

## 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  $\tau$  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.

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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  $\alpha$ ,  $\beta$ , 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

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

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  $\delta$  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

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

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

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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

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

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

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

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:

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

The pattern of lines (9.8.1.10a, b) has lattice periodicity. Indeed, it is invariant under the shift  $t \rightarrow t + 1$  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  $t \rightarrow t - \mathbf{q} \cdot \mathbf{n}$ . Therefore, (9.8.1.10a, b) is invariant under translations from a four-dimensional lattice with basis

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

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

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

with

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

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 (9.8.1.10b) is left invariant by  $(\{R|\mathbf{v}\}, \{\varepsilon|\Delta\})$  if

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

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

$$\begin{aligned} a_{s1}^* &= (\mathbf{a}^*, 0), & a_{s2}^* &= (\mathbf{b}^*, 0), \\ a_{s3}^* &= (\mathbf{c}^*, 0), & a_{s4}^* &= (\mathbf{q}, 1). \end{aligned} \quad (9.8.1.14)$$

A general reciprocal-lattice vector is now

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

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

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

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This set of vectors is a vector module  $M^*$ . The vectors  $\mathbf{a}_1^*$ ,  $\mathbf{a}_2^*$ ,  $\mathbf{a}_3^*$  form a basis of the reciprocal lattice  $\Lambda^*$  of the basic structure and  $\mathbf{q}$  is the modulation wavevector. The choice of the basis of  $\Lambda^*$  has the usual freedom, the wavevector  $\mathbf{q}$  is only determined up to a sign and up to a reciprocal-lattice vector of the basic structure.

A vector module  $M^*$  has point-group symmetry  $K$ , which is the subgroup of all elements  $R$  of  $O(3)$  leaving it invariant.

In the case of an incommensurate one-dimensional modulation,  $M^*$  is generated by the lattice  $\Lambda^*$  of main reflections and the modulation wavevector  $\mathbf{q}$ . It then follows that  $K$  is characterized by the following properties:

(1) It leaves  $\Lambda^*$  invariant. (Only in this way are main reflections transformed into main reflections and satellites into satellites.)

(2) Any element  $R$  of  $K$  then transforms  $\mathbf{q}$  into  $\pm\mathbf{q}$  (modulo reciprocal-lattice vectors of  $\Lambda^*$ ).

An element  $R$  of  $K$  then transforms the basic vectors  $\mathbf{a}_1^*$ ,  $\mathbf{a}_2^*$ ,  $\mathbf{a}_3^*$ ,  $\mathbf{q}$  into ones of the form (9.8.1.15). If one denotes, as in (9.8.1.2),  $\mathbf{q}$  by  $\mathbf{a}_4^*$ , this implies

$$R\mathbf{a}_i^* = \sum_{j=1}^4 \Gamma^*(R)_{ji} \mathbf{a}_j^*, \quad i = 1, \dots, 4, \quad (9.8.1.16)$$

with  $\Gamma^*(R)$  a  $4 \times 4$  matrix with integral entries. In the case of an incommensurate modulated crystal structure, only two vectors with the same length as  $\mathbf{q}$  are  $\mathbf{q}$  and  $-\mathbf{q}$ . As  $\Lambda^*$  is left invariant, it follows that for a one-dimensionally modulated structure  $\Gamma^*(R)$  has the form

$$\Gamma^*(R) = \begin{pmatrix} \Gamma_E^*(R) & \Gamma_M^*(R) \\ 0 & \varepsilon(R) \end{pmatrix}, \quad \text{where } \varepsilon(R) = \pm 1. \quad (9.8.1.17)$$

This matrix represents the orthogonal transformation  $R$  when referred to the basis vectors  $\mathbf{a}_i^*$  ( $i = 1, 2, 3, 4$ ) of the vector module  $M^*$ . As in the case of lattices, two vector modules of modulated crystals are equivalent if they have bases (*i.e.* a basis for the reciprocal lattice  $\Lambda^*$  of the basic structure together with a modulation wavevector  $\mathbf{q}$ ) such that the set of matrices  $\Gamma^*(K)$  representing their symmetry is the same for both vector modules. Equivalent vector modules form a *Bravais class*.

