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Investigation of the surface terminations of icosahedral AlPdMn quasicrystal based on a modified non-spherical model

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Abstract

The atomic positions are obtained from a modified non-spherical model of icosahedral AlPdMn quasicrystal (Fang *et al* 2003 *J. Phys.: Condens. Matter* **15** 4947) by the cut method. The four-shell pseudo-Mackay clusters (PMCs) were searched for in a box of 400 Å × 400 Å × 400 Å. The results show that the number of atoms in the fourth shell, an icosidodecahedron, of the pseudo-Mackay cluster can vary from 15 to 30 because of the cluster overlap, and about 99.96% of the total atoms are included in such incomplete pseudo-Mackay clusters. The characteristics of the atom distribution in the planes perpendicular to a fivefold axis indicate that the planes, which are 1.56 Å apart from their neighbouring planes, are expected to be the terminal surfaces. If one such a plane and its closest neighbouring plane, between which the spacing is 0.48 Å, are considered as a thin layer or a corrugated surface, these layers are also the layers with the maximum density. The pair of corrugated surfaces that are 1.56 Å apart have almost identical chemical composition. These planes form terraces that follow the rule of the Fibonacci sequence with two step heights, 6.60 and 4.08 Å. On the corrugated surfaces perpendicular to a fivefold axis the pentagonal holes arise from the interspaces of adjacent incomplete PMCs. For the atomic planes normal to a twofold axis, the planes with spacing of 1.48 Å from their adjacent planes might be expected to be the terminal surfaces, which form terraces with step heights of 6.28 and 3.88 Å following the rule of the Fibonacci sequence. For the atomic planes normal to a threefold axis, the planes with spacing of 0.86 Å from their adjacent planes might be expected to be the terminal surfaces. No similar results were found for the atomic layers perpendicular to a pseudo-twofold axis.

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1. Introduction

Methods for the determination of quasicrystal structures have been greatly improved with the introduction of the superspace formalism (for review, see [1]). Using this approach, Boudard *et al* [2] investigated the structure of icosahedral AlPdMn (i-AlPdMn) quasicrystal with neutron and x-ray diffraction and obtained a spherical model for describing the atomic surfaces (atomic occupation domains). In the physical structure of icosahedral AlPdMn phase obtained from the spherical model by using the cut method there exist two kinds of pseudo-Mackay clusters (PMCs). The so-called PMC consists of 4 shells: a core atom as the first shell; a small cube of 8 atoms as the second shell; an icosahedron of 12 atoms as the third shell; and an icosidodecahedron of 30 atoms as the fourth shell. The PMC type 1 has a large icosahedron intermediate shell of Mn + Al and an icosidodecahedron external shell of Pd + Al, while the PMC type 2 has a large icosahedron intermediate shell of Mn + Pd and an icosidodecahedron external shell of Al. The inner shells of these two kinds of pseudo-Mackay clusters are pieces of an Al dodecahedron. On the basis of the structure example of the i-AlPdMn quasicrystal, self-similarity rules were derived and were then used for explaining the inelastic neutron scattering data and thermal conductivity behaviour [3]. According to electronic structure calculations, the clustered structure corresponds to a stable and low-energy state [4]. Assuming that the area of intersection of a plane with the clusters determines its energy cost, Yang *et al* [5] investigated the low-energy planes in the icosahedral AlPdMn quasicrystal on the basis of the atomic positions calculated according to the spherical model of Boudard *et al* [2]. It shows that the positions of the local energy minima of fivefold and twofold planes follow a Fibonacci sequence, whereas an almost constant energy cost is found for pseudo-twofold planes [5]. Evidence for a cluster-based structure of the icosahedral AlPdMn quasicrystal has been obtained with scanning tunnelling microscopy, which demonstrates that cracks propagate along zones of lower strength between clusters [6]. Recently, a number of theoretical investigations [7–9] showed that the Bergman clusters are the basic dominant elements for the icosahedral AlPdMn phase.

Using the spherical model of icosahedral AlPdMn [2] as a starting point, Fang *et al* [10] refined the structure of the icosahedral AlPdMn quasicrystal by using quantitative convergent beam electron diffraction and by describing the shape of the atomic surface with symmetry-adapted parameters. Finally, they obtained a more precise non-spherical model in which the percentage of unphysically short inter-atom distances is reduced.

Subdividing a large occupation domain into several small ones, Yamamoto and co-workers [11, 12] constructed a six-dimensional (6D) cluster model of i-AlPdMn quasicrystal. This model includes 91 structural parameters, such as the shifts of the small occupation domains along some parallel space directions from the ideal positions, the occupation probabilities and the temperature factors. After refinement, this model gave small R factors ($R_w = 0.053$, $R = 0.049$) for 377 independent reflections [12]. On the basis of this model, two kinds of 20 Å clusters, which are located at even- and odd-parity 12-fold vertices of the inflated three-dimensional (3D) Penrose pattern, were obtained by using a cut method. This model is considered the most sophisticated and the best available so far.

Recently, there has been great interest in research on the quasicrystal surface structure, composition and surface preparation technique because of the unusual properties of quasicrystals such as oxidation resistance, low surface friction and superior wear resistance. These studies have made great progress in the past few years, especially in the case of the aluminium-based icosahedral quasicrystals. The surface structure of icosahedral AlPdMn quasicrystal has been studied with scanning tunnelling microscopy (STM) [6, 13–18], helium diffraction [17], low-energy electron diffraction (LEED) [19–22] and x-ray photoemission

spectroscopy (XPS) [22]. The STM observations of fivefold and twofold surfaces of i-AlPdMn, which were prepared by *in situ* cleavage in ultrahigh vacuum, revealed significant atomic-scale roughness [6]. The STM measurements [13–16] on the surfaces of i-AlPdMn prepared by sputtering and annealing in ultrahigh vacuum showed that well-defined relatively flat terraces formed on the fivefold surface and twofold surface, and that the step heights of successive terraces followed the Fibonacci sequence. High-resolution STM images of the fivefold surface also showed that the dominant structure motif was dark fivefold stars [13–16]. The terrace–step structure of the threefold surface of i-AlPdMn was also observed with STM [18]. However, the fine structure on the terraces is rougher than on the fivefold surface, and the steps can be very straight. Shen *et al* [21] studied the structural stabilities of the fivefold, twofold and threefold surfaces of i-AlPdMn with LEED. They found that the lateral density of the twofold face is the highest and the density of the threefold face is the lowest among the three high-symmetry faces, while the fivefold face is more stable than the others. Hence, some factors other than density must be involved in stabilizing the quasicrystalline surface. Some evidence of surface relaxation was observed [13, 20].

