
Charge density minimum inside a pentagon	*M*	−4.81	1.82
Charge density minimum inside a pentagon	*J*	−4.77	1.82
Charge density minimum inside a rhombus	*H*	−4.66	2.10
Charge density minimum inside a pentagon	*O*	−4.47	2.20
Charge density minimum inside a pentagon	*I*	−4.42	2.22
Top of a TM atom	*Q*	−4.34	2.34
Top of a TM atom	*A*	−4.27	2.36
Top of a TM atom	*L*	−4.08	2.37
Midpoint between two Al atoms	*F*	−3.95	2.36
Top of Al atom	*K*	−3.64	2.51
Top of Al atom	*B*	−3.48	2.55
Top of Al atom	*C*	−3.47	2.54
Top of Al atom	*E*	−3.45	2.56
Surface *B*			
Charge density minimum inside a pentagon	*H*	−4.87	1.94
Position between two TM atoms	*E*	−4.76	1.83
Charge density minimum inside a rhombus	*J*	−4.76	2.16
Charge density minimum inside a pentagon	*D*	−4.72	2.14
Charge density minimum inside a pentagon	*K*	−4.47	2.07
Charge density minimum inside a rhombus	*C*	−4.39	1.92
Charge density minimum inside a pentagon	*B*	−4.38	2.20
Charge density minimum inside a pentagon	*L*	−4.30	2.00
Top of a TM atom	*G*	−4.26	2.37
Midpoint between three Al atoms	*M*	−4.00	2.43
Top of a TM atom	*A*	−3.92	2.41
Top of a TM atom	*O*	−3.75	2.43
Top of Al atom	*F*	−3.44	2.50
Top of Al atom	*I*	−3.34	2.54
Top of Al atom	*N*	−2.97	2.69

B. Stable positions for adsorbed atoms

The mapping of the potential energy landscape of an isolated adatom on the surface provides a guideline for constructing structural models for adsorbed monolayers. As a probe we have chosen a single Bi atom bound to specific sites on the surface and calculated the binding energy in a relaxed position. The systematic repetition of this procedure for selected points on the surface serves to identify the most stable positions of the adsorbed atoms. As for each site the equilibrium distance above the surface must be found, the procedure is computationally very demanding. 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 us to reduce the number of investigated sites. Of course, the approximate local pentagonal symmetry does not guarantee that the binding energies on the symmetry-equivalent sites all are the same. We have verified that the differences between the binding energies of symmetry-equivalent sites ($\approx$0.2 eV) are much smaller than the binding energy differences between the inequivalent sites (0.5–1.5 eV). The results for series of special positions of adatoms (as defined in Fig. 1) are listed in Table I. The table presents the binding energies E_b and vertical positions h of Bi adatoms at specific sites on the *A* and *B* surfaces of the *W*-(AlCoNi) approximant. In the case of the flat surface *A* the vertical position is measured with respect to the surface plane; in the case of the slightly puckered surface *B* the vertical positions of the adatoms are measured with respect to an average height of the atoms in the surface layer.

1. Bi adsorbed on the surface A

The least attractive sites for Bi adatoms are on top of the Al atoms. The binding energy of a Bi atom on top of Al atoms (sites marked as *B*, *C*, *E*) is in the range from −3.49 to −3.45 eV. A slightly larger binding energy of −3.64 eV is calculated for a Bi atom on top of an Al atom located in the center of a TM pentagon (site *K*). The site *F* located at the midpoint between two covalently bonded Al atom has a binding energy of −3.95 eV. The Bi atom adsorbed on the TM sites has intermediate binding energies in the range from −4.42 to −4.27 eV (sites *Q*, *A*, and *L*). Sites *O* and *P* were chosen between two TM atoms or between one TM and a neighboring Al atom. The binding energies at these sites is −4.47 eV (site *O*) and −4.86 eV (site *P*)—i.e., somewhat larger than on top of TM atoms. The most stable sites for Bi adatoms are obviously various charge density minima at the surface (sites *R*, *N*, *D*, *G*, *M*, *J*, *H*, *O*, *I* in the sequence of decreasing binding energies), where the adatom can bind simultaneously to a number of surface and subsurface atoms. Their binding energies range from −4.98 eV to −4.66 eV. The strongest adatom binding is found at sites *R*, *N*, *D*, and *G*. At sites *R*, *N*, and *G* the Bi atom binds to one TM and two Al surface atoms; at site *D* the adatom sinks deeply into a local electron density minimum. Note, however, that these sites do not form a regular skeleton for an ordered adlayer. It is also interesting to compare vertical positions of the adsorbed atoms. For the least attractive sites on top of the Al atoms an average height of the center of a Bi adatom is 2.54 Å. For the transition-metal sites this average height is of 2.3 Å. The vertical position of Bi atoms in various charge density minima ranges between 1.82 Å and 2.22 Å.

