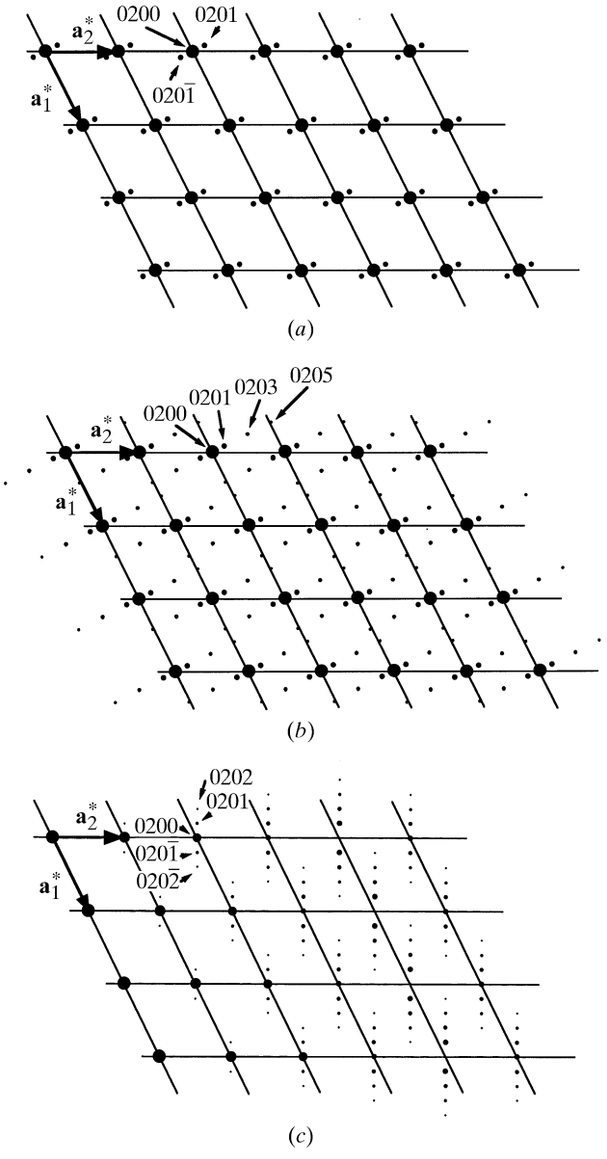

Fig. 4.6.3.3. Schematic diffraction patterns for 3D IMSs with (*a*) 1D harmonic and (*b*) rectangular density modulation. The modulation direction is parallel to $\mathbf{a}_2$. In (*a*) only first-order satellites exist; in (*b*), all odd-order satellites can be present. In (*c*), the diffraction pattern of a harmonic displacive modulation along $\mathbf{a}_1$ with amplitudes parallel to $\mathbf{a}_2^*$ is depicted. Several reflections are indexed. The areas of the circles are proportional to the reflection intensities.

$$F_0(\mathbf{H}) = \sum_{k=1}^{N} f_k(\mathbf{H}^{\parallel}) T_k(\mathbf{H}^{\parallel}) J_0(2\pi \mathbf{H}^{\parallel} \cdot \mathbf{A}_k) \exp\left(2\pi i \sum_{i=1}^{3} h_i x_{ik}\right),$$

$$F_m(\mathbf{H}) = \sum_{k=1}^{N} f_k(\mathbf{H}^{\parallel}) T_k(\mathbf{H}^{\parallel}) J_m(2\pi \mathbf{H}^{\parallel} \cdot \mathbf{A}_k) \times \exp\left[2\pi i \left(\sum_{i=1}^{3} h_i x_{ik} + m\varphi_k\right)\right].$$

The structure-factor magnitudes of the *m*th-order satellite reflections are a function of the *m*th-order Bessel functions. The arguments of the Bessel functions are proportional to the scalar products of the amplitude and the diffraction vector. Consequently, the intensity of the satellites will vary characteristically as a function of the length of the diffraction vector. Each main reflection is accompanied by an infinite number of satellite reflections (Figs. 4.6.3.3*c* and 4.6.3.4).

