Note that no new names have been introduced for the underlying crystallographic concepts like Bravais classes, geometric and arithmetic crystal classes, even if in those cases also the equivalence relation is not simply that of four-dimensional Euclidean crystallography, an explicit distinction always being possible by specifying the dimension as $(3+1)$ instead of four.

9.8.1.5. *Occupation modulation*

Another type of modulation, the occupation modulation, can be treated in a way similar to the displacive modulation. As an example consider an alloy where the positions of the basic structure have space-group symmetry, but are statistically occupied by either of two types of atoms. Suppose that the position $\mathbf{r}$ is occupied by an atom of type A with probability $p(\mathbf{r})$ and by one of type B with probability $1-p(\mathbf{r})$ and that p is periodic. The probability of finding an A atom at site $\mathbf{n}+\mathbf{r}_j$ is

$$P_A(\mathbf{n}+\mathbf{r}_j) = p_j[\mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j)], \tag{9.8.1.27}$$

with $p_j(x) = p_j(x+1)$. In this case, the structure factor becomes

$$S_{\mathbf{H}} = \sum_{\mathbf{n}}\sum_{j}\left[\left(f_A p_j[\mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j)] + f_B\{1-p_j[\mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j)]\}\right) \times \exp[2\pi i\mathbf{H}\cdot(\mathbf{n}+\mathbf{r}_j)]\right], \tag{9.8.1.28}$$

where f_A and f_B are the atomic scattering factors. Because of the periodicity, one has

$$p_j(x) = \sum_m w_{jm}\exp(2\pi i m x). \tag{9.8.1.29}$$

Hence,

$$S_{\mathbf{H}} = \sum_j\left\{f_B\Delta(\mathbf{H})\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_j) + (f_A - f_B)\sum_m \Delta(\mathbf{H}+m\mathbf{q})w_{jm} \times \exp[2\pi i(\mathbf{H}+m\mathbf{q})\cdot\mathbf{r}_j]\right\}, \tag{9.8.1.30}$$

where $\Delta(\mathbf{H})$ is the sum of δ functions over the reciprocal lattice of the basic structure:

$$\Delta(\mathbf{H}) = \sum_{h_1h_2h_3}\delta\left(\mathbf{H} - \sum_{i=1}^{3} h_i\mathbf{a}_i^*\right).$$

Consequently, the diffraction peaks occur at positions $\mathbf{H}$ given by (9.8.1.7). For a simple sinusoidal modulation [$m=\pm1$ in (9.8.1.29)], there are only main reflections and first-order satellites ($m=\pm1$). One may introduce an additional coordinate t and generalize (9.8.1.27) to

$$P_A(\mathbf{n}+\mathbf{r}_j, t) = p_j[\mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j)+t], \tag{9.8.1.31}$$

which has $(3+1)$-dimensional space-group symmetry. Generalization to more complex modulation cases is then straightforward.

9.8.2. Outline for a superspace-group determination

In the case of a modulated structure, the diffraction pattern consists of main reflections and satellites. The main reflections span a reciprocal lattice generated by $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$. Considerations are here restricted for simplicity to the one-dimensional modulated case, *i.e.* to the $n=4$ case. Extension to the more general $n=3+d$ case is conceptually not difficult and does not modify the general procedure outlined here.

(1) *The first step* is the determination of the *Laue group* P_L of the diffraction pattern: it is the point group in three dimensions that transforms every diffraction peak into a peak of the same intensity.†

As P_L leaves invariant the subset of main reflections, this Laue group belongs to one of the 11 Laue symmetry classes. Accordingly, the Laue group determines a three-dimensional holohedral point group which determines a crystallographic system.

(2) *The second step* consists of choosing a basis according to the conventions of *IT* A for the main reflections and choosing a modulation wavevector.

From the centring extinctions, one can deduce to which Bravais class the main reflections belong. This is one of the 14 three-dimensional Bravais classes. Notice that the cubic Bravais classes do not occur because a one-dimensional (incommensurate) modulation is incompatible with cubic symmetry. For this same reason, only the nine non-cubic Laue-symmetry classes occur in the one-dimensional incommensurate case.

The main reflections are indexed by $hkl0$ and the satellite reflections by $hklm$. The Fourier wavevector of a general reflection $hklm$ is given by

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}. \tag{9.8.2.1}$$

Note that this step involves a choice because the system of satellite reflections is only defined modulo the main reflections. When a satellite is in the vicinity of a main reflection, it is reasonable to assign it to that reflection. But one has, especially when deciding whether or not situations are equivalent, to be aware of the fact that each satellite may be assigned to an arbitrary main reflection. It is even possible to assign a satellite to an extinct main reflection. One takes by preference the $\mathbf{q}$ vector along a symmetry axis or in a mirror plane. According to equation (9.8.2.1), the fourth basis vector $\mathbf{a}_4^*$ is equal to the chosen $\mathbf{q}$, the modulation wavevector.

