The $(3+d)\times(3+d)$ matrices $\Gamma^T(R)$ form a finite group of integral matrices which are reducible, since R is already an orthogonal transformation in 3D physical space. Consequently, R can be expressed as pair of orthogonal transformations $(R^{\parallel}, R^{\perp})$ in 3D physical and dD perpendicular space, respectively. Owing to their mutual orthogonality, no symmetry relationship exists between the set of main reflections and the set of satellite reflections. $\Gamma^T(R)$ is the transpose of $\Gamma(R)$ which acts on vector components in direct space.

For the $(3+d)$D direct-space (*superspace*) symmetry operator $(R_s, \mathbf{t}_s)$ and its matrix representation $\Gamma(R_s, \mathbf{t}_s)$ on Σ, the following decomposition can be performed:

$$\Gamma(R_s) = \begin{pmatrix} \Gamma^{\parallel}(R) & 0 \\ \Gamma^{M}(R) & \Gamma^{\perp}(R) \end{pmatrix} \text{ and } \mathbf{t}_s = (\mathbf{t}_3, \mathbf{t}_d).$$

$\Gamma^{\parallel}(R)$ is a 3×3 matrix, $\Gamma^{\perp}(R)$ is a $d\times d$ matrix and $\Gamma^{M}(R)$ is a $d\times 3$ matrix. The translation operator $\mathbf{t}_s$ consists of a 3D vector $\mathbf{t}_3$ and a dD vector $\mathbf{t}_d$. According to Janner & Janssen (1979), $\Gamma^{M}(R)$ can be derived from $\Gamma^{M}(R) = \sigma\Gamma^{\parallel}(R) - \Gamma^{\perp}(R)\sigma$. $\Gamma^{M}(R)$ has integer elements only as it contains components of primitive-lattice vectors of Λ^*, whereas σ in general consists of a rational and an irrational part: $\sigma = \sigma^{i} + \sigma^{r}$. Thus, only the rational part gives rise to nonzero entries in $\Gamma^{M}(R)$. With the order of the Laue group denoted by N, one obtains $\sigma^{i} \equiv (1/N)\sum_R \Gamma^{\perp}(R)\sigma\Gamma^{\parallel}(R)^{-1}$, where $\Gamma^{\perp}(R)\sigma^{i}\Gamma^{\parallel}(R)^{-1} = \sigma^{i}$, implying that $\Gamma^{M}(R) = \sigma^{r}\Gamma^{\parallel}(R) - \Gamma^{\perp}(R)\sigma^{r}$ and $0 = \sigma^{i}\Gamma^{\parallel}(R) - \Gamma^{\perp}(R)\sigma^{i}$.

Example

In the case of a 3D IMS with 1D modulation ($d = 1$) the $3\times d$ matrix

$$\sigma = \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{pmatrix}$$

has the components of the wavevector $\mathbf{q} = \sum_{i=1}^{3}\alpha_i \mathbf{a}_i^* = \mathbf{q}^{i} + \mathbf{q}^{r}$. $\Gamma^{\perp}(R) = \varepsilon = \pm 1$ because for $d = 1$, $\mathbf{q}$ can only be transformed into $\pm\mathbf{q}$. Corresponding to $\mathbf{q}^{i} \equiv (1/N)\sum_R \varepsilon R\mathbf{q}$, one obtains $R^T\mathbf{q}^{i} \equiv \varepsilon\mathbf{q}^{i}$ (modulo Λ^*). The 3×1 row matrix $\Gamma^{M}(R)$ is equivalent to the difference vector between $R^T\mathbf{q}$ and $\varepsilon\mathbf{q}$ (Janssen *et al.*, 2004).

For a monoclinic modulated structure with point group $2/m$ for M^* (unique axis $\mathbf{a}_3$) and satellite vector $\mathbf{q} = (1/2)\mathbf{a}_1^* + \alpha_3\mathbf{a}_3^*$, with α_3 an irrational number, one obtains

$$\begin{aligned}\mathbf{q}^{i} &\equiv (1/N)\sum_R \varepsilon R\mathbf{q} \\ &= \tfrac{1}{4}\left(+1\cdot\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\begin{pmatrix}1/2\\0\\\alpha_3\end{pmatrix} \right. \\ &\quad +1\cdot\begin{pmatrix}\bar1&0&0\\0&\bar1&0\\0&0&1\end{pmatrix}\begin{pmatrix}1/2\\0\\\alpha_3\end{pmatrix} - 1\cdot\begin{pmatrix}\bar1&0&0\\0&\bar1&0\\0&0&\bar1\end{pmatrix}\begin{pmatrix}1/2\\0\\\alpha_3\end{pmatrix} \\ &\quad \left. -1\cdot\begin{pmatrix}1&0&0\\0&1&0\\0&0&\bar1\end{pmatrix}\begin{pmatrix}1/2\\0\\\alpha_3\end{pmatrix}\right) \\ &= \begin{pmatrix}0\\0\\\alpha_3\end{pmatrix}.\end{aligned}$$

