Comparison between experimental surface data and bulk structure models for quasicrystalline AlPdMn: Average atomic densities and chemical compositions

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We have examined bulk structure models for icosahedral AlPdMn in terms of the densities, compositions, and interplanar spacings for the fivefold planes that might represent physical surface terminations. We focus on four models that contain no partial or mixed occupancies, but some comparison is made to a fifth model containing such sites. Each of the four models contains paired planes (layers) that can be separated into two main families on the basis of three features: the relative densities of the two planes, the gap separating the layer from the nearest atomic plane, and the Pd content in the topmost plane. The experimental data and other arguments lead to the conclusion that the family with no Pd in the top plane is favored. Finally, all models show that correlations should be expected between the heights of steps that delineate terraces and average compositional and/or structural features of the terraces.

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I. INTRODUCTION

Quasicrystals are solid materials that are well ordered but not periodic.[1–3] They typically exhibit evidence of a forbidden rotational symmetry. Their intriguing atomic structure engenders unusual physical properties, including surface properties such as good oxidation resistance and low friction. This is well established, at least for the Al-rich icosahedral (*i*) intermetallics, which comprise a large fraction of the hundred or so known quasicrystals.

This type of quasicrystal has proven to be a rich and versatile platform for investigating basic surface phenomena, such as film growth and friction.[4–8] This is largely because the bulk atomic structure propagates up to the surface plane, provided that surface preparation conditions are chosen appropriately.[4–8] Furthermore, clean surfaces with flat terraced morphologies such as that shown in Fig. 1 can be prepared by using fairly standard techniques.[4–8]

Nonetheless, uncertainty remains about significant aspects of the surface structure. This is true in part because different models exist for the bulk structures of these quasicrystals: about seven different bulk models exist for *i*-AlPdMn,[9–20] although not all have been derived independently. Until now, each surface experiment has been compared to a single bulk structural model.[5,7,17,21–32] This limited approach leaves open the question of whether different models might yield different degrees of agreement with experimental surface data. The present paper provides an analysis or comparison of measurable surface properties that are predicted from *different* models.

Another source of uncertainty about the surface structure lies in the fact that within even a single model, there are a large number of bulk planes that can serve as the surface termination—in principle, no two planes are identical.[13,33] The solution to this conundrum was originally recognized by Boudard *et al.*[13] and later exploited by Gierer *et al.*,[22,23] who realized that the bulk structure can be classified into groups of self-similar planes and that one or more groups are probably favored over others as surface terminations. At present, there is a debate as to which group of planes is favored.[29,34,35]

A third subtlety arises from the different emphasis that can be placed on the two main components of the "structure:" the atomic positions and their chemical decorations. When comparing experimental data with bulk models, atomic positions have often been emphasized,[24,26,27,29,31] but chemical identities are important as well, particularly for understanding chemical reactivity of surfaces.

This paper deals with the long-range average surface structure and surface composition of quasicrystals. Our main goal is to find and differentiate among viable terminations for the fivefold surface of *i*-AlPdMn and to see how such terminations vary among different structural models. (Because *i*-AlCuFe and *i*-AlCuRu are considered isomorphic with *i*-AlPdMn, some data for their fivefold surfaces are included as well.) We choose the surface with fivefold symmetry because it has been documented more extensively than the other high-symmetry icosahedral surfaces. The strongest most consistent experimental data lead to the conclusion that three families of planes are possible surface terminations. We discuss the similarities and differences between these families and conclude that one particular family is more likely than the others. We also analyze whether there is a correla-

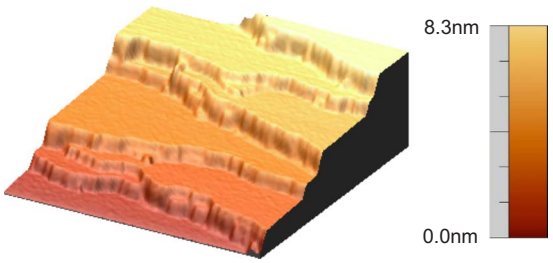

FIG. 1. (Color online) Semi-three-dimensional STM image of the fivefold surface of icosahedral AlPdMn. The size of the image is 250×250 nm^2; the tunneling conditions are +0.97 V and 0.47 nA.

TABLE I. Information about the bulk structure models of the quasicrystal, *i*-AlPdMn, used in this paper. In calculating total number of atoms in the Yamamoto model, sites are weighted according to occupancy. In the four deterministic models, a layer is a pair of planes. In the Yamamoto model, a layer is a group of planes, as defined in Sec. VI and Fig. 4.