(3) In the *third step*, one determines the space group of the *average structure* (from the main reflections).

The average structure is unique but possibly involves split atoms. The space group of the average structure is often the symmetry group of the undistorted phase. That helps to make a good choice for the basic structure and also gives an insight as to how the satellite reflections split from the main reflections at the phase transition.

(4) *Step four* is the identification of the $(3+1)$-dimensional Bravais lattice type. In superspace also, centring gives rise to *centring extinctions*, and that corresponds to making the choice of a *conventional unit cell* in $(3+1)$ dimensions.

The previous three steps establish $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, the three-dimensional Bravais class and $\mathbf{q} = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*$, where the components α, β, and γ are given with respect to the three-dimensional conventional basis.

$$\alpha = \mathbf{q}\cdot\mathbf{a}, \quad \beta = \mathbf{q}\cdot\mathbf{b}, \quad \gamma = \mathbf{q}\cdot\mathbf{c}. \tag{9.8.2.2}$$

The $(3+1)$-dimensional Bravais class is fixed by that three-dimensional Bravais class and the components α, β, γ of $\mathbf{q}$.

Just as for three-dimensional lattices, a conventional cell can be chosen for $(3+1)$-dimensional lattices. To this end, the

† Except for deviations from Friedel's law caused by dispersion; see *IT* B (1993, p. 241, Subsection 2.3.4.1).

vector $\mathbf{q}$ must be considered. The vector $\mathbf{q}$ can be split into an invariant (or irrational) and a rational component according to:

$$\mathbf{q} = \mathbf{q}^i + \mathbf{q}^r \quad \text{with} \quad \mathbf{q}^i = \frac{1}{N}\sum_R \varepsilon(R)(R\mathbf{q}), \tag{9.8.2.3}$$

where summation is over the elements R of the Laue group P_L, N is the order of P_L, and $\varepsilon = \pm 1$ follows from the property (valid in the one-dimensional modulated case):

$$R\mathbf{q} = \varepsilon\mathbf{q} \text{ (modulo main-reflection vectors).} \tag{9.8.2.4}$$

If the splitting (9.8.2.3) results in $\mathbf{q}^r = 0$, there is no problem. For $\mathbf{q}^r \neq 0$ we choose $\mathbf{q}^i$ as the new modulation wavevector. This may cause satellites to be assigned to extinct main reflections, or even to 'main reflections' with non-integer indices. In this case, it is desirable to choose a new basis $\mathbf{a}_c^*, \mathbf{b}_c^*, \mathbf{c}_c^*$ such that all reflections can be written as

$$H\mathbf{a}_c^* + K\mathbf{b}_c^* + L\mathbf{c}_c^* + m\mathbf{q}^i \tag{9.8.2.5}$$

with H, K, L, and m integer numbers. The basis obtained is the conventional basis for the M^* module and corresponds to the choice of a conventional cell for the $(3+1)$-dimensional Bravais lattice.

Observed (possible) centring conditions for the reflections can be applied to determine the $(3+1)$-dimensional Bravais class.

Example 1. As an example, consider a C-centred orthorhombic lattice with modulation wavevector $\mathbf{q} = (\alpha 0 \tfrac{1}{2})$, or $\mathbf{q}^i = (\alpha 00)$ and $\mathbf{q}^r = (00\tfrac{1}{2})$. The general reflection condition is: $hklm$, $h + k =$ even. A reflection

$$h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m(\alpha\mathbf{a}^* + \tfrac{1}{2}\mathbf{c}^*) \tag{9.8.2.6}$$

can be described on a conventional basis with $\mathbf{a}_c^* = \mathbf{a}^*$, $\mathbf{b}_c^* = \mathbf{b}^*$, $\mathbf{c}_c^* = \mathbf{c}^*/2$ as

$$H\mathbf{a}_c^* + K\mathbf{b}_c^* + L\mathbf{c}_c^* + m\alpha\mathbf{a}_c^*. \tag{9.8.2.7}$$

Because $H = h$, $K = k$, $L/2 = l + m/2$, and h, k and l are integers with $h + k$ even, one has the conditions $H + K =$ even and $L + m =$ even. The adopted conventional basis has centring $(\tfrac{1}{2}\tfrac{1}{2}00, 00\tfrac{1}{2}\tfrac{1}{2}, \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})$. The conditions $H + K =$ even and $L + m =$ even become, after interchange of H and L, $K + L =$ even and $H + m =$ even, which according to Table 9.8.3.6 gives $mmmA(\tfrac{1}{2}0\gamma)$. Changing back to the original setting gives the Bravais class $mmmC(\alpha 0\tfrac{1}{2})$.