2. Bi adsorbed on the surface B

A mapping of the energy landscape of the *B* surface provides a similar picture as for the *A* surface. Bi atoms are most weakly bound on top of Al atoms (sites *F*, *I*, *N*), with binding energies between −2.98 and −3.34 eV. The most attractive sites are again various charge density minima at the surface (sites *H*, *J*, *D*, *K*, *C*, *B*, *L*) with binding energies between −4.87 eV and −4.30 eV. A strongly attractive site with a binding energy of −4.76 eV is also the midpoint between two TM atoms (site *E*) in the TM pentagons. The binding energies of Bi on the TM sites (*G*, *A*, *O*) are again intermediate from −3.75 to −4.26 eV; a Bi atom in a threefold hollow between Al atoms has a binding energy of −4.00 eV.

Bi atoms on top of Al sites found their equilibrium positions at an average height of 2.58 Å. The average vertical position of Bi atoms on top of the TM atoms is 2.40 Å. The vertical position of Bi atoms in the charge density minima ranges between 1.83 Å and 2.20 Å. These results show that the puckering of the *B* surface has only minimal influence on the vertical positions of the adsorbed atoms and confirms a general trend: adatoms on the more attractive sites are closer to the surface than the atoms with lower binding energies.

C. Adsorbed monolayer

On the basis of the potential energy mapping we propose a model for the structure of a Bi monolayer with a quasiperiodic order. However, it is not possible to proceed simply by occupying the sites in the sequence of decreasing binding energies. As some of the most stable sites (*N*, *D*) occur only once on the *A* surface of the approximant, this will evidently not provide a skeleton for an ordered adlayer. Instead we begin by placing a Bi atom on top of all TM sites occupying the vertices of the pentagonal tiling. These sites have intermediate binding energies of −4.27 eV (site *A*) and −4.08 eV (site *L*). On the *A* surface this already provides a complete decoration of all rhombic and boat tiles. Inside the pentagonal tiles, the decoration depends on the local structure of the adsorbate: If the interior of a pentagonal tile contains only two Al atoms, we place two Bi atoms along a local mirror plane such as to exploit the strong binding in the electron density minima (sites *N*, *G*, *R*, *I*). If a pentagonal tile is decorated with an inner pentagon of Al atoms, a single Bi atom is placed above its center (site *J*). On the *B* surface, the larger tiles leave more freedom in designing the structure of the adlayer, but in return the task is facilitated by a greater regularity of the tile's decoration. Again we start by putting Bi atoms on top of the TM atoms located at the vertices of the *B* tiling (site *O*). The large pentagonal tiles are occupied in three different ways: (i) On tiles with a pentagon of TM atoms around the center, Bi adatoms are placed on bridge sites between these atoms (site *E*). (ii) On pentagonal tiles centered by a TM atom surrounded by five Al atoms, Bi adatoms are placed on the central TM atom (site *A*) and into the electron density minima surrounded by four Al atoms (site *B* or *K*). (iii) On pentagonal tiles with a vacant center, Bi adatoms are placed into the central charge density minimum (site *H*) and into the five minima close to the tiles edges (site *L*). Finally, Bi atoms are placed also into the charge density minima inside the rhombic tiles (site *J*).

With these adsorption sites, almost all positions that are energetically favorable for single adatoms are occupied in the complete monolayer structure. The exceptions are sites *G* and *D* on the *B* surface which cannot be occupied simultaneously with the *E* site. Placing Bi atoms on either of these sites would not only increase the site energy, but also leads to too short a Bi-Bi distance between the atoms on the *O* and *L* sites. Similarly on the *A* surface, occupation of the *P* sites is overruled because of their too short distances to the vertices (site *A*).

These steps already lead to dense coverage of the surfaces. Figure 2 shows the distribution of Bi atoms in the monolayer at both surfaces in their ideal positions. On the *A* surface of the unit cell of the *W* approximant with a size of 39.59 Å × 23.30 Å it is possible to accommodate 81 Bi atoms. This already leads to the coverage density of 0.087 atoms/Å^2. This value is 9% more than the medium of the experimental value 0.08±0.02 atoms/Å^2 reported by Franke *et al.*[6] On the *B* surface of the unit cell of the *W* approximant it is possible to accommodate 66 Bi atoms. This leads to the coverage density of 0.071 atoms/Å^2. This value is 9% less than the medium of the observed experimental value. In the center of one pentagonal tile, which corresponds just to the center of the 20-Å cluster we intentionally left one void. The reason for this "experiment" was to find out whether the point defect eventually destabilizes the