	Composition			Size of the region analyzed		Total number of layer identified as viable terminations in the analyzed space
Model	Al	Pd	Mn	Total number of atoms	Volume (nm^3)	
KG	70.2	21.3	8.5	29 938	4.5×10^2	26
Boudard	68.7	21.9	9.5	293 061	4.4×10^3	36
PK	72.6	20.8	6.6	65 439	1.0×10^3	35
QG	70.4	21.3	8.3	375 825	5.6×10^3	66
Yamamoto	73.0	18.8	8.2	123 204	2.0×10^3	18

tion between the characteristics of a termination (terrace) and the height of the step which bounds it.

In the following section, we introduce the bulk structure models. In Sec. III, we define the two main families of possible terminations and subsequently compare them with respect to atomic densities, gaps between planes, and chemical compositions. These three factors are known to affect or reflect surface stabilities. We then compare the two families with regard to cut clusters. In Sec. IV, we introduce a third (minority) family. Section V gives some ideas on surface equilibration and how that may affect the surface terminations. Section VI presents a nondeterministic model, and Sec. VII points out correlations between characteristics of terminations and heights of adjoining steps.

II. BULK STRUCTURE MODELS

The first structure model reported for an icosahedral quasicrystal was based on neutron diffraction data for *i*-AlCuFe.[36] With time, it was modified and became known as the Katz–Gratias (KG) model.[11,12] Second, using x-ray and neutron diffraction, Boudard *et al.*[13] constructed a bulk structural model for *i*-AlPdMn, and this is commonly referred to as the Boudard model. Although its structure was mainly based on the KG model, the Boudard model originally contained unreasonably short bond lengths between some pairs of atoms. Therefore, it was slightly modified to alleviate this problem. In this work, we use the modified version.[23] Recently, using the skeleton of the KG model, Quiquandon and Gratias (QG) proposed another global structural model for both *i*-AlPdMn and *i*-AlCuFe quasicrystals[20] based on the previous neutron[36] and x-ray[13] diffraction data combined with magnetic properties. The fourth model used in this paper was proposed by Papadopolos and Kasner (PK).[16,18]

The above four models contain no sites with mixed or partial occupancy. Models without such sites are sometimes called "deterministic" within the quasicrystal community. These four models are analyzed in this paper. Nondeterministic models have also been reported by Elser[9] and by Yamamoto.[10] In Sec. VI, we include some analysis of the Yamamoto model as well.

Each of the four deterministic models was originally derived in six-dimensional (6D) space. The structures analyzed here are three-dimensional (3D) slabs. The atomic coordinates within the slabs were provided by the authors of the respective models, either directly (by private communication) or indirectly (by posted information on a public web site). Table I gives information about the compositions and sizes of the volumes that were analyzed in this work. It should be noted that each analyzed volume was selected in a way that areas of each fivefold plane in that slab were the same within a factor of 2. For this reason, the analyzed volumes did not always encompass the entire volume available from the source. In calculating average quantities, the characteristics of each plane were weighted according to its area, although we tested different weighting schemes and found that average quantities varied by less than 2%.

Figure 2 shows an example of the density and composition of planes of atoms versus their location (x coordinate) in one of the deterministic models (KG). It is assumed that vacuum is on the right and bulk solid is on the left, i.e., a viewer looks "down" at a fivefold surface plane from right to left. Independent of model, most of the distances (gaps) between any two adjacent planes take values of 0.048, 0.078, and 0.156 nm. Gaps of 0.030 nm can also be found, but rarely and only between planes with very low density. The four deterministic models are very similar with regard to atomic positions and planar densities, and they are virtually identical when represented in the style of Fig. 2. Figures showing the other three models in the same fashion are given in the supplemental material.[37]

The reason for the similarity between the deterministic models can be found in their 6D representations. The 6D space is conventionally divided into two three-dimensional (3D) subsets, called physical or parallel space, and inverse or perpendicular space.[1,3]

In perpendicular space, each bulk structural model has at least *three atomic surfaces* (also called acceptance domains or occupation domains) which contain information about the positions of the atoms and their chemical identities. The sizes and the shapes of the atomic surfaces differ from each other within a given model. Indeed, most of the atoms are confined in two large atomic surfaces, while a small fraction of atoms are in the third atomic surface.[12,13,20,30] In perpendicular

