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Wyckoff Positions used for the Classification of Bravais Classes of Modulated Crystals

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Abstract

Wyckoff positions of centrosymmetric symmorphic space groups, if properly interpreted, can be used to derive the Bravais classes of modulated crystals. This program is worked out here for the incommensurate case and assuming that the modulation wave vectors are symmetry related, *i.e.* are (integral combinations of) vectors of one star. The corresponding classes are called elementary Bravais classes (EBC's). It is shown that for three-dimensional crystals the maximal internal dimension for these EBC's is nine. It is explained in what sense this approach leads to a complete list.

I. Introduction

The symmetry of an incommensurate crystal phase is very low if one considers only the usual symmetry transformations, *i.e.* the rigid motions. As has been shown earlier (de Wolff, Janssen & Janner, 1981, and papers cited therein), one can nevertheless use crystallographic concepts if one generalizes the notion of crystal symmetry. From a certain point of view one can consider these generalized symmetry groups as crystallographic space groups in a higher-dimensional space. This is, however, not the essential point: the higher-dimensional space is only introduced for convenience. Anyhow, the introduction of this new type of symmetry transformation is very useful in the description and in the structure determination of incommensurate crystal phases (Yamamoto, 1982). For the latter, in particular, it is highly desirable to have a complete classification.

Since the symmetry groups considered here have the structure of crystallographic space groups a first step towards their classification is the determination of the lattice types, *i.e.* the Bravais classes. If one denotes by d the number of additional dimensions, which can be interpreted as the number of independent modulation wave vectors, one wants to know the $(3 + d)$-dimensional Bravais classes corresponding to incommensurate crystal structures. The latter restriction is necessary because using the definition of Bravais class as in n-dimensional crystallography one obtains many more classes and one does not take into account the dimensionality 3 of the crystal. For d smaller than or equal to 3 this classification has already been done (Janner, Janssen & de Wolff, 1983, here denoted by I) and covers all the cases of incommensurate crystals known so far. It is to be expected, however, that higher internal dimensions also occur in nature. The reason is the following.

Very often a modulated structure originates at a phase transition from the condensation of a vibrational eigenmode of the crystal. In general there are other modes which are symmetry related to the one considered and also condense. Two cases are then expected: one where point-group-related domains appear of single-mode-modulated crystal structures, and a second, without domains, where a multi-mode-modulated single crystal is observed. If the condensation occurs at a point with high symmetry in the Brillouin zone, the number of condensing modes involved is small and the internal dimension required will also be small. If, however, the wave vectors of the condensing modes are in a general position, their number can be as high as 48 in the cubic crystal case and can lead to a fairly high internal dimension.

The number of Bravais classes for each value of the internal dimension is finite, but increases substantially with increasing value of d. Here we restrict ourselves to the Bravais classes of those incommensurate crystal structures that originate from one set of symmetry-related wave vectors. In solid-state physics these sets are known as 'stars'. As in I we call the corresponding Bravais classes 'elementary Bravais classes' (EBC's). In the present paper we intend to derive a list of all EBC's. As explained further on, this goal is achieved in a restrictive sense only, which seems, however, to be physically reasonable.

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The EBC's are of course included in the general derivation of Bravais classes for an arbitrary dimension described in I. Upon analysis of that result it appeared that another, more specific way to find EBC's exists, using concepts relating to the well-known crystallographic Wyckoff positions. This alternative approach is set out in the present paper.