From the relations $R^T\mathbf{q}^{i} \equiv \varepsilon\mathbf{q}^{i}$ (modulo Λ^*), it can be shown that the symmetry operations 1 and 2 are associated with the perpendicular-space transformations $\varepsilon = 1$, and m and $\bar1$ with $\varepsilon = -1$. The matrix $\Gamma^{M}(R)$ is given by

$$\begin{aligned}\Gamma^{M}(2) &= \sigma^{r}\Gamma^{\parallel}(2) - \Gamma^{\perp}(2)\sigma^{r} \\ &= \begin{pmatrix}1/2\\0\\0\end{pmatrix}\begin{pmatrix}\bar1&0&0\\0&\bar1&0\\0&0&1\end{pmatrix} - (+1)\begin{pmatrix}1/2\\0\\0\end{pmatrix} = \begin{pmatrix}\bar1\\0\\0\end{pmatrix}\end{aligned}$$

for the operation 2, for instance.

The matrix representations $\Gamma^T(R_s)$ of the symmetry operators R in reciprocal $(3+d)$D superspace decompose according to

$$\Gamma^T(R_s) = \begin{pmatrix} \Gamma^{\parallel T}(R) & \Gamma^{MT}(R) \\ 0 & \Gamma^{\perp T}(R) \end{pmatrix}.$$

Phase relationships between modulation functions of symmetry-equivalent atoms can give rise to systematic extinctions of different classes of satellite reflections. The extinction rules may include indices of both main and satellite reflections. A full list of systematic absences is given in the table of $(3+1)$D superspace groups (Janssen *et al.*, 2004). Thus, once point symmetry and systematic absences are found, the superspace group can be obtained from the tables in a way analogous to that used for regular 3D crystals. A different approach for the symmetry description of IMSs from the 3D Fourier-space perspective has been given by Dräger & Mermin (1996).

4.6.3.1.3. 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):

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

The same is valid in the case of the $(3+d)$D description of IMSs. The parallel- and perpendicular-space components are orthogonal to each other and can be separated. The Fourier transform of the parallel-space component of the electron-density distribution of a single atom gives the usual atomic scattering factors $f_k(\mathbf{H}^{\parallel})$. For the structure-factor calculation, one does not need to use $\rho(\mathbf{r})$ explicitly. The hyperatoms correspond to the convolution of the electron-density distribution in 3D physical space with the modulation function in dD perpendicular space. Therefore, the Fourier transform of the $(3+d)$D hyperatoms is simply the product of the Fourier transform $f_k(\mathbf{H}^{\parallel})$ of the physical-space component with the Fourier transform of the perpendicular-space component, the modulation function.

For a general *displacive modulation* one obtains for the ith coordinate x_{ik} of the kth atom in 3D physical space

$$x_{ik} = \bar{x}_{ik} + u_{ik}(\bar{x}_4, \ldots, \bar{x}_{3+d}),\ \ i = 1, \ldots, 3,$$

where $\bar{x}_{ik}$ are the basic-structure coordinates and $u_{ik}(\bar{x}_4, \ldots, \bar{x}_{3+d})$ are the modulation functions with unit periods in their arguments (Fig. 4.6.3.2). The arguments are $\bar{x}_{3+j} = \alpha_{ij}\bar{x}_{ik}^0 + t_j,\ j = 1, \ldots, d$, where $\bar{x}_{ik}^0$ are the coordinates of the kth atom referred to the origin of its unit cell and t_j are the phases of the modulation functions. The modulation functions $u_{ik}(\bar{x}_4, \ldots, \bar{x}_{3+d})$ themselves can be expressed in terms of a Fourier series as

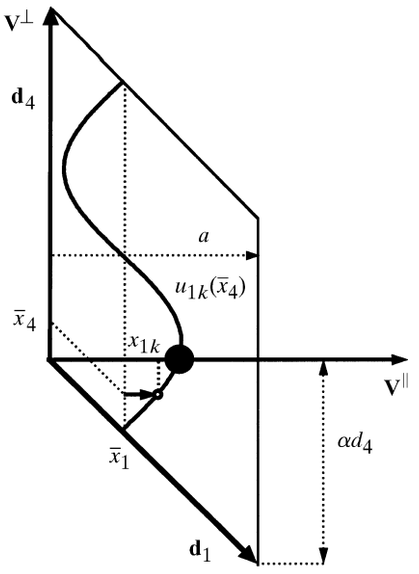

Fig. 4.6.3.2. The relationships between the coordinates $x_{1k}, x_{4k}, \bar{x}_1, \bar{x}_4$ and the modulation function u_{1k} in a special section of the $(3+d)$D space.