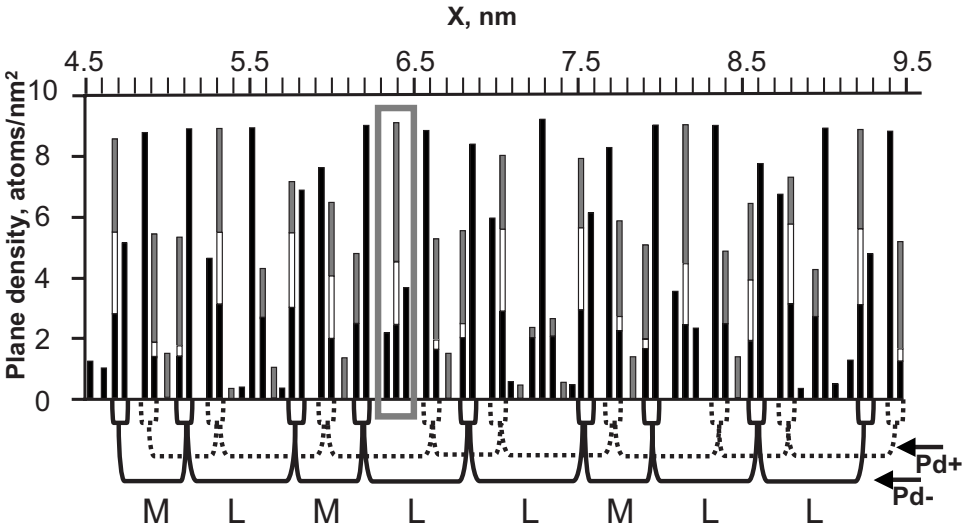

FIG. 2. Schematic depiction of atomic planes in the KG model. The x axis is the fivefold axis. The spatial coordinate is labeled x because this is the notation used by the authors of the model. The height of each line is proportional to the planar atomic density. Within each vertical bar, black is Al, gray is Pd, and white is Mn. The light rectangle encloses a triplet.

space, the atomic surfaces are 3D objects composed of several concentric shells. The shape and the size of the shells vary from model to model, as well as their chemical decoration. However, in all of the bulk structural models, the two main atomic surfaces are located at the same two kinds of nodes in the 6D lattice. For example, in the Boudard model,[13] one of the large atomic surfaces is located at the (000000) or n_0 node, while the other large one is centered at the (100000) or n_1 node. This is a robust property for all the deterministic models discussed in this paper (see Table 1 in Papadopolos *et al.*[38] for comparison of the nodes in several 6D models). The location of the third atomic surface is model dependent but since its contribution is much smaller than the others, we will not discuss it here.

By projecting the atomic surfaces from 6D space to 2D space following known procedures, the planes perpendicular to any direction can be generated.[39] Our interest here is in the planes orthogonal to any fivefold axis. It has been reported that each fivefold plane is generated by *only one* atomic surface.[27,30] Therefore, since all the bulk models have the main two atomic surfaces at the same nodes, each fivefold plane can be classified according to their atomic surfaces in all those models. In addition, the densities and compositions of the planes depend very much on the part of the atomic surfaces from which the planes are generated.[27] For example, in the KG model, there are dense fivefold planes that contain only Al atoms. This means that these planes are formed by the central part of the atomic surface at (000000) nodes since the atomic surface at these nodes has only Al atoms.[27] The other dense planes contain Al, Pd, and Mn atoms so those planes are generated from the central part of the atomic surface at (100000) nodes. Projections from the periphery of any atomic surface will result in less dense planes.

III. TWO MAIN FAMILIES

Several experiments have shown that the preferred terminations of fivefold surfaces of *i*-AlPdMn and *i*-AlCuFe exhibit a structural fingerprint. That is, they consist of two dense planes (a "layer" herein) that are closely spaced. This has been deduced from the analysis of intensity-voltage (I-V) data in the low-energy electron diffraction (LEED),[22,23,25] from x-ray photoelectron diffraction (XPD),[40] from low-energy ion scattering (LEIS),[41] and from x-ray scattering.[42,43] The spacing between the planes at the surface is about 0.04 nm, which is a contraction of 20% from the bulk value of 0.05 nm.

Another useful input is the heights of steps on surfaces exhibiting terrace-step morphology, such as shown in Fig. 1. A number of groups have reported heights of 0.660 nm (L) and 0.408 nm (M) based on STM results for the fivefold surface of *i*-AlPdMn. SPA-LEED analysis of step heights have shown similar values.[44] Analogous values have been reported for fivefold *i*-AlCuRu and *i*-AlCuFe. Step heights that are combinations of L and M have also been observed.[31,45] The L and M heights sometimes, but not always, constitute a Fibonacci sequence in reported STM images.[31,46,47]

In selecting viable surface terminations from the bulk structure models, we only consider layers as defined above. Furthermore, the layers must be separated from adjacent planes by L and M distances or by linear combinations of L and M. Layers that are viable terminations are labeled at the bottom of Fig. 2 with brackets. They fall into two distinct families or sets. For reasons presented later, we call them Pd− (without Pd) and Pd+ (with Pd). Note that if the volume is inspected from the opposite direction (with vacuum on the left), then the Pd− terminations become Pd+ terminations, and vice versa. Analyzing from both directions increases the number of terminations in each set, which we employ to maximize the statistical significance of our conclusions. An example of an atomic plane is shown in Fig. 3.