From the viewpoint of thermodynamics, faceting results from minimizing the total surface free energy of given quasicrystalline matter. The orientation dependence of the surface free-energy density has been derived from the broken-bond model [23, 24]. It is found that the major effect determining the stability of facets is the possibility of finding an optimum cutting position of the surface plane for orientations corresponding to facets with small indices, thus avoiding strong bonds being cut [24]. It is normally assumed that the shorter the bond distance, the stronger the bond. The surface structures of i-AlPdMn phase were explained with a termination of the bulk structure based on truncated pseudo-Mackay icosahedra [5, 6], or Bergman clusters [17], or the geometric model in which the F-phase three-dimensional tiling is decorated by Bergman polytopes [14, 15, 25].

The aim of the present paper is to investigate the surface structure of i-AlPdMn phase on the basis of the atomic positions in three-dimensional (3D) physical space obtained from the non-spherical model [10]. The choice of the non-spherical model [10] in the present study is based on the following considerations. First, the non-spherical model [10] for i-AlPdMn is more precise than the spherical model [2]. Second, this model is much simpler than the 6D cluster model of Yamamoto *et al* [11, 12], and easier to use in describing the shape of the atomic surface with a limited number of parameters. Third, the shapes of the outermost boundaries of the atomic surfaces at n_0, n_1 and bc_1 of the non-spherical model [10] (figure 3 of [10]) are very close to the shapes of the envelopes of the corresponding total occupation domains of the 6D cluster model shown in figure 4 of [11]. For example, the envelope of the total occupation domain at n_1 is basically a sphere with some dimples on the surface, and the envelope of the total occupation domain at n_0 is nearly a sphere with few slightly raised pieces on the surface. Further, the volumes of the three main occupation domains of the non-spherical model are very close to the corresponding ones of the 6D cluster model. For example, the radius of 10.3 Å of the envelope of the occupation domain at n_0 in the non-spherical model is slightly smaller than the corresponding value of 10.9 Å for the 6D cluster model (the distance between the centres of small occupation domains Nos 16 and 29), which is calculated with the positions of the small occupation domains given in [12]. The radius of 10.2 Å for the envelope of the occupation domain at n_1 in the non-spherical model is very close to the corresponding value of 10.3 Å for the 6D cluster model (the distance between the centres of small occupation domains Nos 3 and 15). The radii of the envelopes at bc_1 for the two models are nearly the same, i.e. 4.8 Å. It is noticed that the atomic occupations of the non-spherical model are not precisely described as in the 6D cluster model. However, when it is mainly the atomic plane spacings and the atomic densities of the planes that are considered, the non-spherical model can

give reasonable results. The organization of the paper is as follows. We first briefly describe the non-spherical model. Then we show the results for our statistics of the numbers of PMCs, incomplete PMCs and Bergman clusters in a box of 400 Å × 400 Å × 400 Å. Positions and chemical compositions of a series of atomic planes perpendicular to a fivefold axis, twofold axis, threefold axis and pseudo-twofold axis are analysed. Finally the structures of the fivefold surface, twofold surface, threefold surface and pseudo-twofold surface are discussed.

2. The non-spherical model of the icosahedral AlPdMn quasicrystal

In the non-spherical model [10], the icosahedral AlPdMn phase has a six-dimensional (6D) face-centred hypercubic lattice. The 3D atomic surfaces are located on three special positions of the hypercubic unit cell. (1) Three successive shells located on $n_0 = [\,0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0\,]$: Mn is in the region within boundary B1, Pd lies between boundaries B1 and B2, Al occupies the space between B2 and B3. (2) Two successive shells located on $n_1 = (1/2)[\,1 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0\,]$: Mn within B4 and Al between B4 and B5. (3) Pd occupies the domain within B6 which is located at $bc_1 = (1/4)[\,1 \quad 1 \quad 1 \quad 1 \quad 1 \quad -1\,]$. Since the site symmetries of n_0, n_1, bc_1 are all $\bar{5}\bar{3}m$, the boundaries B1–B6 can be expressed as

$$r(\theta,\phi) = a_0 Y_0^0(\theta,\phi) + a_6\left\{\frac{\sqrt{11}}{5}Y_6^0(\theta,\phi) + \frac{\sqrt{7}}{5}[Y_6^5(\theta,\phi) + Y_6^{-5}(\theta,\phi)]\right\} + a_{10}\{\cdots\} + \cdots \tag{1}$$

where $Y_l^m(\theta,\phi)$ are spherical harmonics. The refined coefficients a_0 and a_6 are respectively 19.1 and 0.323 Å for boundary B1, 28.5 and 3.43 Å for B2, 36.5 and 0.819 Å for B3, 12.3 and −0.819 Å for B4, 36.3 and −4.09 Å for B5, 16.8 and 0.397 Å for B6 where the lattice constant of the six-dimensional face-centred cubic lattice equals 12.902 Å [10].

3. The cluster structure of the i-AlPdMn phase

According to the modified non-spherical model [10], the atoms around the origin form an extended Mackay cluster (MC) [7] if the origin of the 6D superspace is located at the 6D lattice node n_0. When the origin of the 6D superspace is located at the 6D lattice node bc_1, the atoms near the origin form a Bergman dodecahedron [26] or the first three shells of the extended Bergman cluster [7] including a Pd atom at the cluster centre as the first shell.

The first four shells of the extended Mackay cluster [10] consist of a Mn atom at the centre, a small dodecahedron of 20 atoms with the radius of the shell r equal to 2.567 Å, an intermediate icosahedron of 12 atoms with r equal to 4.561 Å and an external icosidodecahedron of 30 atoms with r equal to 4.796 Å. Figure 1 shows the atomic positions of this cluster on the planes perpendicular to a fivefold axis. It is obvious that the distances between two adjacent planes for such a cluster only have two values: 0.48 and 1.56 Å. As shown later, for most of the cluster there is only a piece of the small dodecahedron and the number of atoms in the piece differs from cluster to cluster. This is in fact the so-called pseudo-Mackay cluster (PMC) [2].

