

4.6. Reciprocal-space images of aperiodic crystals

BY W. STEURER AND T. HAIBACH

4.6.1. Introduction

The discovery of materials with icosahedral diffraction symmetry (Shechtman *et al.*, 1984) was the main reason for the reassessment of the definition of *crystallinity* and for the introduction of the concept of *aperiodic crystals*. The first aperiodic crystal, *i.e.* a material with Bragg reflections not located only at reciprocal-lattice nodes, was identified long before (Dehlinger, 1927). In the following decades a wealth of incommensurately modulated phases and composite crystals were discovered. Nevertheless, only a few attempts have been made to develop a crystallography of aperiodic crystals; the most powerful of these was the higher-dimensional approach (see de Wolff, 1974, 1977; Janner & Janssen, 1979, 1980*a,b*; de Wolff *et al.*, 1981). In fact, incommensurate structures can be easily described using the higher-dimensional approach and also, fully equivalently, in a dual way: as a three-dimensional (3D) combination of one or more periodic basic structures and one or several modulation waves (de Wolff, 1984). However, with the discovery of quasicrystals and their noncrystalline symmetries, the latter approach failed and geometrical crystallography including the higher-dimensional approach received new attention. For more recent reviews of the crystallography of all three types of aperiodic crystals see van Smaalen (1995), of incommensurately modulated structures see Cummins (1990), of quasicrystals see Steurer (1990, 1996), of quasicrystals and their crystalline approximants see Goldman & Kelton (1993) and Kelton (1995). Textbooks on quasicrystals have been written by Janot (1994) and Senechal (1995).

According to the traditional crystallographic definition, an *ideal crystal* corresponds to an infinite 3D periodic arrangement of identical structure motifs. Its symmetry can be described by one of the 230 3D space groups. Mathematically, a periodic structure can be generated by the convolution of a function representing the structure motif with a lattice function. The structure motif can be given, for instance, by the electron-density distribution $\rho(\mathbf{r})$ of one primitive unit cell of the structure. The lattice function $g(\mathbf{r})$ is represented by a set of δ functions at the nodes $\mathbf{r} = \sum_{i=1}^3 k_i \mathbf{a}_i$ of a 3D lattice Λ with basis \mathbf{a}_i , $i = 1, \dots, 3$, and $k_i \in \mathbb{Z}$ (\mathbb{Z} is the set of integer numbers). In reciprocal space, this convolution corresponds to the product of the Fourier transform $G(\mathbf{H})$ of the lattice function $g(\mathbf{r})$ and the Fourier transform $F(\mathbf{H}) = \int_V \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) \, d\mathbf{r}$ of the structure motif $\rho(\mathbf{r})$. $G(\mathbf{H})$ is represented by the reciprocal lattice Λ^* decorated with δ functions on the reciprocal-lattice nodes $\mathbf{H} = \sum_{i=1}^3 h_i \mathbf{a}_i^*$, with the reciprocal-basis vectors \mathbf{a}_i^* , $i = 1, \dots, 3$, defined by $\mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij}$ and $h_i \in \mathbb{Z}$. The product $G(\mathbf{H}) \times F(\mathbf{H})$ is called the weighted reciprocal lattice; the weights are given by the structure factors $F(\mathbf{H})$. Thus, the characteristic feature of an ideal crystal in direct and reciprocal space is the existence of a lattice. In direct space, this lattice is decorated with identical structure motifs preserving translational and point symmetry in the framework of *space-group symmetry*. In reciprocal space, only the point symmetry between structure factors is maintained. The *Fourier spectrum* (or *Fourier image*, *i.e.* the Fourier transform) of the electron-density distribution of an ideal crystal consists of a countably infinite set of discrete Bragg peaks with a strictly defined minimum distance.

This crystal definition can be generalized to $n > 3$ dimensions. A dD -dimensional (dD) *ideal aperiodic crystal* can be defined as a dD irrational section of an n -dimensional (nD , $n > d$) crystal with nD lattice symmetry. The intersection of the nD *hypercrystal* with the dD physical space is equivalent to a projection of the weighted nD reciprocal lattice $\Sigma^* = \{\mathbf{H} = \sum_{i=1}^n h_i \mathbf{d}_i^* | h_i \in \mathbb{Z}\}$ onto the dD physical space. The resulting set (Fourier module) $M^* =$

$\{\mathbf{H}^\parallel = \sum_{i=1}^n h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ is countably dense. *Countably dense* means that the dense set of Bragg peaks can be mapped one-to-one onto the set of natural numbers. Hence, the Bragg reflections can be indexed with integer indices on an appropriate basis. The Fourier module of the projected reciprocal-lattice vectors \mathbf{H}^\parallel has the structure of a \mathbb{Z} module of rank n . A \mathbb{Z} module is a free Abelian group, its rank n is given by the number of free generators (rationally independent vectors). The dimension of a \mathbb{Z} module is that of the vector space spanned by it. The vectors \mathbf{a}_i^* are the images of the vectors \mathbf{d}_i^* projected onto the physical space \mathbb{V}^\parallel . Thus, by definition, the 3D reciprocal space of an ideal *aperiodic crystal* consists of a countably dense set of Bragg reflections only. Contrary to an ideal *crystal*, a minimum distance between Bragg reflections does not exist in an aperiodic one. In summary, it may be stressed that the terms *aperiodic* and *periodic* refer to properties of crystal structures in dD space. In nD space, as considered here, lattice symmetry is always present and, therefore, the term *crystal* is used.

