In the case of modulated crystals, such an equivalence relation has been worked out explicitly, giving rise to the concept of the $(3+d)$-dimensional *superspace group*.

The concepts of point group, lattice holohedry, Bravais classes, systems of non-primitive translations, and so on, then follow from the general properties of $n$-dimensional space groups together with the (appropriate) equivalence relations.

A glossary of symbols is given in Appendix *A* and a list of definitions in Appendix *B*.

### 9.8.1.3. *The simple case of a displacively modulated crystal*

#### 9.8.1.3.1. *The diffraction pattern*

To introduce what follows, the simple case of a displacively modulated crystal structure is considered. The point-atom approximation is adopted and the modulation is supposed to be a sinusoidal plane wave.

This means that the structure can be described in terms of atomic positions of a *basic structure* with three-dimensional space-group symmetry, periodically displaced according to the modulation wave. Writing for the position of the $j$th particle in the unit cell of the basic structure given by the lattice vector $\mathbf{n}$:

$$\mathbf{r}_0(\mathbf{n}, j) = \mathbf{n} + \mathbf{r}_j, \tag{9.8.1.3}$$

the position of the same particle in the modulated structure is given by

$$\mathbf{r}(\mathbf{n}, j) = \mathbf{n} + \mathbf{r}_j + \mathbf{U}_j \sin[2\pi\mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j) + \varphi_j], \tag{9.8.1.4}$$

where $\mathbf{q}$ is the wavevector of the modulation and $\mathbf{U}_j$ is the polarization vector for the $j$th particle's modulation. (This is not the most general sinusoidal modulation, because different components $U_{j\alpha}$ may have different phases $\varphi_{j\alpha}, \alpha = 1, 2, 3$.) In general, the symmetry of the modulated structure is different from that of the basic structure and the only translations that leave the modulated structure invariant are those lattice translations $\mathbf{m}$ of the basic structure satisfying the condition $\mathbf{q}\cdot\mathbf{m} =$ integer. If the components $\alpha$, $\beta$, and $\gamma$ of the wavevector $\mathbf{q}$ with respect to the basis $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ are all rational numbers, there is a full lattice of such translations, the structure then is a *superstructure* of the original one and has space-group symmetry. If at least one of the $\alpha, \beta$, and $\gamma$ is irrational, the structure does not have three-dimensional lattice translation symmetry. Nevertheless, the crystal structure is by no means disordered: it is fully determined by the basic structure and the modulation wave(s).

The crystalline order is reflected in the structure factor, which is given by the expression

$$\begin{aligned} S_{\mathbf{H}} &= \sum_{\mathbf{n},j} f_j \exp[2\pi i \mathbf{H}\cdot\mathbf{r}(\mathbf{n}, j)] \\ &= \sum_{\mathbf{n},j} f_j \exp[2\pi i \mathbf{H}\cdot(\mathbf{n}+\mathbf{r}_j)] \\ &\quad \times \exp\{2\pi i \mathbf{H}\cdot\mathbf{U}_j \sin[2\pi\mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j)+\varphi_j]\}, \end{aligned} \tag{9.8.1.5}$$

where $f_j$ is the atomic scattering factor (which still, in general, depends on $\mathbf{H}$). Using the Jacobi–Anger relation, one can rewrite (9.8.1.5) as

$$\begin{aligned} S_{\mathbf{H}} &= \sum_{\mathbf{n}} \sum_{j} \sum_{m=-\infty}^{\infty} \exp[2\pi i(\mathbf{H} - m\mathbf{q})\cdot(\mathbf{n}+\mathbf{r}_j)] \\ &\quad \times f_j \exp(-im\varphi_j) J_{-m}(2\pi\mathbf{H}\cdot\mathbf{U}_j), \end{aligned} \tag{9.8.1.6}$$

where $J_m(x)$ is the $m$th-order Bessel function. The summation over $\mathbf{n}$ results in a sum of $\delta$ functions on the positions of the reciprocal lattice:

$$\Delta(\mathbf{H} - m\mathbf{q}) = \sum_{h,k,l} \delta(\mathbf{H} - m\mathbf{q} - h\mathbf{a}^* - k\mathbf{b}^* - l\mathbf{c}^*).$$

