This results in a change for τ. For example, the $(3+1)$-dimensional space group $Pmmm(\frac{1}{2}0\gamma)000 = A^{Pmmm}_{1\,1\,\bar{1}}$ has a mirror perpendicular to the a axis with associated value $\tau = 0$. The parallel mirror at a distance $a/2$ has $\mathbf{v} = \mathbf{a}$ and consequently $\tau = \frac{1}{2}$. Hence, the symbols $Pmmm(\frac{1}{2}0\gamma)000$ and $Pmmm(\frac{1}{2}0\gamma)s00$ indicate the same group. This non-uniqueness in the symbol, however, does not have serious practical consequences.

Another source of ambiguity is the fact that the assignment of a satellite to a main reflection is not unique. For example, the reflection conditions for the group $I2cb(00\gamma)0s0 = P^{I2cb}_{\bar{1}s\bar{1}}$ are $h+k+l =$ even because of the centring and $l+m =$ even and $h+m =$ even for $h0lm$ because of the two glide planes perpendicular to the b axis. When one takes for the modulation vector $\mathbf{q} = \gamma'\mathbf{c}^* = (1-\gamma)\mathbf{c}^*$, the new indices are h, k, l', and m' with $l' = l+m$ and $m' = -m$. Then the reflection conditions become $l' =$ even and $h+m =$ even for $h0l'm'$. The first of these conditions implies the symbol $I2cb(00\gamma)000 = P^{I2cb}_{\bar{1}\,1\,\bar{1}}$ for the group considered. This, however, is the symbol for the nonequivalent group with condition $h =$ even for $h0lm$. This difficulty may be avoided by sometimes using a non-standard setting of the three-dimensional space group (see Yamamoto *et al.*, 1985). In this case, the setting $I2ab$ instead of $I2cb$ avoids the problem.

9.8.4. Theoretical foundation

9.8.4.1. *Lattices and metric*

A periodic crystal structure is defined in a three-dimensional Euclidean space V and is invariant with respect to translations $\mathbf{n}$ which are integral linear combinations of three fundamental ones $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$:

$$\mathbf{n} = \sum_{i=1}^{3} n_i \mathbf{a}_i, \quad n_i \text{ integers.} \tag{9.8.4.1}$$

These translations are linearly independent and span a lattice Λ. The *dimension* of Λ is the dimension of the space spanned by $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ and the *rank* is the (smallest) number of free generators of those integral linear combinations. In the present case, both are equal to three. Accordingly,

$$\{\Lambda\} = V \quad \text{and} \quad \Lambda \approx Z^3. \tag{9.8.4.2}$$

The elements of Z^3 are triples of integers that correspond to the coordinates of the lattice points. The Bragg reflection peaks of such a crystal structure are at the positions of a reciprocal lattice Λ^*, also of dimension and rank equal to three. Furthermore, the Fourier wavevectors $\mathbf{H}$ belong to Λ^* (after identification of lattice vectors with lattice points):

$$\mathbf{H} = \sum_{i=1}^{3} h_i \mathbf{a}_i^*, \quad h_i \text{ integers} \tag{9.8.4.3}$$

where $\{\mathbf{a}_i^*\}$ is the reciprocal basis

$$\mathbf{a}_i \cdot \mathbf{a}_k^* = \delta_{ik}.$$

The two corresponding metric tensors g and g^*,

$$g_{ik} = \mathbf{a}_i \cdot \mathbf{a}_k \quad \text{and} \quad g_{ik}^* = \mathbf{a}_i^* \cdot \mathbf{a}_k^*, \tag{9.8.4.4}$$

are positive definite and dual:

$$\sum_{k=1}^{3} g_{ik} g_{kj}^* = \delta_{ij}.$$

We now consider crystal structures defined in the same three-dimensional Euclidean space V with Fourier wavevectors that are integral linear combinations of $n = (3+d)$ fundamental ones $\mathbf{a}_1^*, \ldots, \mathbf{a}_n^*$:

$$\mathbf{H} = \sum_{i=1}^{n} h_i \mathbf{a}_i^*, \quad h_i \text{ integers.} \tag{9.8.4.5}$$

The components $(h_1, \ldots, h_n)$ are the indices labelling the corresponding Bragg reflection peaks.

A crystal is *incommensurate* when $d > 0$ and the vectors $\mathbf{a}_i^*$ linearly independent over the rational numbers. In that case, the crystal does not have lattice periodicity and is said to be *aperiodic*. The above description can still be convenient, even in the case that the vectors $\mathbf{a}_i^*$ are not independent over the rationals: one or more of them is then expressed as rational linear combinations of the others. A typical example is that of a superstructure arising from the (commensurate) modulation of a basic structure with lattice periodicity.

Let us denote by M^* the set of all integral linear combinations of the vectors $\mathbf{a}_1^*, \ldots, \mathbf{a}_n^*$. These are said to form a *basis*. It is a set of free Abelian generators, therefore the *rank* of M^* is n. The *dimension* of M^* is the dimension of the Euclidean space spanned by M^*

$$\{M^*\} = V \quad \text{and} \quad M^* \approx Z^n. \tag{9.8.4.6}$$

The elements of Z^n are precisely the set of indices introduced above. Mathematically speaking, M^* has the structure of a (free Abelian) module. Its elements are vectors. So we call M^* a *vector module*. This nomenclature is intended as a *generic* characterization. When a series of structures is considered with different values of the components of the last d vectors with respect to the first three, the generic values of these components are irrational, but accidentally they may become rational as well. This situation typically arises when considering crystal structures under continuous variation of parameters like temperature, pressure or chemical composition. In the case of an ordinary crystal, rank and dimension are equal, the crystal structure is *periodic*, and the vector module becomes a (reciprocal) lattice.

