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 $n$D 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 $n$D 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 $n$D *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 $n$D reciprocal lattice and restricts the number of possible $n$D symmetry groups.

In the following sections, the $n$D 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 $n$D description: it relates the $d$D aperiodic incommensurately modulated structure to a periodic structure in $n$D space. This simplifies the symmetry analysis and structure-factor calculation, and allows more powerful structure-determination techniques.

The $n$D 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 $\alpha$ 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 $\alpha$ 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 $\mathbf{r}$

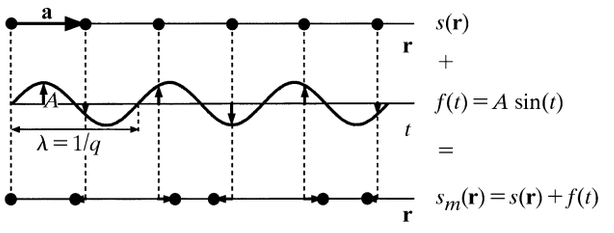


Fig. 4.6.2.1. The combination of a basic structure $s(\mathbf{r})$, with period $a$, and a sinusoidal modulation function $f(t)$, with amplitude $A$, period $\lambda$ and $t = \mathbf{q}\cdot\mathbf{r}$, gives a modulated structure (MS) $s_m(\mathbf{r})$. The MS is aperiodic if $a$ and $\lambda$ are on incommensurate length scales. The filled circles represent atoms.

of the BS is displaced by an amount given by the modulation function $f(t)$, with $f(t) = f(\mathbf{q}\cdot\mathbf{r})$. Hence, the perpendicular-space variable $t$ has to adopt the value $\mathbf{q}\cdot\mathbf{r} = \alpha\mathbf{a}^*\cdot r\mathbf{a} = \alpha r$ for the physical-space variable $\mathbf{r}$. This can be achieved by assigning the slope $\alpha$ to the basis vector $\mathbf{d}_1$. The choice of the parameter $c$ has no influence on the actual MS, *i.e.* the way in which the 2D structure is cut by the parallel space (Fig. 4.6.2.2*c*).

The basis of the lattice $\Sigma^* = \{\mathbf{H} = \sum_{i=1}^{2} h_i\mathbf{d}_i^* | h_i \in \mathbb{Z}\}$, reciprocal to $\Sigma$, can be obtained from the condition $\mathbf{d}_i\cdot\mathbf{d}_j^* = \delta_{ij}$:

$$\mathbf{d}_1^* = \begin{pmatrix} a^* \\ 0 \end{pmatrix}_V, \mathbf{d}_2^* = \begin{pmatrix} \alpha a^* \\ c \end{pmatrix}_V,$$

with $a^* = 1/a$. The metric tensors for the reciprocal and direct 2D lattices for $c = 1$ are

$$G^* = \begin{pmatrix} a^{*2} & \alpha a^{*2} \\ \alpha a^{*2} & 1+\alpha^2 a^{*2} \end{pmatrix} \quad \text{and} \quad G = \begin{pmatrix} a^2+\alpha^2 & -\alpha \\ -\alpha & 1 \end{pmatrix}.$$

The choice of an arbitrary number for $c$ has no influence on the metrics of the physical-space components of the IMS in direct or reciprocal space.

The Fourier transform of the *hypercrystal* depicted in Fig. 4.6.2.2 gives the weighted reciprocal lattice shown in Fig. 4.6.2.3. The 1D diffraction pattern $M^* = \{\mathbf{H}^{\parallel} = \sum_{i=1}^{2} h_i\mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ in physical space is obtained by a projection of the weighted 2D reciprocal lattice $\Sigma^*$ along $\mathbf{V}^{\perp}$ as the Fourier transform of a section in direct space corresponds to a projection in reciprocal space and *vice versa*:

$$M^* = \{\mathbf{H}^{\parallel}\} \xleftarrow{\text{projection } \pi^{\parallel} \text{ onto } \mathbf{V}^{\parallel}} \Sigma^* = \{\mathbf{H} = (\mathbf{H}^{\parallel}, \mathbf{H}^{\perp})\}.$$

Reciprocal-lattice points lying in physical space are referred to as *main reflections*, all others as *satellite reflections*. All Bragg reflections can be indexed with integer numbers $h_1, h_2$ in the 2D description $\mathbf{H} = h_1\mathbf{d}_1^* + h_2\mathbf{d}_2^*$. In the physical-space description, the diffraction vector can be written as $\mathbf{H}^{\parallel} = h\mathbf{a}^* + m\mathbf{q} = \mathbf{a}^*(h_1 + \alpha h_2)$, with $\mathbf{q} = \alpha\mathbf{a}^*$ for the satellite vector and $m \in \mathbb{Z}$ the order of the satellite reflection. For a detailed discussion of the embedding and symmetry description of IMSs see, for example, Janssen *et al.* (1999).