II. The internal dimension of elementary Bravais classes

We recall that the diffraction spots of an incommensurate crystal can be written in the form

$$\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + \sum_{j=1}^{d} m_j \mathbf{q}_j, \tag{1}$$

where h, k, l and m_j are integers and $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ basis vectors of the lattice A^* of main reflections. We denote the set of all vectors of the form (1) by M^* (I, equation 2). We recall that an incommensurate crystal belongs to an EBC if all d modulation vectors can be generated from a single $\mathbf{q}$ by transformations belonging to the point group K of M^*. This means that there are elements $R_1, R_2, \ldots, R_d$ in the point group K such that

$$\mathbf{q}_j = \mathbf{R}_j \mathbf{q}. \tag{2}$$

Since K is centrosymmetric, in an EBC at most $\frac{1}{2}m_K$ of these operators are needed (m_K = order of K). Often d is even smaller because of the existence of integral linear relations

$$\sum_j z_j R_j = 0 \quad (R_j \text{ in } K) \tag{3}$$

corresponding to identities $\sum_j z_j \mathbf{q}_j = 0$.

As an example consider the point group $K = mmm$. If R_1, R_2, R_3 are rotations by π around the three binary axes, respectively, and E is the unit matrix, one has

$$E + R_1 + R_2 + R_3 = 0. \tag{4}$$

This relation implies that for each R in $K = mmm$ one has

$$R = z_0(R)\, E + z_1(R)\, R_1 + z_2(R)\, R_2 \tag{5}$$

and that each integral linear combination of vectors $R\mathbf{q}$ may be expressed as a linear combination of $\mathbf{q}_1 = \mathbf{q}$, $\mathbf{q}_2 = R_1\mathbf{q}$, and $\mathbf{q}_3 = R_2\mathbf{q}$. Therefore, in this case, for a vector in general position one finds $d = 3$, which is smaller than half the order (8) of K.

In this way one can determine the maximal dimension d for each of the Laue point groups and for each case one can determine d elements R_j ($j = 1, \ldots, d$) such that

$$R = \sum_{j=1}^{d} z_j(R)\, R_j \tag{6}$$

for any of the point-group elements R and such that there are no relations of the type (3) between them.

The nine elements of a matrix R_j can also be regarded as the components of a vector in nine-dimensional space. So any number of R_j's larger than nine obeys a relation of the type (3). The coefficients z_j of such a relation can be made integral, because there exist bases for which the elements of all R_j's are integers. It follows that d (being defined as the minimum number of $\mathbf{q}$'s) cannot exceed nine for any EBC. This upper limit actually occurs, namely for a general $\mathbf{q}$ vector in the cubic system.

The dimension d may be smaller than the maximal one for the point group under consideration if the vectors $\mathbf{q}$ are in special positions. To see that, it is convenient to consider the point pattern of M^* as a crystal in reciprocal space with lattice A^*. Let the symmetry of that pattern be described by the (centrosymmetrical symmorphic) space group G. Note that its point group is the Laue point group K of M^* and that A^* is the lattice of the main reflections of M^*. When there exist for a specific vector $\mathbf{q}$ linear integral relations between the vectors $R\mathbf{q}$ of the form

$$\sum_{R \in K} z(R)\, R\mathbf{q} = \mathbf{t}^*, \quad \text{integers } z(R) \text{ and } \mathbf{t}^* \text{ in } A^*, \tag{7}$$

which are different from (3) and such that one of the integers $z(R)$ is equal to one, the dimension d is lower than the maximal one for the Laue group under consideration. Looking at (7) as an equation to be solved for $\mathbf{q}$, for a given $\mathbf{t}^*$, we observe that the solution should be variable (like $0, x, \frac{1}{2}$) rather than fixed (like $0, \frac{1}{2}, \frac{1}{2}$) because incommensurability requires a variable $\mathbf{q}$.

III. EBC's and Wyckoff positions

Relations of the type (6) hold when $\mathbf{q}$ is in a special position ('Wyckoff position') in the space group G (with point group K and lattice A^*) of the symmorphic centrosymmetric type considered here. In that case there are elements R of K such that

$$R\mathbf{q} = \mathbf{q} + \mathbf{t}^*, \tag{8}$$

for some $\mathbf{t}^*$ in A^*. These elements form the point symmetry group of the Wyckoff position. If one adds to this group all corresponding elements $-R$ one obtains again a group which we denote by H_q and which consists of all elements R such that

