where $p_j(x) = p_j(x+1)$. By g_s, the position $\mathbf{n}+\mathbf{r}_j$ is transformed to the equivalent position $\mathbf{n}'+\mathbf{r}_{j'} = R\mathbf{n}+R\mathbf{r}_j+\mathbf{v}$. As the crystal is left invariant by the superspace group, the occupation probability on equivalent points has to be the same:

$$P_A(\mathbf{n}', j', t) = P_A[\mathbf{n}, j, \varepsilon(t-\upsilon_I)]. \tag{9.8.4.38}$$

This implies that for the structure in the three-dimensional space one has the relation

$$P_A(\mathbf{n}', j', 0) = P_A(\mathbf{n}, j, -\varepsilon\upsilon_I). \tag{9.8.4.39}$$

In terms of the modulation function p_j this means

$$p_{j'}[\mathbf{q}\cdot(\mathbf{n}'+\mathbf{r}_{j'})] = p_j[\mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j)-\varepsilon\upsilon_I]. \tag{9.8.4.40}$$

In the same way, one derives the following property of the modulation function:

$$p_{j'}(x) = p_j[\varepsilon(x-\delta)+\mathbf{K}\cdot(\mathbf{r}_{j'}-\mathbf{v})], \quad \text{where } R\mathbf{q} = \varepsilon\mathbf{q}+\mathbf{K}. \tag{9.8.4.41}$$

Analogously, for a displacive modulation, the position $\mathbf{n}+\mathbf{r}_j$ with displacement $\mathbf{u}_j(t_o)$, where $t_o = \mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j)$, is transformed to $\mathbf{n}'+\mathbf{r}_{j'}$ with displacement

$$\mathbf{u}_{j'}(t_o') = R\mathbf{u}_j(t_o-\varepsilon\upsilon_I). \tag{9.8.4.42}$$

To be invariant, the displacement function has to satisfy the relation

$$\mathbf{u}_{j'}(x) = R\mathbf{u}_j[\varepsilon x-\varepsilon\delta+\mathbf{K}\cdot(\mathbf{r}_{j'}-\mathbf{v})], \quad \text{where } R\mathbf{q} = \varepsilon\mathbf{q}+\mathbf{K}. \tag{9.8.4.43}$$

The expressions for $d > 1$ are straightforward generalizations of these.

9.8.4.4.3. *Structure factor*

The scattering from a set of atoms at positions $\mathbf{r}_n$ is described in the kinematic approximation by the structure factor:

$$S_{\mathbf{H}} = \sum_n f_n(\mathbf{H})\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_n), \tag{9.8.4.44}$$

where $f_n(\mathbf{H})$ is the atomic scattering factor. For an incommensurate crystal phase, this structure factor $S_{\mathbf{H}}$ is equal to the structure factor S_{H_s} of the crystal structure embedded in $3+d$ dimensions, where $\mathbf{H}$ is the projection of H_s on V_E. This structure factor is expressed by a sum of the products of atomic scattering factors f_n and phase factors $\exp(2\pi i H_s\cdot r_{sn})$ over all particles in the unit cell of the higher-dimensional lattice. For an incommensurate phase, the number of particles in such a unit cell is infinite: for a given atom in space, the embedded positions form a dense set on lines or hypersurfaces of the higher-dimensional space. Disregarding pathological cases, the sum may be replaced by an integral. Including the possibility of an occupation modulation, the structure factor becomes (up to a normalization factor)

$$S_{\mathbf{H}} = \sum_A\sum_j\int_\Omega \mathrm{d}\mathbf{t}\, f_A(\mathbf{H})P_{Aj}(\mathbf{t}) \times \exp\{2\pi i(\mathbf{H},\mathbf{H}_I)\cdot[\mathbf{r}_j+\mathbf{u}_j(\mathbf{t}),\mathbf{t}]\}, \tag{9.8.4.45}$$

where the first sum is over the different species, the second over the positions in the unit cell of the basic structure, the integral over a unit cell of the lattice spanned by $\mathbf{d}_1,\ldots,\mathbf{d}_d$ in V_I; f_A is the atomic scattering factor of species A, $P_{Aj}(\mathbf{t})$ is the probability of atom j being of species A when the internal position is $\mathbf{t}$.