We calculated the atomic positions in a box of 400 Å × 400 Å × 400 Å by using the non-spherical model [10] and the cut method. The coordinate system A2P–A2–A5, i.e. with the x axis parallel to a pseudo-twofold axis, the y axis parallel to a twofold axis and the z axis parallel to a fivefold axis, as used in [27], is adopted here. The origin of the 6D superspace is located at n_0. A shift of the origin along the parallel space components represents a uniform translation of the entire system. All sections with different perpendicular space components belong to the same local isomorphism class [28]. This means that identical atomic clusters

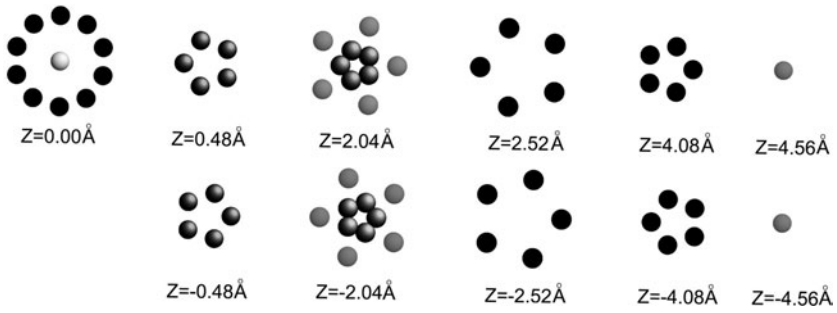

Figure 1. The atomic positions in the first four shells of the extended MC on planes perpendicular to a fivefold axis. z is the coordinate of the plane in the direction of the fivefold axis. The centre of the extended MC is located at the coordinate origin.

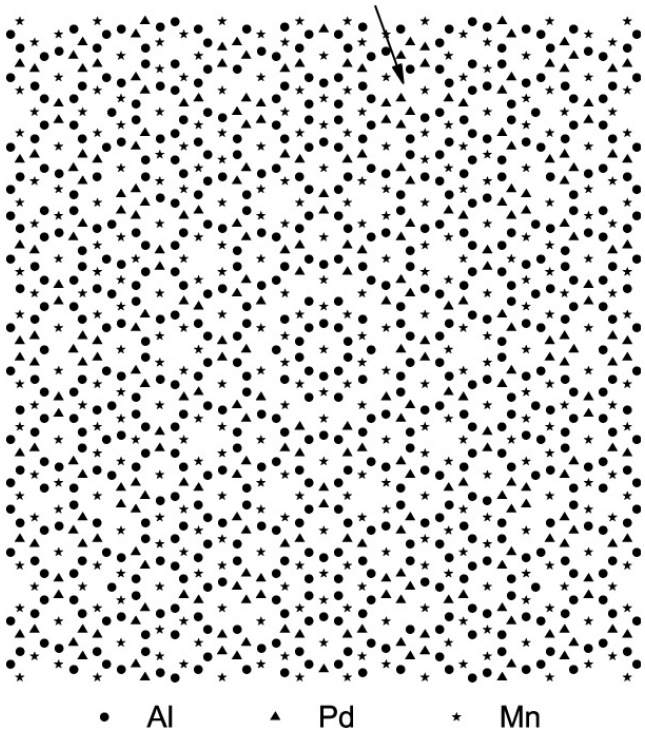

Figure 2. Atomic positions within an area of 120 Å $\times$ 120 Å of the plane perpendicular to a fivefold axis when the origin of the 6D superspace is located at the 6D lattice node n_0 during the cutting.

of any size can be found at distances apart of about twice the size [4]. We compared the calculation results with the origin of 6D superspace located at n_0, n_1 and bc_1, and found that the characteristics of the atomic distribution remain the same. Hence, the atomic positions obtained in a large enough box in the parallel subspace are representative. The total number of atoms in this box is 4239917. The average composition obtained is $Al_{69.7}Pd_{21.6}Mn_{8.7}$. Figure 2 shows the atomic positions within an area of 120 Å $\times$ 120 Å on the fivefold plane at $z = 0$. The fundamental pattern has ten atoms in a circle surrounding another atom. Comparing with figure 1, this pattern should be the PMC whose centre is on the plane at z equal to 0. It is

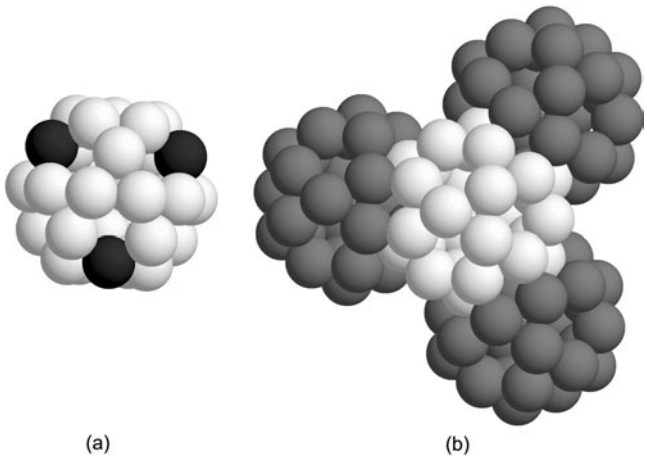

Figure 3. (a) The atomic positions of the 27 atoms (white balls) and three vacancies (dark balls) of the outer shell in an incomplete PMC. (b) Overlapping of the incomplete PMC (white balls) with the other three PMCs (dark balls).

