A maximum density rule for surfaces of quasicrystals

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Abstract

A rule due to Bravais of wide validity for crystals is that their surfaces correspond to the densest planes of atoms in the bulk of the material. Comparing a theoretical model of i-AlPdMn with experimental results, we find that this correspondence breaks down and that surfaces parallel to the densest planes in the bulk are not the most stable, i.e. they are not so-called bulk terminations. The correspondence can be restored by recognizing that there is a contribution to the surface not just from one geometrical plane but from a layer of stacked atoms, possibly containing more than one plane. We find that not only does the stability of high-symmetry surfaces match the density of the corresponding layer-like bulk terminations but the exact spacings between surface terraces and their degree of pittedness may be determined by a simple analysis of the density of layers predicted by the bulk geometric model.

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The surfaces of quasicrystals offer rich potential both for technological applications and for fundamental science. Their tribological properties, such as low coefficient of friction, low surface energy and oxidation resistance have been well documented and have motivated many studies of the clean surfaces of these materials, see Ref. [2] and work cited there. These studies have led to significant progress in the past few years, especially in the case of the aluminium-based icosahedral quasicrystals. The surfaces of these materials have been shown to be perfect “slices” of the bulk structure, with only 3 distinct step heights being observed. However a significant limitation of this work has been that there was no understanding of which bulk planes might be expected to be seen as surface terminations.

A rule with wide validity for crystals, first suggested by Bravais and later refined by others, is that “the largest facets have the densest packing of atoms”, usually interpreted as meaning that, by and large, the most stable surfaces are those parallel to the densest atomic planes in the bulk. It has been observed that this does not hold for i-AlPdMn, where the most stable surfaces are orthogonal to the fivefold axes but the densest planes in the bulk model of Boudard et al. are orthogonal to the twofold axes. For quasicrystals we propose modifying the rule to use densities of thin layers of bulk planes instead of densities of single bulk planes. For icosahedral quasicrystals we consider 0.6 Å layers. This is suggested by the fact that, whereas the distances between neighboring high density planes in the bulk of an ordinary crystal are 1.5-2.0 Å, in the geometric bulk model of F phase icosahedral quasicrystals the distances are 0.2-1.5 Å. We show that the observed surface structure of i-AlPdMn is consistent with this modified rule.

To demonstrate this new rule we first present experimental evidence on the stability and appearance of surfaces of i-AlPdMn derived from scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) measurements. The fivefold surfaces of i-AlPdMn (Fig. I) show large scale terraces and are stable. In Ref. [8] we showed that the intervals between terraces on the fivefold surfaces of i-AlPdMn match a Fibonacci sequence of planes in the model \( M \) with \( S = 4.08 \) Å and \( L = \tau S = 6.60 \) Å. In Refs. [2, 10] it was found that the fivefold bulk terminations of i-AlPdMn consist of two atomic planes 0.48 Å apart.

According to Ref. [2] both twofold and threefold surfaces facet, i.e. they are less stable. The twofold surfaces show pitted small scale terraces, see Fig. II(a-c). The threefold surfaces of i-AlPdMn show clear medium scale terraces with depressions (pits), see Fig. III.

We explain this experimental evidence in terms of the particular geometric model \( M \).
FIG. 1: [see file F1.jpg] (I) STM image (1750 × 1750 nm$^2$) of the fivefold surface of i-AlPdMn. (II) twofold surface of i-AlPdMn: (a) STM image of a terrace-stepped twofold surface [500 × 500 nm$^2$]. (b) Flattened image covering three terraces and two steps [160 × 160 nm$^2$]. (c) Height profile along the line in (a) with step height value. (d) LEED pattern at 50 eV. (III) Two STM images of a threefold surface of i-AlPdMn, each 800 × 800 nm$^2$. These images overlap in about half their area.

FIG. 2: [see file F2.jpg] The coding windows $W_q$, $W_a$, $W_b$ define the geometric model $M$ of atomic positions based on the icosahedral $D_5$ module $M_F$: (a) $W_q$ with edge lengths $\tau^{-1} \sqrt{5}$ and $\sqrt{5}$. (b) $W_a$ is a triacontahedron of edge length $\tau^{-1} \sqrt{5}$. (c) $W_b$ is obtained by taking the marked tetrahedra away from the triacontahedron of edge length $\tau \sqrt{5}$.