Below, we analyze four aspects of these two families. The first three of these are known to influence or reflect surface stability in crystalline materials: atomic densities, interplanar spacings, and chemical compositions. The atomic density is covered by Bravais' rule, which is an empirical generalization. It states that surface planes with high two-dimensional densities, and correspondingly small interplanar spacings, are most common (although exceptions exist). This is usually taken to mean that these surfaces are most stable.[30] Indeed, calculated surface energies of a single element in the solid

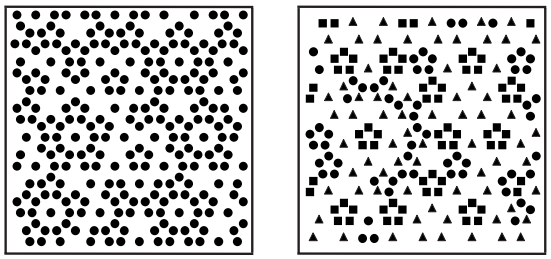

FIG. 3. Atomic arrangements in two adjacent, dense, fivefold planes in the KG model. The two planes combined would be one layer. The sizes of the figures are 6×6 nm^2. (a) Pure Al, $x=8.58$ nm. This would be a top plane in the Pd− family. (b) A mixture of Al, Pd, and Mn, $x=8.53$ nm. This would be a top plane in the Pd+ family. Circle is Al, square is Pd and triangle is Mn.

phase are usually lowest for the hexagonally close-packed surface.[48] In alloys, one expects chemical composition to also play a major role, which can be predicted to first order from the surface energy of the constituent elements. In the quasicrystals under consideration here, Al has a surface energy that is lower than that of the transition metals. For example, the surface energy of Al is 1.2–1.3 J/m^2, whereas that of Pd is 1.9–2.1 J/m^2.[48] Thus, if atomic densities are equal, one would expect the Al-richest planes to be preferred terminations. Both density and composition may be reflected in interplanar gaps, then, with larger gaps corresponding to more stable terminations.

A. Atomic densities

Densities, both of planes and layers, are shown in Table II. Consider first the total density of the terminating layer. This is very similar for the two families. For all models, this ranges from 13.1 to 14.3 nm^{-2}, with an average of about 13.6 nm^{-2}. Turning to individual planes, the *average* density of the topmost plane is clearly different for the two families; it is about 7.6 for the Pd− set and 6.2 for the Pd+ set, with a range of 4.3–9.1 nm^{-2}. The numbers reflect different *relative* densities of the two top planes in the two families. About 70% of layers in the Pd− set have top planes that are more dense than the plane that is 0.05 nm beneath, while about 70% in the Pd+ set have top planes that are less dense. This complementarity stems from the fact that any given layer can belong to either family, depending only on the viewing direction as noted above.

Experimental data are currently insufficient to distinguish between the two families on the basis of relative or absolute densities. A value of 13.5 nm^{-2} is frequently quoted from the LEED *I-V* analysis[22,23] for the composite density averaged over many terraces.[22] However, this value actually rests upon the assumption of a particular bulk structure model (the modified Boudard model). The number was calculated from the densities of planes that provided the optimal fit to the experimental data *within that model* and, hence, cannot be regarded as a model-independent value. Another potential source of atomic densities is STM, but several assumptions and ambiguities are involved in this approach too.[49] One problem is that an image of a single terrace may not represent the ensemble average. In our experience, different terraces are more or less amenable to high-resolution imaging. It is natural to select terraces that provide the best images, but this may result in the selection of nonrepresentative terminations (e.g., those with lowest density in the top plane might provide poorer images). Keeping these reservations in mind, numbers can be derived from STM. An atomic density of 8 nm^{-2} has been reported for the top plane,[31] and values of about 4 nm^{-2} can be derived from other images.[27,50] These values fall within the range of densities (4.3–9.1 nm^{-2}) of the topmost plane for either the Pd− or the Pd+ set in the models (see Table II). Comparison with average values is not useful since the available STM data do not provide averages.)

B. Gaps between planes

A second point of comparison between the two families is the width of the gaps that are cleaved to form the surface. From Fig. 2, it can be seen that all of the Pd− terminations cleave the bulk at 0.156 nm wide gaps, the widest possible spacing between two adjacent planes. (This value of

TABLE II. Densities of planes and layers in the Pd− and Pd+ types of terminations. Densities are in atoms nm^{-2}. For information about individual planes, see supplemental material. (Ref. 37). In the four deterministic models, a layer is a pair of planes. In the Yamamoto model, a layer is a group of planes, as defined in Sec. VI and Fig. 4.