$$R\mathbf{q} = \pm\mathbf{q} + \mathbf{t}^*, \tag{9}$$

for some $\mathbf{t}^*$ in A^*. Then one can write

$$K = \sum_{\mu=1}^{s} R'_\mu H_q, \tag{10}$$

which means that each element of K can be written in a unique way as the product of an element R'_μ and an element of H_q. If now R_i and R_j belong to the same coset $R'_\mu H_q$, there is an element T of H_q such that $R_i = R_j T$ and consequently

$$\mathbf{q}_i = R_i\,\mathbf{q} = R_j\,T\mathbf{q} = \pm R_j(\mathbf{q} + \mathbf{t}^*) = \pm\mathbf{q}_j + \mathbf{t}'^*. \qquad (11)$$

In that case one of the $\mathbf{q}_i$'s may be eliminated from the basis set considered in (2). So for wave vectors in special Wyckoff positions, the internal dimension can be derived step-wise.

The question then comes up whether each variable special position of each centrosymmetrical symmorphic space group G, as listed in *International Tables for X-ray Crystallography* (1969) (IT), yields one EBC. The answer is: yes it does, but sometimes the result is equivalent to one or more of the other Wyckoff positions. There are three types of such equivalent positions.

Type 1

Special positions in the orthorhombic case (*mmm*), which result from permutations of x,y,z (three or six such positions).

Example: positions (*i*), (*m*) and (*q*) for $G = Pmmm$.

Type 2

Starting from a special position in a space group G it can happen that the actual symmetry group of this Wyckoff position contains elements not included in the point group but belonging to a bigger group that leaves the translations (Λ^*) also invariant.

Example: position (*g*) $(0,0,z)$ of $G = P4/m$ clearly generates a point set with space group $P4/mmm$. So that is where the resulting EBC belongs.

Type 3

Because of the rational independence of the basis vectors of M^*, integral linear combinations of $\mathbf{q}_1, \ldots, \mathbf{q}_d$ do not belong to the lattice of main reflections. This implies that the vectors $\mathbf{q}_1, \ldots, \mathbf{q}_d$ should be rationally independent. If this is not the case the vectors $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ should be redefined.

Example 1: position (*i*) $(0,\frac{1}{2},z)$ of $G = P4/mmm$ generates a star which has in its span vectors with only rational components: $(\frac{1}{2},\frac{1}{2},0) = (\frac{1}{2},0,z) + (0,\frac{1}{2},-z)$. If one takes for the lattice of main reflections the basis $(\frac{1}{2},\frac{1}{2},0)$, $(-\frac{1}{2},\frac{1}{2},0)$, $(0,0,1)$ the lattice Λ^* is again tetragonal and one can choose for characterizing this EBC the vector $\mathbf{q}$ with components $(\frac{1}{2},\frac{1}{2},z)$. This case as well as several others are identifiable in IT because they give rise to 'special reflection conditions' for (hkl).

Example 2: in $G = P6/mmm$, the sum vector $(\frac{1}{2},\frac{1}{2},0) = (\frac{1}{2},0,z) + (0,\frac{1}{2},-z)$ for position (*i*) indicates a rational

Table 1. *Elementary Bravais classes*

Given are the Bravais classes either by their number in the tables of I (for d smaller than four) or by the internal dimension in parentheses. The one-line symbol of the Bravais class is the column heading followed by the row heading.

I. Triclinic	$P\bar{1}$	II. Monoclinic	$P2/m$	$B2/m$
(α,β,γ)	1–1	$(\alpha,\beta,0)$	1–2	1–4
		$(\alpha,\beta,\frac{1}{2})$	1–3	–
		$(0,0,\gamma)$	1–5	1–7
		$(\frac{1}{2},0,\gamma)$	1–6	–
		$(0,\frac{1}{2},\gamma)$	–	1–8
		(α,β,γ)	2–16	2–17

