# Aperiodic crystals

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**Introduction**

Crystals are assemblies of atoms that exhibit a long-range positional order. The vast majority of the crystal structures are three-dimensionally (3D) periodic. That means that the structure of the whole crystal can be constructed as a periodic repetition of a small part of the crystal (unit cell) along three linearly independent directions. Aperiodic crystals lack this 3D periodicity, while they are still long-range ordered. Aperiodic crystals can be divided into three main classes:

1) Incommensurately modulated structures: These structures have an average 3D periodic structure, but the atoms are periodically shifted from their average position according to a modulation function with a period that is incommensurate with the periodicity of the basic structure*. The real structure is therefore not periodic (Fig. 1).
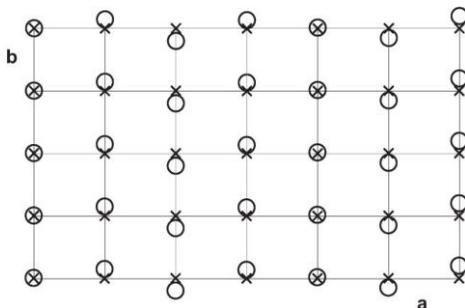


**Figure 1.** Schematic representation of a two-dimensional modulated crystal structure with one atom in the origin of the unit cell of the basic structure. Crosses represent the periodic basic structure, circles represent the positions in the modulated structure.

2) Composite crystal structures: These structures can be described as an intergrowth of two or more substructures (subsystems), each of them periodic in first approximation. The subsystems have a mutually incommensurate ratio of the unit cell dimensions in at least one direction. This incommensurability disturbs the periodicity of the whole composite structure. Moreover, the interactions between the subsystems lead to incommensurate modulations in both subsystems (Fig. 2).

*Incommensurate means that their ratio is not a rational number
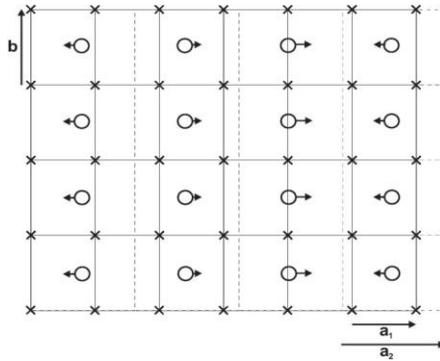
**Figure 2.** Schematic representation of a two-dimensional composite crystal with two subsystems. Crosses represent the first subsystem with one atom in the origin of the unit cell. Circles represent the second subsystem with one atom in the center of the unit cell. The arrows schematically denote the shifts of the atoms of the second subsystem due to the interactions with the atoms of the first subsystem. Shifts in the first subsystem are omitted for clarity.

3) Quasicrystals: Quasicrystals exhibit a non-crystallographic point-symmetry, for example a 5-fold or 8-fold axis. Such symmetry is forbidden in periodic structures. Quasicrystalline structures are found mainly in intermetallic alloys. They are different from modulated or composite structures in one important aspect: they do not have any chemically meaningful average structure. Instead, they can be described as a non-periodic tiling of several types of tiles/clusters (Fig.3). The structures of quasicrystals are described using a different approach from incommensurately modulated crystals and composite crystals, although in both cases the formalism involves embedding of the structures in higher-dimensional superspace.

**Reciprocal space of modulated crystals**
The diffraction pattern of both periodic and aperiodic crystals is discrete. This is a direct consequence of the long-range order in both structures. However, there is an important difference between the two classes of crystals: In contrast to periodic structures, the diffraction pattern of aperiodic crystals is not indexable with three integer indices. The diffraction pattern of modulated crystals consists of reflections corresponding to the periodicity of the basic structure (main reflections) and reflections corresponding to the modulation wave (satellites, Fig.4).
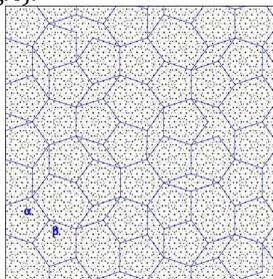


**Figure 3.** A projected electron density of a decagonal quasicrystal AlCoNi, with characteristic tile shapes (decagons, pentagons, rhombs and squashed hexagons). From Katrych et al. (2007)
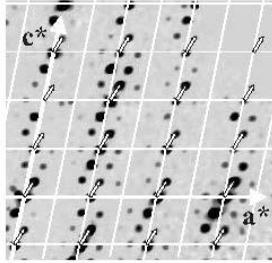
**Figure 4.** Diffraction pattern of the modulated -phase of $Na_2CO_3$ in the $h0l$ plane. Thin white lines connect main reflections. Satellites can be indexed with one wavevector $\mathbf{q}$ = $0.182\mathbf{a}^*+0.322\mathbf{c}^*$ (small white arrows). Satellites up to fourth order are visible. From Dušek et al. (2003).

Main reflections can be indexed with three basic vectors, while $d$ additional vectors (modulation vectors, called also commonly q-vectors) are necessary to index the satellites. These q-vectors can be expressed as a linear combination of the first three reciprocal vectors. For the most common case of d=1 (single modulation vector) we get:

$$\mathbf{q} = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*$$

Frequently, one or two components of the modulation vector are fixed to zero by the crystal symmetry. For a truly incommensurately modulated structure, at least one the components must be an irrational number.