In particular, for a given atomic species, without occupational modulation and a sinusoidal one-dimensional displacive modulation

$$P_j(t) = 1; \quad \mathbf{u}_j(t) = \mathbf{U}_j\sin[2\pi(\mathbf{q}\cdot\mathbf{r}_j+t+\varphi_j)]. \tag{9.8.4.46}$$

According to (9.8.4.45), the structure factor is

$$S_{\mathbf{H}} = \sum_j\int_0^1 \mathrm{d}t f_j(\mathbf{H})\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_j)\exp(2\pi imt) \times \exp[2\pi i\mathbf{H}\cdot\mathbf{U}_j\sin 2\pi(\mathbf{q}\cdot\mathbf{r}_j+t+\varphi_j)]. \tag{9.8.4.47}$$

For a diffraction vector $\mathbf{H} = \mathbf{K}+m\mathbf{q}$, this reduces to

$$S_{\mathbf{H}} = \sum_j f_j(\mathbf{H})\exp(2\pi i\mathbf{K}\cdot\mathbf{r}_j)J_{-m}(2\pi\mathbf{H}\cdot\mathbf{U}_j) \times \exp(-2\pi im\varphi_j). \tag{9.8.4.48}$$

For a general one-dimensional modulation with occupation modulation function $p_j(t)$ and displacement function $\mathbf{u}_j(t)$, the structure factor becomes

$$S_{\mathbf{H}} = \sum_j\int_0^1 \mathrm{d}t\, f_j(\mathbf{H})p_j(\mathbf{q}\cdot\mathbf{r}_j+t+\psi_j)\exp[2\pi i(\mathbf{H}\cdot\mathbf{r}_j+mt)] \times \exp[2\pi i\mathbf{H}\cdot\mathbf{u}_j(\mathbf{q}\cdot\mathbf{r}_j+t+\varphi_j)]. \tag{9.8.4.49}$$

Because of the periodicity of $p_j(t)$ and $\mathbf{u}_j(t)$, one can expand the Fourier series:

$$p_j(\mathbf{q}\cdot\mathbf{r}_j+t+\psi_j)\exp[2\pi i\mathbf{H}\cdot\mathbf{u}_j(\mathbf{q}\cdot\mathbf{r}_j+t+\varphi_j)] = \sum_k C_{j,k}(\mathbf{H})\exp[2\pi ik(\mathbf{q}\cdot\mathbf{r}_j+t)], \tag{9.8.4.50}$$

and consequently the structure factor becomes

$$S_{\mathbf{H}} = \sum_j f_j(\mathbf{H})\exp(2\pi i\mathbf{K}\cdot\mathbf{r}_j)C_{j,-m}(\mathbf{H}), \quad \text{where } \mathbf{H} = \mathbf{K}+m\mathbf{q}. \tag{9.8.4.51}$$

The diffraction from incommensurate crystal structures has been treated by de Wolff (1974), Yamamoto (1982*a*,*b*), Paciorek & Kucharczyk (1985), Petricek, Coppens & Becker (1985), Petříček & Coppens (1988), Perez-Mato *et al*. (1986, 1987), and Steurer (1987).

9.8.5. Generalizations

9.8.5.1. *Incommensurate composite crystal structures*

The basic structure of a modulated crystal does not always have space-group symmetry. Consider, for example, composite crystals (also called intergrowth crystals). Disregarding modulations, one can describe these crystals as composed of a finite number of subsystems, each with its own space-group symmetry. The lattices of these subsystems can be mutually incommensurate. In that case, the overall symmetry is not a space group, the composite crystal is incommensurate and so also is its basic structure. The superspace approach can also be applied to such crystals. Let the subsystems be labelled by an index ν. For the subsystem ν, we denote the lattice by Λ_ν with basis vectors $\mathbf{a}_{\nu i}$ $(i = 1, 2, 3)$, its reciprocal lattice by Λ_ν^* with basis vectors $\mathbf{a}_{\nu i}^*$ $(i = 1, 2, 3)$, and the space group by G_ν. The atomic positions of the basic structure are given by

$$\mathbf{n}_\nu+\mathbf{r}_{\nu j}, \tag{9.8.5.1}$$

where $\mathbf{n}_\nu$ is a lattice vector belonging to Λ_ν. In the special case that the subsystems are mutually commensurate, there are three basis vectors $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ such that all vectors $\mathbf{a}_{\nu i}^*$ are integral linear combinations of them. In general, however, more than three basis vectors are needed, but never more than three times the number of subsystems. Suppose that the vectors $\mathbf{a}_i^*$ $(i = 1,\ldots,n)$

form a basis set such that every $\mathbf{a}^*_{\nu i}$ can be expressed as an integral linear combination of them:

$$\mathbf{a}^*_{\nu i} = \sum_{k=1}^{n} Z^{\nu}_{ik}\mathbf{a}^*_k, \quad Z^{\nu}_{ik} \text{ integers}, \tag{9.8.5.2}$$

with $n = 3 + d_o$ and $d_o > 0$. Then the vectors of the diffraction pattern of the unmodulated system are again of the form (9.8.4.5) and generate a vector module M^*_o of dimension three and rank $(3 + d_o)$, which can be considered as projection of a $(3 + d_o)$-dimensional lattice Σ^*_o.