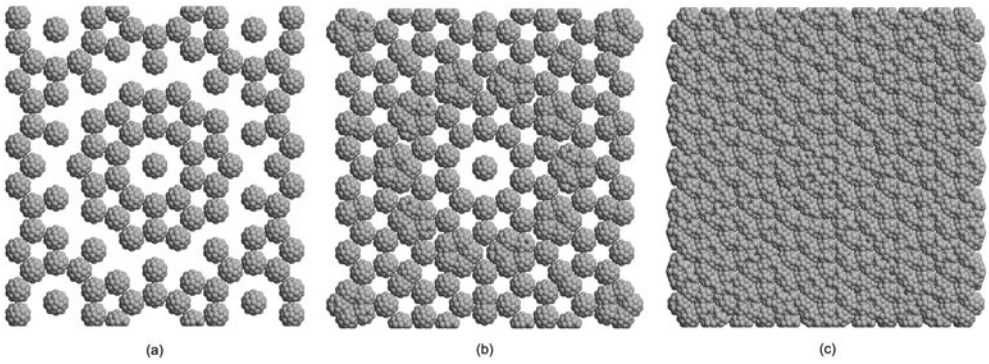

Figure 4. Cluster distributions within an area of 160 Å $\times$ 160 Å on a fivefold plane at $z = 0$ in the A2P–A2–A5 coordinate system. (a) The distribution of PMCs with 30 atoms in the outer shell. (b) The distributions of incomplete PMCs with 27–30 atoms in the outer shell. (c) The distribution of incomplete PMCs with 15–30 atoms in the outer shell.

also noted that sometimes the number of atoms in a circle which surrounds another atom is less than 10, such as at the position pointed to by an arrow. They should belong to imperfect PMCs, because the number of atoms in the outer shell is less than 30. Figure 3(a) shows the atomic positions in the outer shell of an imperfect PMC in which the number of atoms in the outer shell is 27 (represented by white balls). The vacant positions are indicated with three dark balls. Figure 3(b) shows how this imperfect PMC (white balls) overlaps with the other three PMCs (dark balls). From our calculation, the number of atoms in the outer shell can take various values from 15 to 30. We call this kind of PMC an incomplete pseudo-Mackay cluster. Figure 4(a) shows the distribution of PMCs whose centres are within a area of 160 Å $\times$ 160 Å on the plane of $z = 0$. Figure 4(b) is the distribution of incomplete PMCs with 27–30 atoms in the outer shell within the same area as in figure 4(a). Figure 4(c) gives the distribution of incomplete PMCs with 15–30 atoms in the outer shell within the same area as in figures 4(a) and (b). It is seen that some clusters penetrate each other, which makes the numbers and

positions of atoms in the outer shell alter from cluster to cluster. Meanwhile, it seems that there is a covering model based on the incomplete PMC in the icosahedral quasicrystal.

We searched for PMCs in the box of 400 Å × 400 Å × 400 Å by using the following algorithm. Every atomic position is sequentially taken as the centre of the cluster. We then search for the atoms at the given distances from the centre, 4.561 and 4.796 Å, which are the radii of the intermediate icosahedron shell and the outer icosidodecahedron shell, respectively. If the number of detected atoms amounts to 12 and 30 for these two shells, respectively, the central atom is accepted as a centre of the PMC. The atoms for which the distances to the central atom are less than or equal to 4.796 Å are considered as belonging to the same PMC. The positions and numbers of the atoms in the inner core are not taken into account. For accuracy of the statistic results, we do not take the marginal atoms (272 866 in total), for which the distances from the atoms to the surface of the box are less than 4.796 Å, as the centres of clusters. The number of Bergman clusters [26], in which there are 1–3 vacancies in the intermediate icosahedron, is also counted. The statistical results are listed in table 1. It is found that there is no Bergman cluster without vacancies. The incomplete PMCs cover about 99.96% of the total atomic positions, while PMCs only cover 76.52% of the total atoms, and the Bergman clusters with vacancies only cover 51.99% of the total atoms.

4. The characteristics of atomic layers and the surface structure

To explain the experimental results on the surface structure of i-AlPdMn phase, we investigated the positions, chemical compositions, atomic arrangements and atomic densities of the planes perpendicular to fivefold, twofold, threefold and pseudo-twofold axes by using the atomic positions in a box of 400 Å × 400 Å × 400 Å calculated with the non-spherical model [10] of the icosahedral AlPdMn phase. (The data for the planes perpendicular to fivefold, twofold, threefold and pseudo-twofold axes are given in tables 2 to 5, respectively, in the supplementary material.)

4.1. Terminal surfaces perpendicular to a fivefold axis

Most of the distances between two adjacent planes are 0.48, 0.78 and 1.56 Å, and only few distances are 0.30 Å. The value 0.78 Å equals $\tau \times 0.48$ Å, where τ is the golden mean $(\sqrt{5}+1)/2$. The value 0.30 Å equals 0.48 Å$/\tau$, and 1.56 Å equals 2×0.78 Å. As mentioned in section 3, the distances of 0.48 and 1.56 Å are the spacings between two adjacent planes perpendicular to a fivefold direction in a single PMC. Since the largest 'gap' between two adjacent planes is 1.56 Å, if the quasicrystal is cut along a plane within this largest 'gap', the chemical compositions and structures of the terminated surfaces on the two sides of the cutting plane share a common feature: the outermost two planes are so close (with spacing of 0.48 Å) that they might be considered as a single corrugated surface. This is in good agreement with the STM observation [13] that the average corrugation in undisturbed regions is about 0.5 Å. The density of these thin layers with the thickness of 0.48 Å is effectively the largest among all thin layers with thickness less than 0.6 Å [29] as also compared with the layers normal to the twofold axis, threefold axis and pseudo-twofold axis. The outer planes of the two corrugated surfaces are composed primarily of Al, and sometimes mixed with less than 10% Mn. For example, the plane located at $z = 0.48$ Å is composed of Al. The plane located at $z = 2.04$ Å contains 93.2% Al and 6.8% Mn. The inner planes of the two corrugated surfaces normally contain large amounts of Al and Pd atoms and a small amount of Mn atoms. For example, the plane located at $z = 0.0$ Å contains 47.1% Al, 24.8% Pd, 28.1% Mn. The plane located at $z = 2.52$ Å contains 81.6% Al and 18.4% Pd. These results are generally in agreement with the results from LEED [19] and Auger electron spectroscopy [17], which show that the

fivefold surface of $Al_{70}Pd_{21}Mn_9$ is a mixture of very similar terminations with a dense, Al-rich outermost atomic layer followed by a layer containing about 50% Al and 50% Pd. These two corrugated surfaces can also be considered as the surface with the lowest surface free energy, because the total atomic density of these corrugated surfaces is about 0.13 atoms $Å^{-2}$ which is close to the value of 0.141 atoms $Å^{-2}$ for the close-packed (111) surface of face-centred cubic crystal Al [19]. For metals, the closest-packed face generally has the lowest surface free energy.

