of the direct and reciprocal $(3+d)$ lattices (Janner & Janssen, 1980*b*)

$$\Sigma^*: \begin{cases} \mathbf{a}_i^* & = (\mathbf{a}_i^*, \mathbf{0}) & i = 1, \ldots, 3 \\ \mathbf{a}_{3+j}^* & = (\mathbf{a}_{3+j}^*, \mathbf{e}_j^*) & j = 1, \ldots, d \end{cases}$$

$$\Sigma: \begin{cases} \mathbf{a}_i & = (\mathbf{a}_i, -\sum_{j=1}^{d} \sigma_{ji} \mathbf{e}_j) & i = 1, \ldots, 3 \\ \mathbf{a}_{3+j} & = (\mathbf{0}, \mathbf{e}_j) & j = 1, \ldots, d. \end{cases}$$

4.6.3.2.1. Indexing

The indexing of diffraction patterns of composite structures can be performed in the following way:

(1) find the minimum number of reciprocal lattices Λ_ν^* necessary to index the diffraction pattern;

(2) find a basis for M^*, the union of sublattices Λ_ν^*;

(3) find the appropriate superspace embedding.

The $(3+d)$ vectors $\mathbf{a}_i^*$ forming a basis for the 3D Fourier module $M^* = \{\sum_{i=1}^{3+d} h_i \mathbf{a}_i^*\}$ can be chosen such that $\mathbf{a}_1^*$, $\mathbf{a}_2^*$ and $\mathbf{a}_3^*$ are linearly independent. Then the remaining d vectors can be described as a linear combination of the first three, defining the $d \times 3$ matrix σ: $\mathbf{a}_{3+j}^* = \sum_{i=1}^{3+d} \sigma_{ji} \mathbf{a}_i^*$, $j = 1, \ldots, d$. This is formally equivalent to the reciprocal basis obtained for an IMS (see Section 4.6.3.1) and one can proceed in an analogous way to that for IMSs.

4.6.3.2.2. Diffraction symmetry

The symmetry of CSs can be described with basically the same formalism as used for IMSs. This is a consequence of the formally equivalent applicability of the higher-dimensional approach, in particular of the superspace-group theory developed for IMSs [see Janner & Janssen (1980*a*,*b*); van Smaalen (1991, 1992); Yamamoto (1992*a*)].

4.6.3.2.3. Structure factor

The structure factor $F(\mathbf{H})$ of a composite structure consists of the weighted contributions of the subsystem structure factors $F_\nu(\mathbf{H}_\nu)$:

$$F(\mathbf{H}) = \sum_\nu |J_\nu| F_\nu(\mathbf{H}_\nu);$$

$$F_\nu(\mathbf{H}) = \sum_{(R^\nu, \mathbf{t}^\nu)}^{\infty} \sum_{k=1}^{N'} \int_0^1 \mathrm{d}\bar{x}_{4,k}^\nu \ldots \int_0^1 \mathrm{d}\bar{x}_{3+d,k}^\nu f_k^\nu(\mathbf{H}^\parallel) p_k^\nu \times \exp\left(- \sum_{i,j=1}^{3+d} h_i^\nu [R^\nu B_{ijk}^\nu R^{\nu T}] h_j^\nu + 2\pi i \sum_{j=1}^{3+d} h_j^\nu R^\nu x_{jk}^\nu + h_j^\nu t_j^\nu \right),$$

with coefficients similar to those for IMSs.

The weights are the Jacobians of the transformations from $\mathbf{t}_\nu$ to $\mathbf{t}$, and $\mathbf{H}_\nu$ are the reflection indices with respect to the subsystem Fourier modules M_ν^* (van Smaalen, 1995, and references therein). The relative values of $|J_\nu|$, where $J_\nu = \det\left[(V_{d\nu} - \sigma_\nu \cdot Z_{d\nu})^{-1}\right]$, are related to the volume ratios of the contributing subsystems. The subsystem structure factors correspond to those for IMSs (see Section 4.6.3.1). Besides this formula, based on the publications of Yamamoto (1982) and van Smaalen (1995), different structure-factor equations have been discussed (Kato, 1990; Petricek, Maly, Coppens *et al.*, 1991).

