

Dodecagonal oxide quasicrystals deciphered

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Since the discovery of dodecagonal quasicrystals in two-dimensional oxides a decade ago, a variety of related periodic approximant structures have been observed in the different combinations of ternary oxides and supporting metal substrates [1-5]. With the recent experimental validation of the structure model by Cockayne *et al.*, a new level of understanding for this class of aperiodic materials is reached [1, 6]. It allows to classify the wealth of related periodic structures by stoichiometric means and structural aspects.

In this talk, the validated atomic structure of oxide quasicrystals will be presented together with an overlap-free recursion rule for the Niizeki-Gähler tiling and a tiling decoration scheme [1]. In addition, the most recent results obtained for two-dimensional films of Ba-Ti-O on Pd(111) are discussed. We will demonstrate how the six different ordered phases in this system are explained by Ba density variations [4]. Going beyond this exemplary case, at least 13 periodic structures related to oxide quasicrystals have been observed in the different materials combinations so far. Almost all of these structures include a patch of the parent quasicrystal (pQC) tiling in their unit cells. However, in a strict sense only those structures should be called approximants that are purely consist of a given motif of the pQC. We will present a classification scheme that extends the notion of approximants. It covers structures that periodically repeat pQC patches, in which the tiling element sequence is flipped, or include vertex configurations that are not allowed for the pQC. In addition, we introduce pseudo-approximants as structures that host tiles in the unit cell, which are not present in the pQC. We distinguish structures that are indexable by the projected unit vectors of the higher dimensional periodic lattice and that aren't and introduce a measure for the deviation of the unit cell from a patch of the pQC. The signatures of all classes of approximants for the two-dimensional square-triangle-rhombus tiling are discussed not only in parallel space, but also in reciprocal space and internal space.

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Driving honeycomb networks into dodecagonal quasicrystals

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Recently, the atomic structure of the 2D oxide quasicrystal (OQC) has been solved by SXRD [1]. OQCs are made from Ti_nO_n rings with $n = 4, 7, 10$ with Ba or Sr occupying the 7- and 10-member rings (Figure 1). The underlying Ti_nO_n network of the dodecagonal square-triangle-rhombus tiling can be derived from a honeycomb network by a sequence of ring transformations. The most important mechanism in this context is the Stone-Wales transformation that turns four $n = 6$ rings in two $n = 5$ and two $n = 7$ [2]. In OQCs, this transformation is facilitated due to alkaline earth metal ions residing in the honeycomb pores. DFT calculations for a Ba decorated Ti_2O_3 honeycomb on Au(111) found electron transfer from the Ba to the metal support and subsequent dipole formation [3]. This leads to in-plane electrostatic repulsion of the Ba atoms governing the structure formation. The minimization of these electrostatic forces is a driving force towards OQC formation, since the individual dipole strength is reduced due to a lower height above the metal substrate for Ba and Sr residing in rings of $n > 6$ [1].

In application of this structural relationship, we present here the transformation of oxide honeycomb networks into dodecagonal quasicrystals. Starting from a bare Ti_2O_3 honeycomb structure on Pt(111), Ba has been gradually deposited until a coverage of 80% of $n = 6$ rings of the Ti_2O_3 honeycomb. Monitoring the work function, we find a decrease of 2 eV in total due to the increasing number of dipoles added to the oxide network. An annealing step in presence of oxygen at 870 K transforms the overlayer completely into the dodecagonal OQC. This transformation is accompanied with a work function increase by 0.8 eV. This increase confirms the reduction of the individual dipole strength for Ba in the OQC network sketched in Figure 1. The same approach is applied to a new materials combination, which is Sr-Ti-O/Pd(111). Using STM we follow the evolution of the pristine Ti_2O_3 honeycomb on Pd(111) upon incremental Sr deposition on the local scale. In this system, several Sr arrangements on the intact honeycomb grid are found for coverages below 2/3 of the $n = 6$ rings. At a coverage of 80% of the $n = 6$ rings, the honeycomb is again transformed into the dodecagonal square-triangle-rhombus tiling (OQC). This first-time observation of a dodecagonal quasicrystal in this system, illustrates the flexibility of this fabrication approach in the quest of designing 2D dodecagonal quasicrystals.

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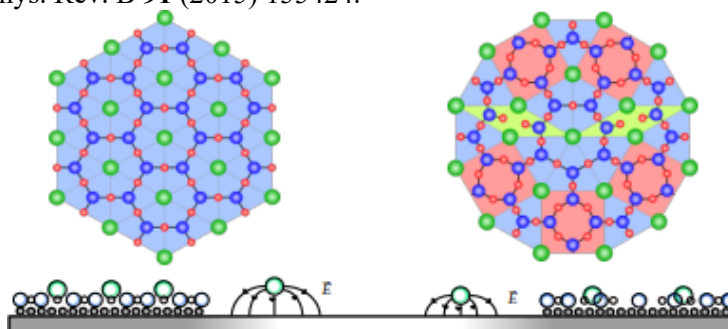


Figure 1: Left: Ba decorated Ti_2O_3 honeycomb and its sideview below. Right: Characteristic dodecagon tiling motif of the OQC. In the OQC network, the Ba height is reduced, which decreases the resulting dipole with its image charge. Ba: green, Ti: blue, O: red.

Structural investigation of the Ho-Au-Si(100) approximant surface

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RE-Au-Si (RE=Gd,Tb,Ho) quasicrystalline approximants have been identified for their remarkable magnetic and thermoelectric properties derived from their complex structure. As Tsai-type 1/1 approximants, their structures are built from a specific cluster type where the central disordered tetrahedron can be partially or totally replaced by a RE atom leading to alteration of magnetic and thermoelectric properties [1].