By assuming that the termination takes place at the largest gap of 1.56 Å, we can also find that the distances between two neighbouring upper terminal planes (for example, the planes located at 2.04 and 6.12, 6.12 and 12.72 Å) or between two neighbouring lower terminal planes (such as the planes located at 0.48 and 4.56 Å, 4.56 and 11.16 Å) take the values $S = 4.08$ Å or $L = \tau S = 6.60$ Å, which matches a Fibonacci sequence. This means that if the termination position in a fivefold direction lies in the largest 'gap', the step heights of the terraces are 4.08 and 6.60 Å on both surfaces of the termination, for instance, a set of planes at $z = 2.04$, 6.12, 12.72, 16.80, 23.40, 30.00, 34.08 Å, on one side, and a set of planes at $z = 0.48$, 4.56, 11.16, 15.24, 21.84, 28.44, 32.52 Å, on the other side. This is in line with the STM observations of Schaub *et al* [13]. In the STM investigation [13] the fivefold surface of icosahedral AlPdMn quasicrystal shows a terrace-like structure, and the heights of the successive terraces obey a Fibonacci sequence for which the short and long intervals, i.e. the heights of 'low' and 'high' terraces, are $L = 4.22 \pm 0.26$ Å and $H = 6.78 \pm 0.24$ Å, respectively. Therefore, the two adjacent planes with spacing of 1.56 Å might be expected to be the terminal surfaces perpendicular to the fivefold axis. We take one of them as an example in the following paragraphs.

4.2. Pentagonal holes in the fivefold surface

If we cut i-AlPdMn phase along a plane between two fivefold planes at $z = 4.56$ and 6.12 Å, the planes located at $z = 4.08$ and 4.56 Å will form a single corrugated surface. Figure 5 shows the atomic distributions in this corrugated surface within a square of 160 Å × 160 Å. Dark and white balls represent atoms on the planes located at $z = 4.08$ Å (lower) and 4.56 Å (upper), respectively. Some objects showing fivefold symmetry immediately attract attention: there are many empty fivefold stars—the same as is seen in atomic resolution images of the fivefold surface of i-AlPdMn [13–16]. Every empty fivefold star appears as a pentagonal hole (such as the pentagon indicated by '3') surrounded by five inner lower atoms (dark balls) on the plane at $z = 4.08$ Å and by five outer higher atoms (white balls) on the plane at $z = 4.56$ Å. The edge lengths of these pentagonal holes (the distance between two adjacent white balls) are 4.8 Å, which agrees well with the STM measurements, 4.8 Å [16]. By calculation, the atoms below the fivefold stars are located on the plane at $z = 2.52$ Å. This means that the depth of the pentagonal holes is 2.04 Å, which is equal to the value predicted with the geometric model [14]. The STM estimation of the minimum depth of the pentagonal hollows is about 1.2 ± 0.2 Å [16] and 1.5 Å [14].

It is also shown in figure 5 that there are two kinds of pentagons. One kind of pentagon, e.g. the pentagon denoted with number '1', consists of a dark ball (lower atom at $z = 4.08$ Å) and five surrounding white balls (higher atoms at $z = 4.56$ Å). Pentagons of another kind, such as that indicated with number '2', consist of a white ball (higher atom at $z = 4.56$ Å) and five surrounding dark balls (lower atoms at $z = 4.08$ Å). Pentagons of the first kind belong to the lowest two fivefold planes of the PMCs whose centres are located on the plane at $z = 8.64$ Å. Pentagons of the second kind belong to the highest two fivefold planes of the PMCs whose centres are located on the plane at $z = 0.0$ Å (refer to figure 1). It is seen from figure 5 that the

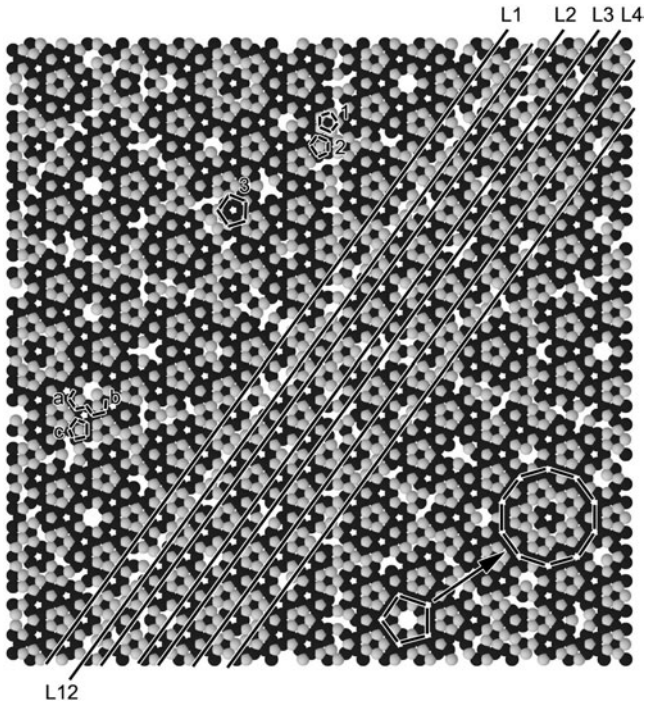

Figure 5. The distribution of atoms within an area of 160 Å × 160 Å of a corrugated surface perpendicular to a fivefold axis. The corrugated surface consists of the atoms on the plane at $z = 4.56$ Å (white balls) and the atoms on the plane at $z = 4.08$ Å (dark balls). Pentagonal holes (hollows), such as the pentagon denoted by '3', are formed with five inner lower atoms on the plane at $z = 4.08$ Å (dark balls) and five outer higher atoms on the plane at $z = 4.56$ Å (white balls). The black lines connect the similar points of the pentagonal holes. The distances between two adjacent lines are either 4.56 or 7.38 or 11.94 Å.