4.6.3.3. Quasiperiodic structures (QSs)

4.6.3.3.1. 3D structures with 1D quasiperiodic order

Structures with quasiperiodic order in one dimension and lattice symmetry in the other two dimensions are the simplest representatives of quasicrystals. A few phases of this structure type have been identified experimentally (see Steurer, 1990). Since the Fibonacci chain represents the most important model of a 1D quasiperiodic structure, it will be used in this section to represent the quasiperiodic direction of 3D structures with 1D quasiperiodic order. As discussed in Section 4.6.2.4, 1D quasiperiodic structures are on the borderline between quasiperiodic and incommensurately modulated structures. They can be described using either of the two approaches. In the following, the quasiperiodic description will be preferred to take account of the scaling symmetry.

The electron-density-distribution function $\rho(\mathbf{r})$ of a 1D quasiperiodically ordered 3D crystal can be represented by a Fourier series:

$$\rho(\mathbf{r}) = (1/V) \sum_{\mathbf{H}} F(\mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}).$$

The Fourier coefficients (*structure factors*) $F(\mathbf{H})$ differ from zero only for reciprocal-space vectors $\mathbf{H} = \sum_{i=1}^{3} h_i^\parallel \mathbf{a}_i^*$ with $h_1{}^\parallel \in \mathbb{R}$, $h_2{}^\parallel, h_3{}^\parallel \in \mathbb{Z}$ or with integer indexing $\mathbf{H} = \sum_{i=1}^{4} h_i \mathbf{a}_i^*$ with $h_i \in \mathbb{Z}$. The set of all vectors $\mathbf{H}$ forms a Fourier module $M^* = \{\mathbf{H}^\parallel = \sum_{i=1}^{4} h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ of rank 4 which can be decomposed into two rank 2 submodules $M^* = M_1^* \oplus M_2^*$. $M_1^* = \{h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^*\}$ corresponds to a $\mathbb{Z}$ module of rank 2 in a 1D subspace, $M_2^* = \{h_3 \mathbf{a}_3^* + h_4 \mathbf{a}_4^*\}$ corresponds to a $\mathbb{Z}$ module of rank 2 in a 2D subspace. Consequently, the first submodule can be considered as a projection from a 2D reciprocal lattice, $M_1^* = \pi^\parallel(\Sigma^*)$, while the second submodule is of the form of a reciprocal lattice, $M_2^* = \Lambda^*$.

Hence, the reciprocal-basis vectors $\mathbf{a}_i^*$, $i = 1, \ldots, 4$, can be considered to be projections of reciprocal-basis vectors $\mathbf{d}_i^*$, $i = 1, \ldots, 4$, spanning a 4D reciprocal lattice, onto the physical space $\Sigma^* = \{\mathbf{H} = \sum_{i=1}^{4} h_i \mathbf{d}_i^* | h_i \in \mathbb{Z}\}$, with

$$\mathbf{d}_1^* = a_1^* \begin{pmatrix} 1 \\ -\tau \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{d}_2^* = a_1^* \begin{pmatrix} \tau \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{d}_3^* = a_3^* \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad \mathbf{d}_4^* = a_4^* \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}.$$

A direct lattice Σ with basis $\mathbf{d}_i$, $i = 1, \ldots, 4$ and $\mathbf{d}_i \cdot \mathbf{d}_j^* = \delta_{ij}$, can be constructed according to (compare Fig. 4.6.2.8) $\Sigma = \{\mathbf{r} = \sum_{i=1}^{4} m_i \mathbf{d}_i | m_i \in \mathbb{Z}\}$, with

$$\mathbf{d}_1 = \frac{1}{a_1^*(2+\tau)} \begin{pmatrix} 1 \\ -\tau \\ 0 \\ 0 \end{pmatrix}, \mathbf{d}_2 = \frac{1}{a_1^*(2+\tau)} \begin{pmatrix} \tau \\ 1 \\ 0 \\ 0 \end{pmatrix},$$

$$\mathbf{d}_3^* = \frac{1}{a_3^*} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad \mathbf{d}_4^* = \frac{1}{a_4^*} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}.$$

Consequently, the structure in physical space $\mathbf{V}^\parallel$ is equivalent to a 3D section of the 4D hypercrystal.