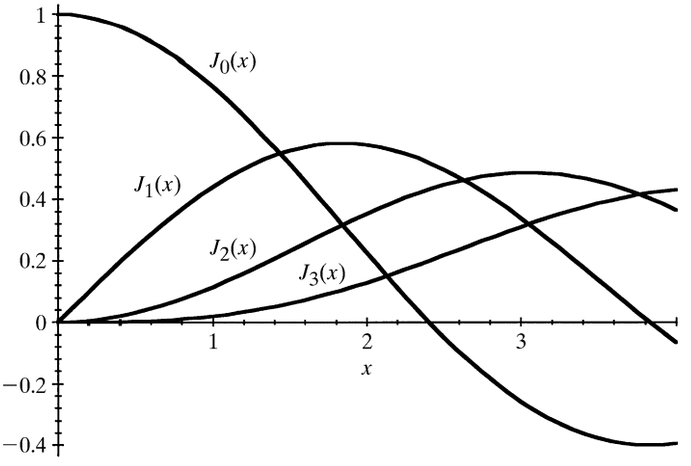

Fig. 4.6.3.4. The relative structure-factor magnitudes of *m*th-order satellite reflections for a harmonic displacive modulation are proportional to the values of the *m*th-order Bessel function $J_m(x)$.

4.6.3.2. Composite structures (CSs)

Composite structures consist of N mutually incommensurate substructures with N basic sublattices $\Lambda_\nu = \{\mathbf{a}_{1\nu}, \mathbf{a}_{2\nu}, \mathbf{a}_{3\nu}\}$, with $\nu = 1, \ldots, N$. The reciprocal sublattices $\Lambda_\nu^* = \{\mathbf{a}_{1\nu}^*, \mathbf{a}_{2\nu}^*, \mathbf{a}_{3\nu}^*\}$, with $\nu = 1, \ldots, N$, have either only the origin of the reciprocal lattice or one or two reciprocal-lattice directions in common. Thus, one needs $(3 + d) < 3N$ reciprocal-basis vectors for integer indexing of diffraction patterns that show Bragg reflections at positions given by the Fourier module M^*. The CSs discovered to date have at least one lattice direction in common and consist of a maximum number of $N = 3$ substructures. They can be divided in three main classes: channel structures, columnar packings and layer packings (see van Smaalen, 1992, 1995).

In the following, the approach of Janner & Janssen (1980*b*) and van Smaalen (1992, 1995, and references therein) for the description of CSs is used. The set of diffraction vectors of a CS, *i.e.* its Fourier module $M^* = \{\sum_{i=1}^{3+d} h_i \mathbf{a}_i^*\}$, can be split into the contributions of the ν subsystems by employing $3 \times (3 + d)$ matrices $Z_{ik\nu}$ with integer coefficients $\mathbf{a}_{i\nu}^* = \sum_{k=1}^{3+d} Z_{ik\nu} \mathbf{a}_k^*$, $i = 1, \ldots, 3$. In the general case, each subsystem will be modulated with the periods of the others due to their mutual interactions. Thus, in general, CSs consist of several intergrown incommensurately modulated substructures. The satellite vectors $\mathbf{q}_{j\nu}$, $j = 1, \ldots, d$, referred to the νth subsystem can be obtained from M^* by applying the $d \times (3 + d)$ integer matrices $V_{jk\nu}$: $\mathbf{q}_{j\nu} = \sum_{k=1}^{3+d} V_{jk\nu} \mathbf{a}_k^*$, $j = 1, \ldots, d$. The matrices consisting of the components σ_ν of the satellite vectors $\mathbf{q}_{j\nu}$ with regard to the reciprocal sublattices Λ_ν^* can be calculated by $\sigma_\nu = (V_{3\nu} + V_{d\nu}\sigma)(Z_{3\nu} + Z_{d\nu}\sigma)^{-1}$, where the subscript 3 refers to the 3×3 submatrix of physical space and the subscript d to the $d \times d$ matrix of the internal space. The juxtaposition of the $3 \times (3 + d)$ matrix Z_ν and the $d \times (3 + d)$ matrix V_ν defines the non-singular $(3 + d) \times (3 + d)$ matrix W_ν,

$$W_\nu = \begin{pmatrix} Z_\nu \\ V_\nu \end{pmatrix}.$$

This matrix allows the reinterpretation of the Fourier module M^* as the Fourier module $M_\nu^* = M^* W_\nu$ of a d-dimensionally modulated subsystem ν. It also describes the coordinate transformation between the superspace basis Σ and Σ_ν.

The superspace description is obtained analogously to that for IMSs (see Section 4.6.3.1) by considering the 3D Fourier module M^* of rank $3 + d$ as the projection of a $(3 + d)$D reciprocal lattice Σ^* upon the physical space. Thus, one obtains for the definition

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