Tiling of the five-fold surface of Al$_{70}$Pd$_{21}$Mn$_9$

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The nature of the five-fold surface of Al$_{70}$Pd$_{21}$Mn$_9$ has been investigated using scanning tunnelling microscopy. From high resolution images of the terraces, a tiling of the surface has been constructed using pentagonal prototiles. This tiling matches the bulk model of Boudard et al. (J. Phys.: Cond. Matter 4, 10149 (1992)), which allows us to elucidate the atomic nature of the surface. Furthermore, it is consistent with a Penrose tiling $T^{s((P1)r)}$ obtained from the geometric model based on the three-dimensional tiling $T^{d(2F)}$. The results provide direct confirmation that the five-fold surface of i-Al-Pd-Mn is a termination of the bulk structure.

61.44 Br, 68.35 Bs, 82.65 Mn

Since their discovery, quasicrystals have extended the boundaries of our knowledge, most strikingly in the redefinition of the crystal undertaken by the International Union of Crystallography in 1991 [2]. The reason for this lies in their unusual aperiodic structure, which in the case of i-Al-Pd-Mn and i-Al-Cu-Fe has been described mathematically with reference to a six-dimensional lattice $D_6$ [3,4]. The fact that a three-dimensional atomic model [2] can be based on a three-dimensional tiling projected from the $D_6$ lattice [5] leads us to expect the five-fold planes of the model to be related to a two-dimensional Penrose-like tiling [6,7].

The unusual tribological behavior observed for quasicrystals raises questions concerning the nature of their surfaces [8]. Systematic studies by Gellman and coworkers indicate that the static friction coefficient for i-Al-Pd-Mn (on itself) is lower than that of most pure metals, and the slip-stick behavior commonly observed on crystalline surfaces is not present [8]. A complete understanding of these observations requires a knowledge of the quasicrystal surface structure [9]. It can not be assumed a priori that a quasicrystal surface is aperiodic itself or that it reflects a perfect truncation of the bulk structure. If this is the case, however, we would expect the structure of that surface to reflect the symmetry of a two-dimensional Penrose tiling [6,7]. Until now, however, this direct link between theory and experiment has not been made.

This is partly because the aperiodic nature of quasicrystals makes it difficult to determine their surface structure. Surface diffraction techniques can not be exploited to achieve a full structural determination as they rely on a formalism developed largely for periodic structures [10]. Scanning probe microscopies offer an alternative, but even with these methods atomic resolution has so far proved elusive. It has been variously suggested that this is an inherent limitation of the electronic structure of these surfaces [11] or a consequence of defect-like protrusions observed in all studies to date [12,13]. In previous work, we introduced an approach based on tiling of scanning tunnelling microscopy (STM) images using regions of high contrast as vertices [14]. Though this approach produced partial tilings, the presence of large protrusion defects on the surface introduced breaks in the tiling and comparison with models of the surface was not possible.

In this study we carry this tiling approach to fruition, using a combination of experimental and theoretical methods. A refined surface preparation technique has led to terraces which are free from the protrusions found in previous STM studies [13,14]. This in turn has led to better resolution STM images which together with the structural perfection, allows us to derive an experimental tiling over a lateral range of ~100 Å. By comparison with the experimentally derived bulk model of Boudard et al. [7], we identify possible structural entities on the surface. We also demonstrate that the experimental tiling matches the two-dimensional tiling $T^{s((P1)r)}$, derived from a well established geometric model of the bulk [5,8].

The quasicrystal sample was grown using the Bridgman method and polished using 6µm, 1µm and 0.25µm diamond paste on Texmet cloth for one hour. The ultra-
high vacuum (UHV) preparation consisted of five sputter/anneal cycles. The sputtering angle was at grazing incidence (20°-30°); Ar gas was used at 500 eV and each sputter lasted 90 minutes. Each annealing was to 970 K for 120-150 minutes. After this procedure, the LEED pattern had five-fold rotational axes and exhibited a low background, with sharp peaks. We note that this temperature is at the upper end of the range known to produce quasicrystalline surfaces [18].

FIG. 1. (a) 100 × 100 Å² high resolution STM image of a flat terrace (V = 1 V, I = 0.3 nA). A pentagonal hole (circled) and a pentagon have been outlined. (b) 50 × 50 Å² high resolution STM image (V = 1 V, I = 0.3 nA). Several pentagons have been outlined. A Fast Fourier Transform (FFT) of the image in (b) is shown as an inset.

This preparation procedure leads to very large flat terraces (up to 1500 Å wide). Images from the terraces were then obtained which display a higher resolution than those in any previously published STM work [13-16].

FIG. 2. Tiling of Fig. 1(a) derived as described in the text.
This tiling is not necessarily unique, and the tiles themselves contain internal structure; but this is precisely what is to be expected for this surface, as can be shown by comparison with the experimentally derived model of Boudard et al., based on x-ray and neutron scattering measurements [17]. Fig. 3(a) shows one plane from this model, which contains only aluminum atoms. The experimentally derived tiling of Fig. 2 is shown superimposed on this plane without scaling. Fig. 3(b) shows that within the pentagons described above, other atoms are also expected to be present, which in turn will give rise to high contrast areas within the pentagons on the STM images. This is demonstrated in Fig. 3(c) [17].