4.6.3.3.1.1. Indexing

The reciprocal space of the Fibonacci chain is densely filled with Bragg reflections (Figs. 4.6.2.9 and 4.6.3.5). According to the nD embedding method, the shorter the parallel-space distance $\Delta\mathbf{H}^\parallel = \mathbf{H}_2^\parallel - \mathbf{H}_1^\parallel$ between two Bragg reflections, the larger the corresponding perpendicular-space distance $\Delta\mathbf{H}^\perp = \mathbf{H}_2^\perp - \mathbf{H}_1^\perp$ becomes. Since the structure factor $F(\mathbf{H})$ decreases rapidly as a

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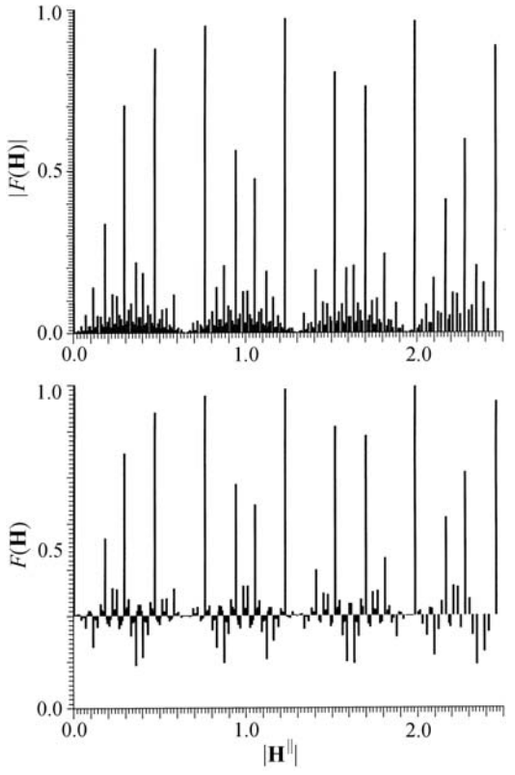

Fig. 4.6.3.5. The structure factors $F(\mathbf{H})$ (below) and their magnitudes $|F(\mathbf{H})|$ (above) of a Fibonacci chain decorated with equal point atoms are shown as a function of the parallel-space component $|\mathbf{H}^{\parallel}|$ of the diffraction vector. The short distance in the Fibonacci chain is S = 2.5 Å, all structure factors within $0 \leq |\mathbf{H}| \leq 2.5$ Å^{-1} have been calculated and normalized to $F(00) = 1$.

function of $\mathbf{H}^{\perp}$ (Fig. 4.6.3.6), 'neighbouring' reflections of strong Bragg peaks are extremely weak and, consequently, the reciprocal space appears to be filled with *discrete* Bragg peaks even for low-resolution experiments.

This property allows an unambiguous identification of a correct set of reciprocal-basis vectors. However, infinitely many sets allowing a correct indexing of the diffraction pattern with integer indices exist. Nevertheless, an optimum basis (low indices are assigned to strong reflections) can be derived: the intensity distribution, not the metrics, characterizes the best choice of indexing. Once the minimum distance S in the structure is identified from chemical considerations, the reciprocal basis should be chosen as described in Section 4.6.2.4. It has to be kept in mind, however, that the identification of the metrics is not sufficient to distinguish in the 1D aperiodic case between an incommensurately modulated structure, a quasiperiodic structure or special kinds of structures with fractally shaped atomic surfaces.