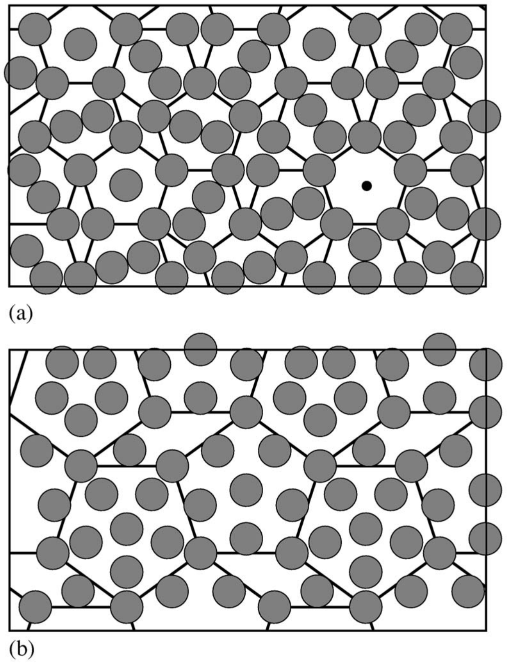

FIG. 2. The ideal positions of Bi atoms in the proposed structural model of a monolayer on surfaces *A* (a) and *B* (b). Sites are labeled according to the nomenclature defined in Fig. 1. On the *A* surface of the unit cell of the *W* approximant it is possible to accommodate 81 Bi atoms. On the *B* surface of the unit cell of the *W* approximant it is possible to accommodate 66 Bi atoms. At the *A* surface in the center of one pentagonal tile (marked by the black dot) that corresponds to the center of the 20 Å cluster we intentionally left a void; cf. text.

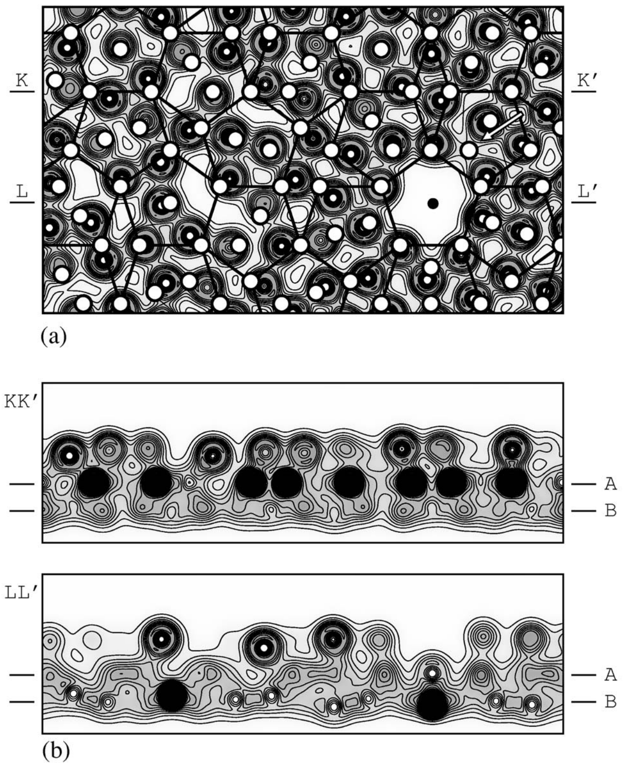

FIG. 3. Part (a) shows a valence electron density distribution in the Bi adlayer adsorbed at the *A* surface of *d*-Al-Co-Ni after the relaxation. For comparison the ideal positions of adsorption sites are marked by small open circles. The superposed tiling demonstrates that despite quite large deviations of the Bi atoms from their ideal positions the quasiperiodic order in the monolayer is maintained. The Bi atom marked by an arrow is shifted to a higher position, indicating that the structure is slightly overpacked. Interestingly, the void in the monolayer marked by a black dot did not shrink upon relaxation. Part (b) presents side views on the same model in two intersection planes perpendicular to the quasiperiodic plane: along the line KK' (top panel) and LL' (bottom panel). The contour plots of the valence charge density distribution provide a qualitative information on the character of bonding of the adsorbed Bi atoms on the substrate and on buckling of the adsorbed monolayer.

adlayer. The stability of the proposed structures has been tested by relaxation with Hellmann-Feynman forces.

1. Bi monolayer on the surface A

Figure 3(a) shows the distribution of Bi atom in the monolayer at the *A* surface after the relaxation. The Bi atoms located in the charge density minima of the surface were shifted only little from their ideal positions. On the other hand, the Bi atoms put on top of the TM atoms considerably drift away from their ideal positions. One of the Bi atoms (marked by an arrow) jumped up to the next layer. It is one of the atoms next to the pentagon surrounding the vacancy. A look at the substrate shows that the charge density minimum that should stabilize this atom is particularly shallow at this position. The vertical position of this particular atom is 4.27 Å above the surface plane. Figure 3(b) presents side views of the *A* surface with the adsorbed Bi monolayer. The contour plot shows the valence charge density distribution in a plane perpendicular to the quasiperiodic plane. We selected two intersection planes: along the line KK' and LL'; see Fig. 3(a). The KK' intersection shows bonding of the adsorbed Bi atoms on the TM atoms in the *A* plane of the surface. A weak covalency in the bonding can be recognized. The LL' intersection is led through the centers of the 20-Å columnar clusters. This plane intersects only a few adsorbed Bi atoms. These atoms sit in the charge density minima. The charge density distribution shows that the bonding of these atoms to the surface has purely metallic character. The side views provide qualitative information on the buckling of the adsorbed monolayer.