Consequently, the structure factor $S_{\mathbf{H}}$ vanishes unless there are integers $h$, $k$, $l$, and $m$ such that

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}. \tag{9.8.1.7}$$

If $\mathbf{q}$ is incommensurate, *i.e.* if there is no integer $N$ such that $N\mathbf{q}$ belongs to the reciprocal lattice spanned by $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$, one needs more than three integers (in the present case four) for indexing $\mathbf{H}$. This is characteristic for incommensurate crystal phases.

In the diffraction pattern of such a modulated phase, one distinguishes between main reflections (for which $m = 0$) and satellites (for which $m \neq 0$). The intensities of the satellites fall off rapidly for large $m$ so that the observed diffraction spots remain separated, although vectors of the form (9.8.1.7) may come arbitrarily close to each other.

In the commensurate case also, there are main reflections and satellites, but, since here there is an integer $N$ such that $N\mathbf{q}$ belongs to the reciprocal lattice, one may restrict the values of $m$ in (9.8.1.7) to the range from 0 to $N-1$.

#### 9.8.1.3.2. *The symmetry*

There is more than one way for expressing the long-range order present in an incommensurate crystal in terms of symmetry. One natural way is to adopt the point of view that the measuring process limits the precision in the determination of a modulation wavevector. Accordingly, one can try an *approximation* of the modulation wavevector $\mathbf{q}$ *by a commensurate one*: an irrational number can be approximated arbitrarily well by a rational one.

There are two main disadvantages in this approach. Firstly, a good approximation implies, in general, a large unit cell for the corresponding superstructure, which involves a large number of parameters. Secondly, the space group one finds may depend essentially on the rational approximation adopted. Consider, for example, an orthorhombic basic structure with space group $Pcm2_1$ and modulation with wavevector $\mathbf{q} = \gamma\mathbf{c}^*$, polarization along the $b$ direction and positions of the particles given by

$$\mathbf{r}(\mathbf{n}, j) = \mathbf{n} + \mathbf{r}_j + \mathbf{U}\sin[2\pi\mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j)], \tag{9.8.1.8}$$

where for convenience the polarization has been taken as independent of $j$. Under the glide reflection $\{m_x|(m+\frac{1}{2})\mathbf{c}\}$ (integer $m$) present in the basic structure, the transformed positions are

$$\begin{aligned} \mathbf{r}'(\mathbf{n}, j) &= \mathbf{r} + \mathbf{U}\sin\{2\pi[\mathbf{q}\cdot\mathbf{r} - \gamma(m+\tfrac{1}{2})]\}, \\ &\qquad \text{with } \mathbf{r} = \mathbf{n} + \mathbf{r}_j. \end{aligned} \tag{9.8.1.9}$$

Consider the rational approximation of $\gamma$ given by $P/Q$, with $P$ and $Q$ relatively prime integers. Then such a glide transformation as given above is (for certain values of $m$) a symmetry of the modulated structure only if $P$ is even and $Q$ odd, because only in that case does the equation $P(m+\frac{1}{2}) = lQ$ have a solution for integers $l$ and $m$. Analogously, the mirror $m_y$ only occurs as a glide plane if $P/Q$ is odd/even, whereas the screw axis along the $z$ axis requires the case odd/odd. Hence, if, for example, one approximates the same irrational number successively by 5/12, 7/17 or 8/19, one finds different symmetry groups. Furthermore, in all the cases, the point group is monoclinic and the information contained in the orthorhombic point-group symmetry of the main reflections is lost.