Besides the *aperiodic crystals* mentioned above, other classes of *aperiodic structures* with strictly defined construction rules exist (see Axel & Gratias, 1995). Contrary to the kind of aperiodic crystals dealt with in this chapter, the Fourier spectra of aperiodic structures considered in the latter reference are continuous and contain only in a few cases additional sharp Bragg reflections (δ peaks).

Experimentally, the borderline between aperiodic crystals and their periodic approximations (*crystalline approximants*) is not sharply defined. Finite crystal size, static and dynamic disorder, chemical impurities and defects broaden Bragg peaks and cause diffuse diffraction phenomena. Furthermore, the resolution function of the diffraction equipment is limited.

However, the concept of describing an aperiodic structure as a dD physical-space section of an nD crystal (see Section 4.6.2) is only useful if it significantly simplifies the description of its structural order. Thus, depending on the shape of the *atomic surfaces*, which gives information on the atomic ordering, incommensurately modulated structures (IMs, Sections 4.6.2.2 and 4.6.3.1), composite structures (CSs, Sections 4.6.2.3 and 4.6.3.2), or quasiperiodic structures (Qs, Sections 4.6.2.4 and 4.6.3.3) can be obtained from irrational cuts. The atomic surfaces are continuous $(n-d)$ -dimensional objects for IMs and CSs, and discrete $(n-d)$ -dimensional objects for Qs. A class of aperiodic crystals with discrete fractal atomic surfaces also exists (Section 4.6.2.5). In this case the Hausdorff dimension (Hausdorff, 1919) of the atomic surface is not an integer number and smaller than $n-d$. The most outstanding characteristic feature of a fractal is its scale invariance: the object appears similar to itself 'from near as from far, that is, whatever the scale' (Gouyet, 1996).

To overcome the problems connected with experimental resolution, the translational symmetry of periodic crystals is used as a hard constraint in the course of the determination of their structures. Hence, space-group symmetry is taken for granted and only the local atomic configuration in a unit cell (actually, asymmetric unit) remains to be determined. In reciprocal space, this assumption corresponds to a condensation of Bragg reflections with finite full width at half maximum (FWHM) to δ peaks accurately located at the reciprocal-lattice nodes. Diffuse diffraction phenomena are mostly neglected. This extrapolation to the existence of an ideal crystal is generally out of the question even if samples of very poor quality (high mosaicity, microdomain structure, defects, . . .) are investigated.

The same practice is convenient for the determination of real aperiodic structures once the type of idealized aperiodic ordering is 'known'. Again, the global ordering principle is taken as a hard

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constraint. For instance, the question of whether a structure is commensurately or incommensurately modulated can only be answered within a given experimental resolution. Experimentally, the ratio of the wavelength of a modulation to the period of the underlying lattice can always be determined as a rational number only. Saying that a structure is incommensurately modulated, with the above ratio being an irrational number, simply means that the experimental results can be better understood, modelled and interpreted assuming an incommensurate modulation. For example, an incommensurate charge-density wave can be moved through an ideal crystal without changing the energy of the crystal. This is not so for a commensurate modulation. In some cases, the modulation period changes with temperature in discrete steps ('devil's staircase'), generating a series of commensurate superstructures ('lock-in structures'); in other cases, a continuous variation can be observed within the experimental resolution. The latter case will be described best by an incommensurately modulated structure.

However, if only the local structure of an aperiodic crystal is of interest, a structure analysis does not take much more experimental effort than for a regular crystal. In contrast, for the analysis of the global structure, *i.e.* the characterization of the type of its 'aperiodicity', diffraction experiments with the highest possible resolution are essential. Some problems connected with the structure analysis of aperiodic crystals are dealt with in Section 4.6.4.

To determine the long-range order – whether a real 'quasicrystal' is perfectly quasiperiodic, on average quasiperiodic, a crystalline approximant or a nanodomain structure – requires information from experiments that are sensitive to changes of the global structure. Hence, one needs diffraction experiments that allow the accurate determination of the spatial intensity distribution. Consequently, the limiting factors for such experiments are the maximum spatial and intensity resolution of the diffraction and detection equipment, as well as the size and quality of the sample. Nevertheless, the resolution available on state-of-the-art standard synchrotron-beamline equipment is sufficient to test whether the ordering of atoms in an aperiodic crystal reaches the same degree of perfection as found in high-quality silicon. Of course, the higher the sample quality the more necessary it is to account for dynamical diffraction effects such as reflection broadening and displacement. Otherwise, a misinterpretation may bias the global structure modelling.