The heights of the other Bi atoms above the substrate range between 1.92 Å and 2.81 Å. These distances are somewhat larger than for isolated Bi adatoms. In particular, Bi atoms placed at weakly bonding sites drift farther away from the surface, leading to an increased buckling amplitude of the monolayer of 0.88 Å (compared to a maximal height difference of 0.54 Å for isolated adsorbed Bi atoms). The positions of the closest and farthest atoms are consistent with the results of the potential-energy landscape: the atom closest to the surface is located in a charge density minimum inside a pentagonal tile; the Bi atom located at the largest distance is pushed up by its neighbors on a top of an Al atom. It was also interesting to observe the behavior of the vacancy in the adlayer just above the center of the 20-Å cluster during the relaxation. It is evident that the Bi atoms surrounding the void do not relax inward, indicating that the quasiperiodic network is sufficiently stable. It is also noteworthy that the regular pentagon of Bi atoms on top of TM atoms in the center of the figure is quite strongly distorted. This is not surprise since the potential-energy analysis had shown that the Bi atoms on top of TM atoms receive only moderate stabilization and that the five sites forming the pentagon are energetically inequivalent. Altogether despite the observed deviations of the positions of the Bi atoms in the monolayer from the ideal sites the regularity of the quasiperiodic order is conserved. The quasiperiodicity is enforced by the stabilizing effect of the pairs of Bi atoms in the pentagonal tiles.

The average binding energy of a Bi atom in the adsorbed monolayer, calculated with respect to a free Bi atom is $E_{ads}=-4.464$ eV/atom. This is almost exactly equal to the average over the adsorption energies of the isolated Bi atom (we estimate a value of -4.45eV/atom—it must be emphasized that this is only an estimate, because the adsorption energies for topologically equivalent sites in the surface tiling can differ by up to 0.2 eV/atom). However, this agreement is largely coincidental and could be misleading. The binding energy between adlayer and substrate can be calculated from the difference between the total energy of the adlayer-substrate complex and the total energy of the substrate plus the same monolayer removed to a distance of 6.5 Å—which is large enough so that all bonds between the Bi monolayer and the substrate are broken. This binding energy is $E_{ML\ bind}=-1.06$eV/atom. The difference between these two energies can be attributed to the binding between Bi atoms in the adlayer, for which we find -3.40 eV/atom. This Bi-Bi binding energy is only slightly smaller than the cohesive energy of Bi in its native *hR*2 structure ($E_{hR2}=-3.89$ eV/atom) and larger than the cohesive energy of Bi in a structurally relaxed triangular ($E_{tri}=-3.29$ eV/atom) or square ($E_{square}=-3.31$ eV/atom) monolayer.[11] We conclude that the structure of the adsorbed Bi monolayer on the *A* surface is particularly well adapted to the formation of strong Bi-Bi bonds.

2. Bi monolayer on the surface B

Figure 4(a) shows the distribution of Bi atoms in the monolayer after relaxation. It is remarkable that after relaxation the Bi atoms remained very close to their ideal positions. Slightly larger shifts are calculated only for the Bi atoms bound to the vertices of the pentagonal tiles—i.e., on top of the transition-metal atoms. Again this shows the moderate stabilization of these sites. The pentagons of Bi atoms inside the pentagonal tiles close to upper edge of Fig. 4(a) are rotated by $\pi/10$ with respect to the pentagons of TM atoms beneath them in the substrate. Each Bi atom is thus located in the stable bridge site *E*; see Table I. We also tested a configuration where the orientation of the pentagon of Bi atoms was aligned with the pentagon of TM atoms beneath them (Bi atoms on site *G*). It was interesting to observe the change of the orientation of this configuration during the relaxation. The Bi pentagon rotated by $\pi/10$ to assume stable orientation. In comparison with the monolayer formed on the surface *A*, the Bi monolayer on the surface *B* exhibits much higher regularity. The quasiperiodic arrangement of the atoms in the monolayer is substrate induced.