Example 2. As a second example, consider a C-centred orthorhombic lattice of main reflections. Suppose that an arbitrary reflection is given by

$$H\mathbf{a}^* + K\mathbf{b}^* + L\mathbf{c}^* + m\gamma\mathbf{c}^* \tag{9.8.2.8}$$

with respect to the conventional basis $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ of the C-centred lattice and that the general reflection condition is

$$H + K + m = \text{even}. \tag{9.8.2.9}$$

This is in agreement with the C-centring condition $H + K =$ even for the main reflections. Equation (9.8.2.9) implies a centring $(\tfrac{1}{2}\tfrac{1}{2}0\tfrac{1}{2})$ of the $(3+1)$-dimensional lattice Σ. Its conventional basis corresponding to (9.8.2.8) is

$$(\mathbf{a}, 0), (\mathbf{b}, 0), (\mathbf{c}, -\gamma), (0, 1). \tag{9.8.2.10}$$

Because of the centring translation $[(\mathbf{a} + \mathbf{b})/2, 1/2]$, a primitive basis of Σ is

$$\left(\frac{\mathbf{a}+\mathbf{b}}{2}, -1/2\right), \left(\frac{\mathbf{a}-\mathbf{b}}{2}, -1/2\right), (\mathbf{c}, -\gamma), (0, 1), \tag{9.8.2.11}$$

which corresponds, according to (9.8.1.11), to a choice $\mathbf{q} = \mathbf{a}^* + \gamma\mathbf{c}^*$. In terms of this modulation vector, an arbitrary reflection (9.8.2.8) can be described as

$$h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m(\mathbf{a}^* + \gamma\mathbf{c}^*). \tag{9.8.2.12}$$

Because $H = h + m$, $K = k$, and $L = l$, the reflection condition (9.8.2.9) now becomes $h + k =$ even, again in agreement with the fact that the lattice of main reflections is C-centred.

(5) *Step five*: one lists all point groups (more precisely, the arithmetic crystal classes) compatible with the external Bravais class (*i.e.* the three-dimensional one), the components of the modulation vector $\mathbf{q}$ with respect to the conventional basis of this class, and the observed general extinctions. These groups are listed in Table 9.8.3.3.

The external part of the $(3+1)$-dimensional point group does not need to be the same as the point group of the average structure: it can never be larger, but is possibly a subgroup only.

(6) *Step six* consists of finding the superspace groups compatible with the previously derived results and with the special extinctions observed in the diffraction pattern.

For each arithmetic point group, the non-equivalent superspace groups are listed in Table 9.8.3.5.

Example 3. Continue with example 2 of step 4. The external Bravais class of the modulated crystal is $mmmC$ and $q = (10\gamma)$. Consider the two cases of special reflection conditions.

(1) The observed condition is: $00Lm, m = 2n$. Then there is only one superspace group that obeys this condition: No. 21.4 with symbol $C222(10\gamma)00s$ in Table 9.8.3.5. [See Subsection 9.8.3.3 for explanation of symbols; note that $C222$ denotes the external part of the $(3+1)$-dimensional space group.]

(2) There is no special reflection condition. Possible superspace groups are:

$C222(10\gamma)$, No. 21.3,	$Cmm2(10\gamma)$, No. 35.4,
$C2mm(10\gamma)$, No. 38.3,	$Cmmm(10\gamma)$, No. 65.4.

In this second case, there are thus four possible superspace groups, three without and one with inversion symmetry. The difficulty stems from the fact that (in the absence of anomalous dispersion) the Laue group always has an inversion centre. Just as in three-dimensional crystallography, the ambiguity can only be solved by a complete determination of the structure, or by non-diffraction methods.

In the determination of modulated structures, one generally starts with the assumption that the external part of the $(3+1)$-dimensional point group is equal to the point group of the basic structure. This is, however, not necessarily true. The former may be a subgroup of the latter. Especially when the basic structure contains atoms at special positions, the point-group symmetry may be lowered by the modulation.

