MS29-O4 Quasiperiodic canonical-cell tiling with cubic symmetry

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In canonical-cell tiling models [1] for icosahedral quasicrystals and their approximants, the atomic structure is presented as a packing of icosahedral clusters sitting on the vertices of a tiling composed of four standard polyhedra (A, B, C, and D), called the canonical cells. The canonical-cell geometry has indeed been observed in many approximants to icosahedral quasicrystals in different alloy systems. It is hence naturally expected that the same geometry holds also for icosahedral quasicrystals, and if so the canonical cells should be able to tile the space in a quasiperiodic manner so that icosahedral symmetry is globally retained. However, the existence of a tiling like the latter one has never been proved. In this work, an inflation rule for the canonical cells is worked out, and the existence of a quasiperiodic canonical-cell tiling has been confirmed for the first time. In the present inflation step, each canonical cell is expanded by a factor of τ^3 (τ: golden mean), and it is then divided into cells of the original sizes. Importantly, there are several different ways to divide expanded cells of the same shape (e.g. A) depending on their surrounding environment, still the division rules are determined locally. The atomic surface of this quasiperiodic canonical-cell tiling is studied by taking the perp-space images of the vertices. Interestingly, the atomic surface exhibits cubic symmetry rather than icosahedral symmetry.

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Keywords: quasiperiodicity, canonical-cell tiling, inflation rule, icosahedral, cubic

MS29-O5 Unit-cell twinning in quasicrystals

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The discovery of quasicrystals [1] rose questions about some basic concepts of crystallography [2,3]. Their structure and the corresponding electron diffraction patterns are explained by means of unit-cell twinning. The twinning operation is applied onto primitive golden rhombohedra, obtained by a small deformation of a parent cubic close-packed structure. The deformation accounts for the required space filling and for the five-fold point symmetry. Stacking of the multiply twinned star polyhedra ("stellae dodecangulae") keeps the golden rhombohedra of adjacent nano-domains in-phase, regardless of their actual separation. The golden rhombohedra form a kind of an intergrown multiply twinned structure, with no obvious boundaries between individual twins.

By taking into account only low-index first order reflections it is shown that unit cell twinning enables a complete reconstruction of the quasicrystalline reciprocal space, with all remaining reflections being accounted for by strong dynamical scattering or belonging to weak higher-order reflections at the outskirts of the zero-Laue zone (Fig.1). Simulated diffraction patterns are in good accord with the published experimental ones of $MnAl_6$ [4].

Twinning and tiling are two fully compatible approaches and quasicrystals do not violate any of the existing crystallographic concepts. The golden rhombohedra, which represent the basic building elements, are small in comparison with the huge cubic cells, suggested in the past. No atoms, and the close packed ones in particular, can be ordered at distances of the order of a few nanometers, because there are no natural forces acting at such distances. When structures with huge unit cells indeed appear, they can only be a result of at least two competing periodicities, which lock-in after relatively large distances. That is also the case in quasicrystals, where the star polyhedra are a result and not the origin of multiple twinning, whose driving force is obviously the need to fill the space exactly with the slightly collapsed parent structure.

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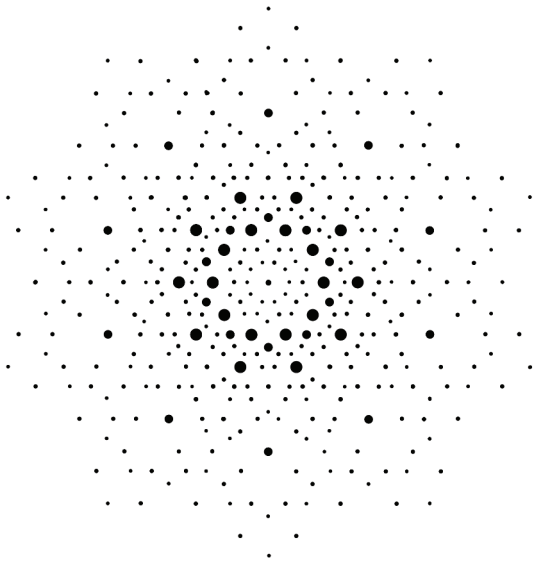

Figure 1. The simulated diffraction pattern along a quasicrystalline five-fold axis, composed of contributions from the multiply twinned golden rhombohedra and completed by dynamical scattering (the smallest radii).

Keywords: quasicrystals, unit-cell twinning, long-range order

MS30. Structure and function in coordination compounds

Chairs: Marijana Đaković, Janusz Lipkowski

MS30-O1 Hybrid porous materials

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That composition and structure profoundly impact the properties of crystalline solids has provided impetus for exponential growth in the field of crystal engineering [1] over the past 25 years. This lecture will address how crystal engineering has evolved from structure design (form) to control over bulk properties (function) with particular emphasis upon an underexplored class of porous material: hybrid organic-inorganic compounds. Whereas porous crystalline materials such as purely inorganic materials (e.g. zeolites) and those based upon coordination chemistry (e.g. Metal-Organic Frameworks and Porous Coordination Polymers) are well studied and offer great promise for separations and catalysis, they can be handicapped by cost or performance (e.g. chemical stability, interference from water or low selectivity) limitations. Hybrid Porous Materials, HPMs, are much less studied. HPMs are built from metal or metal cluster "nodes" and combinations of organic and inorganic "linkers" and they represent an opportunity to overcome the weaknesses associated with existing classes of porous material. Two prototypal families of HPMs will be addressed: (i) Pillared square grids with pcu topology can afford exceptional control over pore chemistry, pore size and binding energy for CO2.[2] Further, their performance is typically unaffected by moisture. (ii) mmo nets are based upon square grids linked by angular inorganic linkers such as chromate anions.[3] They also offer exceptional performance with respect to capture of CO2 and other polarizable gases. New results related to the structure and properties of pcu and mmo HPMs will be presented. 1. (a) Desiraju, G.R. Crystal engineering: The design of organic solids Elsevier, 1989; (b) Moulton, B.; Zaworotko, M.J. Chemical Reviews 2001, 101, 1629-1658. 2. (a) Burd, S.D.; Ma, S.; Perman, J.A.; Sikora, B.J.; Snurr, R.Q.; Thallapally, P.K.; Tian, J.; Wojtas, L.; Zaworotko, M.J. J. Amer. Chem. Soc. 2012, 134, 3663-3666. (b) Nugent, P.; Belmabkhout, Y.; Burd, S.D.; Cairns, A.J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M.J. Nature 2013, 495, 80-84, 2013. 3. Mohamed, M.; Elsaidi, S.; Wojtas, L.; Pham, T.; Forrest, K.A.; Tudor, B.; Space, B.; Zaworotko, M.J. J. Amer. Chem. Soc. 2012, 134, 19556-19559.

Keywords: crystal engineering, porous materials, carbon capture