Unlike the bulk, the atomic structure and surface properties of these Au-Si-RE approximants remain unexplored. Several key questions await answers, including the stability of the clusters once exposed to the surface [2]. Here we propose a characterization of the (100) surface of the Tsai-type approximant $\text{Ho}_{1.04}\text{Au}_{4.85}\text{Si}_{1.324}$ using both experimental techniques and density functional theory (DFT). Low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) show a (2x1) surface reconstruction. The patterns present on the surface are comparable to the patterns present on one of the bulk planes for which DFT calculations were performed. The ultraviolet photoemission spectroscopy measurements and the bulk calculation of the electronic density of states show that the valence band is dominated by Au 5d states.

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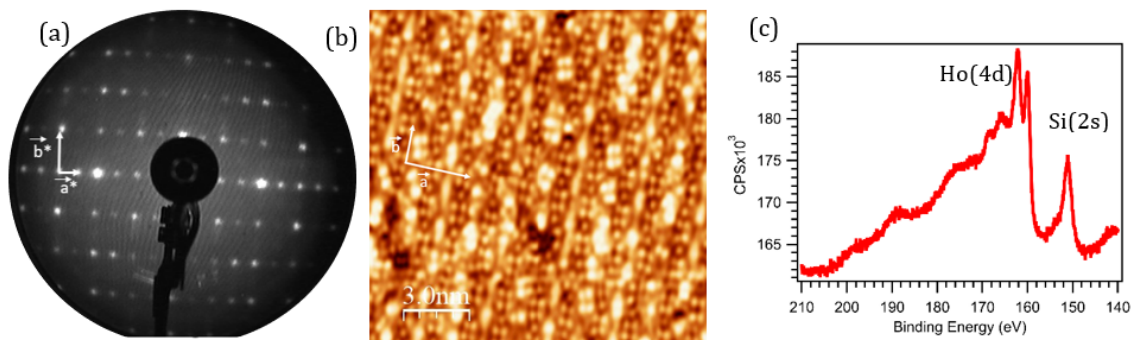


Fig.1: (a) LEED pattern at 22eV and (b) STM image of Ho-Au-Si(100); (c) XPS spectrum of Ho 4d and Si 2s core levels.

Quasiperiodic moiré patterns in twisted bilayers

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We see here that standard moiré patterns generated by twisting 2D layers on top of each other by a small angle $\alpha=2\delta$, are quasiperiodic of rank 4 in the general case and governed by the periodicity of the so-called 0-lattice introduced long ago by W. Bollmann [1,2] in the study of grain boundaries in metals and alloys. Using complex numbers for describing vectors in the layers plane, we find the explicit analytical form of the 0-lattice to be:

$$\mathcal{O} = \frac{i}{2 \sin \delta} e^{i\delta} (\Lambda + \tau)$$

where Λ is the lattice of the layer and τ the rigid body translation between the two layers. As typical moiré pattern of the bilayer, we choose the complex interference function:

$$\mu(z) = \varrho(ze^{-i\delta}) + \varrho((z + \tau)e^{i\delta}) \text{ with } \varrho(z) = \sum_{\chi \in \Lambda^*} f_{\chi} e^{2i\pi(\chi \cdot z)} \text{ where } \chi \cdot z = \Re(\bar{\chi}z)$$

leading to:

$$\mu(z) = \sum_{\chi \in \Lambda^*} 2f_{\chi} e^{2i\pi(\cos \delta(\chi \cdot z) + \varphi/2)} \cos 2\pi(\sin \delta(i\chi) \cdot z - \varphi/2)$$

showing that the moiré pattern decomposes in a sum of products of short wavelength terms (of arguments in blue), close to the periods of the layer structure, and long wavelength ones (in red) of periods twice the 0-lattice. We shall discuss the case where the quasiperiodicity of the pattern reduces to simple 2D periodicity when the rotation angle generates a coincidence lattice [3] in a way similar to quasicrystals transforming in periodic approximants for rational cuts.

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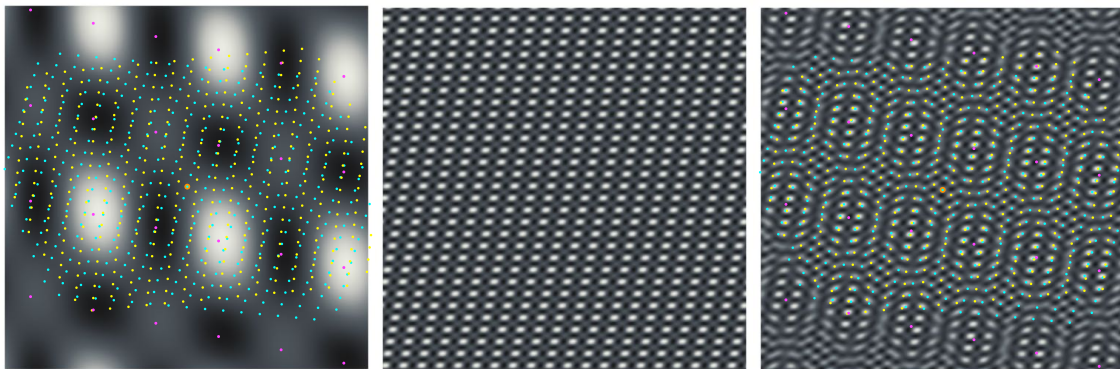


Fig.1: Example of moiré pattern (on the right) generated in an oblique bilayer decomposed into the sum of products of slow (on the left) and fast (in the middle) oscillating terms. Atom positions of the layers are the yellow and blue dots and the 0-lattice nodes are in red.