Lattices and vector modules are, mathematically speaking, free Z modules. For such a module, there exists a dual one that is also free and of the same rank. In the periodic crystal case, that duality can be expressed by a scalar product, but for an aperiodic crystal this is no longer possible. It is possible to keep the metrical duality by enlarging the space and considering the vector module M^* as the projection of an n-dimensional (reciprocal) lattice Σ^* in an n-dimensional Euclidean space V_s.

$$M^* \to \Sigma^*, \quad \{\Sigma^*\} = V_s \quad \text{and} \quad \Sigma^* \approx Z^n, \tag{9.8.4.7}$$

with the orthogonal projection π_E of V_s onto V defined by

$$M^* = \pi_E \Sigma^*. \tag{9.8.4.8}$$

This corresponds to attaching to the diffraction peak with indices $(h_1, \ldots, h_n)$ the point of an n-dimensional reciprocal lattice having the same set of coordinates. The orthocomplement of V in V_s is called internal space and denoted by V_I. The embedding is uniquely defined by the relations

$$a_{si}^* = (\mathbf{a}_i^*, \mathbf{a}_{Ii}^*), \quad i = 1, \ldots, n, \tag{9.8.4.9}$$

where $\{a_{si}^*\}$ is a basis of Σ^* and $\{\mathbf{a}_i^*\}$ a basis of M^*. The vectors $\mathbf{a}_{Ii}^*$ span V_I.

The crystal density ρ in V can also be embedded as ρ_s in V_s by identifying the Fourier coefficients $\hat{\rho}$ at points of M^* and of Σ^* having correspondingly the same components.

$$\hat{\rho}_s(h_1, \ldots, h_n) \equiv \hat{\rho}(h_1, \ldots, h_n). \tag{9.8.4.10}$$

Then ρ_s is invariant with respect to translations of the lattice Σ with basis

$$a_{si} = (\mathbf{a}_i, \mathbf{a}_{Ii}) \tag{9.8.4.11}$$

dual to (9.8.4.9). In the commensurate case, this correspondence requires that the given superstructure be considered as the limit of an incommensurate crystal [for which the embedding (9.8.4.10) is a one-to-one relation].

As discussed below, point-group symmetries R of the diffraction pattern, when expressed in terms of transformation of the set of indices, define n-dimensional integral matrices that can be considered as being n-dimensional orthogonal transformations R_s in V_s, leaving invariant the Euclidean metric tensors:

$$g_{sik} = a_{si} \cdot a_{sk} \quad \text{and} \quad g^*_{sik} = a^*_{si} \cdot a^*_{sk}. \tag{9.8.4.12}$$

The crystal classes considered in the tables suppose the existence of main reflections defining a three-dimensional reciprocal lattice. For that case, the embedding can be specialized by making the choice

$$\begin{aligned} a^*_{si} &= (\mathbf{a}^*_i, 0) \qquad i = 1, 2, 3, \\ a^*_{s(3+j)} &= (\mathbf{a}^*_{3+j}, \mathbf{d}^*_j) \qquad j = 1, 2, \ldots, d = n - 3, \end{aligned} \tag{9.8.4.13}$$

and, correspondingly,

$$\begin{aligned} a_{si} &= (\mathbf{a}_i, \mathbf{a}_{Ii}) \qquad i = 1, 2, 3, \\ a_{s(3+j)} &= (0, \mathbf{d}_j) \qquad j = 1, 2, \ldots, d, \end{aligned} \tag{9.8.4.14}$$

with $\mathbf{d}^*_i \cdot \mathbf{d}_k = \delta_{ik}$ and $\mathbf{a}^*_i \cdot \mathbf{a}_k = \delta_{ik}$. These are called *standard lattice bases*.

9.8.4.2. *Point groups*

9.8.4.2.1. *Laue class*

Definition 1. The *Laue point group* P_L of the diffraction pattern is the point group in three dimensions that transforms every diffraction peak into a peak of the same intensity.†

Because all diffraction vectors are of the form (9.8.4.5), the action of an element R of the Laue group is given by

$$R\mathbf{a}^*_i = \sum_{j=1}^{3+d} \Gamma^*(R)_{ji}\mathbf{a}^*_j, \quad i = 1, \ldots, 3 + d. \tag{9.8.4.15}$$

The $(3 + d) \times (3 + d)$ matrices $\Gamma^*(R)$ form a finite group of integral matrices $\Gamma^*(K)$ for K equal to P_L or to one of its subgroups. A well known theorem in algebra states that then there is a basis in $3 + d$ dimensions such that the matrices $\Gamma^*(R)$ on that basis are orthogonal and represent $(3 + d)$-dimensional orthogonal transformations R_s. The corresponding group is a $(3 + d)$-dimensional crystallographic group denoted by K_s. Because R is already an orthogonal transformation on V, R_s is reducible and can be expressed as a pair (R, R_I) of orthogonal transformations, in 3 and d dimensions, respectively. The basis on which (R, R_I) acts according to $\Gamma^*(R)$ is denoted by $\{(\mathbf{a}^*_i, \mathbf{a}^*_{Ii})\}$. It spans a lattice Σ^* that is the reciprocal of the lattice Σ with basis elements $(\mathbf{a}_i, \mathbf{a}_{Ii})$. The pairs (R, R_I), sometimes also noted (R_E, R_I), leave Σ invariant:

$$(R, R_I)(\mathbf{a}_i, \mathbf{a}_{Ii}) \equiv (R\mathbf{a}_i, R_I\mathbf{a}_{Ii}) = \sum_{j=1}^{3+d} \Gamma(R)_{ji}(\mathbf{a}_j, \mathbf{a}_{Ij}), \tag{9.8.4.16}$$

where $\Gamma(R)$ is the transpose of $\Gamma^*(R^{-1})$.

In many cases, one can distinguish a lattice of main reflections, the remaining reflections being called satellites. The main reflections are generally more intense. Therefore, main reflections are transformed into main reflections by elements of the Laue group. On a standard lattice basis (9.8.4.13), the matrices $\Gamma(R)$ take the special form

$$\Gamma(R) = \begin{pmatrix} \Gamma_E(R) & 0 \\ \Gamma_M(R) & \Gamma_I(R) \end{pmatrix}. \tag{9.8.4.17}$$

The transformation of main reflections and satellites is then given by $\Gamma^*(R)$ as in (9.8.4.15), the relation with $\Gamma(R)$ being (as already said)

$$\Gamma^*(R) = \tilde{\Gamma}(R^{-1}),$$

where the tilde indicates transposition. Accordingly, on a standard basis one has

$$\Gamma^*(R) = \begin{pmatrix} \Gamma^*_E(R) & \Gamma^*_M(R) \\ 0 & \Gamma^*_I(R) \end{pmatrix}. \tag{9.8.4.18}$$

The set of matrices $\Gamma_E(R)$ for R elements of K forms a crystallographic point group in three dimensions, denoted K_E, having elements R of $O(3)$, and the corresponding set of matrices $\Gamma_I(R)$ forms one in d dimensions denoted by K_I with elements R_I of $O(d)$.