(7) *Step seven* concerns the restrictions imposed on/by the displacive or occupation modulation waves. For each occupied special Wyckoff position of the basic structure, one has to verify the validity of the restrictions imposed by the elements of the superspace group on the modulation as expressed in equation (9.8.1.24).

During the structure determination, one should check for each Wyckoff position which is occupied by an atom of the basic

structure, whether the assumed displacive or occupation modulations obey the site symmetry of the Wyckoff position considered. An atom at a special position transforms into itself by the site symmetry of the position. For such a symmetry transformation, $j' = j$, $\mathbf{v} = 0$, and thus $\Delta(\varepsilon = 1) = \tau$, $\Delta(\varepsilon = -1) = 0$ (*cf.* Subsection 9.8.3.3). In the modulated structure, the site symmetry is preserved only if, for each of its symmetry operations, the appropriate relation is obeyed by the modulations [*cf.* (9.8.1.24)].

For displacive modulations, the conditions are

$$\begin{aligned} \mathbf{u}_j(\mathbf{q}\cdot\mathbf{r}) &= R\mathbf{u}_j(\mathbf{q}\cdot\mathbf{r}-\tau) \quad \text{for } \varepsilon = 1, \\ \mathbf{u}_j(\mathbf{q}\cdot\mathbf{r}) &= R\mathbf{u}_j(\mathbf{q}\cdot\mathbf{r}) \quad \text{for } \varepsilon = -1 \end{aligned} \tag{9.8.2.13}$$

and, for occupation modulation,

$$\begin{aligned} p_j(\mathbf{q}\cdot\mathbf{r}) &= p_j(\mathbf{q}\cdot\mathbf{r}-\tau) \quad \text{for } \varepsilon = 1, \\ p_j(\mathbf{q}\cdot\mathbf{r}) &= p_j(\mathbf{q}\cdot\mathbf{r}) \quad \text{for } \varepsilon = -1. \end{aligned} \tag{9.8.2.14}$$

Example 4. Assume, as for the case discussed above, that the basic structure has the space group *Cmmm*. Can the superspace group be *Cmmm*(10γ)? In this superspace group, $\tau = 0$ for all symmetry operations with $\varepsilon = 1$. Displacive modulations at special positions must thus obey $\mathbf{u}_j(\mathbf{q}\cdot\mathbf{r}) = R\mathbf{u}_j(\mathbf{q}\cdot\mathbf{r})$ for the superspace group to be correct. For an atom at special position *mmm*, this is not possible for all site symmetry operations unless $\mathbf{u}_j = 0$. Suppose that the structure model contains a displacive modulation polarized along **a** for that atom. The allowed site symmetry is then lowered to 2*mm*, and as a consequence the superspace group is *C*2*mm*(10γ) rather than *Cmmm*(10γ).

9.8.3. Introduction to the tables

In what follows, the tables dealing with the $(3+1)$-dimensional case will be presented. The explanations can easily be applied to the $(2+d)$-dimensional case also [Tables 9.8.3.1(*a*), (*b*) and 9.8.3.4(*a*), (*b*)].

9.8.3.1. *Tables of Bravais lattices*

The $(3+1)$-dimensional lattice Σ^* is determined by the three-dimensional vectors $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ and the modulation vector **q**. The former three vectors give by duality **a**, **b**, and **c**, the external components of lattice basis vectors, and the products $-\mathbf{q}\cdot\mathbf{a} = -\alpha$, $-\mathbf{q}\cdot\mathbf{b} = -\beta$, and $-\mathbf{q}\cdot\mathbf{c} = -\gamma$ the corresponding internal components. Therefore, it is sufficient to give the arithmetic crystal class of the group $\Gamma_E(K)$ and the components σ_j ($\sigma_1 = \alpha$, $\sigma_2 = \beta$, and $\sigma_3 = \gamma$) of the modulation vector **q** with respect to a conventional basis $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$. The arithmetic crystal class is denoted by a modification of the symbol of the three-dimensional symmorphic space group of this class (see Chapter 1.4) plus an indication for the row matrix σ (having entries σ_j). In this way, one obtains the so-called one-line symbols used in Tables 9.8.3.1(*a*), (*b*) and 9.8.3.2(*a*), (*b*).