We now assume that one can choose $\mathbf{a}^*_{li} = 0$ for $i = 1, 2, 3$ and we denote $\mathbf{a}^*_{l3+j}$ by $\mathbf{d}^*_j$. This corresponds to assuming the existence of a subset of Bragg reflections at the positions of a three-dimensional reciprocal lattice Λ^*. Then there is a standard basis for the lattice Σ_o, which is the reciprocal of Σ^*_o, given by

$$(\mathbf{a}_i, \mathbf{a}_{li}), \quad (0, \mathbf{d}_j), \quad i = 1, 2, 3, \quad j = 1, \ldots, d_o. \tag{9.8.5.3}$$

In order to find the $(3 + d_o)$-dimensional periodic structure for which this composite crystal is the three-dimensional intersection, one associates with a translation $\mathbf{t}$ in the internal space V_I three-dimensional independent shifts, one for each subsystem. These shifts of the subsystems replace the phase shifts adopted for the modulated structures: V_I is now the space of the variable relative positions of the subsystems. Again, a translation in the superspace can give rise to a non-Euclidean transformation in the three-dimensional space of the crystal, because of the variation in the relative positions among subsystems. Each subsystem, however, is rigidly translated. For the basis vectors $\mathbf{d}_j$, the shift of the subsystem ν is defined in terms of projection operators π_ν:

$$\pi_\nu \mathbf{d}_j = \sum_{i=1}^{3} Z^{\nu}_{i3+j}\mathbf{a}_{\nu i}, \quad j = 1, \ldots, d_o. \tag{9.8.5.4}$$

Then an arbitrary translation $\mathbf{t} = \sum_j t_j \mathbf{d}_j$ in V_I displaces the subsystem ν over a vector $\sum_j t_j(\pi_\nu \mathbf{d}_j)$. A translation $(\mathbf{a}, \mathbf{a}_I + \mathbf{d})$ belonging to the $(3 + d_o)$-dimensional lattice Σ_o induces for the subsystem ν in ordinary space a relative translation over vector $\mathbf{a} + \pi_\nu(\mathbf{a}_I + \mathbf{d})$. The statement is that this translation is a vector of the lattice Λ_ν and leaves therefore the subsystem ν invariant. So the lattice translations belonging to Σ_o form a group of symmetry operations for the composite crystal as a whole.

The proof is as follows. If $\mathbf{k}$ belongs to Λ^*_ν, the vector $(\mathbf{k}, \mathbf{k}_I)$ belongs to Σ^*_o. In particular, for $\mathbf{k} = \mathbf{a}^*_{\nu i}$, one has, because of (9.8.5.2) and (9.8.5.4),

$$\mathbf{a}^*_{\nu i} \cdot \pi_\nu \mathbf{d}_j = Z^{\nu}_{i3+j}, \quad j = 1, \ldots, d_o, \tag{9.8.5.5}$$

and

$$\mathbf{k}_I = \sum_{j=1}^{d_o} Z^{\nu}_{i3+j}\mathbf{d}^*_j \quad \text{and therefore} \quad \mathbf{k}_I \cdot \mathbf{d}_j = Z^{\nu}_{i3+j}.$$

Note that one has $\mathbf{k}_I \cdot \mathbf{t} = \mathbf{k} \cdot \pi_\nu \mathbf{t}$, for any $\mathbf{t}$ from V_I as π_ν is a linear operator. Because of the linearity, this holds for every $\mathbf{k}$ from Λ^*_ν as well. Since $(\mathbf{k}, \mathbf{k}_I)$ belongs to Σ^*_o and $(\mathbf{a}, \mathbf{a}_I + \mathbf{d})$ to Σ_o, one has for their inner product:

$$\mathbf{k} \cdot \mathbf{a} + \mathbf{k}_I \cdot \mathbf{a}_I + \mathbf{k}_I \cdot \mathbf{d} = \mathbf{k} \cdot (\mathbf{a} + \pi_\nu \mathbf{a}_I + \pi_\nu \mathbf{d}) \equiv 0 \pmod 1,$$

which implies that $\mathbf{a} + \pi_\nu \mathbf{a}_I + \pi_\nu \mathbf{d}$ is an element of Λ_ν.