For a modulated crystal, one can choose the $\mathbf{a}^*_i$ $(i = 1, 2, 3)$ of a standard basis. These span the (reciprocal) lattice of the basic structure. One can then express the additional vectors $\mathbf{a}^*_{3+j}$ (which are modulation wavevectors) in terms of the basis of the lattice of main reflections:

$$\mathbf{a}^*_{3+j} = \sum_{i=1}^{3} \sigma_{ji}\mathbf{a}^*_i, \quad j = 1, 2, \ldots, d. \tag{9.8.4.19}$$

The three components of the jth row of the $(d \times 3)$-dimensional matrix σ are just the three components of the jth modulation wavevector $\mathbf{q}_j = \mathbf{a}^*_{3+j}$ with respect to the basis $\mathbf{a}^*_1, \mathbf{a}^*_2, \mathbf{a}^*_3$. It is easy to show that the internal components $\mathbf{a}_{Ii}$ $(i = 1, 2, 3)$ of the corresponding dual standard basis can be expressed as

$$\mathbf{a}_{Ii} = -\sum_{j=1}^{d} \sigma_{ji}\mathbf{d}_j, \quad i = 1, 2, 3. \tag{9.8.4.20}$$

This follows directly from (9.8.4.19) and the definition of the reciprocal standard basis (9.8.4.13). From (9.8.4.16) and (9.8.4.17), a simple relation can be deduced between σ and the three constituents $\Gamma_E(R)$, $\Gamma_I(R)$, and $\Gamma_M(R)$ of the matrix $\Gamma(R)$:

$$-\Gamma_I(R)\sigma + \sigma\Gamma_E(R) = \Gamma_M(R). \tag{9.8.4.21}$$

Notice that the elements of $\Gamma_M(R)$ are integers, whereas σ has, in general, irrational entries. This requires that the irrational part of σ gives zero when inserted in the left-hand side of equation (9.8.4.21). It is therefore possible to decompose formally σ into parts σ^i and σ^r as follows.

$$\sigma = \sigma^i + \sigma^r, \quad \text{with} \quad \sigma^i \equiv \frac{1}{N}\sum_R \Gamma_I(R)\sigma\Gamma_E(R)^{-1}, \tag{9.8.4.22}$$

where the sum is over all elements of the Laue group of order N. It follows from this definition that

$$\Gamma_I(R)\sigma^i\Gamma_E(R)^{-1} = \sigma^i. \tag{9.8.4.23}$$

This implies

$$\Gamma_M(R) = -\Gamma_I(R)\sigma^r + \sigma^r\Gamma_E(R). \tag{9.8.4.24}$$

The matrix σ^r has rational entries and is called the rational part of σ. The part σ^i is called the irrational (or invariant) part.

The above equations simplify for the case $d = 1$. The elements $\sigma_{1i} = \sigma_i$ are the three components of the wavevector $\mathbf{q}$, the row matrix $\sigma\Gamma_E(R)$ has the components of $R^{-1}\mathbf{q}$ and $\Gamma_I(R) = \varepsilon = \pm 1$

† See footnote on p. 913.

since, for $d = 1$, $\mathbf{q}$ can only be transformed into $\pm\mathbf{q}$. One has the corresponding relations

$$\mathbf{q} = \mathbf{q}^i + \mathbf{q}^r, \quad \text{with} \quad \mathbf{q}^i \equiv \frac{1}{N}\sum_R \varepsilon R\mathbf{q}, \tag{9.8.4.25}$$

and

$$R\mathbf{q} \equiv \varepsilon\mathbf{q} \text{ (modulo reciprocal lattice } \Lambda^*); \quad R\mathbf{q}^i = \varepsilon\mathbf{q}^i. \tag{9.8.4.26}$$

The reciprocal-lattice vector that gives the difference between $R\mathbf{q}$ and $\varepsilon\mathbf{q}$ has as components the elements of the row matrix $\Gamma_M(R)$.

9.8.4.2.2. *Geometric and arithmetic crystal classes*

According to the previous section, in the case of modulated structures a standard basis can be chosen (for M^* and correspondingly for Σ^*). According to equation (9.8.4.15), for each three-dimensional point-group operation R that leaves the diffraction pattern invariant, there is a point-group transformation R_E in the external space (the physical one, so that $R_E = R$) and a point-group transformation R_I in the internal space, such that the pair (R, R_I) is a $(3+d)$-dimensional orthogonal transformation R_s leaving a $(3+d)$-dimensional lattice Σ invariant. For incommensurate crystals, this internal transformation is unique and follows from the transformation by R of the modulation wavevectors [see equations (9.8.4.15) and (9.8.4.18) for the $\mathbf{a}^*_{3+j}$ basis vectors]: there is exactly one R_I for each R. This is so because in the incommensurate case the correspondence between M^* and Σ^* is uniquely fixed by the embedding rule (9.8.4.10) (see Subsection 9.8.4.1). Because the matrices $\Gamma(R)$ and the corresponding transformations in the $(3+d)$-dimensional space form a group, this implies that there is a mapping from the group K_E of elements R_E to the group K_I of elements R_I that transforms products into products, *i.e.* is a group homomorphism. A point group K_s of the $(3+d)$-dimensional lattice constructed for an incommensurate crystal, therefore, consists of a three-dimensional crystallographic point group K_E, a d-dimensional crystallographic point group K_I, and a homomorphism from K_E to K_I.

Definition 2. Two $(3+d)$-dimensional point groups K_s and K'_s are *geometrically equivalent* if they are connected by a pair of orthogonal transformations (T_E, T_I) in V_E and V_I, respectively, such that for every R_s from the first group there is an element R'_s of the second group such that $R_E T_E = T_E R'_E$ and $R_I T_I = T_I R'_I$.

A point group determines a set of groups of matrices, one for each standard basis of each lattice left invariant.

Definition 3. Two groups of matrices are *arithmetically equivalent* if they are obtained from each other by a transformation from one standard basis to another standard basis.

The arithmetic equivalence class of a $(3+d)$-dimensional point group is fully determined by a three-dimensional point group and a standard basis for the vector module M^* because of relation (9.8.4.15).

In three dimensions, there are 32 geometrically non-equivalent point groups and 73 arithmetically non-equivalent point groups. In one dimension, these numbers are both equal to two. Therefore, one finds all $(3+1)$-dimensional point groups of incommensurately modulated structures by considering all triples of one of the 32 (or 73) point groups, for each one of the two one-dimensional point groups and all homomorphisms from the first to the second.