fivefold holes are formed by the atoms in the topmost two layers of three adjacent incomplete PMCs such as the clusters denoted by letters 'a', 'b' and 'c'. In other words, the top interspace of three adjacent incomplete PMCs whose centres are located on an identical fivefold plane forms the fivefold hole. The five outer higher atoms (white balls) of a pentagonal hole are divided into two groups: three atoms (for example, the atoms denoted with 'a', 'b' and 'c') are from the incomplete PMCs whose centres are on the plane at $z = 0.0$ Å, and the other two higher atoms are from the incomplete PMCs whose centres are on the plane at $z = 8.64$ Å. Most of atoms on the planes of $z = 4.56$ and 4.08 Å are either from the topmost two layers of the incomplete PMCs with the centres at $z = 0.0$ Å or from the lowest two layers of the incomplete PMCs with the centres at $z = 8.64$ Å. When the quasicrystal is cut along a plane between $z = 4.56$ and 6.12 Å, this plane will be tangential to the lower PMCs and cut with the upper PMCs. In this case the intersection area of the plane with the clusters will be small; thus we call the plane the low-energy plane [5]. Hence, the largest 'gap' must correspond to lower strength between clusters.

Furthermore, five pentagonal holes often create a larger pentagon, as marked with the black line near the lower left side of the arrow in figure 5. Sometimes, ten pentagonal holes form a decagonal ring as marked on the upper right side of the arrow in figure 5. The arrangements of pentagonal holes in figure 5 show Fibonacci relationships. This is illustrated in figure 5 by the black lines that join the similar points of the pentagonal holes. According to the calculated atomic positions, there are three distinct distances, 4.56, 7.38 and 11.94 Å, between

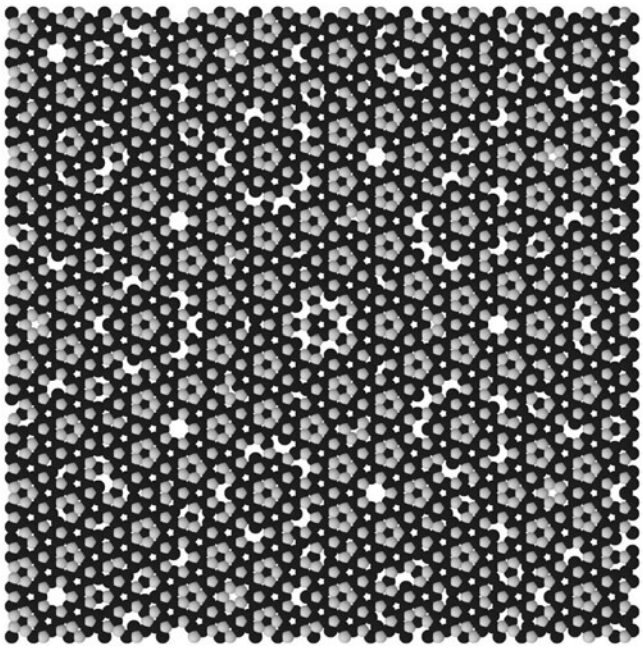

Figure 6. The distribution of atoms within an area of 160 Å × 160 Å on a corrugated surface perpendicular to a fivefold axis. The corrugated surface consists of the atoms on the plane at $z = 11.16$ Å (white balls) and the atoms on the plane at $z = 10.68$ Å (dark balls).

two adjacent lines. The ratios of the distances, 7.38/4.56 and 11.94/7.38, equal the golden mean τ within calculation errors. The distance 11.94 Å between lines L1 and L2 in figure 5 can be separated into two parts, 7.38 and 4.56 Å, by line L12 that connects the similar points of the imperfect pentagonal holes. These values are in agreement with STM measurements: narrower separation $N = 7.38 \pm 0.38$ Å and wider separation $W = 11.81 \pm 0.39$ Å from [13], and narrower separation $N = 4.6 \pm 0.2$ Å and wider separation $W = 7.4 \pm 0.2$ Å from [16]. In fact, the sequential lines with the distances of 7.38 and 4.56 Å make the arrangement of line separations LSLSLL which is a segment of a Fibonacci sequence.

Figures 6 and 7 are another two 160 Å × 160 Å pictures showing the atomic distributions on the corrugated surfaces perpendicular to the fivefold axis formed by the atoms (white balls) on the higher plane at $z = 11.16$ Å and the atoms (dark balls) on the lower plane at $z = 10.68$ Å, and by the higher atoms (white balls) at $z = 15.24$ Å and the lower atoms (dark balls) at $z = 14.76$ Å, respectively. The fundamental features of figures 6 and 7 are the same as those of figure 5.

To summarize, the fivefold surface with terraces is a termination of the bulk structure, and the terminal plane is one of the two planes between which the spacing is the largest.

4.3. Terminal surfaces perpendicular to a twofold axis

The calculation shows that the inter-plane spacings have only three values, 0.56, 0.92 and 1.48 Å. The ratios of these spacings, 0.92/0.56 and 1.48/0.92, also equal the golden mean τ within calculation errors. The largest 'gap' is 1.48 Å. The smallest interval is 0.56 Å. If we consider the densities of thin layers with thickness less than 0.6 Å instead of densities of single bulk planes as proposed in [29], the two atomic planes with the spacing of 0.56 Å can be

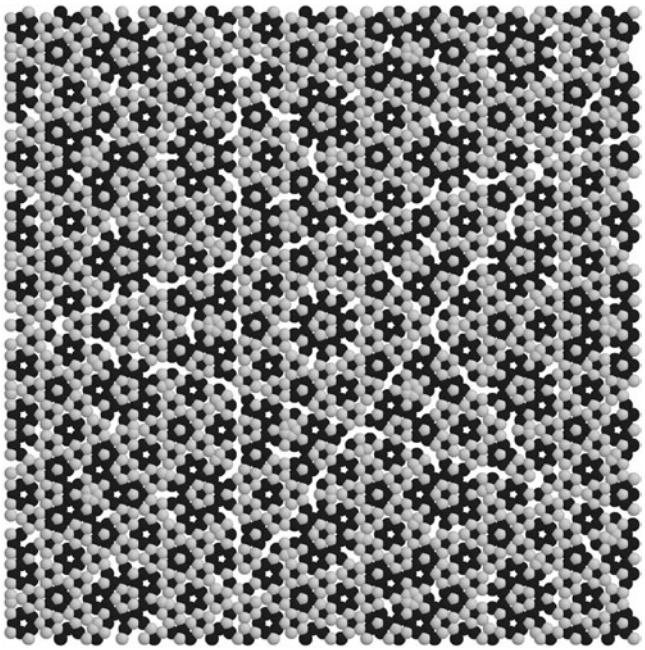

Figure 7. The distribution of atoms within an area of 160 Å × 160 Å on a corrugated surface perpendicular to a fivefold axis. The corrugated surface consists of the atoms on the plane at $z = 15.24$ Å (white balls) and the atoms on the plane at $z = 14.76$ Å (dark balls).