Again, as in the case of three-dimensional lattices, it is sometimes convenient to consider a vector module that includes as subset the one spanned by all diffraction spots as in (9.8.1.15). Within such a larger vector module, the actual diffraction peaks then obey *centring conditions*. For a vector module associated with a modulated structure, centring may involve main reflections (the basic structure then has a centred lattice), or satellites, or both. For example, if in a structure with primitive orthorhombic basic structure the modulation wavevector is given by  $\alpha\mathbf{a}_1^* + \frac{1}{2}\mathbf{a}_2^*$ , one may describe the diffraction spots by means of the non-primitive lattice basis  $\mathbf{a}_1^*$ ,  $\frac{1}{2}\mathbf{a}_2^*$ ,  $\mathbf{a}_3^*$  and by the modulation wavevector  $\alpha\mathbf{a}_1^*$ .

Crystallographic point groups are denoted generally by the same letter  $K$ .

### 9.8.1.4.2. Description in four dimensions

The matrices  $\Gamma^*(R)$  form a faithful integral representation of the three-dimensional point group  $K$ . It is also possible to consider them as four-dimensional orthogonal transformations leaving a lattice with basis vectors (9.8.1.14) invariant. Indeed, one can consider the vectors (9.8.1.15) as *projections* of four-dimensional lattice vectors  $H_s = (\mathbf{H}, H_I)$ , which can be written as

$$H_s = \sum_{i=1}^4 h_i \mathbf{a}_{si}^*, \quad (9.8.1.18)$$

where [cf. (9.8.1.14)]  $m$  has now been replaced by  $h_4$  and

$$\mathbf{a}_{si}^* = (\mathbf{a}_i^*, 0), \quad i = 1, 2, 3; \quad \mathbf{a}_{s4}^* = (\mathbf{q}, 1). \quad (9.8.1.19)$$

As will be explained in Section 9.8.4, these vectors span the four-dimensional reciprocal lattice for a periodic structure having as three-dimensional intersection (say defined by the hyperplane  $t = 0$ ) the modulated crystal structure (a specific example has been given in Subsection 9.8.1.3). In direct space, the point group  $K_s$  in four dimensions with elements  $R_s$  of  $O(4)$  then acts on the corresponding dual basis vectors (9.8.1.11) of the four-dimensional *direct lattice* as

$$R_s \mathbf{a}_{si} = \sum_{j=1}^4 \Gamma(R)_{ji} \mathbf{a}_{sj} \quad (i = 1, 2, 3, 4), \quad (9.8.1.20a)$$

where  $\Gamma(R)$  is the transpose of the matrix  $\Gamma^*(R^{-1})$  appearing in (9.8.1.17) and therefore for incommensurate one-dimensionally modulated structures it has the form

$$\Gamma(R) = \begin{pmatrix} \Gamma_E(R) & 0 \\ \Gamma_M(R) & \varepsilon(R) \end{pmatrix}. \quad (9.8.1.20b)$$

### 9.8.1.4.3. Four-dimensional crystallography

Let us summarize the results obtained in the previous paragraph. The matrices  $\Gamma(R)$  form a faithful integral representation of the three-dimensional point group  $K$  with a four-dimensional carrier space  $V_s$ . It is a reducible representation having as invariant subspaces the physical three-dimensional space, denoted by  $V$  (or sometimes also by  $V_E$ ), and the additional one-dimensional space, denoted by  $V_I$ . In  $V$ , the four-dimensional point-group transformation acts as  $R$  (sometimes also denoted by  $R_E$ ), in  $V_I$  it acts as one of the two one-dimensional point-group transformations: the identity or the inversion. Therefore, the space  $V_s$  can be made Euclidean with  $\Gamma(R)$  defining a four-dimensional point-group transformation  $R_s$ , which is an element of a crystallographic subgroup  $K_s$  of  $O(4)$ . The four-dimensional point-group transformations are of the form  $(R, \varepsilon)$ , with  $\varepsilon = \pm 1$  and they act on the four-dimensional lattice basis as

$$(R, \varepsilon) \mathbf{a}_{si} = \sum_{j=1}^4 \Gamma(R)_{ji} \mathbf{a}_{sj}, \quad i = 1, \dots, 4, \quad (9.8.1.21)$$

where  $\varepsilon$  stands for  $\varepsilon(R)$  as in (9.8.1.20b). So the point-group symmetry operations are crystallographic and given by pairs of a three-dimensional crystallographic point-group transformation and a one-dimensional  $\varepsilon = \pm 1$ , respectively. The case  $\varepsilon = -1$  corresponds to an *inversion of the phase of the modulation function*.

As in the three-dimensional case, one can define equivalence classes among those four-dimensional point groups.

