vectors $\mathbf{d}_i^*, i = 1, \ldots, 3+d$, spanning a $(3+d)$D reciprocal lattice Σ^*:

$$\Sigma^* = \left\{ \mathbf{H} = \sum_{i=1}^{3+d} h_i \mathbf{d}_i^* \middle| h_i \in \mathbb{Z} \right\},$$

$$\mathbf{d}_i^* = (\mathbf{a}_i^*, \mathbf{0}),\ i = 1, \ldots, 3 \text{ and } \mathbf{d}_{3+j}^* = (\mathbf{a}_{3+j}^*, c\mathbf{e}_j^*),\ j = 1, \ldots, d.$$

The first vector component of $\mathbf{d}_i^*$ refers to the physical space, the second to the perpendicular space spanned by the mutually orthogonal unit vectors $\mathbf{e}_j$. c is an arbitrary constant which can be set to 1 without loss of generality.

A direct lattice Σ with basis $\mathbf{d}_i, i = 1, \ldots, 3+d$ and $\mathbf{d}_i \cdot \mathbf{d}_j^* = \delta_{ij}$, can be constructed according to

$$\Sigma = \left\{ \mathbf{r} = \sum_{i=1}^{3+d} m_i \mathbf{d}_i \middle| m_i \in \mathbb{Z} \right\},$$

$$\mathbf{d}_i = \left(\mathbf{a}_i, -\sum_{j=1}^{d} \alpha_{ij}(1/c)\mathbf{e}_j \right),\ i = 1, \ldots, 3$$

$$\text{and } \mathbf{d}_{3+j} = \left(\mathbf{0}, (1/c)\mathbf{e}_j^* \right),\ j = 1, \ldots, d.$$

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

4.6.3.1.1. *Indexing*

The 3D reciprocal space M^* of a $(3+d)$D IMS consists of two separable contributions,

$$M^* = \left\{ \mathbf{H} = \sum_{i=1}^{3} h_i \mathbf{a}_i^* + \sum_{j=1}^{d} m_j \mathbf{q}_j \right\},$$

the set of main reflections $(m_j = 0)$ and the set of satellite reflections $(m_j \neq 0)$ (Fig. 4.6.3.1). In most cases, the modulation is only a weak perturbation of the crystal structure. The main reflections are related to the average structure, the satellites to the difference between average and actual structure. Consequently, the satellite reflections are generally much weaker than the main reflections and can be easily identified. Once the set of main reflections has been separated, a conventional basis $\mathbf{a}_i^*, i = 1, \ldots, 3$, for Λ^* is chosen.

The only ambiguity is in the assignment of rationally independent satellite vectors $\mathbf{q}_i$. They should be chosen inside the reciprocal-space unit cell (Brillouin zone) of Λ^* in such a way as to give a minimal number d of additional dimensions. If satellite vectors reach the Brillouin-zone boundary, centred $(3+d)$D Bravais lattices are obtained. The star of satellite vectors has to be invariant under the point-symmetry group of the diffraction pattern. There should be no contradiction to a reasonable physical modulation model concerning period or propagation direction of the modulation wave. More detailed information on how to find the optimum basis and the correct setting is given by Janssen *et al.* (1999) and Janner *et al.* (1983*a*,*b*).

4.6.3.1.2. *Diffraction symmetry*

The Laue symmetry group $K^L = \{R\}$ of the Fourier module M^*,

$$M^* = \left\{ \mathbf{H} = \sum_{i=1}^{3} h_i \mathbf{a}_i^* + \sum_{j=1}^{d} m_j \mathbf{q}_j = \sum_{i=1}^{3+d} h_i \mathbf{a}_i^* \right\}, \Lambda^* = \left\{ \mathbf{H} = \sum_{i=1}^{3} h_i \mathbf{a}_i^* \right\},$$

is isomorphous to or a subgroup of one of the 11 3D crystallographic Laue groups leaving Λ^* invariant. The action of the point-group symmetry operators R on the reciprocal basis $\mathbf{a}_i^*, i = 1, \ldots, 3+d$, can be written as

$$R\mathbf{a}_i^* = \sum_{j=1}^{3+d} \Gamma_{ij}^T(R)\mathbf{a}_j^*, i = 1, \ldots, 3+d.$$

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.*, 1999).

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

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

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 $\bar{1}$ with $\varepsilon = -1$. The matrix $\Gamma^M(R)$ is given by

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

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.*, 1999). 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):

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

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 $\bar{x}_{3+j} = \alpha_{ij}\bar{x}^0_{ik} + t_j$, $j = 1, \ldots, d$, where $\bar{x}^0_{ik}$ 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

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

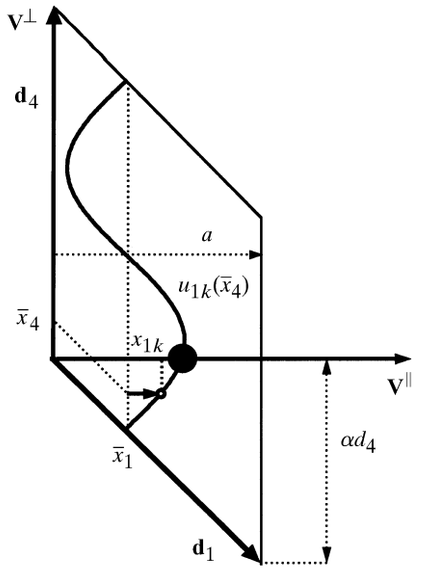

Fig. 4.6.3.2. The relationships between the coordinates $x_{1k}, x_{4k}, \bar{x}_1, \bar{x}_4$ and the modulation function u_{1k} in a special section of the $(3+d)$D space.

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 $p_k(\bar{x}_4, \ldots, \bar{x}_{3+d})$:

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

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

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

The resulting structure-factor formula is

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

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