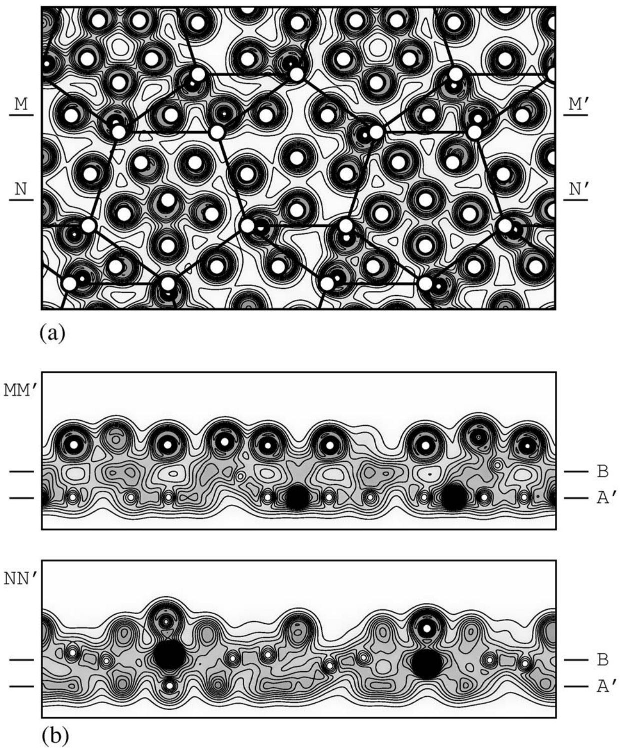

FIG. 4. Part (a) presents a topview on a valence electron density distribution in the Bi adlayer adsorbed at the surface *B* of *d*-Al-Co-Ni. For comparison the ideal positions of the adorption sites are marked by small open circles. In contrast to the surface *A* (see Fig. 3), here the Bi atoms after relaxation remain very close to their ideal positions. Part (b) shows sideviews of the *B* surface with the adsorbed Bi monolayer in two intersection planes: along the line *MM′* (top panel) and *NN′* (bottom panel).

Figure 4(b) presents side views of the *B* surface with the adsorbed Bi monolayer. The views are shown in two intersection planes: along the lines *MM′* and *NN′*; see Fig. 4(a). The contour plots of the valence charge density distribution provide qualitative information on the character of bonding of the adsorbed Bi atoms on the substrate and on buckling of the adsorbed monolayer.

The lowest vertical positions of an atom in the monolayer is 1.90 Å for an atom located in a charge density minimum. This distance is even smaller than the distance of closest approach of an isolated adatom (1.94 Å for an adatom in the center of a pentagonal tile, position *H*). The largest distance above the substrate is calculated for a Bi atom placed on the top of the central TM(Co) atom in the left pentagonal tile. Its height is 2.92 Å, about 0.5 Å larger than for isolated Bi atoms adsorbed on top of a TM atom. The buckling amplitude of the monolayer on the *B* surface is thus 1.02 Å—i.e., twice as large as calculated from the positions of single Bi atoms and also 16% higher than in a monolayer adsorbed on the surface *A*. The stronger buckling also reflects the puckering of the substrate.

The average binding energy for Bi atoms in the monolayer on the *B* surface is $E_{ads}=-4.561$ eV/atom, which is

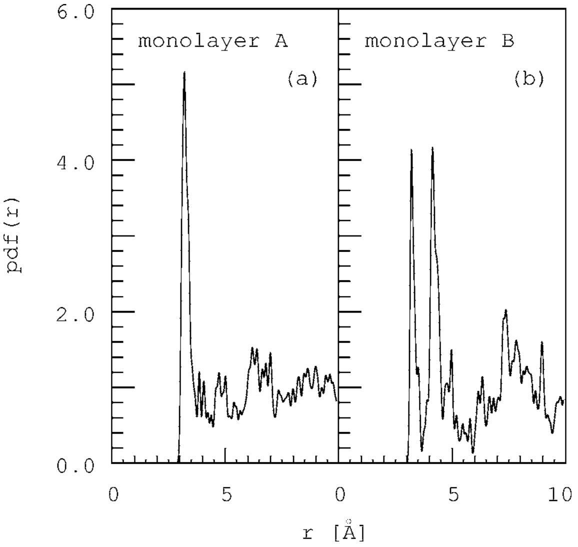

FIG. 5. The pair distribution function (PDF) of Bi atom ion the surfaces *A* (a) and *B* (b) calculated from the relaxed interatomic distances of Bi atoms in the monolayers. While the PDF of the Bi atoms on the surface *A* exhibits a single nearest-neighbors peak with the maximum at the separation ≈3.2 Å, the nearest neighbors of Bi atoms on the *B* surface are separated at two distinctly different distances. The nearest-neighbor peak in the PDF is thus split into two subpeaks with the maxima at the distances at ≈3.2 Å and ≈4.1 Å.

somewhat higher than on the *A* surface and also larger than the value estimated from the average of the adsorption energies of adsorbed single Bi atoms, for which we find a value of −4.22 eV/atom. The binding energy between adlayer and substrate is $E_{ML\ bind}=-1.70$ eV/atom; the Bi atoms are thus more strongly bonded to the surface *B* than to the surface *A*. The binding between the Bi atoms in the monolayer contributes only −2.86 eV/atom to the total adsorption energy, which is now considerably lower than the cohesive energy of bulk Bi. We conclude that in contrast to the dense adlayer on the *A* surface, a monolayer on the *B* surface is under considerable tensile strain. However, the energy difference is more than compensated by a stronger bonding to the substrate.