Model	Range of densities of first (top) plane in Pd− or second plane in Pd+	Average density of first plane in Pd− or second plane in Pd+	Range of densities of second plane in Pd− or first plane in Pd+	Average density of second plane in Pd− or first plane in Pd+	Range of lateral densities of terminating layer	Average density of terminating layer
KG	4.60–9.12	7.52	4.25–8.91	6.48	13.51–14.30	13.92
Boudard	4.63–8.85	7.57	4.27–8.58	5.95	13.07–13.71	13.53
PK	4.67–8.96	7.61	4.48–8.80	6.21	13.31–14.15	13.82
QG	4.59–8.95	7.56	4.34–8.72	6.02	13.16–13.89	13.59
Yamamoto	n/a	n/a	n/a	n/a	11.44–13.54	12.45

TABLE III. Compositions of planes and layers in the Pd− and Pd+ types of terminations, in at. %. Ranges and averages are given here. For information about individual planes, see supplemental material (Ref. 37). In the four deterministic models, a layer is a pair of planes. In the Yamamoto model, a layer is a group of planes, as defined in Sec. VI and Fig. 4.

Model	Range of compositions of first (top) plane in Pd− or second plane in Pd+	Average composition of first plane in Pd− or second plane in Pd+	Range of compositions of second plane in Pd− or first plane in Pd+	Average composition of second plane in Pd− or first plane in Pd+	Range of compositions of terminating layer	Average composition of terminating layer
KG	Al(100.00)	Al(100.00)	Al(23.84–50.60) Pd(18.86–69.58) Mn(0.59–36.93)	Al(36.20) Pd(44.56) Mn(19.24)	Al(56.49–83.40) Pd(9.91–26.12) Mn(0.20–19.74)	Al(70.58) Pd(19.38) Mn(10.04)
Boudard	Al(87.10–100.00) Mn(0.00–12.90)	Al(95.41) Mn(3.59)	Al(26.40–78.20) Pd(21.80–66.83) Mn(0.00-26.25)	Al(38.52) Pd(49.20) Mn(12.18)	Al(57.58–84.22) Pd(7.05–25.55) Mn(2.50–17.04)	Al(69.86) Pd(21.39) Mn(8.76)
PK	Al(82.88–100.00) Mn(0.00–17.12)	Al(95.04) Mn(4.96)	Al(26.11–87.79) Pd(12.21–72.62) Mn(0.00–14.62)	Al(51.77) Pd(43.99) Mn(4.24)	Al(64.56–87.09) Pd(4.16–31.37) Mn(0.00–11.29)	Al(74.67) Pd(19.97) Mn(5.36)
QG	Al(69.35–100.00) Mn(0.00–30.88)	Al(84.83) Mn(15.17)	Al(34.95–82.67) Pd(17.33–65.05) Mn(0.00)	Al(58.38) Pd(41.62) Mn(0.00)	Al(62.12–78.17) Pd(5.69–36.00) Mn(0.00–19.71)	Al(71.06) Pd(19.48) Mn(9.46)
Yamamoto	n/a	n/a	n/a	n/a	Al(72.56–89.75) Pd(2.69–23.37) Mn(2.46–8.86)	Al(79.14) Pd(14.52) Mn(6.34)

0.156 nm is not the step height since that would be the spacing *between adjacent* 0.156 nm gaps.) All of the Pd+ terminations cleave the bulk at smaller gaps of 0.078 nm. In quasicrystals, it has been proposed that the spacing between adjacent planes influences the selection of terminations.[13,31] This reflects the fact that a large interplanar gap implies weaker bonding between planes and, hence, a lower total surface energy for the two adjacent planes. This correlation between interplanar spacing and surface energy suggests that the Pd− set should be the preferred type of termination.

C. Chemical composition

Table III shows that in the Pd− set, the top plane is mainly or completely Al. It may contain some Mn, but *never* Pd. In the Pd+ set, the top plane *always* contains Pd (on average in excess of 40 at. %), typically being a mixture of Al, Pd, and Mn. This general description applies to all four models. Papadopolos *et al.*[29] have proposed that the Pd+ set are terminations on fivefold surfaces of *i*-AlPdMn (although we wish to note that Papadopolos *et al.* have expressed reservations about the chemical decoration used.[51,52]) On the other hand, a termination similar to those in the Pd− family has been used in density functional simulations of surface properties of AlPdMn rational approximants.[35,53–55] In addition, a termination belonging to the Pd− family was used for generating potential energy surfaces and subsequent kinetic Monte Carlo simulations of Al adatoms.[56,57]

The models can be compared to experimental data for both Pd and Mn contents. Regarding the Pd content, LEED *I-V* data for fivefold *i*-AlPdMn were fit best by terminations that contained an average of 93 at. % Al, 7 at. % Mn, and no Pd in the top plane, within the context of the modified Boudard model. In other words, there was a clear preference for the Pd− set over the Pd+ set. An analogous result was obtained for the fivefold surface of *i*-AlCuFe, i.e., no Fe was found in the topmost plane.[25] LEIS also indicated that the top plane is Al rich, whereas the second plane is relatively rich in Pd.[41] Other types of surface sensitive analyses—x-ray photoelectron spectroscopy or Auger electron spectroscopy—have provided information that is not useful in the present context since these techniques average over many layers and therefore give bulk compositions. Overall, the LEED *I-V* data and the LEIS data indicate that the majority of surface planes belong to the Pd− set.