$[7, 8, 9]$ of the quasicrystals i-AlPdMn $[6]$. This model is a superposition of three icosahedral quasilattices, $q$, $a$ and $b$, of atomic positions in the physical space $E_\|$. As described in Ref. $[2]$ and references cited there, there is a coding space, $E_\perp$, containing three windows, $W_q$, $W_a$ and $W_b$ (shown in Fig. 2), and a $*$-map that takes each point of one of the quasilattices into a point of the corresponding window. The $*$-map is not continuous: it maps discrete unbounded quasilattices to dense point sets bounded by a window. Its usefulness is that it maps planes to planes and that the density function on planes orthogonal to a given axis, which is an erratic discrete function ($\rho(z_\|)$) in $E_\|$, is a continuous function ($\rho(z_\perp)$) in $E_\perp$ which can be graphed as in Figs. 3(I)-(III). For each of the five, two and threefold axes we use a standard distance, denoted by $\sqrt{5}$, $\sqrt{2}$ and $\sqrt{3}$, respectively. These are related by $\sqrt{3}/\sqrt{5} = \sqrt{5}/(\tau + 2) = \sqrt{2}/2 = 1/\sqrt{2(\tau + 2)}$, where $\tau = (1 + \sqrt{5})/2$. Below we take $\sqrt{5} = 4.56$ Å—the value for i-AlPdMn.

For ordinary lattices the density of points in a plane depends only on the orientation of the plane. For the $q$, $a$, $b$ quasilattices the density $\rho$ is a product of two factors: the module factor $[11]$ that depends on the orientation of the plane ($1/\sqrt{5}$, $1/4$ and $1/3$, respectively, for five, two and threefold planes) and the window factor which is the area of the section of the window by the corresponding plane in coding space (see Fig. 12 in Ref. $[2]$). We also use the fact that each plane orthogonal to a threefold or fivefold axis contains points of one quasilattice only and each plane orthogonal to a twofold axis contains points of all three quasilattices, $q$, $a$ and $b$. The top row of Table [I] gives the maximum density of planes in the main symmetry directions and the bottom row the maximum density of terminations.
TABLE I: Row 1 gives the maximum atomic densities of planes in the model \( M \) and Row 2 the maximum atomic densities of the layer-like terminations.

|            | fivefold | twofold | threefold |
|------------|----------|---------|-----------|
| Densest planes | 0.086 Å\(^{-2}\) | 0.101 Å\(^{-2}\) | 0.066 Å\(^{-2}\) |
| Densest layers | 0.133 Å\(^{-2}\) | 0.101 Å\(^{-2}\) | 0.066 Å\(^{-2}\) |

(described below). As for the similar model with spherical windows \([6]\) used in Ref. \([5]\), there are twofold planes denser than the densest fivefold or threefold planes even though experimental evidence indicates that the fivefold surfaces are the most stable \([5]\).

In the light of this, and the fact that fivefold terminations are observed to consist of a pair of neighboring planes, we propose a modification to the Bravais rule to take into account close neighboring planes. We consider bulk layers of a quasicrystal, unions of close neighboring planes (for icosahedral quasicrystals, modeled by \( M \), within a 0.6 Å range), and define a bulk termination to be a layer with close to maximum density among all parallel layers. We then expect the more stable surfaces to correspond to the denser terminations.

To test this we now describe the terminations of our model \( M \) in the five, two and threefold directions and compare them with the experimental data. In each of these directions three different inter-plane distances occur, in each case in the ratios 1 : \( \tau \) : \( \tau^2 \). In Å units these are: 0.30, 0.48, 0.78 (fivefold); 0.57, 0.92, 1.48 (twofold); and 0.20, 0.33, 0.53 (threefold).

