Structures with 2D Quasiperiodicity

Axial quasicrystals have just one special axis $N$ with multiplicity $n$ larger than two. Along this axis they show a periodic sequence of atomic layers, which are ordered quasiperiodically in two dimensions. Theoretically, $n$ could be any integer and there are no principal geometrical restrictions. However, all stable axial quasicrystals known so far show five- or ten-fold symmetry only (cf. [99] and references therein). This is not too surprising since icosahedral coordination is the most frequent atomic environment type (AET) in intermetallic phases [26]. However, since polyhedra with icosahedral symmetry cannot be packed without gaps, they are distorted and/or mixed with other AET. There are a few reports on quasicrystals with 8- or 12-fold symmetry. However, these quasiperiodic phases are either metastable or of poor quality. Not a single quasicrystal with any other noncrystallographic symmetry has ever been reported.

For the hypothetical case of 2D structures, it has been argued that only quasicrystals based on quadratic irrationalities, $a + b\sqrt{c}$ ($a, b, c \ldots$ rational numbers), could be energetically stable [71]. Consequently, only quasicrystals with 5-, 8-, 10-, and 12-fold symmetries would be allowed. In the more realistic case of 3D QC, however, symmetries based on cubic irrationalities, such as 7-, 9-, 14- and 18-fold could also be possible according to this approach [84, 98].

It was also shown that weak matching rules, based on the alternation condition, exist for tilings with $n$-fold symmetry, where $n$ is either a prime number or the double of a prime number. This means that a ground state could exist for structures based on such tilings. Generally, in case of $n$-fold rotational symmetry the irrationality would be of order $\phi(n)/2$, i.e. a root of the algebraic equation $a_n x^n + a_{n-1} x^{n-1} + \cdots + a_1 x + a_0 = 0$, where $a_i$ are integers. $\phi(n)$ is Euler’s totient function, i.e. the number of all positive integers $k$ that are relatively prime to (do not contain any factor with) $n$, $\gcd(k, n) = 1$ and $k \leq n$ (see Table 8.1). The number $\phi(n)$ is also equal to the number of possible generators of the cyclic group $C_n$.

In 1985, the discovery of the first (metastable) axial quasicrystals, decagonal Al–Mn [11, 20], and dodecagonal Ni–Cr [53] was reported. The first stable
decagonal quasicrystal, Al$_{10}$FeNi$_3$, was actually discovered in 1982 [61], but not identified as quasiperiodic before 1994 [70]. The first report on a stable decagonal phase, Al$_{65}$Cu$_{20}$Co$_{15}$, was published in 1988 [46]. There are no stable heptagonal and octagonal phases known so far, and only one, rather poorly ordered, dodecagonal phase, Ta$_{1.6}$Te, has been reported in 1998 [25]. It should be mentioned here that the local axial symmetry and scaling properties in some proteins show rotational orders $n = 5, 7, 8, 9, 11$ [54–56].

8.1 Heptagonal Phases

No regular or semiregular polyhedra (Platonic or Archimedean solids) exist with rotational symmetry larger than five-fold. However, polyhedra with only axial $n$-fold symmetry (e.g. prisms or pyramids) are possible for arbitrary $n$. Indeed, (distorted) seven-membered rings are very common in the structures of ternary borides and borocarbides (see later). These structures can be seen as approximants of heptagonal quasicrystals. If approximants exist, why are no heptagonal quasicrystals known so far?

A tiling with seven-fold (or any other) symmetry can be constructed by the dual-grid method as easily as one with 5-fold symmetry (see also Sect. 1.2.4). It gets more complicated, however, if one tries to construct a structure based on a cluster with seven-fold symmetry. We demonstrate this by the example of local polysynthetic twinning of pentagonal and heptagonal clusters (e.g., pentagonal and heptagonal bipyramids, respectively) (Fig. 8.1).

The first pentagon P (nucleus) is twinned along its edges: $P + 5P \to P5P$. The twinning is repeated at the edges of the $\tau^2$-times larger (in diameter) aggregates: $P5P + 5P5P \to (P5P)5(P5P)$ and so forth. The local twinning procedure applied to heptagons, already leads in the first shell of neighbors to overlaps, which may cause problems in the case of real atomic clusters. This problem can be overcome if one does not try to build the quasiperiodic structure by overlapping heptagonal clusters but build the structure based on at least three different unit tiles.

The heptagonal tiling consists of three different rhombic prototiles (Fig. 8.2). The prototiles have a different frequency in the heptagonal tiling and the approximant, respectively. In the tiling the frequency of the three prototiles is proportional to their areas [119], while in the approximant it depends on the order of the approximant.