A commensurately modulated structure with $\alpha' = m/n$ and $\lambda = (n/m)a$, $m, n \in \mathbb{Z}$, and with $c = 1$, can be generated by

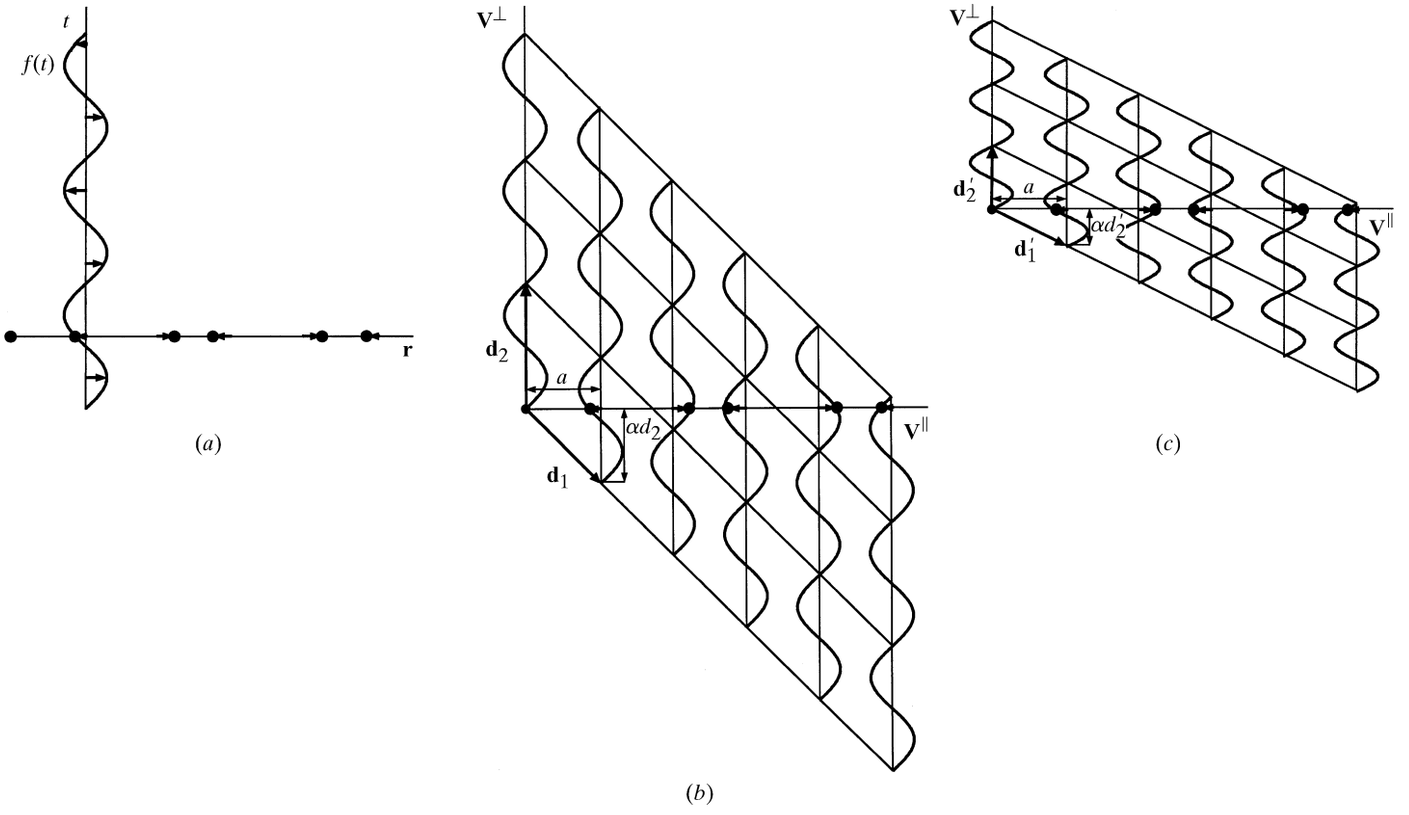


Fig. 4.6.2.2. 2D embedding of the sinusoidally modulated structure illustrated in Fig. 4.6.2.1. The correspondence between the actual displacement of an atom in the 1D structure and the modulation function defined in one additional dimension is illustrated in part (*a*). Adding to each atom its modulation function in this orthogonal dimension (perpendicular space $\mathbf{V}^{\perp}$) yields a periodic arrangement in 2D space $\mathbf{V}$, part (*b*). The MS results as a special section of the 2D periodic structure along the parallel space $\mathbf{V}^{\parallel}$. It is obvious from a comparison of (*b*) and (*c*) that the actual MS is independent of the perpendicular-space scale.