Two point groups  $K_s$  and  $K'_s$  belong to the same *geometric crystal class* if their three-dimensional (external) parts (forming the point group  $K_E$  and  $K'_E$ , respectively) are in the same three-dimensional crystal class [*i.e.* are conjugated subgroups of  $O(3)$ ] and their one-dimensional internal parts (forming the point groups  $K_I$  and  $K'_I$ , respectively) are equal. The latter condition implies that corresponding point-group elements have the same value of  $\varepsilon$ .

Such a geometric crystal class can then be denoted by the symbol of the three-dimensional crystal class together with the values of  $\varepsilon$  that correspond to the generators.

Also, the notion of *arithmetic equivalence* can be generalized to these four-dimensional point groups, as they admit the same faithful integral representation  $\Gamma(K)$  given above. This means

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that two such groups are arithmetically equivalent if there is a basis transformation for the reciprocal-vector module, which transforms main reflections into main reflections and satellites into satellites and which transforms one of the matrix groups into the other. The arithmetic classes are determined by the arithmetic equivalence class of the three-dimensional group  $K_E$  [*i.e.* by  $\Gamma_E(K)$ ] and by the components of the modulation wavevector with respect to the corresponding reciprocal-lattice basis. This is because the elements  $\varepsilon$  are fixed by the relation

$$R\mathbf{q} \equiv \varepsilon\mathbf{q} \text{ (modulo reciprocal-lattice vectors of the basic structure).} \quad (9.8.1.22)$$

Note that these  $(3+1)$ -dimensional equivalence classes are not simply those one obtains in four-dimensional crystallography, as the relation between the higher-dimensional space  $V_s$  and the three-dimensional physical space  $V$  plays a fundamental role.

The embedded structures in four dimensions have lattice periodicity. So the symmetry groups are four-dimensional space groups, called *superspace groups*. The new name has been introduced because of the privileged role played by the three-dimensional subspace  $V$ . A superspace-group element  $g_s$  consists of a point-group transformation  $(R, \varepsilon)$  and a translation  $(\mathbf{v}, \Delta)$ . The action of such an element on the four-dimensional space is then given by

$$g_s r_s = \{(R, \varepsilon)|(\mathbf{v}, \Delta)\}(\mathbf{r}, t) = (R\mathbf{r} + \mathbf{v}, \varepsilon t + \Delta). \quad (9.8.1.23)$$

It is important to realize that a superspace-group symmetry of an embedded crystal induces three-dimensional transformations leaving the original modulated structure invariant. Corresponding to (9.8.1.23), one obtains the following relations [cf. (9.8.1.13)]:

$$\mathbf{u}_{j'}[\mathbf{q} \cdot (\mathbf{n}' + \mathbf{r}_{j'})] = R\mathbf{u}_j[\mathbf{q} \cdot (\mathbf{n} + \mathbf{r}_j) - \varepsilon\Delta] \quad (9.8.1.24)$$

with

$$\mathbf{n}' + \mathbf{r}_{j'} = R(\mathbf{n} + \mathbf{r}_j) + \mathbf{v}.$$

These are purely three-dimensional symmetry relations, but of course not Euclidean ones.

In three-dimensional Euclidean space, the types of space-group transformation are translations, rotations, rotoinversions, reflections, central inversion, screw rotations, and glide planes. Only the latter two transformations have intrinsic non-primitive translations. For superspace groups, the types of transformation are determined by the point-group transformations. By an appropriate choice of the basis in  $V_s$ , each of the latter can be brought into the form

$$\begin{pmatrix} \cos \varphi & -\sin \varphi & 0 & 0 \\ \sin \varphi & \cos \varphi & 0 & 0 \\ 0 & 0 & \delta & 0 \\ 0 & 0 & 0 & \varepsilon \end{pmatrix}; \quad \varepsilon, \delta = \pm 1. \quad (9.8.1.25)$$

By a choice of origin, each translational part can be reduced to its intrinsic part, which in combination with the point-group element  $(R, \varepsilon)$  gives one of the transformations in  $V$  indicated above together with the inversion, or the identity, or a shift in  $V_I$ . So, for phase inversion (when  $\varepsilon = -1$ ), the intrinsic shift in  $V_I$  vanishes. When  $\varepsilon = +1$ , the intrinsic shift in  $V_I$  is given by  $\tau$ . It will be shown in Subsection 9.8.3.3 that the value of  $\tau$  is one of

$$0, \frac{1}{2}, \frac{\pm 1}{3}, \frac{\pm 1}{4}, \frac{\pm 1}{6}. \quad (9.8.1.26)$$

Therefore, a superspace-group element can be denoted by a symbol that consists of a symbol for the three-dimensional part following the conventions given in Volume A of *International*

*Tables for Crystallography*, a symbol that determines  $\varepsilon$ , and one for the corresponding intrinsic internal translation  $\tau$ .