D. Structural properties of an adsorbed monolayer

The structural properties of the monolayers on the *A* and *B* surfaces are quite different. Figure 5 shows the pair-distribution functions (PDF's) calculated from the interatomic distances between the Bi atoms in the monolayers. The PDF of the Bi atoms on the surface *A* exhibits a single nearest-neighbor (NN) peak with a maximum at a nearest-neighbor distance of 3.18 Å and a second peak at a next-nearest-neighbor (NNN) distance of 4.7 Å. The NN distance corresponds to the short interatomic distances between atoms decorating the interior of the pentagonal tiles; it is only slightly larger than the optimized NN distance in a triangular Bi monolayer. The NNN distance is equal to the edge length of the pentagonal tiles. Hence the structure of the Bi monolayer adsorbed on the *A* surface represents a good compromise between the Bi-Bi bonding within the monolayer and the structure of the substrate. The PDF of the monolayer on the *B* surface shows a split NN peak with maxima at the distances of 3.21 Å and 4.14 Å, a smaller subpeak at about 4.7 Å, and a further peak at 7.5 Å. The 3.21-Å peak is a nearest-neighbor bonding distance analogous to that in the monolayer on the surface *A*, but now under tensile strain. The 4.14-Å peak corresponds to the distance between, e.g., the central atoms inside the pentagonal tiles and the neighboring five atoms forming a pentagon inside the tile; see Fig. 4(a). The subpeak at 4.7 Å corresponds to the distance between the atoms forming the inscribed pentagons (which is just equal to the edge length of the pentagon forming the tiling on the *A* surface—cf. our discussion of the relation between the *A* and *B* tilings in Ref. 18); the peak at 7.5 Å corresponds to the distance between the atoms decorating the vertices of the large pentagons on the *B* surface. Distances larger than 4 Å are, of course, already too large to represent a bonding distance; the atoms at this distance are stabilized by the bonding to the substrate. Hence the analysis of the PDF's of the monolayer confirms the conclusions drawn on the basis of the adsorption energies: The structure of the Bi monolayer on the *A* surface allows the formation of strong Bi-Bi bonds, but there is a certain mismatch with the substrate (which also leads to the relaxation effects discussed above). The monolayer adsorbed on the *B* surface is under tensile strain, but is optimally adapted to the substrate geometry.

Bi crystallizes in the As structure, the *hR*2 structure in Pearson's notation. It is a trigonal structure with space group No. 166. A closer look at the structure shows that it is a slightly deformed simple cubic structure. Each atom has three neighbors at a distance of 3.06 Å and three neighbors at a distance of 3.51 Å, so the average nearest-neighbor distance is 3.285 Å. Recently we studied[11] the stability of unsupported monolayers. In a square network of Bi atoms the equilibrium bonding distance is 3.12 Å. In a slightly less stable (by 25 meV/atom) triangular-network Bi atoms prefer an equilibrium separation at 3.29 Å. The first nearest-neighbor distance of Bi atoms on the *A* surface and the position of the first nearest-neighbor subpeak in the PDF of Bi atoms on the *B* surface are within this range of distances. The existence of the second nearest-neighbor subpeak in the PDF of Bi atoms on the *B* surface thus demonstrates that the adsorbate-substrate interaction can stabilize a regular nanostructure where the nearest atoms are located at distances significantly larger than the equilibrium bond distances. It is also noteworthy that the Bi-Bi bonds are particularly flexible. Our study of the stability of unsupported monolayers[11] has shown not only a very small angular stiffness of the Bi-Bi bonds as demonstrated by the small structural energy difference between square and triangular layers, but also a modest increase of the total energy on varying the bond lengths (high compressibility). This flexibility of Bi-Bi bonds seems to be essential for adapting the structure of the adsorbed monolayer to the quasiperiodic order of the substrate. In contrast to Bi, Al exhibits a strong preference for a triangular network and a lower compressibility. Al is therefore not a suitable element for the formation of the quasiperiodic adlayers. These results could explain the observed crystalline textures of Al films deposited on the quasicrystalline surfaces[1,2] and the success in formation of quasiperiodic Bi overlayers on the surfaces of quasicrystals.[6,10]