$$u_{ik}(\bar{x}_4, \ldots, \bar{x}_{3+d}) = \sum_{n_1=1}^{\infty} \ldots \sum_{n_d=1}^{\infty} \{{}^{u}C_{ik}^{n_1 \ldots n_d} \cos[2\pi(n_1\bar{x}_4 + \ldots + n_d\bar{x}_{3+d})] + {}^{u}S_{ik}^{n_1 \ldots n_d} \sin[2\pi(n_1\bar{x}_4 + \ldots + n_d\bar{x}_{3+d})]\},$$

where n_j are the orders of harmonics for the jth modulation wave of the ith component of the kth atom and their amplitudes are ${}^{u}C_{ik}^{n_1 \ldots n_d}$ and ${}^{u}S_{ik}^{n_1 \ldots n_d}$.

Analogous expressions can be derived for a *density modulation*, *i.e.*, the modulation of the occupation probability $p_k(\bar{x}_4, \ldots, \bar{x}_{3+d})$:

$$p_k(\bar{x}_4, \ldots, \bar{x}_{3+d}) = \sum_{n_1=1}^{\infty} \ldots \sum_{n_d=1}^{\infty} \{{}^{p}C_{k}^{n_1 \ldots n_d} \cos[2\pi(n_1\bar{x}_4 + \ldots + n_d\bar{x}_{3+d})] + {}^{p}S_{k}^{n_1 \ldots n_d} \sin[2\pi(n_1\bar{x}_4 + \ldots + n_d\bar{x}_{3+d})]\},$$

and for the modulation of the tensor of thermal parameters $B_{ijk}(\bar{x}_4, \ldots, \bar{x}_{3+d})$:

$$B_{ijk}(\bar{x}_4, \ldots, \bar{x}_{3+d}) = \sum_{n_1=1}^{\infty} \ldots \sum_{n_d=1}^{\infty} \{{}^{B}C_{ijk}^{n_1 \ldots n_d} \cos[2\pi(n_1\bar{x}_4 + \ldots + n_d\bar{x}_{3+d})] + {}^{B}S_{ijk}^{n_1 \ldots n_d} \sin[2\pi(n_1\bar{x}_4 + \ldots + n_d\bar{x}_{3+d})]\}.$$

The resulting structure-factor formula is

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

for summing over the set $(R, \mathbf{t})$ of superspace symmetry operations and the set of N' atoms in the asymmetric unit of the $(3+d)$D unit cell (Yamamoto, 1982). Different approaches without numerical integration based on analytical expressions including Bessel functions have also been developed. For more information see Paciorek & Chapuis (1994), Petricek, Maly & Cisarova (1991), and references therein.

For illustration, some fundamental IMSs will be discussed briefly (see Korekawa, 1967; Böhm, 1977).

Harmonic density modulation. A harmonic density modulation can result on average from an ordered distribution of vacancies on atomic positions. For an IMS with N atoms per unit cell one obtains for a harmonic modulation of the occupancy factor

$$p_k = (p_k^0/2)\{1 + \cos[2\pi(\bar{x}_{4,k} + \varphi_k)]\}, \quad 0 \le p_k^0 \le 1,$$

the structure-factor formula for the mth order satellite $(0 \le m \le 1)$

$$F_0(\mathbf{H}) = (1/2)\sum_{k=1}^{N} f_k(\mathbf{H}^{\parallel}) T_k(\mathbf{H}^{\parallel}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_k),$$
$$F_m(\mathbf{H}) = (1/2)\sum_{k=1}^{N} f_k(\mathbf{H}^{\parallel}) T_k(\mathbf{H}^{\parallel}) (p_k^0/2)^{|m|} \exp\left[2\pi i\left(\sum_{i=1}^{3} h_i x_{ik} + m\varphi_k\right)\right].$$

Thus, a linear correspondence exists between the structure-factor magnitudes of the satellite reflections and the amplitude of the density modulation. Furthermore, only first-order satellites exist, since the modulation wave consists only of one term. An important criterion for the existence of a density modulation is that a pair of satellites around the origin of the reciprocal lattice exists (Fig. 4.6.3.3).

Symmetric rectangular density modulation. The box-function-like modulated occupancy factor can be expanded into a Fourier series,

$$p_k = p_k^0(4/\pi)\left\{\sum_{n=1}^{\infty}[(-1)^{n+1}/(2n-1)]\cos[2\pi(2n-1)(\bar{x}_{4,k} + \varphi_k)]\right\}, \quad 0 \le p_k^0 \le 1,$$

and the resulting structure factor of the mth order satellite is

$$F_0(\mathbf{H}) = (1/2)\sum_{k=1}^{N} f_k(\mathbf{H}^{\parallel}) T_k(\mathbf{H}^{\parallel}) \exp\left(2\pi i \sum_{i=1}^{3} h_i x_{ik}\right),$$
$$F_m(\mathbf{H}) = (1/\pi m)\sin(m\pi/2)\sum_{k=1}^{N} f_k(\mathbf{H}^{\parallel}) T_k(\mathbf{H}^{\parallel}) p_k^0 \times \exp\left[2\pi i\left(\sum_{i=1}^{3} h_i x_{ik} + m\varphi_k\right)\right].$$

According to this formula, only odd-order satellites occur in the diffraction pattern. Their structure-factor magnitudes decrease linearly with the order $|m|$ (Fig. 4.6.3.3*b*).