These difficulties are avoided if one embeds the modulated crystal according to the basic ideas expressed in the previous section. Conceptually, it corresponds (de Wolff, 1974, 1977;

Janner & Janssen, 1977) to *enlarging the class of symmetry transformations* admitted, from Euclidean in three dimensions to Euclidean in $n$ dimensions (here $n = 4$). A four-dimensional Euclidean operation transforms the three-dimensional structure but does not leave distances invariant in general. To illustrate this phenomenon, consider the effect of a lattice translation of the basic structure on the modulation: it gives rise to a shift of the phase. Combining such a translation with an appropriate (compensating) shift of the phase, one obtains a transformation that leaves the basic structure *and* the modulation invariant. Such a transformation corresponds precisely to a lattice translation in four dimensions for the embedded crystal structure. In the real space, however, a shift of the phase is not an admitted Euclidean transformation as it does not leave invariant the distance between the particles, so that the combination of lattice translation and (compensating) phase shift also is not admitted as such, even if for an incommensurate modulation it simply corresponds to a relabelling of the atoms leaving the global structure invariant.

From what has been said, it should be apparent that the four-dimensional embedding of the modulated structure according to the superspace approach can also be obtained directly by considering as additional coordinate the phase $t$ of the modulation. The positions in three dimensions are then the intersection of the lines of the atomic positions (parametrized by $t$) with the hyperplane $t = 0$. For the modulated structure of (9.8.1.4), these lines are given by

$$(\mathbf{n} + \mathbf{r}_j + \mathbf{U}_j \sin\{2\pi[\mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j)+t]+\varphi_j\}, t) \quad \text{any real } t, \qquad (9.8.1.10a)$$

and for a more general, not necessarily sinusoidal, modulation by

$$(\mathbf{n} + \mathbf{r}_j + \mathbf{u}_j\{\mathbf{q}\cdot[\mathbf{n}+\mathbf{r}_j]+t\}, t), \qquad (9.8.1.10b)$$

where $\mathbf{u}_j(x)$ is a periodic vector function: $\mathbf{u}_j(x+1) = \mathbf{u}_j(x)$. A general point in four-dimensional space is $r_s = (\mathbf{r}, t)$ with $\mathbf{r} = (x, y, z)$.

The notation adopted here for the $(3+1)$-dimensional embedding of the modulated structure is a shorthand notation intended to stress the double role of the variable $t$ as a parameter in the three-dimensional description of the structure and as a coordinate in the $(3+1)$-dimensional embedding. In the latter case, it implicitly assumes the choice of a fourth basis vector $\mathbf{d}$ perpendicular to the physical space of the crystal, so that the following four-dimensional vector notations are considered to be equivalent:

$$r_s = (\mathbf{r}, \mathbf{t}) = (\mathbf{r}, t\mathbf{d}) = (\mathbf{r}, t).$$

The pattern of lines (9.8.1.10$a, b$) has lattice periodicity. Indeed, it is invariant under the shift $t \to t+1$ and, for every lattice translation $\mathbf{n}$ from the basic structure, there is a compensating phase shift: the pattern is left invariant under the combination of the translation $\mathbf{n}$ and the phase shift $t \to t - \mathbf{q}\cdot\mathbf{n}$. Therefore, (9.8.1.10$a, b$) is invariant under translations from a four-dimensional lattice with basis

$$a_{s1} = (\mathbf{a}, -\mathbf{q}\cdot\mathbf{a}), \quad a_{s2} = (\mathbf{b}, -\mathbf{q}\cdot\mathbf{b}), \quad a_{s3} = (\mathbf{c}, -\mathbf{q}\cdot\mathbf{c}), \quad a_{s4} = (0, 1). \qquad (9.8.1.11)$$

In accordance with the equivalent descriptions given for $r_s$, equivalent descriptions for $a_{s4}$ are $a_{s4} = (0, 1) = (0, \mathbf{d})$ with dual basis vector $a^*_{s4} = (\mathbf{q}, 1) = (\mathbf{q}, \mathbf{d}^*)$, where $\mathbf{d}^*$ is reciprocal to $\mathbf{d}$ in the fourth direction. With respect to the axes (9.8.1.11), a general point in four dimensions can be written as

$$r_s = \sum_{i=1}^{4} x_i a_{si} = (\mathbf{r}, r_I),$$

with

$$\mathbf{r} = x_1\mathbf{a} + x_2\mathbf{b} + x_3\mathbf{c}, \quad \text{and} \quad r_I = t = x_4 - \mathbf{q}\cdot\mathbf{r}. \qquad (9.8.1.12)$$