Analogously, in $(3+d)$ dimensions, one takes one of the 32 (73) groups, one of the d-dimensional groups, and all homomorphisms from the first to the second. If one takes all triples of a three-dimensional group, a d-dimensional group, and a homomorphism from the first to the second, one finds, in general, groups that are equivalent. The equivalent ones still have to be eliminated in order to arrive at a list of non-equivalent groups.

9.8.4.3. *Systems and Bravais classes*

9.8.4.3.1. *Holohedry*

The Laue group of the diffraction pattern is a three-dimensional point group that leaves the positions (and the intensities)† of the diffraction spots as a set invariant, thus the vector module M^* also. As discussed in Subsection 9.8.4.2, each of the elements of the Laue group can be combined with an orthogonal transformation in the internal space. The resulting point group in $3+d$ dimensions leaves the lattice Σ^* invariant for which the vector module M^* is the projection. Conversely, if one has a point group that leaves the $(3+d)$-dimensional lattice invariant, its three-dimensional (external) part with elements $R_E = R$ leaves the vector module invariant.

Definition 4. The holohedry of the lattice Σ^* is the subgroup of the direct product $O(3) \times O(d)$, *i.e.* the group of all pairs of orthogonal transformations $R_s = (R, R_I)$ that leave the lattice invariant.

This choice is possible because the point groups are reducible, *i.e.* leave the subspaces V and V_I of the direct sum space V_s invariant. In the case of an incommensurate crystal, the projection of Σ^* on M^* is one-to-one as one can see as follows. The vector

$$H_s = \sum_{i=1}^{3} h_i(\mathbf{a}_i^*, 0) + \sum_{j=1}^{d} m_j(\mathbf{q}_j, \mathbf{d}_j^*) \tag{9.8.4.27}$$

of Σ^* is projected on $\mathbf{H} = \sum_i h_i\mathbf{a}_i^* + \sum_j m_j\mathbf{q}_j$. The vectors projected on the null vector satisfy, therefore, the relation $\sum_i h_i\mathbf{a}_i^* + \sum_j m_j\mathbf{q}_j = 0$. For an incommensurate phase, the basis vectors are rationally independent, which means that $h_i = 0$ and $m_j = 0$ for any i and j. Consequently, precisely one vector of Σ^* is projected on each given vector of M^*.

Suppose now $R = 1$. This transformation leaves the component of every vector belonging to Σ^* in V invariant. If R_I is the corresponding orthogonal transformation in V_I of an element R_s of the point group, a vector with component $\mathbf{H}_I$ is transformed into a vector with component H'_I. Since a given $\mathbf{H}$ is the component of only one vector of Σ^*, this implies $\mathbf{H}_I = \mathbf{H}'_I$. Consequently, R_I is also the identity transformation. Therefore, for incommensurate modulated phases, there are no point-group elements with $R = R_E = 1$ and $R_I \neq 1$. For commensurate crystal structures embedded in the superspace, this is different: point-group elements with internal component different from the identity associated with an external component equal to unity can occur.

For modulated crystal structures, the holohedral point group can be expressed with respect to a lattice basis of standard form

† See footnote on p. 913.

(9.8.4.13). It is then faithfully represented by integral matrices that are of the form indicated in (9.8.4.17) and (9.8.4.18).

9.8.4.3.2. *Crystallographic systems*

Definition 5. A *crystallographic system* is a set of lattices having geometrically equivalent holohedral point groups.

In this way, a given holohedral point group (and even each crystallographic point group) belongs to exactly one system. Two lattices belong to the same system if there are orthonormal bases in V and in V_I, respectively, such that the holohedral point groups of the two lattices are represented by the same set of matrices.

9.8.4.3.3. *Bravais classes*

Definition 6. Two lattices belong to the same *Bravais class* if their holohedral point groups are arithmetically equivalent.

This means that each of them admits a lattice basis of standard form such that their holohedral point group is represented by the same set of integral matrices.

9.8.4.4. *Superspace groups*

9.8.4.4.1. *Symmetry elements*

The elements of a $(3+d)$-dimensional superspace group are pairs of Euclidean transformations in 3 and d dimensions, respectively:

$$g_s = (\{R|\mathbf{v}\}, \{R_I|\mathbf{v}_I\}) \in E(3) \times E(d), \tag{9.8.4.28}$$

i.e. are elements of the direct product of the corresponding Euclidean groups. The elements $\{R|\mathbf{v}\}$ form a three-dimensional space group, but the same does not hold for the elements $\{R_I|\mathbf{v}_I\}$ of $E(d)$. This is because the internal translations $\mathbf{v}_I$ also contain the 'compensating' transformations associated with the corresponding translation $\mathbf{v}$ in V [see (9.8.4.32)]. In other words, a basis of the lattice Σ does not simply split into one basis for V and one for V_I.

As for elements of a three-dimensional space group, the translational component $\upsilon_s = (\mathbf{v}, \mathbf{v}_I)$ of the element g_s can be decomposed into an intrinsic part υ_s^o and an origin-dependent part υ_s^a:

$$(\upsilon, \upsilon_I) = (\mathbf{v}^o, \mathbf{v}_I^o) + (\mathbf{v}^a, \mathbf{v}_I^a),$$

with

$$(\mathbf{v}^o, \mathbf{v}_I^o) = \frac{1}{n}\sum_{m=1}^{n} (R^m\mathbf{v}, R_I^m\mathbf{v}_I), \tag{9.8.4.29}$$

where n denotes the order of the element R. In particular, for $d = 1$ the intrinsic part $\mathbf{v}_I^o$ of $\mathbf{v}_I$ is equal to $\mathbf{v}_I$ if $R_I = \varepsilon = +1$ and vanishes if $\varepsilon = -1$. The latter means that for $d = 1$ there is always an origin in the internal space such that the internal shift $\mathbf{v}_I$ can be chosen to be zero for an element with $\varepsilon = -1$.

