

Quasicrystals Investigated Using Density-Functional Methods: Bulk, Surface and Thin Films

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Even a quarter of a century after the discovery of this new class of solids quasicrystals and their fascinating and sometimes puzzling properties continue to challenge both theory and experiment. The non-crystallographic point-group symmetry of quasicrystals with a 5-, 8-, 10- or 12-fold rotational axis is incompatible with translational periodicity, quasicrystals are aperiodic. Such structures can be described as regular periodic structures in n -dimensional ($n > 3$) space. For example, the structure of icosahedral quasicrystals with 5-fold rotational symmetry can be described by projecting a 6D hypercubic lattice onto 3D physical space. The challenge is to specify the atomic surfaces (or occupation domains) in the 3D “perpendicular” subspace. The precise determination of these atomic surfaces requires, in principle, the determination of the phase of the diffraction intensities. A further problem arises from the need to specify the chemical ordering determined by the shell structure of the occupation domains. But even if the quasicrystalline structure should be perfectly well known, theoretical calculations of their electronic, magnetic and dynamical properties are severely hampered by the absence of translational periodicity. Calculations must rely on a hierarchy of structures – so-called periodic or rational approximants which approach the quasiperiodic structure in the limit of infinite cell size. Even low-order approximants have a few hundred atoms per cell, simulations of quasiperiodic systems therefore also represent a challenge to current computational methods.

In my contribution I shall discuss the state-of-the-art of ab-initio calculations of the structural, electronic and magnetic properties of icosahedral quasicrystals in the bulk and at their free surfaces and investigate the possibility that the quasicrystallinity propagates to clusters and thin films condensed at the surface. Icosahedral (i) AlPdMn quasicrystals have been extensively studied by both experiment and theory. There is now a general agreement that their structure is reasonably well described in terms of triacontahedral occupation domains centred at the sites of a face-centred 6D hypercubic lattice. The distribution of the three chemical species is determined by the internal shell structure of the occupation domains. The physical properties of i-AlPdMn are characterized by (i) a deep minimum (a “pseudogap”) in the electronic density of states at the Fermi level and (ii) the observation of very large magnetic moments on a small percentage of the Mn atoms. As the formation of a large magnetic moment is usually dependent on a high local electronic density of states at E_F (the Stoner-Wohlfarth model), these two observations are not easily re-conciled – which property is intrinsic to the quasicrystalline structure and which is a consequence of defects ?

Structural refinements, based on total-energy minimization of large periodic approximants and electronic structure calculations have been used to demonstrate that in the ground-state i-AlPdMn is in fact a zero-gap semiconductor.¹ Gap-formation is found to be a consequence of the topology of the quasicrystalline lattice and requires a small modification of the surfaces separating the chemical shells of the occupation domains.²

Large magnetic moments on Mn-atoms are formed as a consequence of the presence of certain low-energy structural defects. The possibility to form such defects at a low energetic

cost is related to the cluster structure of the quasicrystals. This structure may be described in terms of interpenetrating Mackay and Bergman clusters. In the regions where the clusters overlap, the principles of their chemical decoration can be in conflict – hence a change in decoration causes only a small change in total energy. If a Mn atom in the center of a Mackay cluster is coordinated by two or more Pd atoms, a high magnetic moment is formed.

The investigation of the structure of quasicrystalline surfaces offers the possibility of a direct observation of the constituent clusters. Scanning tunnelling microscopy (STM) of the 5-fold surface of $i\text{-AlPdMn}$ with atomic resolution shows two very characteristic patterns nicknamed the “white flower” and the “dark star”. Detailed modelling studies³ have demonstrated that the structure of the surface may be described as a P1 tiling consisting of pentagons, pentagonal stars and thin rhombi. The pentagonal tiles are associated with Mackay clusters truncated at the surface. The orientation of the tiles is correlated with the position of the center on the cluster (occupied by a Mn atom) relative to the surface: “top” for Mn in the surface layer, “bottom” for Mn in a subsurface position. The “white flowers” are formed by top pentagons, i.e. by a Mackay truncated by a plane through its center and five surrounding truncated Bergman clusters. The “dark stars” are associated to the bottom pentagons with a sub-surface Mn atom in the center, surrounded by five Al-pentagons. The dark feature in the center is in fact a stable surface vacancy. Mn atoms in surface or near-surface positions have been found to be strongly magnetic.⁴

An interesting question is whether the quasiperiodic symmetry can propagate to nanostructures or thin films supported by the quasicrystalline surface. The nucleation and growth of Pb clusters and films has been studied in detail.⁵ In STM the formation of Pb clusters with 5-fold symmetry has been observed. Ab-initio modelling has demonstrated that these “starfish clusters” consist of 10 Pb atoms adsorbed at equatorially truncated Mackay clusters. At higher coverages these clusters coalesce to form quasiperiodic films – again the combined studies based on STM experiments and ab-initio calculation proved to be very fruitful.⁶ Quasiperiodic thin layers can also be formed by alkali overlayers. Ab-initio simulations showed that Na and K monolayers with an initial structure adapted to the P1 tiling of the surface spontaneously re-arranged to form a structure which is better described by a decorated DHBS tiling (consisting of decagons, hexagons, boats and stars).⁷ In this case, the quasiperiodic symmetry can even propagate to a second monolayer. Experiments have confirmed layer-by-layer growth and a pentagonal symmetry of the films, but are unable to resolve their structure at an atomic level. Finally we will discuss very briefly recent results from both STM and ab-initio calculation on the surfaces of decagonal quasicrystals⁸ and their approximants.⁹

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