A correct set of reciprocal-basis vectors can be identified in the following way:

(1) Find pairs of strong reflections whose physical-space diffraction vectors are related to each other by the factor τ.

(2) Index these reflections by assigning an appropriate value to a^*. This value should be derived from the shortest interatomic distance S expected in the structure.

(3) The reciprocal basis is correct if all observable Bragg reflections can be indexed with integer numbers.

4.6.3.3.1.2. Diffraction symmetry

The possible Laue symmetry group K^{3D} of the Fourier module $M^* = \{\mathbf{H}^{\parallel} = \sum_{i=1}^{4} h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ is any one of the direct product $K^{3D} = K^{2D} \otimes K^{1D} \otimes \bar{1}$. K^{2D} corresponds to one of the ten crystallographic 2D point groups, $K^{1D} = \{1\}$ in the general case of a quasiperiodic stacking of periodic layers. Consequently, the nine Laue groups $\bar{1}$, $2/m$, mmm, $4/m$, $4/mmm$, $\bar{3}$, $\bar{3}m$, $6/m$ and $6/mmm$ are possible. These are all 3D crystallographic Laue groups except for the two cubic ones.

The (unweighted) Fourier module shows only 2D lattice symmetry. In the third dimension, the submodule M_1^* remains invariant under the scaling symmetry operation $S^n M_1^* = \tau^n M_1^*$ with $n \in \mathbb{Z}$. The scaling symmetry operators S^n form an infinite group $s = \{\ldots, S^{-1}, S^0, S^1, \ldots\}$ of reciprocal-basis transformations S^n in superspace,

$$S^n = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}_D^n, \quad S^{-1} = \begin{pmatrix} \bar{1} & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}_D,$$

$$S^0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}_D,$$

and act on the reciprocal basis $\mathbf{d}_i^*$ in superspace.

4.6.3.3.1.3. Structure factor

The structure factor of a periodic structure is defined as the Fourier transform of the density distribution $\rho(\mathbf{r})$ of its unit cell (UC):

$$F(\mathbf{H}) = \int_{\mathrm{UC}} \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) \, \mathrm{d}\mathbf{r}.$$

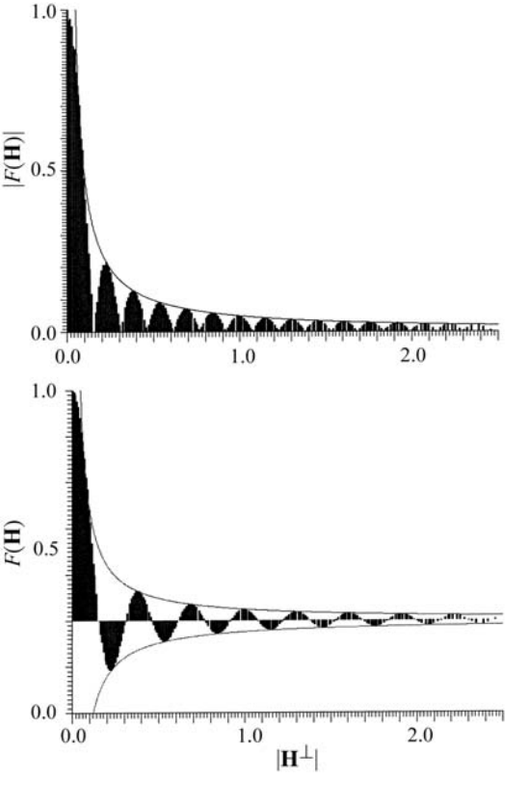

Fig. 4.6.3.6. The structure factors $F(\mathbf{H})$ (below) and their magnitudes $|F(\mathbf{H})|$ (above) of a Fibonacci chain decorated with equal point atoms are shown as a function of the perpendicular-space component $|\mathbf{H}^{\perp}|$ of the diffraction vector. The short distance in the Fibonacci chain is S = 2.5 Å, all structure factors within $0 \leq |\mathbf{H}| \leq 2.5$ Å^{-1} have been calculated and normalized to $F(00) = 1$.

references