The internal part of the intrinsic translation can itself be decomposed into two parts. One part stems from the presence of a translation in the external space. The lattice of the $(3+d)$-dimensional space group has basis vectors

$$(\mathbf{a}_i, \mathbf{a}_{Ii}), (0, \mathbf{d}_j), \quad i = 1, 2, 3, \quad j = 1, \ldots, d. \tag{9.8.4.30}$$

The internal part of the first three basis vectors is

$$\mathbf{a}_{Ii} = -\Delta\mathbf{a}_i = -\sum_{j=1}^{d} \sigma_{ji}\mathbf{d}_j \tag{9.8.4.31}$$

according to equation (9.8.4.20). The three-dimensional translation $\mathbf{v} = \sum_i \upsilon_i\mathbf{a}_i$ then entails a d-dimensional translation $-\Delta\mathbf{v}$ in V_I given by

$$\Delta\mathbf{v} = \Delta\left(\sum_{i=1}^{3} \upsilon_i\mathbf{a}_i\right) = \sum_{i=1}^{3} \upsilon_i\Delta\mathbf{a}_i. \tag{9.8.4.32}$$

These are the so-called compensating translations. Hence, the internal translation $\mathbf{v}_I$ can be decomposed as

$$\mathbf{v}_I = -\Delta\mathbf{v} + \boldsymbol{\delta}, \tag{9.8.4.33}$$

where $\boldsymbol{\delta} = \sum_{j=1}^{d} \upsilon_{3+j}\mathbf{d}_j$.

This decomposition, however, does still depend on the origin. Consider the case $d = 1$. Then an origin shift $\mathbf{s}$ in the three-dimensional space changes the translation $\mathbf{v}$ to $\mathbf{v} + (1-R)\mathbf{s}$ and its internal part $-\Delta\mathbf{v} = -\mathbf{q}\cdot\mathbf{v}$ to $-\mathbf{q}\cdot\mathbf{v} - \mathbf{q}\cdot(1-R)\mathbf{s}$. This implies that for the case that $\varepsilon = 1$ the part δ changes to $\delta + \mathbf{q}\cdot(1-R)\mathbf{s} = \delta + \mathbf{q}^r\cdot(1-R)\mathbf{s}$, because $\mathbf{q}^i$ is invariant under R. Therefore, δ changes, in general. The internal translation

$$\tau = \delta - \mathbf{q}^r\cdot\mathbf{v}, \tag{9.8.4.34}$$

however, is invariant under an origin shift in V.

Definition 7. *Equivalent superspace groups*. Two superspace groups are equivalent if they are isomorphic and have point groups that are arithmetically equivalent.

Another definition leading to the same partition of equivalent superspace groups considers equivalency with respect to affine transformations among bases of standard form.

This means that two equivalent superspace groups admit standard bases such that the two space groups are represented by the same set of $(4+d)$-dimensional affine transformation matrices. We recall that an n-dimensional Euclidean transformation $g_s = \{R_s|v_s\}$ if referred to a basis of the space can be represented isomorphically by an $(n+1)$-dimensional matrix, of the form

$$A(g_s) = \begin{pmatrix} R_s & v_s \\ 0 & 1 \end{pmatrix} \tag{9.8.4.35}$$

with R_s an $n \times n$ matrix and v_s an n-dimensional column matrix, all with real entries.

9.8.4.4.2. *Equivalent positions and modulation relations*

A $(3+d)$-dimensional space group that leaves a function invariant maps points in $(3+d)$-space to points where the function has the same value. The atomic positions of a modulated crystal represent such a pattern, and the superspace group leaving the crystal invariant leads to a partition into equivalent atomic positions. These relations can be formulated either in $(3+d)$-dimensional space or, equally well, in three-dimensional space. As a simple case, we first consider a crystal with a one-dimensional occupation modulation: this implies $d = 1$. Again, as in §9.8.1.3.2, we omit to indicate the basis vectors $\mathbf{d}_1$ and $\mathbf{d}_1^*$ and give only the corresponding components.

An element of the $(3+1)$-dimensional superspace group is a pair

$$g_s = (\{R|\mathbf{v}\}, \{\varepsilon|\upsilon_I\}) \tag{9.8.4.36}$$

of Euclidean transformations in V and V_I, respectively. This element maps a point located at $r_s = (\mathbf{r}, t)$ to one at $(R\mathbf{r} + \mathbf{v}, \varepsilon t + \upsilon_I)$. Suppose the probability for the position $\mathbf{n} + \mathbf{r}_j$ to be occupied by an atom of species A is given by

$$P_A(\mathbf{n}, j, t) = p_j[\mathbf{q}\cdot(\mathbf{n} + \mathbf{r}_j) + t], \tag{9.8.4.37}$$

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

assumption of irrationality. Only some of the statements need to be adapted. The most important change is that there is no longer a one-to-one correspondence between the points of the reciprocal lattice Σ^* and its projection on V defining the positions of the Bragg peaks. Furthermore, the projection of the lattice Σ on the space V_I forms a discrete set. The latter means the following. For an incommensurate modulation, the incommensurate structure, which is the intersection of a periodic structure with the hyperplane $\mathbf{r}_I = 0$, is also the intersection of the same periodic structure with a hyperplane $\mathbf{r}_I = \text{constant}$, where this constant is of the form

$$\sum_{i=1}^{3} h_i \mathbf{a}_{Ii} + \sum_{j=1}^{d} m_j \mathbf{a}_{I3+j}. \qquad (9.8.5.12)$$

Because for an incommensurate structure these vectors form a dense set in V_I, the phase of the modulation function with respect to the basic structure is not determined. For a commensurate modulation, however, the points (9.8.5.12) form a discrete set, even belong to a lattice, and the phase (or the phases) of the modulation are determined within vectors of this lattice. Notice that the grid of this lattice becomes finer as the denominators in the rational components become larger.

When G_s is a $(3+d)$-dimensional superspace group, its elements, in general, do not leave the ordinary space V invariant. The subgroup of all elements that do leave V invariant, when restricted to V, is a group of distance-preserving transformations in three dimensions and thus a subgroup of $E(3)$, the three-dimensional Euclidean group. In general, this subgroup is not a three-dimensional space group. It is so when the modulation wavevectors all have rational components only, *i.e.* when σ is a matrix with rational entries. Because the phase of the modulation function is now determined (within a given rational number smaller than 1), the space group depends in general on this phase.