As an example, the symbol $2/mB(0\frac{1}{2}\gamma)$ denotes a Bravais class for which the main reflections belong to a *B*-centred monoclinic lattice (unique axis **c**) and the satellite positions are generated by the point-group transforms of $\frac{1}{2}\mathbf{b}^* + \gamma\mathbf{c}^*$. Then the matrix σ becomes $\sigma = (0\frac{1}{2}\gamma)$. It has as irrational part $\sigma^i = (00\gamma)$ and as rational part $\sigma^r = (0\frac{1}{2}0)$. The external part of the $(3+1)$-dimensional point group of the Bravais lattice is $2/m$. By use of the relation [*cf.* (9.8.2.4)]

$$R\mathbf{q}^i = \varepsilon\mathbf{q}^i, \quad R\mathbf{q}^r \equiv \varepsilon\mathbf{q}^r \text{ (modulo } \mathbf{b}^*), \tag{9.8.3.1}$$

Table 9.8.3.1(*a*). $(2+1)$-*Dimensional Bravais classes for incommensurate structures*

The holohedral point group K_s is given in terms of its external and internal parts, K_E and K_I, respectively. The reflections are given by $h\mathbf{a}^* + k\mathbf{b}^* + m\mathbf{q}$ where **q** is the modulation wavevector. If the rational part $\mathbf{q}^r$ is not zero, there is a corresponding centring translation in three-dimensional space. The conventional basis $(\mathbf{a}_c^*, \mathbf{b}_c^*, \mathbf{q}^i)$ given for the vector module M^* is shown such that $\mathbf{q}^r = 0$. The basis vectors are given by components with respect to the conventional basis $\mathbf{a}^*, \mathbf{b}^*$ of the lattice Λ^* of main reflections.

No.	Symbol	K_E	K_I	**q**	Conventional basis	Centring
Oblique						
1	$2p(\alpha\beta)$	2	$\bar{1}$	$(\alpha\beta)$	(10), (01), $(\alpha\beta)$	
Rectangular						
2	$mmp(0\beta)$	mm	$1\bar{1}$	(0β)	(10), (01), (0β)	
3	$mmp(\frac{1}{2}\beta)$	mm	$1\bar{1}$	$(\frac{1}{2}\beta)$	$(\frac{1}{2}0)$, (01), (0β)	$\frac{1}{2}0\frac{1}{2}$
4	$mmc(0\beta)$	mm	$1\bar{1}$	(0β)	(10), (01), (0β)	$\frac{1}{2}\frac{1}{2}0$

we see that the operations 2 and m are associated with the internal space transformations $\varepsilon = 1$ and $\varepsilon = -1$, respectively. This is denoted by the one-line symbol $(2/m, 1\bar{1})$ for the $(3+1)$-dimensional point group of the Bravais lattice. In direct space, the symmetry operation $\{R, \varepsilon(R)\}$ is represented by the matrix $\Gamma(R)$ which transforms the components $v_j, j = 1, \ldots, 4$, of a vector v_s to:

$$v_j' = \sum_{k=1}^{4} \Gamma(R)_{jk} v_k.$$

The operations (2, 1) and $(m, \bar{1})$ are represented by the matrices:

$$\Gamma(2) = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 1 \end{pmatrix}; \quad \Gamma(m) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & -1 \end{pmatrix}. \tag{9.8.3.2}$$

The 3×3 part $\Gamma_E(R)$ of each matrix is obtained by considering the action of R on the external part **v** of v_s. The 1×1 part $\Gamma_I(R)$ is the value of the ε associated with R and the remaining part $\Gamma_M(R)$ follows from the relation

$$\Gamma_M(R) = -\Gamma_I(R)\sigma^r + \sigma^r\Gamma_E(R). \tag{9.8.3.3}$$

Bravais classes can be denoted in an alternative way by two-line symbols. In the two-line symbol, the Bravais class is given by specifying the arithmetic crystal class of the external symmetry by the symbol of its symmorphic space group, the associated elements $\Gamma_I(R) = \varepsilon$ by putting their symbol under the corresponding symbols of $\Gamma_E(R)$, and by the rational part σ^r indicated by a prefix. In the following table, this prefix is given for the components of $\mathbf{q}^r$ that play a role in the classification.

P	(000)	R	$(\frac{1}{3}, \frac{1}{3}, 0)$		
A	$(\frac{1}{2}, 0, 0)$	B	$(0, \frac{1}{2}, 0)$	C	$(0, 0, \frac{1}{2})$
L	(1, 0, 0)	M	(0, 1, 0)	N	(0, 0, 1)
U	$(0, \frac{1}{2}, \frac{1}{2})$	V	$(\frac{1}{2}, 0, \frac{1}{2})$	W	$(\frac{1}{2}, \frac{1}{2}, 0)$.

Note that the integers appearing here are not equivalent to zero because they express components with respect to a conventional lattice basis (and not a primitive one). For the Bravais class

references