

Lecture 1 — Symmetry in the solid state -

Part I: Simple patterns and groups

1 Symmetry operators: key concepts

- **Operators:** transform (move) the whole pattern (i.e., the *attributes*, or content, of all points in space). We denote operators in *italic fonts* and we used parentheses ($()$) around them for clarity, if required.
- **Symmetry operators:** a generic operator as described above is said to be a *symmetry operator* if upon transformation, the new pattern is indistinguishable from the original one. Let us imagine that a given operator g transforms point p to point p' . In order for g to be a *symmetry operator*, the *attributes* of the two points must be in some sense “the same”. This is illustrated in a general way in Fig. 1.
- **Application of operators** to points or parts of the pattern, relating them to other points or sets of points. We indicate this with the notation $v = gu$, where u and v are sets of points. We denote sets of points with roman fonts and put square brackets $[\]$ around them for clarity, if required. We will also say that pattern fragment u is *transformed* by g into pattern fragment v . If the pattern is to be symmetric, v must have the same attributes as u in the sense explained above.
- **Operator composition.** It is the sequential ordered application of two operators, and we indicate this with $g \circ h$. The new operator thus generated acts as $(g \circ h)u = g[hu]$. **Important Note:** Symmetry operators in general *do not commute*, so the order is important. We will see later on that translations (which are represented by vectors) can be symmetry operators. The composition of two translations is simply their *vector sum*.
- **Operator Graphs.** They are *sets of points* in space that are invariant (i.e., are transformed into themselves) upon the application of a given operator. We draw graphs with conventional symbols indicating how the operator acts. We denote the graph of the operator g (i.e., the invariant points) as $[g]$. **Note:** graphs can be thought of as parts of the pattern, and are subject to symmetry like everything else (as explained above). Sometimes, as in the above case of the fourfold axis, the graphs of two distinct operators coincide (e.g., left and right rotations around the same axis). In this case, the conventional symbol will account for this fact.
- **Transformation by “graph symmetry”.** Operator graphs can be thought of a parts of the pattern, and they can be transformed like everything else. When the graph of symme-

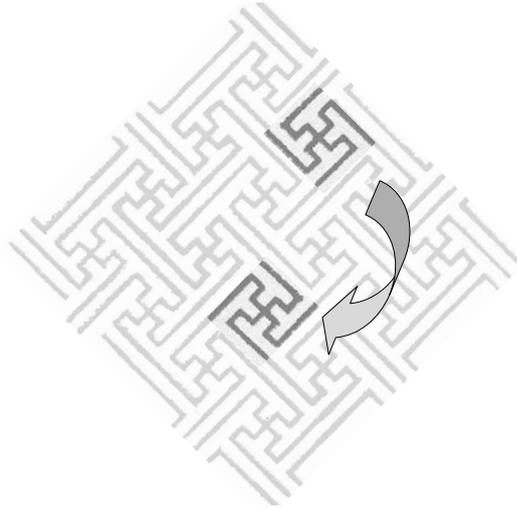


Figure 1: A generic symmetry operator acting on a pattern fragment.

try operator is transformed by the action of another operator, another graph is obtained, which logically represents a new symmetry operator. This is said to be obtained “by graph symmetry” from the original operator.

2 Formal properties of a group

- A binary operation (usually called **composition** or **multiplication**) must be defined. We indicated this with the symbol “ \circ ”.
- Composition must be **associative**: for every three elements f , g and h of the set

$$f \circ (g \circ h) = (f \circ g) \circ h \quad (1)$$

- The “neutral element” (i.e., the identity, usually indicated with E) must exist, so that for every element g :

$$g \circ E = E \circ g = g \quad (2)$$

- Each element g has an **inverse** element g^{-1} so that

$$g \circ g^{-1} = g^{-1} \circ g = E \quad (3)$$

- Another useful concept you should be familiar with is that of **subgroup**. A **subgroup is a subset of a group that is also a group**.

3 Composition (multiplication) of symmetry operators

Fig. 2 illustrates in a graphical way the composition of the operators 4^+ and m_{10} . The fragment to be transformed (here a dot) is indicated with "start", and the two operators are applied in order one after the other, until one reaches the "end" position. It is clear by inspection that "start" and "end" are related by the "diagonal mirror" operator m_{11} .