In conclusion, one may state that the composite structure is the intersection with the ordinary space ($\mathbf{t} = 0$) of a pattern having atomic position vectors given by

$$(\mathbf{n}_\nu + \mathbf{r}_{\nu j} - \pi_\nu \mathbf{t}, \mathbf{t}) \quad \text{for any } \mathbf{t} \text{ of } V_I. \tag{9.8.5.6}$$

Such a pattern is invariant under the $(3 + d_o)$-dimensional lattice Σ_o. Again, orthogonal transformations R of $O(3)$ leaving the vector module M^*_o invariant can be extended to orthogonal transformation R_s of $O(3) \times O(d_o)$ allowing a Euclidean structure to be given to the superspace. One can then consider the superspace-group symmetry of the basic structure defined by atomic positions as in (9.8.5.6). A superspace-group element g_s as in (9.8.4.28) induces (in three-dimensional space) for the subsystem ν the transformation

$$g_s : \mathbf{n}_\nu + \mathbf{r}_{\nu j} \to R\mathbf{n}_\nu + R\mathbf{r}_{\nu j} + \mathbf{v} + R\pi_\nu R_I^{-1}\mathbf{v}_I, \tag{9.8.5.7}$$

changing the position $\mathbf{n}_\nu + \mathbf{r}_{\nu j}$ into an equivalent one of the composite structure, not necessarily, however, within the same subsystem ν.

Finally, the composite structure can also be modulated. For the case of a one-dimensional modulation of each subsystem ν, the positions are

$$\mathbf{n}_\nu + \mathbf{r}_{\nu j} + \mathbf{u}_{\nu j}[\mathbf{q}_\nu \cdot (\mathbf{n}_\nu + \mathbf{r}_{\nu j})]. \tag{9.8.5.8}$$

Possibly the modulation vectors can also be expressed as integral linear combinations of the $\mathbf{a}^*_i$ $(i = 1, \ldots, 3 + d_o)$. Then, the dimension of V_I is again d_o. In general, however, one has to consider $(d - d_o)$ additional vectors, in order to ensure the validity of (9.8.4.5), now for $n = 3 + d$. We can then write

$$\mathbf{q}_\nu = \sum_{j=1}^{3+d} Q^{\nu}_j \mathbf{a}^*_j, \quad Q^{\nu}_j \text{ integers}. \tag{9.8.5.9}$$

The peaks of the diffraction pattern are at positions defined by a vector module M^*, which can be considered as the projection of a $(3 + d)$-dimensional lattice Σ^*, the reciprocal of which leaves invariant the pattern of the modulated atomic positions in the superspace given by

$$\{\mathbf{n}_\nu + r_{\nu j} - \pi_\nu \mathbf{t} + \mathbf{u}_{\nu j}[\mathbf{q}_\nu \cdot (\mathbf{n}_\nu + \mathbf{r}_{\nu j} - \pi_\nu \mathbf{t}) + \mathbf{q}_{I\nu} \cdot \mathbf{t}], \mathbf{t}\}, \quad \text{for any } \mathbf{t} \text{ of } V_I \tag{9.8.5.10}$$

with $\pi_\nu \mathbf{d}_j = 0$ for $j > d_o$, where $\mathbf{q}_{I\nu}$ is the internal part of the $(3 + d)$-dimensional vector that projects on $\mathbf{q}_\nu$. Their symmetry is a $(3 + d)$-dimensional superspace group G_s. The transformation induced in the modulated composite crystal by an element under g_s of G_s is now readily written down. For the case $d = d_o = 1$ and $g_s = (\{R|\mathbf{v}\}, \{\varepsilon|\Delta\})$, the position $\mathbf{n}_\nu + \mathbf{r}_{\nu j}$ is transformed into

$$R(\mathbf{n}_\nu + \mathbf{r}_{\nu j}) + \mathbf{v} + \varepsilon R\pi_\nu \Delta\mathbf{d}_1, \tag{9.8.5.11}$$

and the modulation $\mathbf{u}_{\nu j}[\mathbf{q}_\nu \cdot (\mathbf{n}_\nu + \mathbf{r}_{\nu j})]$ into

$$R\mathbf{u}_{\nu j}[\mathbf{q}_\nu \cdot (\mathbf{n}_\nu + \mathbf{r}_{\nu j} + \varepsilon\pi_\nu \Delta\mathbf{d}_1) - \varepsilon\mathbf{q}_{I\nu} \cdot \Delta\mathbf{d}_1].$$

This shows how the superspace-group approach can be applied to a composite (modulated) structure. Note that composite systems do not necessarily have an invariant set of (main) reflections at lattice positions.

9.8.5.2. *The incommensurate versus the commensurate case*

As said earlier, it sometimes makes sense also to use the description as developed for incommensurate crystal phases for a (commensurate) superstructure. In fact, very often the modulation wavevector also shows, in addition to continuously varying (incommensurate) values, several rational values at various phase transitions of a given crystal or in different compounds of a given structural family. In these cases, there is three-dimensional space-group symmetry. Generally, the space groups of the various phases are different. The description as used for incommensurate phases then gives the possibility of a more unified characterization for the symmetry of related modulated crystal phases. In fact, the theory of higher-dimensional space groups for modulated structures is largely independent of the