### 9.8.1.4.4. Generalized nomenclature

In Section 9.8.4, the theory is extended to structures containing  $d$  modulations, with  $d \geq 1$ . In this case, each point-group transformation in internal space is given by  $R_I$  and the associated internal translation by the ( $d$ -dimensional) vector  $\mathbf{v}_I$ . Thus,

$$g_s = \{(R, R_I)|(\mathbf{v}, \mathbf{v}_I)\}.$$

The transformations  $R$  and  $R_I$  are represented by the matrices  $\Gamma_E(R)$  and  $\Gamma_I(R)$ , respectively. In the following discussion, this nomenclature (but with  $v_I$  rather than  $\mathbf{v}_I$ ) is sometimes also applied for the  $(3+1)$ -dimensional case. The usual formulae are obtained by replacing  $R_I$  by  $\varepsilon$  and  $v_I$  by  $\Delta$ .

### 9.8.1.4.5. Four-dimensional space groups

Four-dimensional space groups were obtained in the  $(3+1)$ -reducible case by Fast & Janssen (1969) and in the general case by Brown, Bülow, Neubüser, Wondratschek & Zassenhaus (1978). The groups were determined on the basis of algorithms developed by Zassenhaus (1948), Janssen, Janner & Ascher (1969), Brown (1969), and Fast & Janssen (1971). In the book by Brown, Bülow, Neubüser, Wondratschek & Zassenhaus, quoted above, a mathematical characterization of the basic crystallographic concepts is given together with corresponding tables for the dimensions one, two, three, and four. One finds there, in particular, a full list of four-dimensional space groups. The list by Fast & Janssen is restricted to space groups with  $(3+1)$ -reducible point groups. The four-dimensional groups in the work of Brown *et al.* are labelled by numbers. For these same groups, alternative symbols have been developed by Weigel, Phan, Veysseyre and Grebille generalizing the principles of the notation adopted by *International Tables for Crystallography*, Volume A, for the three-dimensional space groups (Weigel, Phan & Veysseyre, 1987; Veysseyre & Weigel, 1989; Grebille, Weigel, Veysseyre & Phan, 1990).

The difference in the listing of four-dimensional crystallographic groups one finds in Brown *et al.* and in Weigel *et al.* with respect to that in the present tables is not simply a matter of notation. In the first place, here only those groups appear that can occur as symmetry groups of one-dimensional incommensurate modulated phases (there are 371 such space groups). Furthermore, as already mentioned, a finer equivalence relation has been considered that reflects the freedom one has in embedding a three-dimensional modulated structure in a four-dimensional Euclidean space. Instead of 371, one then obtains 775 inequivalent groups for which the name superspace group has been introduced. A  $(3+1)$ -dimensional superspace group is thus a four-dimensional space group having some additional properties. In Section 9.8.4, the precise definitions are given.

In the commensurate one-dimensionally modulated case, 3833 four-dimensional space groups may occur, out of which 320 already belong to the previous 371. The corresponding additional  $(3+1)$ -dimensional superspace groups are also present in the listing by Fast & Janssen (1969) and have been considered again (and applied to structure determination) by van Smaalen (1987). The Bravais classes for the commensurate  $(3+1)$ -dimensional case are given in Table 9.8.3.2(b).

The relation between modulated crystals and the superspace groups is treated in a textbook by Opechowski (1986). That between the superspace-group symbols of the present tables and those of Weigel *et al.* is discussed in Grebille *et al.* (1990).

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

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

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

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

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

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

Hence,

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

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

$$\Delta(\mathbf{H}) = \sum_{h_1 h_2 h_3} \delta \left( \mathbf{H} - \sum_{i=1}^3 h_i \mathbf{a}_i^* \right).$$

Consequently, the diffraction peaks occur at positions  $\mathbf{H}$  given by (9.8.1.7). For a simple sinusoidal modulation [ $m = \pm 1$  in (9.8.1.29)], there are only main reflections and first-order satellites ( $m = \pm 1$ ). One may introduce an additional coordinate  $t$  and generalize (9.8.1.27) to

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

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 *ITA* 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

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

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  $\alpha$ ,  $\beta$ , and  $\gamma$  are given with respect to the three-dimensional conventional basis.

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

The  $(3 + 1)$ -dimensional Bravais class is fixed by that three-dimensional Bravais class and the components  $\alpha$ ,  $\beta$ ,  $\gamma$  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 *ITB* (1993, p. 241, Subsection 2.3.4.1).