The densest fivefold layers of thickness less than 0.6 Å are pairs of planes 0.48 Å apart. This agrees with experimental evidence \([2, 10]\). Fig. 3(I) graphs the atomic density, \( \rho(z_{\perp}) \), of \((q, b)\) pairs of planes as a function of position along a fivefold \( z_{\perp}\)-axis in coding space \( E_{\perp} \). It is close to its maximum along a clear plateau of width about \((2\tau^2/(\tau + 2)) \frac{\tau}{5} \). The interval of this plateau (a “window” \( W \)) codes a Fibonacci sequence along a fivefold axis of \( E_{\parallel} \) with \( S = (2\tau/(\tau + 2)) \frac{\tau}{5} = 4.08 \) Å and \( L = \tau S = 6.60 \) Å, in agreement with \([8]\). A slightly longer interval codes a decorated Fibonacci sequence \([2]\) that includes steps of height \( \tau^{-1}S = 2.52 \) Å too, detected in Ref. \([12]\). Note that there is not such a clearly defined plateau as in Fig. 3(I) when the windows in Fig. 2 are replaced by spherical approximants. As well as the \((q, b)\) layers there are also \((b, q)\) layers in \( M \) whose density graph is the mirror image of Fig. 3(I) and codes another Fibonacci sequence of equally dense layers. These are not seen as surface terminations, the planes observed on the surface can be identified as type...
FIG. 3: [see file F3.jpg] (I) The densest fivefold layers are \((q,b)\) pairs of planes a distance 0.48 Å apart. The \(q\)-curve is the density of atomic positions on \(q\)-planes and the \(b\)-curve, the density on \(b\)-planes. The full curve is the sum of these densities. The support of the plateau of the full curve defines the terminations and is the coding window of the Fibonacci sequence of terraces of terminations seen on fivefold surfaces. The height of the plateau is the density of fivefold terminations. (II) The densest twofold layers are single planes, which contain atomic positions of types \(q\), \(b\) and \(a\). The curve graphs the density of planes along a twofold axis in coding space. (III) Graphs of the densities of a \((b,q,a)\) triple of threefold planes with spacings: \(b\)-plane, 0.20 Å, \(q\)-plane, 0.33 Å, \(a\)-plane. The plateau in the graph of the combined density defines the terminations, its height giving their density.

\(q\) by the presence of a local configuration called a “ring” [2]. This can perhaps be understood from the densities of the parallel planes next above and below the layers: above a \((q,b)\) layer there is a low density plane and below a high density plane. For the mirror-image \((b,q)\) layer the neighboring planes are mirrored too.

The densest twofold layers are single planes. In Fig. 3(II) we can identify a not very sharply defined plateau of width about \((\tau^2/2)\) that defines the twofold terminations. A window of this width on a twofold axis in \(E_{\perp}\) encodes a Fibonacci sequence of terminations along a twofold axis of \(E_{\parallel}\) with \(S = (\tau^2/2) = 0.63\) nm, \(L = \tau S = 1.02\) nm. These gaps are close to the steps between terraces (0.62 nm and 0.95 nm) in Fig. 1(II)(c). Increasing the width of the window by a factor \(\tau^2\) would reduce the lengths of intervals in the Fibonacci sequence by \(\tau^{-2}\), making them 0.24 nm and 0.36 nm corresponding to the depths of the depressions in the terraces in Fig. 1(II)(c).

The densest threefold layers are \((b,q,a)\) and \((a,q,b)\) triples of planes of with distances 0.20 Å between the \(b\) and \(q\) planes and 0.33 Å between the \(q\) and \(a\) planes. The graph of the densities of the \((b,q,a)\) layers as a function of position in coding space is shown in Fig. 3(III) and has a wide plateau-like area around its maximum. This is in qualitative agreement with the medium scale terraces that spread over an area of about \(1000 \times 1000\) nm\(^2\) on the threefold surface shown in Fig. 1(III). In the threefold case (unlike the fivefold case) there are single \(b\) planes as dense as the densest threefold terminations.

The second row of Table 1 gives the maximum densities of five, two and threefold termi-
nations for the model $\mathcal{M}$, which are in the order fivefold, twofold, threefold.

We suggest that, with our modified definition of “termination”, the Bravais rule that the densest bulk terminations correspond to the most stable surfaces may be widely applicable to quasicrystals. Moreover the shape of the graph of the density of layers as a function of position in coding space determines the appearance of the corresponding surface: if the maximum of the function has the form of a flat plateau, as for the fivefold and threefold layers in Figs. 3(I) and 3(III), then the surfaces have a strong terrace-like character, as in Figs. 1(I) and 1(III). The terraces correspond to bulk layers of almost equal density and are equally probable as surfaces. On the other hand, the sharper peak for the twofold layers in Fig. 3(II) determines the more fragmented appearance of the twofold surface with small scale terraces as in Fig. 1(II)(a): different terraces correspond to bulk layers of different densities, and are not equally probable.

We have also observed that this modified density rule is valid for i-AlCuFe and we expect that it should apply to all icosahedral quasicrystals. We have preliminary indications that this rule can be extended to the so-called two-dimensional aperiodic materials (for example the family of decagonal quasicrystals), and expect that such considerations may apply to the surfaces of quasicrystal approximant phases and other complex metallic alloys.

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