Some, or sometimes all, transformations of the space group of the basic structure give rise to a symmetry transformation for the modulated structure when combined with an appropriate phase shift, possibly together with an inversion of the phase. If $\{R|\mathbf{v}\}$ is an element of the space group of the basic structure, $\Delta$ is a phase shift and $\varepsilon = \pm 1$, then the point $(\mathbf{r}, t)$ is transformed to $(R\mathbf{r} + \mathbf{v}, \varepsilon t + \Delta)$. The pattern (9.8.1.10$b$) is left invariant by $(\{R|\mathbf{v}\}, \{\varepsilon|\Delta\})$ if

$$(R\mathbf{n} + R\mathbf{r}_j + \mathbf{v} + R\mathbf{u}_j[\mathbf{q}\cdot(\mathbf{n}+\mathbf{r}_j) + \varepsilon t - \varepsilon\Delta], t) = (\mathbf{n}' + \mathbf{r}_{j'} + \mathbf{u}_{j'}[\mathbf{q}\cdot(\mathbf{n}'+\mathbf{r}_{j'}) + t], t). \qquad (9.8.1.13)$$

The position $\mathbf{n}' + \mathbf{r}_{j'}$ is the transform of $\mathbf{n} + \mathbf{r}_j$ in the basic structure and therefore also belongs to the basic structure.

One can conclude that the pattern has as symmetry transformations all elements $(\{R|\mathbf{v}\}, \{\varepsilon|\Delta\})$ satisfying (9.8.1.13). These form a space group in four dimensions.

The reciprocal to the basis (9.8.1.11) is

$$a^*_{s1} = (\mathbf{a}^*, 0), \quad a^*_{s2} = (\mathbf{b}^*, 0), \quad a^*_{s3} = (\mathbf{c}^*, 0), \quad a^*_{s4} = (\mathbf{q}, 1). \qquad (9.8.1.14)$$

A general reciprocal-lattice vector is now

$$H_s = \sum_{i=1}^{4} h_i a^*_{si} = (h_1\mathbf{a}^* + h_2\mathbf{b}^* + h_3\mathbf{c}^* + h_4\mathbf{q}, h_4).$$

The projection of this reciprocal-lattice vector is of the form (9.8.1.7), as it should be. Moreover, the projection of the four-dimensional Fourier transform on the hyperplane $t = 0$ is exactly the Fourier transform of the structure in this hyperplane. If, as a consequence of the four-dimensional space-group symmetry, the four-dimensional diffraction pattern shows systematic extinctions, the same extinctions are present in the diffraction pattern of the three-dimensional structure.

There are also other ways to describe the symmetry relations of incommensurate modulated structures. One is based on representation theory. This method has in particular been used when the modulation occurs as a consequence of a soft mode. Then the irreducible representation of the space group to which the soft mode belongs gives information on the modulation function as well. Heine & McConnell have treated the symmetry with a method related to the Landau theory of phase transitions (Heine & McConnell, 1981; McConnell & Heine, 1984). Perez-Mato *et al*. have given a formulation in terms of three-dimensional structures parametrized by what are here the additional coordinates (Perez-Mato, Madariaga & Tello, 1984, 1986; Perez-Mato, Madariaga, Zuñiga & Garcia Arribas, 1987). Other treatments of the problem can be found in Koptsik (1978), Lifshitz (1996), and de Wolff (1984).

### 9.8.1.4. *Basic symmetry considerations*

#### 9.8.1.4.1. *Bravais classes of vector modules*

For a modulated crystal structure with a one-dimensional modulation, the positions of the diffraction spots are given by vectors

$$\mathbf{H} = \sum_{i=1}^{3} h_i \mathbf{a}^*_i + m\mathbf{q}. \qquad (9.8.1.15)$$