As an example, consider a one-dimensional modulation of a basic structure with orthorhombic space group *Pcmn*. Suppose that the modulation wavevector is $\gamma\mathbf{c}^*$. Then the mirror $R = m_z$ perpendicular to the c axis is combined with $R_I = \varepsilon = -1$. Suppose, furthermore, that the glide reflection perpendicular to the a axis and the b mirror are both combined with a phase shift $\frac{1}{2}$. In terms of the coordinates x, y, z with respect to the a, b and c axes, and internal coordinate t, the generators of the $(3+1)$-dimensional superspace group $Pcmn(00\gamma)ss0$ act as

$$(x, y, z, t) \to (x + k, y + l, z + m, t - \gamma m + n), \quad k, l, m, n \text{ integers}, \qquad (9.8.5.13a)$$

$$(x, y, z, t) \to (-x + k + \tfrac{1}{2}, y + l, z + \tfrac{1}{2} + m, t - \gamma/2 - \gamma m + \tfrac{1}{2} + n), \qquad (9.8.5.13b)$$

$$(x, y, z, t) \to (x + k, -y + l + \tfrac{1}{2}, z + m, t - \gamma m + \tfrac{1}{2} + n), \qquad (9.8.5.13c)$$

$$(x, y, z, t) \to (x + \tfrac{1}{2} + k, y + \tfrac{1}{2} + l, -z + \tfrac{1}{2} + m, -t - \gamma/2 - \gamma m + n). \qquad (9.8.5.13d)$$

Note that these positions are referred to a split basis (*i.e.* of basis vectors lying either in V or in V_I) and not to a basis of the lattice Σ. When the superstructure is the intersection of a periodic structure with the plane at $t = t_o$, its three-dimensional space group follows from equation (9.8.5.13) by the requirement $t' = t_o$. When γ has the rational value r/s with r and s relatively prime, the conditions for each of the generators to give an element of the three-dimensional space group are, respectively:

$$-rm + sn = 0 \qquad (9.8.5.14a)$$

$$-2rm + 2sn = r - s \qquad (9.8.5.14b)$$

$$-2rm + 2sn = -s \qquad (9.8.5.14c)$$

$$-2rm + 2sn = 4st, \qquad (9.8.5.14d)$$

for m, n, r, s integers and t real. These conditions are never satisfied simultaneously. It depends on the parity of both r and s which element occurs, and for the elements with $\varepsilon = -1$ it also depends on the value of the 'phase' t, or more precisely on the product $\tau = 4st$. The translation group is determined by the first condition as in (9.8.5.14*a*). Its generators are

$$\mathbf{a}, \mathbf{b}, \text{ and } s\mathbf{c},$$

where the last vector is the external part of the lattice vector $s(\mathbf{c}, -r/s) + r(0, 1)$. The other space-group elements can be derived in the same way. The possible space groups are:

$\gamma = r/s$	τ even integer	τ odd integer	otherwise
r even, s odd	$11\frac{2_1}{n}$	$2_12_12_1$	112_1
r odd, s even	$1\frac{2_1}{c}1$	2_1cn	1c1
r odd, s odd	$\frac{2_1}{c}11$	$c2_1n$	$c11$

In general, the three-dimensional space groups compatible with a given $(3+d)$-dimensional superspace group can be determined using analogous equations.

As one can see from the table above, the orthorhombic $(3+d)$-dimensional superspace group leads in several cases to monoclinic three-dimensional space groups. The lattice of main reflections, however, still has orthorhombic point-group symmetry. Description in the conventional way by means of three-dimensional groups then neglects some of the structural features present. Even if the orthorhombic symmetry is slightly broken, the orthorhombic basic structure is a better characterization than a monoclinic one. Note that in that case the superspace-group symmetry is also only an approximation.

When the denominators of the wavevector components become small, additional symmetry operations become possible. Because the one-to-one correspondence between Σ^* and M^* is no longer present, there may occur symmetry elements with trivial action in V but with nontrivial transformation in V_I. For $d = 1$, these possibilities have been enumerated. The corresponding Bravais classes are given in Table 9.8.3.2(*b*).

APPENDIX *A*
Glossary of symbols

M^* Vector module in m-dimensional reciprocal space ($m = 1, 2, 3$; normally $m = 3$), isomorphic to Z^n with $n \geq m$. The dimension of M^* is m, its rank n.

$\mathbf{a}_i^*$ ($i = 1, \ldots, n$.) Basis of a vector module M^* of rank n; if $n = 4$ and $\mathbf{q}$ is modulation wavevector (the $n = 4$ case is restricted in what follows to modulated crystals), the basis of M^* is chosen as $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*, \mathbf{q}$, with $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ a basis of the lattice of main reflections.

Λ^* Lattice of main reflections, m-dimensional reciprocal lattice.

$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ (Conventional) basis of Λ^* for $m = 3$.

Λ Direct m-dimensional lattice, dual to Λ^*.

V_s Superspace; Euclidean space of dimension $n = m + d$; $V_s = V \oplus V_I$.

V Physical (or external) space of dimension m ($m = 1, 2$ or 3), also indicated by V_E.

V_I Internal (or additional) space of dimension d.

Σ^* Reciprocal lattice in n-dimensional space, whose orthogonal projection on V is M^*.

Σ Lattice in n-dimensional superspace for which Σ^* is the reciprocal one.

a^*_{si} Lattice basis of Σ^* in V_s ($i = 1, \ldots, n$);
if $n = 4$, this basis can be chosen as $\{(\mathbf{a}^*, 0), (\mathbf{b}^*, 0), (\mathbf{c}^*, 0), (\mathbf{q}, 1)\}$ and is called standard. An equivalent notation is $(\mathbf{q}, 1) = (\mathbf{q}, \mathbf{d}^*)$;
for $n = 3 + d$, the general form of a standard basis is $(\mathbf{a}^*, 0)$, $(\mathbf{b}^*, 0)$, $(\mathbf{c}^*, 0)$, $(\mathbf{q}_1, \mathbf{d}^*_1), \ldots, (\mathbf{q}_j, \mathbf{d}^*_j), \ldots, (\mathbf{q}_d, \mathbf{d}^*_d)$.

a_{si} ($i = 1, \ldots, n$.) Lattice basis of Σ in V_s dual to $\{a^*_{si}\}$;
if $n = 4$, the standard basis is $(\mathbf{a}, -\mathbf{q}\cdot\mathbf{a}), (\mathbf{b}, -\mathbf{q}\cdot\mathbf{b}), (\mathbf{c}, -\mathbf{q}\cdot\mathbf{c}), (0, 1) = (0, \mathbf{d})$;
for $n = 3 + d$, a standard basis is dual to the standard one given above.