III. Orthorhombic	$Pmmm$	$Immm$	$Cmmm$	$Ammm$	$Fmmm$
$(0,0,\gamma)$	1–9	1–12	1–13	1–15	1–17
$(\frac{1}{2},0,\gamma)$	–	–	–	1–16	–
$(0,\frac{1}{2},\gamma)$	1–10	–	–	–	–
$(\frac{1}{2},\frac{1}{2},\gamma)$	1–11	–	–	–	–
$(1,0,\gamma)$	–	–	1–14	–	1–18
$(0,\beta,\gamma)$	2–50	2–52	2–53	2–54	2–56
$(\frac{1}{2},\beta,\gamma)$	2–51	–	–	2–55	–
(α,β,γ)	3–148	3–149	3–150	–	3–151

IV. Tetragonal	$P4/m$	$P4/mmm$	$I4/m$	$I4/mmm$
$(0,0,\gamma)$	–	1–19	–	1–21
$(\frac{1}{2},\frac{1}{2},\gamma)$	–	1–20	–	–
$(\alpha,0,0)$	–	2–63	–	2–67
$(\alpha,\frac{1}{2},0)$	–	2–64	–	–
$(\alpha,0,\frac{1}{2})$	–	2–65	–	–
$(\alpha,\frac{1}{2},\frac{1}{2})$	–	2–66	–	–
$(\alpha,\alpha,0)$	–	2–68	–	2–70
$(\alpha,\alpha,\frac{1}{2})$	–	2–69	–	–
$(\alpha,\alpha,1)$	–	–	–	2–71
$(0,\beta,\gamma)$	–	3–177	–	3–179
$(\frac{1}{2},\beta,\gamma)$	–	3–178	–	–
(α,α,γ)	–	3–180	–	3–181
$(\alpha,\beta,0)$	2–57	(4)	2–59	(4)
$(\alpha,\beta,\frac{1}{2})$	2–58	(4)	–	–
(α,β,γ)	3–157	(5)	3–158	(5)

V. Trigonal	$P\bar{3}$	$P\bar{3}1m$	$P\bar{3}m1$	$R\bar{3}$	$R\bar{3}m$
$(0,0,\gamma)$	–	–	–	–	1–22
$(1/3,1/3,\gamma)$	–	1–23	–	–	–
$(\alpha,0,0)$	–	–	–	–	2–79
$(\alpha,0,1/3)$	–	–	2–78	–	–
$(\alpha,\alpha,0)$	–	–	–	–	2–77
$(\alpha,\alpha,1/3)$	–	2–76	–	–	–
$(\alpha,\beta,0)$	–	–	–	2–73	–
$(\alpha,\beta,1/3)$	2–72	–	–	–	–
$(\alpha,0,\gamma)$	–	–	3–198	–	3–199
(α,α,γ)	–	3–197	–	–	–
(α,β,γ)	3–186	(5)	(5)	3–187	(5)

VI. Hexagonal	$P6/m$	$P6/mmm$
$(0,0,\gamma)$	–	1–24
$(\alpha,0,0)$	–	2–82
$(\alpha,\alpha,0)$	–	2–83
$(\alpha,0,\gamma)$	–	3–202
(α,α,γ)	–	3–203
$(\alpha,\beta,0)$	2–80	(4)
(α,β,γ)	3–200	(5)

VII. Cubic	$Pm3$	$Pm3m$	$Im3$	$Im3m$	$Fm3$	$Fm3m$
$(\alpha,0,0)$	–	3–208	–	3–210	–	3–211
$(\alpha,\frac{1}{2},0)$	3–204	–	–	–	–	–
$(\alpha,1,0)$	–	–	–	–	3–205	
$(\alpha,\frac{1}{2},\frac{1}{2})$	–	3–209	–	–	–	–
$(0,\beta,\beta)$	–	3–212	–	3–213	–	3–214
$(\frac{1}{2},\beta+\frac{1}{2},\beta)$	3–206	–	–	–	–	–
$(0,\beta+1,\beta)$	–	–	–	–	3–207	–
(α,α,α)	–	3–215	–	3–216	–	3–217
$(0,\beta,\gamma)$	(6)	(6)	(6)	(6)	(6)	(6)
$(\frac{1}{2},\beta,\gamma)$	(6)	(6)	–	–	–	–
(α,α,γ)	–	(6)	–	(6)	–	(6)
(α,β,γ)	(9)	(9)	(9)	(9)	(9)	(9)