Regarding the Mn content in the top plane, there are two reports based on low-energy ion scattering data. The first indicated a range of 0.4–6.3 at. % Mn, while the second more sophisticated study indicated an upper limit of 1 at. %. The LEED *I-V* analysis set an upper limit of 10 at. %. An STM study reported a mean surface Mn concentration of about 0.2 nm^{-2}, assuming that every adsorbed Si atom occupied a Mn site.[58] This translates into a top-layer Mn concentration of 2.5–3.3 at. %, using the average densities of the top planes in either the Pd− or Pd+ sets (cf. Table II). Taken together, the data indicate that the average Mn concentration

in the topmost plane is between 0 and 10 at. %, and most probably ≤4 at. %.

Table III contains the information needed to predict Mn content from the four models for both the Pd− and Pd+ terminations. It can be seen that the range of average Mn content in the top plane, across the different models, is about the same for the two families: from 0% to 15% in the Pd− set and 0% to 19% in the Pd+ set. These ranges certainly encompass all of the experimental values. Hence, Mn content cannot be used to discriminate between the two main families.

D. Cut clusters

Much past discussion of surface structure has revolved around the local structure, which in turn relates to clusters that can be identified in the bulk.[1–3] These clusters are nested polyhedra consisting of a few tens of atoms. In the deterministic models, two types of clusters are commonly identified, which are called Bergman and Mackay. In icosahedral materials, any plane through the bulk intersects some of these clusters. Cut clusters have been associated with certain local features in STM images of the fivefold surfaces, the so-called dark stars, which are important adsorption sites.[5,56,57,59–61]

The two main families differ in the way that the top planes cut bulk clusters in the models. The Pd− family cuts Mackay clusters 0.252 nm above or 0.204 nm below the equator, thereby producing features that are strong candidates for the dark star sites. The Pd+ family cuts Bergman clusters 0.078 nm below the equator, producing a competing candidate for the dark-star sites. From our assertion that the Pd− family is more likely to be the preferred termination, it follows that the dark-star sites are more likely to be cut Mackay clusters than cut Bergmans.

IV. THIRD FAMILY

A third type of termination can be described as a group of three planes separated by two gaps of 0.05 nm. The middle plane is denser than the two outer ones. We call these groups "triplets." One such group is enclosed by a light rectangle in Fig. 2. Most triplets contain a pair of planes that is comparable in density to the pairs in the two main families.

The triplets cannot account for all of the surface terminations because the experimental M step height is 0.408 nm, while the separation between triplets is at least 0.864 nm, using the dense middle plane of each triplet to define its location. However, it is possible that the triplets coexist with other terminations. Indeed, two LEED I-V studies[22,23,25] and one XPD study[40] previously showed that the ensemble of surface terminations contains 10%–30% triplets. For example, see the terminations labeled B and E in Fig. 4 of Ref. 40 or the fifth arrow from left in Fig. 9 of Ref. 25.

Each of the less dense planes at the edge of a triplet, 0.05 nm from the middle plane, is formed by a projection from the periphery of one of the two main atomic surfaces in six dimensions (see Sec. II). We note that there is no fundamental difference between the dense paired planes in the Pd+ and Pd− families, and the planes in the triplets, with respect to the 6D representation. The distinction between triplets and the other two families appears in three dimensions when we impose the simplifying constraint that planes with very low atomic density (<1 nm^{-2}) are unimportant.

V. SURFACE EQUILIBRATION

The degree to which triplets, or even mixtures of Pd+ and Pd− terminations, are present on a real surface probably depends on conditions of preparation. In all of the data reviewed in this paper, surfaces were prepared by ion bombardment at room temperature, followed by annealing. After the initial structural and chemical disruption caused by ion bombardment, the surface must regenerate, with the bulk sample serving as both template and reservoir. During regrowth, metastable phases and features can appear and disappear. For instance, a cubic phase forms at moderate annealing temperatures and is replaced by the quasicrystalline phase around 700 K.[62]

In one study, it was found that if the quasicrystalline surface phase is annealed no higher than 915 K, it includes metastable terminations.[63] The signature of these transitory terminations is a dense network of voids, through which the more stable termination at the bottom of the voids becomes progressively exposed with increasing annealing temperature.[45,63,64] On i-AlPdMn, the voids have a depth of 0.25 nm.[63] This value can be reconciled with transitions between terminations in different families. These arguments will be presented elsewhere. The main point here is that the voids provide evidence that terminations from different families coexist, at least under some circumstances. Further evidence for coexisting families can be inferred from an XPD study[40] in which the surface was heated to a relatively low temperature, 800 K. Under these conditions, equal contributions from Pd+ and Pd− families were found, together with triplets. It is possible that the Pd+ set is metastable at such low preparation temperatures.

