

9. BASIC STRUCTURAL FEATURES

Bragg reflections can be labelled by a finite set of integral indices as well and the Fourier wavevectors form a vector module as defined above. The difference from the previous case is that the basic structure itself is incommensurate, even if one disregards modulation.

A third class of incommensurate crystals found in nature is represented by the *quasicrystals* (examples of which are the icosahedral phases). In that case also, the basic structure is incommensurate, the difference from the previous case being that the splitting in subsystems of main reflections and/or in main reflections and satellites is not a natural one, even in the lowest approximation.

It is justified to assume that crystal phases allow for an even wider range of ordered structures than those mentioned above. Nevertheless, all the cases studied so far allow a common approach based on higher-dimensional crystallography, *i.e.* on crystallographic properties one obtains after embedding the crystal structure in a higher-dimensional Euclidean space.

To present that approach in its full generality would require a too abstract language. On the other hand, restriction to the simplest case of a modulated crystal would give rise to misleading views. It what follows, the basic ideas are formulated as simply as possible, but still within a general point of view. Their application and the illustrative examples are mainly restricted to the modulated crystal case. The tables presented here, even if applicable to more general cases, cover essentially the one-dimensional modulated case [$d = 1$ in equation (9.8.1.1)].

9.8.1.2. The basic ideas of higher-dimensional crystallography

Incommensurate modulated crystals are systems that do not obey the classical requirements for crystals. Nevertheless, their long-range order is as perfect as that of ordinary crystals. In the diffraction pattern they also show sharp, well separated spots, and in the morphology flat faces. Dendritic crystallization with typical point-group symmetry is observed in both commensurate and incommensurate materials. Therefore, we shall consider both as crystalline phases and generalize for that reason the concept of a crystal. The positions of the Bragg diffraction peaks given in (9.8.1.1) are a special case. In general, they are elements of a vector module M^* and can be written as

$$\mathbf{H} = \sum_{i=1}^n h_i \mathbf{a}_i^*, \quad \text{integers } h_i. \quad (9.8.1.2)$$

This leads to the following *definition of crystal*.

An *ideal crystal* is considered to be a matter distribution having Fourier wavevectors expressible as an integral linear combination of a finite number (say n) of them and such that its diffraction pattern is characterized by a discrete set of resolved Bragg peaks, which can be indexed accordingly by a set of n integers h_1, h_2, \dots, h_n .

Implicit in this definition is the possibility of neglecting diffraction intensities below a given threshold, allowing one to identify and to label individual Bragg peaks even when n is larger than the dimension m of the crystal, which is usually three. Actually, for incommensurate crystals, the unresolved Bragg peaks of arbitrarily small intensities form a dense set, because they may come arbitrarily close to each other.

Here some typical examples are indicated. In the *normal crystal* case, $n = m = 3$ and $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$ are conventionally denoted by $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ and the indices h_1, h_2, h_3 by h, k, l .

In the case of a one-dimensionally *modulated crystal*, which can be described as a periodic plane wave deformation of a normal crystal (defining the basic structure), one has $n = 4$.

Conventionally, $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$ are chosen to be $\mathbf{a}^*, \mathbf{b}^*$, and \mathbf{c}^* generating the positions of the main reflections, whereas $\mathbf{a}_4^* = \mathbf{q}$ is the wavevector of the modulation. The corresponding indices are usually denoted by h, k, l and m . Also, crystals having two- and three-dimensional modulation are known: in those cases, $n = 5$ and $n = 6$, respectively.

In the case of a *composite crystal*, one can identify two or more subsystems, each with its own space-group symmetry. As an example, consider the case where two subsystems share \mathbf{a}^* and \mathbf{b}^* of their reciprocal-lattice basis, whereas they differ in periodicity along the c axis and have, respectively, \mathbf{c}_1^* and \mathbf{c}_2^* as third basis vector. Then again, $n = 4$ and $\mathbf{a}_1^*, \dots, \mathbf{a}_4^*$ can be chosen as $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}_1^*$, and \mathbf{c}_2^* . The indices can be denoted by h, k, l_1, l_2 . In general, the subsystems interact, giving rise to modulations and possibly (but not necessarily) to a larger value of n . In addition to the main reflections from the undistorted subsystems, satellite reflections then occur.

In the case of a *quasicrystal*, the Bragg reflections require more than three indices, but they do not arise from structurally different subsystems having lattice periodicity. So, for the icosahedral phase of AlMn alloy, $n = 6$, and one can take for $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$ a cubic basis $\mathbf{a}^*, \mathbf{b}^*$, and \mathbf{c}^* and for $\mathbf{a}_4^*, \mathbf{a}_5^*, \mathbf{a}_6^*$ then $\tau\mathbf{a}^*, \tau\mathbf{b}^*$, and $\tau\mathbf{c}^*$, respectively, with τ the golden number $[1 + \sqrt{5}]/2$.

The *Laue point group* P_L of a crystal is the point symmetry group of its diffraction pattern. This subgroup of the orthogonal group $O(3)$ is of finite order. The finite order of the group follows from the discreteness of the (resolved) Bragg peak positions, implying a finite number only of peaks of the same intensity lying at a given distance from the origin.

Under a symmetry rotation R , the indices of each reflection are transformed into those of the reflection at the rotated position. Therefore, a symmetry rotation is represented by an $n \times n$ non-singular matrix $\Gamma(R)$ with integral entries. Accordingly, a Laue point group admits an n -dimensional faithful integral representation $\Gamma(P_L)$. Because any finite group of matrices is equivalent with a group of orthogonal matrices of the same dimension, it follows that:

- (1) P_L is isomorphic to an n -dimensional crystallographic point group;
- (2) there exists a lattice basis $\mathbf{a}_{s1}^*, \dots, \mathbf{a}_{sn}^*$ of a Euclidean n -dimensional (reciprocal) space, which projects on the Fourier wavevectors $\mathbf{a}_1^*, \dots, \mathbf{a}_n^*$;
- (3) the three-dimensional Fourier components $\hat{\rho}(h_1, \dots, h_n)$ of the crystal density function $\rho(\mathbf{r})$ can be attached to corresponding points of an n -dimensional reciprocal lattice and considered as the Fourier components of a density function $\rho_s(r_s)$ having lattice periodicity in that higher-dimensional space (r_s is an n -dimensional position vector).

Such a procedure is called the *superspace embedding* of the crystal.

Note that this procedure only involves a reinterpretation of the structural data (expressed in terms of Fourier coefficients): the structural information in the n -dimensional space is exactly the same as that in the three-dimensional description.

The *symmetry group* of a crystal is then defined as the Euclidean symmetry group of the crystal structure embedded in the superspace.

Accordingly, the symmetry of a crystal whose diffraction pattern is labelled by n integral indices is an n -dimensional space group.

The *equivalence relation* of these symmetry groups follows from the requirement of invariance of the equivalence class with respect to the various possible choices of bases and embeddings. Because of that, the equivalence relation is not simply the one valid for n -dimensional crystallography.

9.8. INCOMMENSURATE AND COMMENSURATE MODULATED STRUCTURES

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} :

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

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

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

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 $\mathbf{q} \cdot \mathbf{m} = \text{integer}$. 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

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

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

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

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

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

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

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

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

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

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 $P(m + \frac{1}{2}) = IQ$ 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;