Table 1. The number of clusters and the number of atoms that belong to the PMCs, the incomplete PMCs and Bergman clusters in a box of 400 Å × 400 Å × 400 Å. In searching for the clusters, the marginal atoms, for which the distance from the atom to the surface of the box is less than 4.796 Å (radius of PMC), were not taken as centres of the clusters. The same treatment is also used for counting Bergman clusters for which the radius is 4.154 Å. (Note: inc-PMC_1: incomplete PMC with 27–30 atoms in the outer shell; inc-PMC_2: incomplete PMC with 15–30 atoms in the outer shell; Bergman: a central atom, 9–11 atoms in the inner shell with the radius of 2.819 Å ($r/a_{3D} = 0.618$), 20 atoms in the outer shell with the radius of 4.154 Å ($r/a_{3D} = 0.911$). Here, $a_{3D} = a_p/\sqrt{2}$, $a_p = 6.451$ Å is the lattice constant of the primitive 6D hypercubic lattice of the i-AlPdMn phase. N_c: number of clusters. N_t: total number of atoms. N_i: number of atoms that belong to the clusters. N_o: number of atoms that do not belong to the clusters.)

	N_c	N_t	N_i/N_t	N_o/N_t
PMC	66 879	3967 051	0.7652	0.2348
inc-PMC_1	103 531	3967 051	0.8766	0.1234
inc-PMC_2	543 859	3967 051	0.9996	0.0004
Bergman	75 570	4002 515	0.5199	0.4801

considered as a single thin layer or corrugated surface. The atomic densities of such thin layers are always less than 0.074 atom $Å^{-2}$. If the i-AlPdMn quasicrystal is terminated along the plane perpendicular to a twofold axis, the termination position must lie between the two planes with a spacing of 1.48 Å, because this spacing is the largest and both the terminal surface layers have the effectively largest atomic density (larger than 0.073 atom $Å^{-2}$). It is noted that some other planes, e.g., the plane at $y = 10.16$ Å, have larger atomic densities, e.g., 0.104 atom $Å^{-2}$, while the atomic densities of the neighbouring planes are very low, e.g., 0.001 atom $Å^{-2}$ for the plane at $y = 9.24$ Å and 0.019 atom $Å^{-2}$ for the plane at $y = 11.08$ Å. Thus the plane at

$y = 10.16$ Å cannot be the terminal surface; otherwise another terminal surface would have very low atomic density. Therefore, when the icosahedral AlPdMn quasicrystal is terminated on a twofold plane, a set of lower surfaces, such as the planes at $y = 2.40$, 6.28, 12.56, 18.84, 22.72 and 29.00 Å, or a series of upper surfaces, such as the planes at $y = 3.88$, 7.76, 14.04, 20.32, 24.20 and 30.48 Å, form the terraces normal to a twofold axis. The step heights of the successive terraces follow the rule of the Fibonacci sequence with two incommensurable values, 3.88 and 6.28 Å. These values of the step heights are very close to the STM results, 3.6, 6.2 and 9.5 Å for the twofold surface [29]. It is also noticed that very few step heights may have the value of 2.40 Å that equals $3.88\ \text{Å}/\tau$.

4.4. Terminal surfaces perpendicular to a threefold axis

The distances of neighbouring atomic planes have five values, 0.20, 0.33, 0.53, 0.65 and 0.86 Å. The largest 'gap' is 0.86 Å, which is much smaller than the largest spacing 1.56 Å for fivefold planes and 1.48 Å for twofold planes. The largest atomic density is 0.065 atom Å^{-2}, which is also smaller than the largest densities for the fivefold and twofold planes. In contrast with the case for fivefold and twofold planes, one can frequently find segments that consist of four or three sequential planes with the inter-plane distance of 0.86 Å and the nearly largest atomic density of 0.060–0.065 atom Å^{-2}. If the quasicrystal is separated following the biggest 'gap' of 0.86 Å, the two new surfaces will not be able to share a common feature, or a single smooth atomic plane on the surface will be at the largest distance of 0.86 Å from the inner atomic plane. Although it is difficult to predict definitely the cutting plane positions, the separation may take place in the largest 'gap' of 0.86 Å.

4.5. Atomic planes perpendicular to a pseudo-twofold axis

The distances of neighbouring atomic planes have only three values 0.18, 0.30 and 0.48 Å. The atomic plane spacings and the atomic densities (less than 0.048 atom Å^{-2}) are all very small. It is difficult to judge which position could be the termination position.

Comparing the results for the atomic planes perpendicular to fivefold, twofold, threefold and pseudo-twofold directions, the densest single smooth atomic planes in the bulk quasicrystal are the planes perpendicular to a twofold axis and located at, e.g., $y = 6.28$, 10.16 Å. However, if one considers two planes that are very close to each other as a single thin layer or corrugated surface, for example the two planes with spacing equal to 0.48 Å, the densest atomic layers are the fivefold layers with atomic densities of about 0.13 atom Å^{-2}. In this sense, if the quasicrystal is terminated in the largest gap, i.e. 1.56 Å, along a plane normal to the fivefold axis, both terminal surfaces are exactly the layer with the largest atomic density. The statement that the terminal surface is one of the pair of thin layers with the largest gap is consistent with the maximum density rule for surfaces of quasicrystals [29]. Hence, the surface perpendicular to the fivefold axis is the most stable surface among the three high-symmetry surfaces; the surface perpendicular to the threefold axis is the least stable surface. No flat surface perpendicular to the pseudo-twofold axis could be formed. It is easier to cleave the icosahedral AlPdMn quasicrystal along the plane perpendicular to a fivefold axis than in other directions.