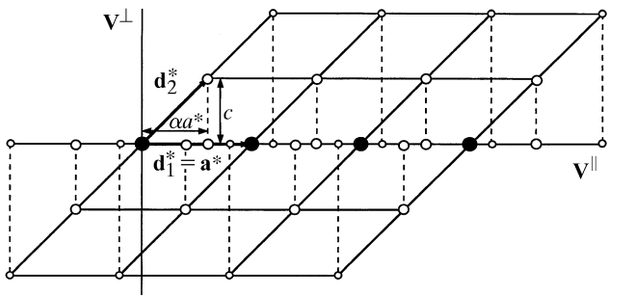


Fig. 4.6.2.3. Schematic representation of the 2D reciprocal-space embedding of the 1D sinusoidally modulated structure depicted in Figs. 4.6.2.1 and 4.6.2.2. Main reflections are marked by filled circles and satellite reflections by open circles. The sizes of the circles are roughly related to the reflection intensities. The actual 1D diffraction pattern of the 1D MS results from a projection of the 2D reciprocal space onto the parallel space. The correspondence between 2D reciprocal-lattice positions and their projected images is indicated by dashed lines.

shearing the 2D lattice $\Sigma$ with a shear matrix $S_m$:

$$\mathbf{d}'_i = \sum_{j=1}^{2} S_{mij}\mathbf{d}_j, \text{ with } S_m = \begin{pmatrix} 1 & -x \\ 0 & 1 \end{pmatrix}_D \text{ and } x = \alpha' - \alpha,$$

$$\mathbf{d}'_1 = \mathbf{d}_1 - x\mathbf{d}_2 = \begin{pmatrix} a \\ -\alpha \end{pmatrix}_V - (\alpha' - \alpha)\begin{pmatrix} 0 \\ 1 \end{pmatrix}_V = \begin{pmatrix} a \\ -\alpha' \end{pmatrix}_V,$$

$$\mathbf{d}'_2 = \mathbf{d}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_V.$$

The subscript $D$ ($V$) following the shear matrix indicates that it is acting on the $D$ ($V$) basis. The shear matrix does not change the distances between the atoms in the basic structure. In reciprocal space, using the inverted and transposed shear matrix, one obtains

$$\mathbf{d}_i^{*\prime} = \sum_{j=1}^{2} (S_m^{-1})_{ij}^T \mathbf{d}_j^*, \text{ with } (S_m^{-1})^T = \begin{pmatrix} 1 & 0 \\ x & 1 \end{pmatrix}_D \text{ and } x = \alpha' - \alpha,$$

$$\mathbf{d}_1^{*\prime} = \mathbf{d}_1^* = \begin{pmatrix} a^* \\ 0 \end{pmatrix}_V,$$

$$\mathbf{d}_2^{*\prime} = x\mathbf{d}_1^* + \mathbf{d}_2^* = (\alpha' - \alpha)\begin{pmatrix} a^* \\ 0 \end{pmatrix}_V + \begin{pmatrix} \alpha a^* \\ 1 \end{pmatrix}_V = \begin{pmatrix} \alpha' a^* \\ 1 \end{pmatrix}_V.$$

### 4.6.2.3. *1D composite structures*

In the simplest case, a *composite structure* (CS) consists of two intergrown periodic structures with mutually incommensurate lattices. Owing to mutual interactions, each subsystem may be modulated with the period of the other. Consequently, CSs can be considered as coherent intergrowths of two or more incommensurately modulated substructures. The substructures have at least the origin of their reciprocal lattices in common. However, in all known cases, at least one common reciprocal-lattice plane exists. This means that at least one particular projection of the composite structure exhibits full lattice periodicity.