VI. NONDETERMINISTIC MODEL

Some characteristics of the Yamamoto model, a nondeterministic model, are included in Tables I–III. In calculating average densities and compositions for this model, we weighted each atomic position according to its statistical occupancy and composition. The bulk atomic density is 61.6 nm^{-3}. This is low compared to the densities of the other models, which fall in the range of 65.4–66.6 nm^{-3}. The lowness of the value may be related to the partial occupation of sites.

The densities and compositions of atomic planes are shown in Fig. 4 for the Yamamoto model. There are many atomic planes, but gaps exist between groups of planes. The clustering of planes suggests a natural grouping, as shown by the brackets at the bottom of the x axis in Fig. 4. Each bracket is 0.11 nm wide. We call each such group of planes a "layer," by analogy with the deterministic models, even though they do not consist of simple paired planes. The layers can be divided into two families of plausible terminations

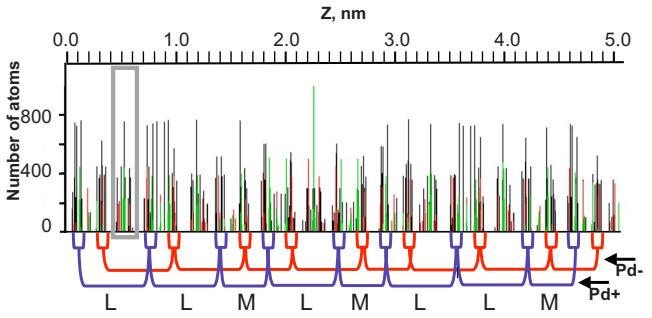

FIG. 4. (Color online) Schematic depiction of atomic planes in the Yamamoto model. The z axis is the fivefold axis. The spatial coordinate is labeled z because this is the notation used by the authors of the model. The height of each line is proportional to the planar atomic density. Planes are color coded for chemical composition, where black is Al, green is Pd, and red is Mn. There are very many planes, but gaps between groups of planes suggest the natural grouping scheme indicated by the series of 0.11 nm wide brackets at the bottom. The light rectangle encloses the equivalent of a triplet.

that are very similar to the Pd+ and Pd− families discussed in Sec. III.

One difference between this model and the deterministic models is that a layer in the Yamamoto model cannot be divided into two planes separated by 0.050 nm, so the composition of a layer is more spatially continuous. Nonetheless, the compositional trends are the same: there is a Pd− family, in which the Pd concentration increases from top to bottom, and vice versa in the Pd+ family. Another difference between this model and the deterministic models is that the atomic density of the terminating layers is only 12.5 nm^{-2} on average, to be compared with 13.6 nm^{-2} in the deterministic models. This mimics the difference in bulk density noted above and undoubtedly has the same origin. Triplets can also be identified in the Yamamoto model, and one example is shown by the gray rectangle in Fig. 4.

VII. CORRELATIONS BETWEEN CHARACTERISTICS OF TERMINATIONS AND HEIGHTS OF ADJOINING STEPS

It has been reported that different terraces can behave much differently as templates for nucleation and growth of metal films.[65,66] It has also been reported that the terrace width is smaller if the terrace is bounded by an M-type step than an L-type step.[67] Furthermore, step bunching on these fivefold surfaces has been attributed to differences between different terminations.[31] Because of such observations, there has been speculation that step heights on quasicrystals, such as L and M, may correspond to certain densities, compositions, or other features on the adjoining terraces.[67] Our analysis of the models shows that such correlations indeed exist.

To assess correlations in atomic structure, we chose to evaluate the density of the top *plane* in the terminating layer. This metric can be applied to the four deterministic models but not to the Yamamoto model because in the latter, terminating layers do not consist of only two planes. Table IV shows the result: the density of the topmost plane, for terraces bordered by L steps, is about 20% lower than the other type of terrace. This is true for the Pd− family. Because of the complementary relationship between the two families, the inverse relationship would hold in the Pd+ family: top planes of terraces bordered by M steps would be about 20% less dense than the other. Table IV shows that the results are nearly identical for the four models, which should be expected since they are so similar in terms of the 6D structure (Sec. II). We do not expect that the Yamamoto model would be significantly different if an analogous metric were devised.

To assess correlations in composition, we evaluate the average Al, Pd, and Mn concentrations in the terminating *layer*. The result is shown in Table IV. Again, there is always a difference between L- and M-type terraces, but now the dif-

TABLE IV. Correlations between densities and compositions of terminations, and step heights, in the Pd− family. Heights of L− and M−type steps are 0.660 and 0.408 nm, respectively, for the five fold surface of i−AlPdMn. In the four deterministic models, a layer is a pair of planes. In the Yamamoto model, a layer is a group of planes, as defined in Sec. VI and Fig. 4.