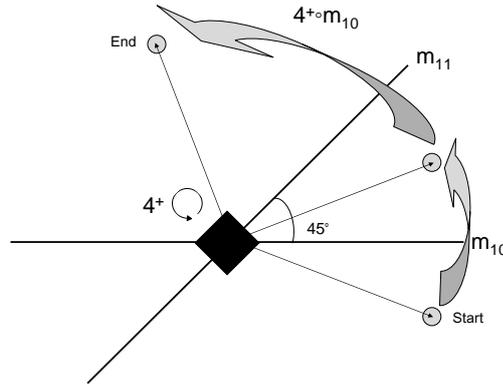


Figure 2: A graphical illustration of the composition of the operators 4^+ and m_{10} to give $4^+ \circ m_{10} = m_{11}$.

Note that the two operators 4^+ and m_{10} *do not commute*:

$$\begin{aligned} 4^+ \circ m_{10} &= m_{11} \\ m_{10} \circ 4^+ &= m_{1\bar{1}} \end{aligned} \quad (4)$$

It is important to note that

Applying a symmetry operator to the graph of another is not the same thing as composing (multiplying) the two operators.

Rather, transformation by graph symmetry is equivalent to *conjugation*

$$g[h] = [g \circ h \circ g^{-1}] \quad (5)$$

We read Eq. 5 in the following way: "The graph of the operator h transformed *by symmetry* with the operator g is equal to the graph of the operator $g \circ h \circ g^{-1}$ ". This relation clearly shows that graph symmetry is *not* equivalent to composition.

4 Conjugation classes

The group operation we just introduced, $g \circ h \circ g^{-1}$, also has special name — it is known as **conjugation**. If $k = g \circ h \circ g^{-1}$ we say that “ k and h are *conjugated* through the operator g ”.

Operators like k and h here above, which are conjugate with each other form distinct non-overlapping subsets¹ (*not* subgroups) of the whole group, known as **conjugation classes** (not to be confused with crystal classes — see below). **conjugation classes group together operators with symmetry-related graphs**

Conjugated operators are very easy to spot in a picture because *their graphs contain the same pattern*. On the other hand, operators such as m_{10} and m_{11} in the square group may look the same, but are not conjugated, so they do not necessarily contain the same pattern. We will see many examples of both kinds in the remainder.

5 The 2D point groups in the ITC

5.1 Symmetry directions: the key to understand the ITC

The group symbols used in the ITC employ the so-called **Hermann-Mauguin notation**² The symbols are constructed with letters and numbers in a particular sequence — for example, $6mm$ is a *point group* symbol and $I4_1/amd$ is an ITC *space group* symbol. This notation is complete and completely unambiguous, and should enables one, with some practice, to construct all the symmetry operator graphs. Nevertheless, the ITC symbols are the source of much confusion for beginners (and even some practitioners). In the following paragraphs we will explain in some detail the point-group notation of the ITC, but here it is perhaps useful to make some general remarks just by looking at the snowflake and its symmetry group diagram ($6mm$) in fig. 3.

- The principal symmetry feature of the $6mm$ symmetry is the 6-fold axis. Axes with order higher than 2 (i.e., 3, 4 and 6) **define the *primary symmetry direction* and always come upfront in the point-group symbol, and right after the lattice symbol (P, I, F , etc.) in the space group symbols**. This is the meaning of the first character in the symbol $6mm$.

¹For the mathematically minded, conjugation is an *equivalence relation*, and conjugation classes are therefore *equivalence classes*

²The Schoenflies notation is still widely used in the older literature and in some physics papers. In the longer version of the notes (Lecture 2), we will illustrate some principles this notation.

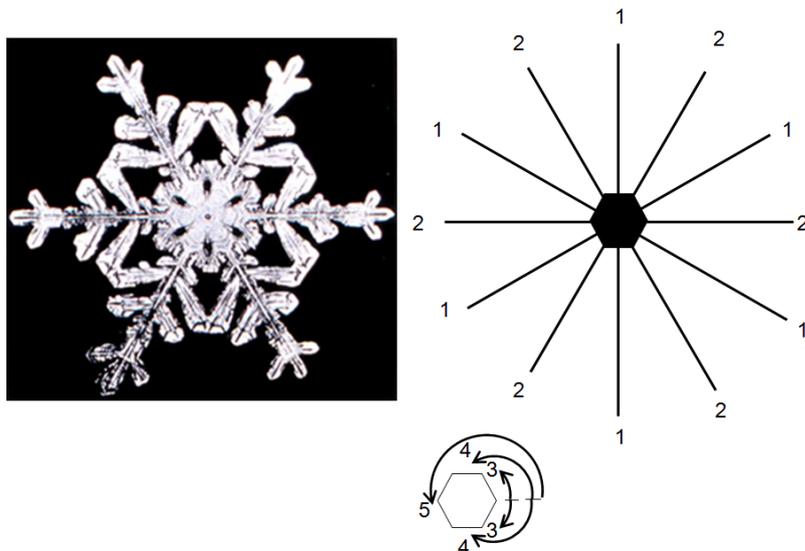


Figure 3: **Left.** A snowflake by Vermont scientist-artist Wilson Bentley, c. 1902. **Right** The symmetry group of the snowflake, $6mm$ in the ITC notation. The group has 6 classes, 5 marked on the drawing plus the identity operator E . Note that there are two classes of mirror planes, marked “1” and “2” on the drawing. One can see on the snowflake picture that their graphs contain *different patterns*.