$\mathbf{q}_j$ Modulation wavevector(s) $\mathbf{q}_j = \sum_{i=1}^{3} \sigma_{ji}\mathbf{a}^*_i$;
if $n = 4$, $\mathbf{q} = \sum_{i=1}^{3} \sigma_i \mathbf{a}^*_i = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*$;
$\sigma = (\alpha, \beta, \gamma)$;
if $n = 4$, $\mathbf{q} = \mathbf{q}^i + \mathbf{q}^r$, with $\mathbf{q}^i = (1/N)\sum_{R \text{ in } K} \varepsilon(R) R\mathbf{q}$, where $\varepsilon(R) = R_I$, and N is the order of K.

$\mathbf{H}$ Bragg reflections: $\mathbf{H} = \sum_{i=1}^{n} h_i \mathbf{a}^*_i = (h_1, h_2, \ldots, h_n)$;
if $n = 4$, $\mathbf{H} = \sum_{i=1}^{4} h_i \mathbf{a}^*_i = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q} = (h, k, l, m)$.

H_s Embedding of $\mathbf{H}$ in V_s: for $\mathbf{H} = (h_1, \ldots, h_n) = \sum_{i=1}^{n} h_i \mathbf{a}^*_i$, one has correspondingly $H_s = (\mathbf{H}, \mathbf{H}_I) = \sum_{i=1}^{n} h_i a^*_{si}$.

P_L Laue point group.

$O(m)$ Orthogonal group in m dimensions.

R Orthogonal point-group transformation, element of $O(m)$.

K Point group, crystallographic subgroup of $O(m)$.

R_s Superspace point-group element: $R_s = (R_E, R_I) = (R, R_I)$ element of $O(m) \times O(d)$ with $R_E = R$ external, and R_I internal part of R_s, respectively;
if $n = 4$, superspace point-group element: $[R, \varepsilon(R)]$ with $\varepsilon(R) = \pm 1$, also written (R, ε).

K_s Point group, crystallographic subgroup of $O(m) \times O(d)$.

K_E External part of K_s, crystallographic point group, subgroup of $O(m)$ with as elements the external part transformations of K_s.

K_I Internal part of K_s, crystallographic point group, subgroup of $O(d)$ with as elements the internal part transformations of K_s.

$\mathbf{r}_o(\mathbf{n}, j)$ Atomic positions in the basic structure: $\mathbf{r}_o(\mathbf{n}, j) = \mathbf{n} + \mathbf{r}_j$ with $\mathbf{n} \in \Lambda$.

$\mathbf{r}(\mathbf{n}, j)$ Atomic positions in the displacively modulated structure;
$(d = 1)$: $\mathbf{r}(\mathbf{n}, j) = \mathbf{r}_o(\mathbf{n}, j) + \mathbf{u}_j[\mathbf{q}\cdot\mathbf{r}(\mathbf{n}, j) + \varphi_j]$. In general, however, different phases $\varphi_{j\alpha}$ may occur for different components $u_{j\alpha}$ along the crystallographic axes.

$\mathbf{u}_j(x)$ Modulation function for displacive modulation with $\mathbf{u}_j(x + 1) = \mathbf{u}_j(x)$.

$p_j(x)$ Modulation function for occupation modulation with $p_j(x + 1) = p_j(x)$.

g Euclidean transformation in m dimensions; $g = \{R|\mathbf{v}\}$ element of the space group G with rotational part R and translational part $\mathbf{v}$.

$\mathbf{v}^o$ Intrinsic translation part (origin independent).

g_s Superspace group transformation ($d = 1$):
$g_s = \{(R, \varepsilon)|(\mathbf{v}, \Delta)\} = (\{R|\mathbf{v}\}, \{\varepsilon|\Delta\}) = \{R_s|\upsilon_s\}$
element of the superspace group G_s.
In the $(3 + d)$-dimensional case:
$g_s = \{(R, R_I)|(\mathbf{v}, \mathbf{v}_I)\} = (\{R|\mathbf{v}\}, \{R_I|\mathbf{v}_I\})$.

υ_I Internal shift ($d = 1$): $\upsilon_I = \Delta = \delta - \mathbf{q}\cdot\mathbf{v}$.

τ Intrinsic internal shift ($d = 1$): $\tau = \delta - \mathbf{q}^r\cdot\mathbf{v}$.

$\Gamma^*(R)$ Point-group transformation R with respect to a basis of M^* and at the same time superspace point-group transformation R_s with respect to a corresponding basis of Σ^*.

$\Gamma(R)$ Superspace point-group transformation with respect to a lattice basis of Σ dual to that of Σ^* leading to $\Gamma^*(R)$. The mutual relation is then $\Gamma^*(R) = \tilde{\Gamma}(R^{-1})$ with the tilde denoting transposition.

$\Gamma_E(R)$, $\Gamma_I(R)$, $\Gamma_M(R)$: external, internal, and mixed blocks of $\Gamma(R)$, respectively.

$\Gamma^*_E(R)$, $\Gamma^*_I(R)$, $\Gamma^*_M(R)$: external, internal, and mixed blocks of $\Gamma^*(R)$, respectively.

$S_{\mathbf{H}}$ Structure factor:

$$S_{\mathbf{H}} = \sum_{\mathbf{n}} \sum_{j} f_j(\mathbf{H}) \exp[2\pi i \mathbf{H}\cdot\mathbf{r}(\mathbf{n}, j)].$$

$f_j(\mathbf{H})$ Atomic scattering factor for atom j.

APPENDIX *B*
Basic definitions

In the following, we give a short definition of the most important notions appearing in the theory and of the equivalence relations used in the tables. The latter are especially adapted to the case of modulated crystal phases.

[i] *Vector module*. A set of all integral linear combinations of a finite number of vectors. The *dimension* of the vector module is the dimension (m) of the space V (also indicated as V_E and called external) generated by it over the real numbers. Its *rank* (n) is the minimal number of rationally independent vectors that generate the vector module. If this rank is equal to the dimension, the vector module is also a lattice. In general, a vector module of rank n and dimension m is the orthogonal projection on the m-dimensional space V of an n-dimensional lattice. We shall restrict ourselves mainly to the case $m = 3$ and $n = 4$, but the following definitions are valid for modulated phases of arbitrary dimension and rank. The *dimension of the modulation* (d) is $n - m$. The modulation phases span a d-dimensional space V_I (called internal or additional).