Harmonic displacive modulation. The displacement of the atomic coordinates is given by the function

$$x_{ik} = x_{ik}^0 + A_{ik}\cos[2\pi(\bar{x}_{4,k} + \varphi_k)], \quad i = 1, \ldots, 3,$$

and the structure factor by

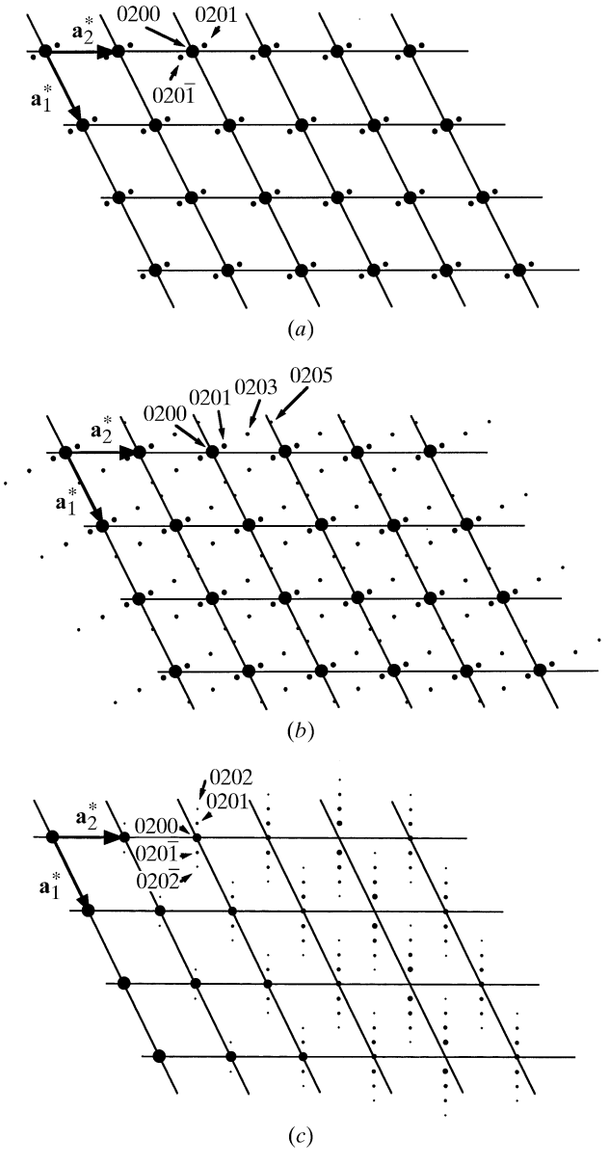

Fig. 4.6.3.3. Schematic diffraction patterns for 3D IMSs with (*a*) 1D harmonic and (*b*) rectangular density modulation. The modulation direction is parallel to $\mathbf{a}_2$. In (*a*) only first-order satellites exist; in (*b*), all odd-order satellites can be present. In (*c*), the diffraction pattern 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).

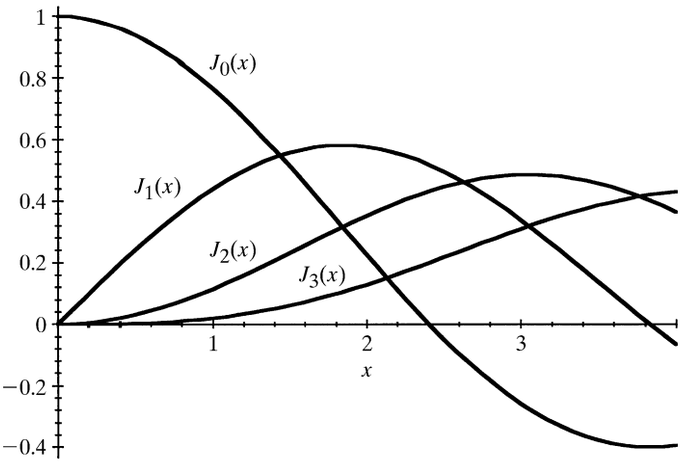

Fig. 4.6.3.4. The relative structure-factor magnitudes of *m*th-order satellite reflections for a harmonic displacive modulation are proportional to the values of the *m*th-order Bessel function $J_m(x)$.

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