The diffraction vector $\mathbf{h}$ of every Bragg reflection can then be indexed by (3+$d$) integers. For d=1 we get:

$$\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$$

**Superspace embedding of the diffraction pattern and electron density**

The diffraction pattern of an aperiodic crystal can be considered to be a projection on 3D space of a (3+$d$)$D$ weighted reciprocal lattice.

In the (3+$d$)$D$ reciprocal space the reciprocal vectors become linearly independent and form a (3+$d$)-dimensional reciprocal lattice.

The theory of the Fourier transform shows that a discrete Fourier spectrum indexable by $n$ integers can be always related to a periodic function defined in $n$ dimensions. Thus, we can always *construct* an $n$-dimensional periodic density function (superspace scattering density) that is the $nD$ inverse Fourier transform of the structure factors indexed in $n$ dimensions by $n$ integers:

For ordinary structures, $n$=3 and the density directly represents the real scattering density of the crystal. For modulated structures, $n$=3+$d$ and it can be shown that the real-space electron density of a modulated crystal can be obtained as a section through the superspace electron density perpendicular to the additional dimensions.

**Structure analysis of incommensurate structures**

Theory related to the description of aperiodic structures may appear rather involved. However, at least for modulated structures and composites the actual structure solution and structure refinement process is not very much different from standard periodic structures. The basic steps are identical: collection of diffraction data, indexing and integration of reflection intensities, symmetry determination and structure solution by one of the established methods, and then structure refinement. The major difference is in the description of the structure model. Instead of describing each atom by its position and displacement parameters, the atomic modulation function must be properly parametrized,

and the parameters refined. The task is facilitated by the dedicated software, especially by the crystallographic computing system Jana2006 (Petříček et al. 2014). This system automates most of the steps in the superspace analysis, and a solution and refinement of a simple incommensurately modulated structure may take only a few hours.

The main difficulty lies understanding the refined model. The structure is aperiodic, and hence there is an infinite variability of atomic arrangements in the structure, and the structure cannot be depicted in the traditional way without loss of information. However, a useful insight into the basic features of the structure can be obtained by plotting a sufficiently large, characteristic part of the structure (Fig. 5).
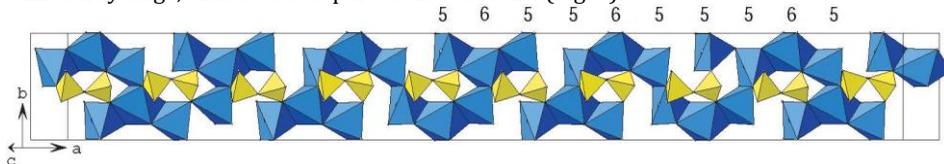


**Figure 5.** Modulated structure of chromium diphosphate. A small but characteristic part of the infinite aperiodic structure is shown. This part shows the principal features of the modulation: the variation of the coordination of the Cr atom between an elongated octahedron and tetragonal pyramid and variation of the bending angle of the $P_2O_7$ group. Numbers above the structure highlight the coordination number of the Cr atoms, showing an aperiodic sequence).

Less intuitive, but more accurate information about all possible configurations present in the structure is provided by so-called t-plots. These plots show a selected structural property (atomic position, interatomic distance, angle, valence etc.) as a function of the modulation phase. Such plots contain all values assumed by the property throughout the structure.

Understanding the structure analysis of incommensurately modulated structures and composites requires some effort. However, it is advisable for every crystallographer to have enough knowledge on the subject to be at least able to recognize such structure, and in case of need, seek advice in the literature or with an expert. An excellent, easy to read, yet accurate introductory article into the subject has been published by Wagner and Schönleber (2009). A book by Sander van Smaalen (2007) is then a comprehensive text covering all aspects of incommensurate crystallography, and is recommended for everybody wishing to study the subject in detail. Book by Janssen Chapuis and de Boissieu (2007) is another useful source of information, which covers both incommensurately modulated crystals and quasicrystals.

**References**

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A quasiperiodic crystal, or quasicrystal, is a structure that is ordered but not periodic. A quasicrystalline pattern can continuously fill all available space, but it lacks translational symmetry. While crystals, according to the classical crystallographic restriction theorem, can possess only two-, three-, four-, and six-fold rotational symmetries, the Bragg diffraction pattern of quasicrystals shows sharp peaks with other symmetry orders — for instance, five-fold. The three main classes of aperiodic crystals, modulated phases, incommensurate composites and quasicrystals are treated from a unified point of view, which stresses similarities of the various systems. Until the 1970s all materials studied consisted of periodic arrays of unit cells, or were amorphous. In the last decades a new class of solid state matter, called aperiodic crystals, has been found. It is a long range ordered structure, but without lattice periodicity. ference on Aperiodic Crystals (Aperiodic-. 2012) held during 2–7 September 2012 at. Cairns, Australia. MEETING REPORT. Aperiodic crystals*. Aperiodic crystals, which exhibit the dis-. crete diffraction patterns in spite of. absence of long-range periodicity, exist.