We now show that this tiling is also contained within the Katz-Gratias-Elser geometric model [3,4]. The metric model consists of the three-dimensional quasicrystalline tiling $T^{(2F)}$ derived from a six-dimensional lattice, face-centered hypercubic lattice $D_6$. This tiling is decorated by Bergman (and automatically Mackay) polytopes to give the atomic positions [3]. All of the vertices of the $T^{(2F)}$ tiling can be embedded in a sequence of planes orthogonal to a five-fold symmetry axis of an icosahedron [20].

In some of these planes a quasiperiodic tiling $T^{*(A_4)}$ appears (20 and refs. therein). The prototiles in $T^{*(A_4)}$ are golden triangles. The edges of the triangles in the tiling are parallel to the two-fold symmetry axes of an icosahedron (“two-fold directions”) and are of two lengths related by the golden ratio $\tau$. As an intermediate step, we locally derive the tiling $T^*$ with pentagon, acute rhombus and hexagon as prototiles from the quasilattice of the tiling $T^{*(A_4)}$, as shown in Fig. 1(left side). The tiling has an inflation factor $\tau$.

Keeping all acute rhombuses from the tiling $T^*$, we replace each hexagon by two overlapping pentagons. Now we randomly choose one of the pentagons from each overlapping pair, and unify the rest of the hexagon(s) with the neighboring acute rhombus. This process is indicated by an arrow in the centre section of Fig. 4. In this way we obtain either a crown or a pentagonal star to replace the neighboring acute rhombus, and the result is a tiling $T^{*(P1)r}$, see the right-hand side of Fig. 4. The tiling $T^{*(P1)r}$ is a partly random variant of the Penrose (P1) tiling, $T^{*(P1)}$ [21].

The tiling $T^{*(P1)r}$ clearly matches the geometry of the experimentally derived tiling shown in Fig. 2. We now compare the edge-length of the tiles to the experimental value of 8.0±0.3Å. The scaling for the tilings derived above from the model is implicit from previous work [23,24]; the edges of the tilings $T^{*(A_4)}$, $T^*$, and $T^{*(P1)r}$ are of length 12.553 Å. However by an investigation of the window in perpendicular space $E_\perp$ of the atomic positions for the plane in the model which we estimate...
most closely corresponds to the experimental one we may show that the minimal edge length for a $P1(\tau)$ tiling is $\tau^{-1}12.55 \text{ Å}=7.758 \text{ Å}$. Therefore within the geometric model, in a plane that corresponds to that of Fig. 2, a tiling such as in Fig. 4 exists with an edge length 7.758 Å, in excellent agreement with the experimental observations.

Our data and analysis provide dramatic confirmation of the bulk termination of this surface which has been suggested by other workers. The LEED analysis of Gierer and co-workers indicated that the surface is consistent with the bulk quasicrystallinity and is an Al termination [1,2]. X-ray photoelectron diffraction (XPD) studies are also consistent with a quasicrystalline surface nature [14]. Previous scanning tunnelling microscopy (STM) studies have all presented similar images of the quasicrystalline surface [12-14] having a lower resolution than those presented here (the degree of resolution can be put on a quantitative basis using radial distribution functions (RDF) from autocorrelation patterns (not shown)). Shen et al., using an autocorrelation analysis showed that the surface structure is consistent with a bulk structure based on truncated pseudo-Mackay icosahedra or Bergman clusters [1,4]. Schaub et al. [1] interpreted their STM images in terms of an Amman pentagrid model with Fibonacci relationships between structural elements within the terraces and across steps on the surface. Later, these measurements were shown to be in correspondence with the Katz-Gratias-Elser geometric model [3,4] for the atomic positions [20,22]. However the lower resolution of these measurements precluded their analysis using the tiling approach described in this paper.

The ability to prepare surfaces having the structural perfection observed here will facilitate the precise characterization of ordered molecular adsorption, friction and adhesion on quasicrystal surfaces. In previous work on the adsorption of $C_{60}$ molecules of the $\alpha$-Al-Pd-Mn surface, although local areas were found in which the molecules had Fibonacci scaling relationships, on a larger scale the correlation was broken by the presence of defects [24]. Surfaces of the quality described above should enable the formation of better ordered overlayers.

To summarize, very high resolution STM images of flat terraces of the five-fold $Al_{12}Pd_{21}Mn_{19}$ surface have been presented. A tiling of the surface based on pentagons of edge $8.0 \pm 0.3\text{Å}$ has been experimentally derived. This tiling is shown to be consistent with the geometric model based on the $T^{(2\theta)}$ tiling, and with the experimentally derived model of Boudard et al. [17]. These results point clearly to a bulk termination of this surface and lend support to the bulk models of this complex material.

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