

9.8. Incommensurate and commensurate modulated structures

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9.8.1. Introduction

9.8.1.1. Modulated crystal structures

Lattice periodicity is a fundamental concept in crystallography. This property is widely considered as essential for the characterization of the concept of a crystal. In recent decades, however, more and more long-range-ordered condensed-matter phases have been observed in nature that do not have lattice periodicity, but nevertheless only differ from normal crystal phases in very subtle and not easy to observe structural and physical properties.

It is convenient to extend the concept of a crystal in such a way that it includes these ordered phases as well. If properly applied, crystallographic symmetry concepts are then still valid and of relevance for structural (and physical) investigation. Instead of limiting the validity of crystallographic notions, these developments show how rich the crystallographic ordering can be.

Incommensurate crystals are characterized by Bragg reflection peaks in the diffraction pattern that are well separated but do not belong to a lattice and cannot be indexed by three integer indices. This means that the description in terms of three-dimensional point and space groups, as given in *ITA* (1992), breaks down. It is possible, however, to generalize the crystallographic concepts on which the usual description is based. The ensuing symmetry groups and their equivalence classes are different from those of three-dimensional crystallography. The main properties of these new groups and the specific problems posed by their application to incommensurate crystal structures form the subject of the following sections.

The tables presented here, and their explanation, have been restricted to cover mainly the simplest case: *modulated crystal structures* (in particular, those with a single modulation wave). Nevertheless, most of the basic concepts also apply for the other classes of incommensurate crystal structures.

A modulation is here considered to be a periodic deformation of a 'basic structure' having space-group symmetry. If the periodicity of the modulation does not belong to the periodicities of the basic structure, the modulated crystal structure is called incommensurate.

That description is based on the observation in the diffraction pattern of modulated structures of main reflections, situated on a reciprocal lattice, and additional reflections, generally of weaker intensity, called satellites.

As far as we know, the first indications that complex crystal structures could exist not having normal lattice periodicity came, at the end of the 19th century, from studies of the morphology of the mineral calaverite. It was found that the faces of this compound do not obey the law of rational indices (Smith, 1903; Goldschmidt, Palache & Peacock, 1931). Donnay (1935) showed that faces that could not be indexed correspond to additional reflections in the X-ray diffraction pattern. From the experience with manufacturing of optical gratings, it was already known that periodic perturbation gives rise to additional diffraction spots. Dehlinger (1927) used this theory of 'Gittergeister' (lattice ghosts) to explain line broadening in Debye–Scherrer diagrams of metals and alloys. Preston (1938) called the 'Gittergeister' he found in diffraction from an aluminium–copper alloy 'satellites'. Periodic displacement (modulation) waves were considered by Daniel & Lipson (1943) as the origin of satellites in a copper–iron–nickel alloy. Complex magnetic ordering giving rise to satellites was found in magnetic crystals (Herpin, Meriel &

Villain, 1960; Koehler, Cable, Wollan & Wilkinson, 1962). In the early 1970's, the importance of the irrationality was realized and the term 'incommensurate phase' was introduced for modulated crystal phases with wavevectors that have irrational components. Such phases were found in insulators as well (Tanisaki, 1961, 1963; Brouns, Visser & de Wolff, 1964). The remarkable morphological properties of calaverite could also be related to the existence of an incommensurate modulation (Dam, Janner & Donnay, 1985). Structures that are well ordered, show sharp incommensurate spots in the diffraction pattern, but cannot be described as a modulation of a lattice periodic system, were also discovered, indicating that incommensurability is not restricted to modulated crystals. Examples are the composite (or intergrowth) crystals (Jellinek, 1972) and, more recently, quasicrystals (Shechtman, Blech, Gratias & Cahn, 1984). The latter not only lack three-dimensional lattice periodicity, but also show non-crystallographic symmetry elements, such as five-, eight- or twelvefold axes. For a review, see Janssen & Janner (1987).

We denote a basis for the lattice of main reflections by \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* . The satellites are separated from the main reflections by vectors that are integral linear combinations of some basic modulation vectors denoted by \mathbf{q}_j ($j = 1, 2, \dots, d$). Accordingly, the positions of the Bragg reflections are given by

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m_1\mathbf{q}_1 + m_2\mathbf{q}_2 + \dots + m_d\mathbf{q}_d \quad (9.8.1.1)$$

If the modulation is incommensurate, the set of all positions (9.8.1.1) does not form a lattice. Mathematically, it has the structure of a \mathbb{Z} -module, and its elements are three-dimensional vectors (of the reciprocal space). Accordingly, we call it a (reciprocal) *vector module*.

The modulation that gives rise to the satellites can be:

- (i) a displacive modulation, consisting of a periodic displacement from the atomic positions of the basic structure;
- (ii) an occupation modulation, in which the atomic positions of the basic structure are occupied with a periodic probability function.

Mixed forms also occur. Other modulation phenomena found are, for example, out-of-phase structures and translation interface modulated structures. The satellite reflections of modulated structures for the various types of modulation were systematically studied by Korekawa (1967).

For an incommensurate structure, at least one component of a basic modulation wavevector \mathbf{q}_j with respect to the lattice of main reflections is irrational. As argued later, even in the case of a commensurate modulation, *i.e.* when all components of these modulation wavevectors are rational, it is sometimes convenient to adopt the description of equation (9.8.1.1) and to apply the formalism developed for the incommensurate crystal case.

The modulated crystal case presented above is only the simplest one giving rise to incommensurate crystal structures. Another class is represented by the so-called *composite* or *intergrowth crystal structures*. Here the basic structure consists of two or more subsystems each with its own space-group symmetry (neglecting mutual interaction) such that, in general, the corresponding lattices are incommensurate. This means that these lattices are not sublattices of a common one. Actually, a mutual interaction is in general present giving rise to periodic deviations, *i.e.* to modulations. These crystals are different from the previous ones, in the sense that they show more than one set of main reflections. In the case of an intergrowth crystal, the

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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.