The unmodulated (basic) 1D subsystems of a 1D incommensurate intergrowth structure can be related to each other in a 2D parameter space $\mathbf{V} = (\mathbf{V}^{\parallel}, \mathbf{V}^{\perp})$ (Fig. 4.6.2.4). The actual atoms result from the intersection of the physical space $\mathbf{V}^{\parallel}$ with the hypercrystal. The hyperatoms correspond to a convolution of the real atoms with infinite lines parallel to the basis vectors $\mathbf{d}_1$ and $\mathbf{d}_2$ of the 2D hyperlattice $\Sigma = \{\mathbf{r} = \sum_{i=1}^{2} n_i\mathbf{d}_i | n_i \in \mathbb{Z}\}$.

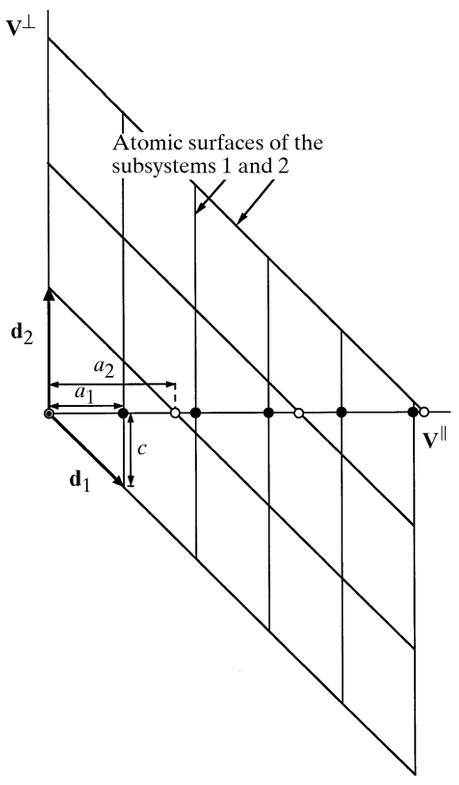


Fig. 4.6.2.4. 2D embedding of a 1D composite structure without mutual interaction of the subsystems. Filled and empty circles represent the atoms of the unmodulated substructures with periods $a_1$ and $a_2$, respectively. The atoms result from the parallel-space cut of the linear atomic surfaces parallel to $\mathbf{d}_1$ and $\mathbf{d}_2$.

An appropriate basis is given by

$$\mathbf{d}_1 = \begin{pmatrix} a_1 \\ -c \end{pmatrix}_V, \mathbf{d}_2 = \begin{pmatrix} 0 \\ c(a_2/a_1) \end{pmatrix}_V,$$

where $a_1$ and $a_2$ are the lattice parameters of the two substructures and $c$ is an arbitrary constant. Taking into account the interactions between the subsystems, each one becomes modulated with the period of the other. Consequently, in the 2D description, the shape of the hyperatoms is determined by their modulation functions (Fig. 4.6.2.5).

A basis of the reciprocal lattice $\Sigma^* = \{\mathbf{H} = \sum_{i=1}^{2} h_i\mathbf{d}_i^* | h_i \in \mathbb{Z}\}$ can be obtained from the condition $\mathbf{d}_i \cdot \mathbf{d}_j^* = \delta_{ij}$:

$$\mathbf{d}_1^* = \begin{pmatrix} a_1^* \\ 0 \end{pmatrix}_V, \mathbf{d}_2^* = \begin{pmatrix} a_2^* \\ (a_2^*/ca_1^*) \end{pmatrix}_V.$$

The metric tensors for the reciprocal and the direct 2D lattices for $c = 1$ are

$$G^* = \begin{pmatrix} a_1^{*2} & a_1^* a_2^* \\ a_1^* a_2^* & (1 + a_1^{*2})(a_2^*/a_1^*)^2 \end{pmatrix} \text{ and } G = \begin{pmatrix} 1 + a_1^2 & -a_2/a_1 \\ -a_2/a_1 & (a_2/a_1)^2 \end{pmatrix}.$$

The Fourier transforms of the hypercrystals depicted in Figs. 4.6.2.4 and 4.6.2.5 correspond to the weighted reciprocal lattices illustrated in Figs. 4.6.2.6 and 4.6.2.7. The 1D diffraction patterns $M^* = \{\mathbf{H}^{\parallel} = \sum_{i=1}^{2} h_i\mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ in physical space are obtained by a projection of the weighted 2D reciprocal lattices $\Sigma^*$ upon $\mathbf{V}^{\parallel}$. All Bragg reflections can be indexed with integer numbers $h_1, h_2$ in both the 2D description $\mathbf{H} = h_1\mathbf{d}_1^* + h_2\mathbf{d}_2^*$ and in the 1D physical-space description with two parallel basis vectors $\mathbf{H}^{\parallel} = h_1\mathbf{a}_1^* + h_2\mathbf{a}_2^*$.



references