It is interesting to compare the average coordination number of Bi atoms in the adsorbed quasiperiodic monolayer on the *A* and *B* surfaces. The nearest-neighbor atoms in the monolayer are defined by a distance smaller than certain cutoff radius r_c defined by the minimum in the PDF following the main peak. From the pair distribution function we find that the cutoff radius separating the first and second nearest neighbors of Bi atoms on the surface *A* is equal to $r_c = 3.7$ Å. The corresponding average coordination number in the monolayer is $Z = 3.4$. Because of the split first-neighbor peak of the PDF of the monolayer adsorbed on the *B* surface, one can define two cutoff radii separating the first and second nearest neighbors. The first one we defined as $r_{c1} = 3.7$ Å, the same as at the surface *A*; the second one is $r_{c2} = 4.59$ Å. The corresponding average coordination numbers are $Z_1 = 1.6$ and $Z_2 = 4.8$, respectively. Between the distances r_{c2} and r_{c1} is thus 3.2 neighbors. The calculated average coordination number of Bi atoms in the adsorbed monolayer on the tenfold decagonal Al-Co-Ni surface *A* is similar to the value for Bi adlayers adsorbed on the fivefold icosahedral Al-Pd-Mn surface[11] where we found a value of $Z = 3.2$. The coordination number $Z_2 \approx 5$ for the adlayer on the *B* surface corresponds to the arrangement in the centered pentagonal motifs on some of the pentagonal tiles, whereas $Z_1 \approx 2$ corresponds to the coordination in the smaller pentagons. Altogether we find that the distances in the close-packed adlayers on the *A* surface are close to those in a freestanding square Bi monolayer, while the coordination is slightly lower. On the *B* surface the packing of Bi atoms in the adlayer is significantly less dense, and this appears to facilitate the matching to the quasiperiodic structure of the substrate.

E. Electronic properties of adsorbed monolayer

Figure 6 presents a comparison of the local densities of states (DOS) of the Bi monolayers adsorbed on both surfaces of *d*-Al-Co-Ni with the DOS of crystalline Bi. From the viewpoint of the electronic structure crystalline Bi is a very interesting compound. The DOS has one highly remarkable feature—a deep pseudogap just at Fermi level. The origin of this pseudogap is well known. A Bi atom has two *s* and three *p* electrons. The *s* band lies at higher bonding energies and is well separated from the *p* band. The *p* band is thus occupied to one-half. In a simple cubic structure the *p* orbitals form a rectangular network of $(pp\sigma)$ bonds extending in all three Cartesian directions. For a half-occupied *p* band the simple cubic structure is instable against Peierls distortion, leading to a rhombohedral structure with three short (strong) and three long (weak) bonds and the formation of a pseudogap at the Fermi level. The clear separation of the *s* band from the *p* band is essentially conserved also in the DOS of the Bi monolayers adsorbed on the quasicrystalline surface. The *s* band is narrowed as a consequence of the reduced dimensionality, whereas the *p* band is substantially broadened by the hybridization of the *p* states of the Bi atom with the substrate orbitals. The surface DOS of *d*-Al-Co-Ni (see dashed curves in Fig. 6) consists of a narrow TM *d* band extending from about −3 eV up to the Fermi level and a broad Al *s*,*p* band with a bottom at ≈−10.4 eV. In bulk *d*-Al-Co-Ni we have found a pronounced structure-induced DOS minimum at the Fermi level which is, however, nearly filled up at the surface. Because of the larger interatomic distances between the Bi atoms and the reduced coordination, the *s* bands of monolayers are narrower than that in the crystalline structure. In both *s* and *p* bands of the Bi layer the characteristic bonding-antibonding splitting induced by Peierls distortion of the crystalline bulk structure has disappeared, reflecting the fact that the structure of the monolayer is imposed by the bonding to the substrate and not the result of the atomic interactions within the adlayer. The formation mechanism of the pseudogap in the bulk is thus very specific and cannot be extended to the monolayer cases. The high DOS at the Fermi level in both quasiperiodic monolayers indicates their metallic character. The metallic character of the Bi monolayers (in contrast to the half-metallic properties of bulk Bi) results both from the adlayer-substrate hybridization and from the internal geometric structure of the adlayer which does not support the bonding-antibonding splitting in a network of *p* bonds.