[ii] *Superspace*. V_s is an n-dimensional Euclidean space that is the direct sum of an m-dimensional *external* space V (of the crystal) and a d-dimensional *internal* space V_I (for the additional degrees of freedom). V is sometimes denoted by V_E.

[iii] *Split basis*. For the space $V_s = V \oplus V_I$, this is a basis with m basis vectors in V and $d = n - m$ basis vectors in V_I.

[iv] *Standard basis*. For the $(m + d)$-dimensional space $V_s = V \oplus V_I$, a standard basis in direct space is one having the last d basis vectors lying in V_I (d = dimension of V_I = dimension of the modulation). A standard basis in

reciprocal space (V^* identified with V) is one with the first m basis vectors lying in V (m = dimension of V).

[v] *Conventional basis*. For a lattice Λ in three dimensions, it is a basis such that (i) the lattice generated by it is contained in Λ as a sublattice and (ii) there is the standard relationship between the basis vectors (*e.g.* for a cubic lattice a conventional basis consists of three mutually perpendicular vectors of equal length).

The lattice Λ is obtained from the lattice spanned by the conventional basis by adding (a small number of) *centring vectors*. [For example, the b.c.c. lattice is obtained from the conventional cubic lattice by centring the unit cell with $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$.] The reciprocal basis for the conventional basis is a conventional basis for the reciprocal lattice Λ^*.

In the $(m+d)$-dimensional superspace, a conventional basis for the lattice Σ satisfies the same conditions (i) and (ii) as formulated above for the three-dimensional case. In addition, however, one requires that the basis is standard and such that the non-vanishing external components satisfy the relations of an ($m=3$) conventional basis and that the corresponding internal components only involve the irrational components of the modulation vector(s) (for $d=1$ the basis is such that $\mathbf{q}^r = 0$, thus $\mathbf{q}^i = \mathbf{q}$). Again a conventional basis for Σ^* is dual to the same for Σ.

[vi] *Holohedry*. The holohedry of a vector module is the group of orthogonal transformations of the same dimension that leaves the vector module invariant. The holohedry of an $(m+d)$-dimensional lattice is the subgroup of $O(m)\times O(d)$ that leaves the lattice invariant.

[vii] *Point group*. An $(m+d)$-dimensional crystallograhic point group $K_s = (K_E, K_I)$ is a subgroup of $O(m)\times O(d)$. With respect to a standard lattice basis its elements $R_s = (R, R_I)$ are of the form

$$\Gamma(R) = \begin{pmatrix} \Gamma_E(R) & 0 \\ \Gamma_M(R) & \Gamma_I(R) \end{pmatrix},$$

where all the entries are integers and R is an element of an m-dimensional point group K, which is actually the same as K_E. For an incommensurate modulated crystal, K_s and K are isomorphic groups. If $d=1$, $\Gamma_I(R) = \varepsilon = \pm 1$.

[viii] *Geometric crystal class*. Two point groups $K_s = (K_E, K_I)$ and $K_s' = (K_E', K_I')$ of pairs (R_E, R_I) of orthogonal transformations [R_E belongs to $O(m)$ and R_I to $O(d)$] are geometrically equivalent if and only if there are orthogonal transformations T_E and T_I of $O(m)$ and $O(d)$, respectively, such that $R_E' = T_E \cdot R_E \cdot T_E^{-1}$ and $R_I' = T_I \cdot R_I \cdot T_I^{-1}$ for some group isomorphism $(R_E, R_I) \rightarrow (R_E', R_I')$. For $d=1$, that condition takes a simpler form because $R_I = \varepsilon = \pm 1$.

[ix] *Arithmetic crystal class*. A group of integral matrices $\Gamma^*(R)$ [for $R \in K$ of $O(m)$] is determined on a basis $\{\mathbf{a}_i^*;\ i=1,\ldots,n\} = \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*, \mathbf{q}_1, \ldots, \mathbf{q}_d$ of a vector module in reciprocal space by an m-dimensional point group K (here $m=3$). For modulated crystals, the transformations in direct space are given by matrices $\Gamma(R) =$ transpose of $\Gamma^*(R^{-1})$ which are of the form (9.8.4.17). Two groups $\Gamma'(K')$ and $\Gamma(K)$ are arithmetically equivalent if and only if there is an $(m+d)$-dimensional matrix S of the form

$$S = \begin{pmatrix} S_E & 0 \\ S_M & S_I \end{pmatrix}$$

with integral entries and determinant ± 1 such that $\Gamma'(K') = S\Gamma(K)\cdot S^{-1}$. Here S_E is $m\times m$ and S_I is $d\times d$ dimensional. An alternative formulation is: the matrix groups $\Gamma(K)$ and $\Gamma'(K')$ determined as in equation (9.8.1.16) or in equation (9.8.1.21) are arithmetically equivalent if

(*a*) the groups K and K' are geometrically equivalent m-dimensional point groups [the corresponding $(m+d)$-dimensional point groups K_s and K_s' are then also geometrically equivalent];

(*b*) there are vector module bases $\mathbf{a}^*, \ldots, \mathbf{q}_d$ and $\mathbf{a}^{*\prime}, \ldots, \mathbf{q}_d'$ such that K on the first basis gives the same group of matrices as K' on the second basis.

[x] *Bravais class*. Two vector modules are in the same Bravais class if the groups of matrices determined by their holohedries are arithmetically equivalent. Two $(m+d)$-dimensional lattices are in the same Bravais class if their holohedries are arithmetically equivalent. In both cases, one can find bases for the two structures such that the holohedries take the same matrix form. In the $(m+d)$-dimensional case, the lattice bases both have to be standard.

[xi] *Superspace group*. An $(m+d)$-dimensional superspace group is an n-dimensional space group ($n=m+d$) such that it has a d-dimensional lattice of internal translations. (This latter property reflects the periodicity of the modulation.) It is determined on a standard lattice basis by the matrices $\Gamma(R)$ of the point-group transformations and by the components $\upsilon_i(R)$ ($i=1,\ldots,m+d$) of the translation parts of its elements. The matrices $\Gamma(R)$ represent at the same time the elements R of the m-dimensional point group K and the corresponding elements R_s of the $(n+d)$-dimensional point groups K_s. Two $(m+d)$-dimensional superspace groups are equivalent if there is an origin and a standard lattice basis for each group such that the collection $\{\Gamma(K), \upsilon_s(K)\}$ is the same for both groups. [In previous formulae, $\upsilon_s(R)$ is often simply indicated as υ_s.]

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9.1

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