5. Summary

According to the atomic positions in a box of 400 Å × 400 Å × 400 Å obtained by using the non-spherical model of i-AlPdMn phase [10] and the cut method, the surface structures of the i-AlPdMn phase are investigated. It is shown that, if the incomplete PMC is regarded as

the building block of the i-AlPdMn phase, 99.96% of the total atoms can be covered by these incomplete PMCs. For the fivefold surface, one of the pair of layers, which are 1.56 Å apart from each other, is expected to be the terminal surface that forms terraces. The pentagonal holes on the surface are the interspaces surrounded by neighbouring incomplete PMCs and have the depth of 2.04 Å. The step heights of the terraces form a Fibonacci sequence with two incommensurable values, 4.08 and 6.60 Å. The distances between two adjacent lines that connect similar points of the pentagonal holes obey the rule of the Fibonacci sequence with two incommensurable values, 4.56 and 7.38 Å. The average corrugation on the surface is 0.48 Å. For the twofold surface, the atomic plane, which is 1.48 Å apart from one of its neighbouring planes, is expected to be the terminal surface. These planes can also form terraces for which the step heights follow the Fibonacci sequence with two values, 6.28 and 3.88 Å. For the threefold surface, it is difficult to predict definitely the termination positions; however, the separation may take place in the largest 'gap' of 0.86 Å. Considering the densities in thin layers with thickness less than 0.6 Å, the densest layers are the layers with atomic density of about 0.13 atom $Å^{-2}$ and perpendicular to a fivefold axis. The layer with the largest spacing to one of its neighbours also possesses the maximum atomic density. Such layers are thought most likely to be the terminal surfaces. Hence, the surface perpendicular to the fivefold axis is the most stable surface, and the surface perpendicular to the threefold axis is the least stable surface among the three high-symmetry surfaces. No flat surface perpendicular to the pseudo-twofold axis could be formed. It is easier to cleave the icosahedral AlPdMn quasicrystal along the plane perpendicular to the fivefold axis than in other directions.

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References

[1] Janot C 1992 *Quasicrystals: a Primer* (Oxford: Clarendon)
[2] Boudard M, de Boissieu M, Janot C, Beeli C, Nissen H-U, Vincent H, Ibberson R, Audier M and Dubois J M 1992 *J. Phys.: Condens. Matter* **4** 10149
[3] Janot C 1996 *Phys. Rev.* B **53** 181
[4] Janot C 1997 *J. Phys.: Condens. Matter* **9** 1493
[5] Yang W, Feuerbacher M and Urban K 2002 *J. Alloys Compounds* **342** 164
[6] Ebert Ph, Feuerbacher M, Tamura N, Wollgarten M and Urban K 1996 *Phys. Rev. Lett.* **77** 3827
[7] Duneau M 2000 *Mater. Sci. Eng.* A **294–296** 192
[8] Quandt A and Elser V 2000 *Phys. Rev.* B **61** 9336
[9] Gratias D, Puyraimond F, Quiquandon M and Katz A 2000 *Phys. Rev.* B **63** 024202
[10] Fang A, Zou H, Yu F, Wang R and Duan X 2003 *J. Phys.: Condens. Matter* **15** 4947
[11] Yamamoto A, Takakura H and Tsai A P 2003 *Phys. Rev.* B **68** 094201
[12] Yamamoto A, Takakura H and Tsai A P 2002 *J. Alloys Compounds* **342** 159
[13] Schaub T M, Bürgler D E, Güntherodt H-J and Suck J B 1994 *Phys. Rev. Lett.* **73** 1255
[14] Papadopolos Z, Kasner G, Ledieu J, Cox E J, Richardson N V, Chen Q, Diehl R D, Lograsso T A, Ross A R and McGrath R 2002 *Phys. Rev.* B **66** 184207
[15] Ledieu J, McGrath R, Diehl R D, Lograsso T A, Delaney D W, Papadopolos Z and Kasner G 2001 *Surf. Sci.* **492** L729
[16] Ledieu J and McGrath R 2003 *J. Phys.: Condens. Matter* **15** S3113
[17] Barbier L, Le Floc'h D, Calvayrac Y and Gratias D 2002 *Phys. Rev. Lett.* **88** 085506
[18] Rouxel D, Cai T-H, Jenks C J, Lograsso T A, Ross A and Thiel P A 2000 *Surf. Sci.* **461** L521
[19] Gierer M, Van Hove M A, Goldman A I, Shen Z, Chang S-L, Jenks C J, Zhang C-M and Thiel P A 1997 *Phys. Rev. Lett.* **78** 467

[20] Diehl R D, Ledieu J, Ferralis N, Szmodis A W and McGrath R 2003 *J. Phys.: Condens. Matter* **15** R63
[21] Shen Z, Raberg W, Heinzig M, Jenks C J, Fournee V, Van Hove M A, Lograsso T A, Delaney D, Cai T, Canfield P C, Fisher I R, Goldman A I, Kramer M J and Thiel P A 2000 *Surf. Sci.* **450** 1
[22] Shen Z, Jenks C J, Anderegg J, Delaney D W, Lograsso T A, Thiel P A and Goldman A I 1997 *Phys. Rev. Lett.* **78** 1050
[23] Ho T L 1991 *Quasicrystals, the State of the Art* ed D P DiVicenzo and P J Steinhardt (Singapore: World Scientific) p 403
[24] Van Samaalen S 1999 *Acta Crystallogr.* A **55** 401
[25] Kasner G, Papadopolos Z, Kramer P and Bürgler D E 1999 *Phys. Rev.* B **60** 3899
[26] Elser V 1996 *Phil. Mag.* B **73** 641
[27] Levine D, Lubensky T C, Ostlund S, Ramaswamy S, Steinhardt P J and Toner J 1985 *Phys. Rev. Lett.* **54** 1520
[28] Steurer W and Haibach T 1999 *Physical Properties of Quasicrystals* ed Z M Stadnik (Berlin: Springer) p 51
[29] Papadopolos Z, Pleasants P, Kasner G, Fournée V, Cai T, Jenks C, Thiel P, Ledieu J and McGrath R 2004 *Phys. Rev.* B **69** 224201