The following sections present an aid to the characterization of aperiodic crystals based on information from diffraction experiments and give a survey of aperiodic crystals from the viewpoint of the experimentally accessible reciprocal space. Characteristic features of the diffraction patterns of the different types of aperiodic crystals are shown. A standard way of determining the metrics and finding the optimum nD embedding is described. Structure-factor formulae for general and special cases are given.

4.6.2. The n -dimensional description of aperiodic crystals

4.6.2.1. Basic concepts

An incommensurate modulation of a lattice-periodic structure destroys its translational symmetry in direct and reciprocal space. In the early seventies, a method was suggested by de Wolff (1974) for restoring the lost lattice symmetry by considering the diffraction pattern of an *incommensurately modulated structure* (IMS) as a projection of an nD reciprocal lattice upon the physical space. n , the dimension of the superspace, is always larger than or equal to d , the dimension of the physical space. This leads to a simple method for the description and characterization of IMSs as well as a variety of new possibilities in their structure analysis. The nD embedding method is well established today and can be applied to all aperiodic crystals with reciprocal-space structure equivalent to a \mathbb{Z} module

with finite rank n (Janssen, 1988). The dimension of the embedding space is determined by the rank of the \mathbb{Z} module, *i.e.* by the number of reciprocal-basis vectors necessary to allow for indexing all Bragg reflections with integer numbers. The point symmetry of the 3D reciprocal space (Fourier spectrum) constrains the point symmetry of the nD reciprocal lattice and restricts the number of possible nD symmetry groups.

In the following sections, the nD descriptions of the four main classes of aperiodic crystals are demonstrated on simple 1D examples of incommensurately modulated phases, composite crystals, quasicrystals and structures with fractally shaped atomic surfaces. The main emphasis is placed on quasicrystals that show scaling symmetry, a new and unusual property in structural crystallography. A detailed discussion of the different types of 3D aperiodic crystals follows in Section 4.6.3.

4.6.2.2. 1D incommensurately modulated structures

A periodic deviation of atomic parameters from a reference structure (*basic structure*, BS) is called a *modulated structure* (MS). In the case of mutual incommensurability of the basic structure and the modulation period, the structure is called incommensurately modulated. Otherwise, it is called commensurately modulated. The modulated atomic parameters may be one or several of the following:

- (a) coordinates,
- (b) occupancy factors,
- (c) thermal displacement parameters,
- (d) orientation of the magnetic moment.

An incommensurately modulated structure can be described in a dual way by its *basic structure* $s(\mathbf{r})$ and a *modulation function* $f(t)$. This allows the structure-factor formula to be calculated and a full symmetry characterization employing representation theory to be performed (de Wolff, 1984). A more general method is the nD description: it relates the dD aperiodic incommensurately modulated structure to a periodic structure in nD space. This simplifies the symmetry analysis and structure-factor calculation, and allows more powerful structure-determination techniques.

The nD embedding method is demonstrated in the following 1D example of a displacively modulated structure. A basic structure $s(\mathbf{r}) = s(\mathbf{r} + n\mathbf{a})$, with period a and $n \in \mathbb{Z}$, is modulated by a function $f(t) = f(\mathbf{q} \cdot \mathbf{r}) = f(\alpha r) = f[\alpha r + (na/\alpha)]$, with the satellite vector $\mathbf{q} = \alpha \mathbf{a}^*$, period $\lambda = 1/q = a/\alpha$, and α a rational or irrational number yielding a commensurately or incommensurately modulated structure $s_m(\mathbf{r})$ (Fig. 4.6.2.1).

If the 1D IMS and its 1D modulation function are properly combined in a 2D parameter space $\mathbf{V} = (\mathbf{V}^{\parallel}, \mathbf{V}^{\perp})$, a 2D lattice-periodic structure results (Fig. 4.6.2.2). The actual atoms are generated by the intersection of the 1D physical (external, parallel) space \mathbf{V}^{\parallel} with the continuous *hyperatoms*. The hyperatoms have the shape of the modulation function along the perpendicular (internal, complementary) space \mathbf{V}^{\perp} . They result from a convolution of the physical-space atoms with their modulation functions.

A basis $\mathbf{d}_1, \mathbf{d}_2$ (D basis) of the 2D hyperlattice $\Sigma = \{\mathbf{r} = \sum_{i=1}^2 n_i \mathbf{d}_i | n_i \in \mathbb{Z}\}$ is given by

$$\mathbf{d}_1 = \begin{pmatrix} a \\ -\alpha/c \end{pmatrix}_V, \mathbf{d}_2 = \begin{pmatrix} 0 \\ 1/c \end{pmatrix}_V,$$

where a is the translation period of the BS and c is an arbitrary constant. The components of the basis vectors are given on a 2D orthogonal coordinate system (V basis). The components of the basis vector \mathbf{d}_1 are simply the parallel-space period a of the BS and α times the perpendicular-space component of the basis vector \mathbf{d}_2 . The vector \mathbf{d}_2 is always parallel to the perpendicular space and its length is one period of the modulation function in arbitrary units (this is expressed by the arbitrary factor $1/c$). An atom at position \mathbf{r}