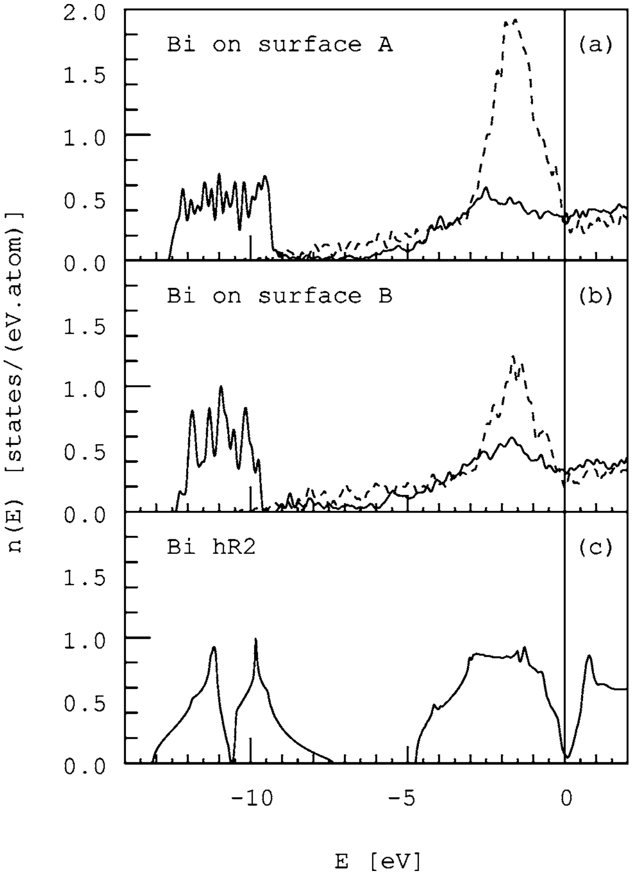

FIG. 6. A comparison of the densities of states (DOS) of the Bi monolayers adsorbed on surfaces *A* (a) and *B* (b) of *d*-Al-Co-Ni with the DOS of a crystalline Bi (c); cf. text. The dashed lines represent the surface DOS of the substrate.

IV. SUMMARY AND CONCLUSION

We have presented a structural model for quasiperiodic monolayers of Bi atoms formed on the tenfold surface of a model for the decagonal Al-Co-Ni quasicrystal, based on *ab initio* density functional calculations. 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 tenfold surface of a *W*-(AlCoNi) approximant to the *d*-Al-Co-Ni quasicrystal. We found stable quasiperiodic monolayers on both possible surfaces: the flat *A* surface and puckered *B* surface. On both surfaces the adsorbed Bi layers show considerable buckling with an amplitude of about 1 Å, reflecting the strength of adatom bonding at the different adsorption sites. The monolayer on the *B* surface is less dense and more regular than that on the *A* surface, the average density of both monolayers is in good agreement with experiment.[6] The dense packing on the *A* surface allows for the formation of strong Bi-Bi bonds within the adlayer, at the expense of a distortion of the quasiperiodic arrangement. Bi-Bi bonds in the less dense monolayer of surface *B* are under tensile strain, but this is overcompensated by strong Bi-substrate bonds, leading to a very regular adlayer structure.

Our present results confirm the conclusions that we reported already in our previous study[11] on the formation of single-atom monolayers on the *i*-Al-Pd-Mn surface. The lateral interactions of Bi atoms in the monolayer do not lead to any spontaneous quasiperiodic ordering. On the other hand, some elements like Bi with flexible interatomic interactions can adopt the quasiperiodic ordering promoted by the interaction with a quasiperiodically ordered substrate. At low coverage when the lateral interactions between adsorbent atoms is weak (as on the *B* surface) the quasiperiodic arrangement of the atoms can be highly regular. At higher coverage the positions of atoms are frequently shifted from their ideal positions and the quasiperiodic arrangement is locally distorted. However, a long-range quasiperiodic order is still maintained by the quasiperiodic distribution of the most stable sites. The adsorbate-substrate interaction can stabilize a regular nanostructure where atoms are separated by the nearest-neighbor distances significantly larger than the equilibrium bonding distances in close-packed monolayers.

It is also instructive to compare our results for adlayers on the *d*-Al-Co-Ni with those we have published for Bi monolayers on a fivefold surface of *i*-Al-Pd-Mn.[11] In both cases the surface structure may be described by a pentagonal tiling, with the vertices occupied by transition-metal atoms. However, while on the *i*-Al-Pd-Mn surface the vertices are occupied by Pd atoms, whose *d*-band DOS is centered far enough below the Fermi level to produce electron-density minima at the vertex sites, for *d*-Al-Co-Ni the *d* bands of both Co and Ni overlap with the Fermi level, producing a high electron density in the surface. The potential-energy mapping shows that adatoms bind more strongly on sites with electron-density minima than on top of TM atoms. Hence, on the fivefold surface of *i*-Al-Pd-Mn, the quasiperiodic order of the substrate is promoted to the adlayer by the strong binding of the Bi atoms to the vertices of the *P*1 tiling. In contrast, on both surfaces of *d*-Al-Co-Ni, the binding of Bi atoms to the vertices of the surface tiling is weaker and the quasiperiodic order of the substrate is transmitted to the film by the strong binding to local electron-density minima inside the tiles, which are also quasiperiodically distributed.

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