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 jth 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 jth 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 α, β, and γ 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 α, β, and γ 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 mth-order Bessel function. The summation over $\mathbf{n}$ results in a sum of δ 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 γ 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;

references