Table 2. *Number of elementary Bravais classes in the various crystal systems*

Internal dimension d	1	2	3	4	5	6	9
System							
Triclinic	1	–	–	–	–	–	–
Monoclinic	7	2	–	–	–	–	–
Orthorhombic	10	7	4	–	–	–	–
Tetragonal	3	12	7	3	2	–	–
Trigonal	2	6	5	–	3	–	–
Hexagonal	1	3	3	1	1	–	–
Cubic	–	–	14	–	–	11	6

dependence of the basic satellites. Taking for the basis vectors of Λ^* the vectors $(\frac{1}{2},0,0)$, $(0,\frac{1}{2},0)$ and $(0,0,1)$ the vector $\mathbf{q}$ gets components $(0,0,z)$ and the EBC is characterized by these instead of the original ones. In all these cases the EBC derived from a Wyckoff position is equivalent to one derived from another position.

When comparing the table of EBC's with the special positions in IT it should be realized that the row headings in the table, which give the components of the vector $\mathbf{q}$, refer to reciprocal space whereas the components in IT are of vectors in direct space. Thus the lattice centerings F and I must be interchanged, as well as the designations $3m1$ and $31m$. In the tetragonal system I remains I but the axes are rotated through 45°. Hexagonal axes make an angle of 60°. Components α,β,γ refer to a basis which yields integer centering translations (1,1,0 instead of $\frac{1}{2},\frac{1}{2},0$, *etc.*). Apart from these changes, EBC's are obtained from the special positions in IT just by replacing (x,y,z) by (α,β,γ).

IV. Tables

For all Wyckoff positions we have derived the nonequivalent EBC's. However, it should be said here that in this way one does not obtain a complete list. One of the reasons is that if one of the free parameters becomes rational, the internal dimension generally decreases. For example, if in an orthorhombic case the vector (α,β,γ) gets a rational component (say $\alpha=\frac{1}{4}$) one can redefine Λ^* (take $\mathbf{a}^*/4$ instead of $\mathbf{a}^*$). Then $\mathbf{q}$ has components $(0,\beta,\gamma)$ and the internal dimension is two instead of three. This would imply a constant and very abrupt change of the internal dimension within the same Wyckoff position. Therefore, it is more convenient to consider these cases as belonging to the same EBC: that for the incommensurate value of α.

A second reason for the change of the EBC when $\mathbf{q}$ has special values of the components not required by the Wyckoff position is the existence of operators which are linear combinations of the point-group elements and which map a vector $\mathbf{q}$ on a reciprocal-lattice vector.

Example: for $K=m3$ the sum $E+R+R^2$, where R is the threefold rotation around a body diagonal of the cubic cell, gives zero when applied to $\mathbf{q}=(\alpha,\beta,-\alpha-\beta)$, although $\mathbf{q}$ is not in a special position. In itself the resulting equation (7) does not characterize any local symmetry in reciprocal space. So from a physical point of view the ensuing EBC's may be less stable than those generated by special positions, implying a change in the local symmetry. For this reason they are omitted for $d>3$.

In the tables the EBC's form a complete list for internal dimensions not larger than three, and are those derived from Wyckoff positions for all other values of d. Each EBC is given either by its number from I (if $d=3$ or smaller) or by its internal dimension. These are arranged in rows and columns. The column headings give the point group K and the centering of the lattice of main reflections, the rows give the components of one vector of the star with respect to a conventional basis of Λ^*. The one-line symbol for the EBC follows by writing the column heading followed by the row heading.

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