Model	Type of step bordering termination in down-going direction	Average atomic density in top plane of termination, (nm^{-2})	Average atomic density in top plane, L:M ratio.	Average concentration of elements in terminating layer (range of values for individual terminating layers is given in parentheses) (at. %)		
				Al	Pd	Mn
KG	L	6.6	0.74	66.39 (56.49–75.38)	18.13 (9.91–25.74)	15.57 (3.15–19.74)
	M	8.9		76.71 (71.32–83.40)	21.56 (16.40–26.12)	1.73 (0.20–2.92)
Boudard	L	6.8	0.78	65.08 (57.58–72.27)	24.32 (23.18–25.25)	10.59 (3.04–17.04)
	M	8.8		76.85 (72.69–83.34)	17.52 (8.05–24.08)	5.62 (2.50–8.60)
PK	L	6.9	0.78	70.61 (64.56–81.24)	24.54 (12.92–31.13)	4.94 (1.11–9.33)
	M	8.8		81.57 (79.62–84.55)	11.67 (4.16–15.25)	6.76 (5.13–11.29)
QG	L	6.8	0.78	69.83 (62.12–75.90)	25.87 (8.98–36.00)	4.29 (0.00–15.18)
	M	8.8		72.68 (67.29–78.17)	8.98 (6.04–13.67)	18.06 (15.45–19.71)
Yamamoto	L	n/a	n/a	76.70 (72.56–86.34)	17.74 (5.85–23.37)	5.56 (2.46–8.86)
	M	n/a		84.03 (77.77–89.75)	8.08 (2.69–13.81)	7.89 (7.15–8.65)

ference depends strongly on the model. Taking Mn concentration in the Pd− set as an example, terminating layers on *L*-type terraces contain *more* Mn than *M*-type terraces in the KG and Boudard models. The *L*-type terraces contain *less* Mn in the other three models. The average Mn concentration on the two types of terraces differs by as much as a factor of 10 (e.g., the KG model).

These results show that there is both a structural and a chemical correlation between step height and characteristics of the terminations. The correlation is model independent for atomic densities of the topmost plane, where the relationship $L<M$ always holds true. However, it is strongly model dependent for the composition in the terminating pair of planes (layer). Either or both of these correlations could be related to the experimental observations mentioned above. Finally, it should be noted that the correlations apply only to *average* quantities. The distributions sometimes overlap, as can be seen by inspecting the ranges given in Table IV.

VIII. DISCUSSION

In the two main families, we hypothesize that the Pd− set is the more stable type of termination. This is partly because of the larger interplanar gap where the surface is formed, which signals a lower surface energy. It is also because experimental data indicate that the top plane contains no Pd in *i*-AlPdMn and (analogously) no Fe in *i*-AlCuFe. Furthermore, LEIS indicates that the top plane is Al rich, while the second plane is relatively Pd rich. The Pd+ family always contains significant Pd in the topmost plane. Our hypothesis has implications for atomic-scale structure on surfaces because it implies that the dark-star features in STM are cut Mackays rather than cut Bergmans, as previously proposed by Papadopolos *et al.*[29]

If one accepts the hypothesis that the Pd− set is the more stable type of termination, can surface science distinguish between the bulk structural models? On the basis of long-range average information (i.e., information averaged over many terraces) of the type that has been emphasized in this paper, we conclude that it cannot. However, future research may provide such a result by taking advantage of the fact that the structural models differ, not so much in their atomic locations as in their chemical decorations. Specifically, an experiment could be designed to determine the correlation between the chemical composition of individual terraces and the adjoining step heights. Our analysis (Sec. VII) reveals that this correlation is quite model dependent. This approach would differ from experiments designed to date, in which it would provide chemical compositions on individual terraces, as opposed to compositions that are averaged over many terraces.

IX. CONCLUSIONS

We have examined four deterministic models and one nondeterministic model for *i*-AlPdMn in terms of the densities, interplanar spacings, and compositions of the fivefold planes, which are viable surface terminations, and we have compared them with available data for fivefold surfaces. Each of the four deterministic models contains sets of paired planes (layers), and the nondeterministic model contains similar groups of planes. Two main families of layers, which we call Pd− and Pd+, are viable terminations based on their planar structure and the step heights associated with them. Each layer can belong to either family, depending only on the viewing direction. Besides the Pd content, these two sets differ in the average relative densities of the two planes (Pd− having the denser plane on top, usually) and the width of the interplanar gap where the surface forms (Pd− having the larger gap by a factor of 2). The experimental data and other arguments lead to the conclusion that the Pd− family is favored over the Pd+. This implies that a distinctive type of adsorption site, known from STM studies as a dark star, is a cut Mackay cluster. There is evidence that a third family, consisting of triplets, is also present as a minority. Finally, the analysis of the models shows correlations between the average structure and composition of terminations and the height of the step adjoining the terrace.

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