- The next important features are the **mirror planes**. We can pick any plane we want and use it to define the **secondary symmetry direction**. For example, in fig. 3, we could define the secondary symmetry direction to be horizontal and perpendicular to the vertical mirror plane marked “1”. This is the meaning of the second character in the symbol $6mm$
- The **tertiary symmetry direction is never symmetry equivalent to the other two**. In other word, the operator “ m ” appearing in the third position as $6mm$ **does not belong to the same class as either of the other two symbols**. It has therefore necessarily to refer to a mirror plane of the *other class*, marked as “2”.
- Therefore, **in $6mm$, secondary and tertiary symmetry directions make an angle of 30° with each other**. Likewise **in $4mm$, (the square group) secondary and tertiary symmetry directions make an angle of 45° with each other**.

Operators listed in the ITC group symbols *never belong to the same conjugation class*.

5.2 Detailed description of the 2D point group tables in the ITC

The 10 2D point groups are listed in ITC-Volume A ([2]) on pages 768–769 (Table 10.1.2.1 therein, see Fig. 4). We have not introduced all the notation at this point, but it is worth examining the entries in some details, as the principles of the notation will be largely the same throughout the ITC.

10. POINT GROUPS AND CRYSTAL CLASSES

Table 10.1.2.1. *The ten two-dimensional crystallographic point groups*

General, special and limiting edge forms and *point forms* (italics), oriented edge and site symmetries, and Miller indices (*hk*) of equivalent edges [for hexagonal groups Bravais-Miller indices (*hk*) are used if referred to hexagonal axes]; for point coordinates see text.

OBLIQUE SYSTEM				
1				
1	<i>a</i>	1	Single edge Single point (<i>a</i>)	(<i>hk</i>)
2				
2	<i>a</i>	1	Pair of parallel edges Line segment through origin (<i>e</i>)	(<i>hk</i>) (<i>hk</i> -)
RECTANGULAR SYSTEM				
<i>m</i>				
2	<i>b</i>	1	Pair of edges Line segment (<i>e</i>)	(<i>hk</i>) (<i>hk</i> -)
			Pair of parallel edges Line segment through origin	(10) (10)
1	<i>a</i>	<i>m</i>	Single edge Single point (<i>a</i>)	(01) or (01-bar)
<i>2mm</i>				
4	<i>c</i>	1	Rhomb Rectangle (<i>i</i>)	(<i>hk</i>) (<i>hk</i> -) (<i>kh</i>) (<i>kh</i> -)
2	<i>b</i>	<i>m</i>	Pair of parallel edges Line segment through origin (<i>g</i>)	(01) (01-bar)
2	<i>a</i>	<i>m</i>	Pair of parallel edges Line segment through origin (<i>e</i>)	(10) (10)
SQUARE SYSTEM				
4				
4	<i>a</i>	1	Square Square (<i>d</i>)	(<i>hk</i>) (<i>hk</i> -) (<i>kh</i>) (<i>kh</i> -)
<i>4mm</i>				
8	<i>c</i>	1	Ditetragon Truncated square (<i>g</i>)	(<i>hk</i>) (<i>hk</i> -) (<i>kh</i>) (<i>kh</i> -)
4	<i>b</i>	<i>m</i>	Square Square (<i>f</i>)	(11) (11-bar) (11) (11)
4	<i>a</i>	<i>m</i>	Square Square (<i>d</i>)	(10) (10) (01) (01-bar)

10.1. CRYSTALLOGRAPHIC AND NONCRYSTALLOGRAPHIC POINT GROUPS

Table 10.1.2.1. The ten two-dimensional crystallographic point groups (cont.)

HEXAGONAL SYSTEM				
3				
3	<i>a</i>	1	Trigon Trigon (<i>d</i>)	(hki) (ihk) (kih)
3m1				
6	<i>b</i>	1	Ditrigon Truncated trigon (<i>e</i>)	(hki) (ihk) (kih) (khi) (ikh) (hik)
			Hexagon Hexagon	$(11\bar{2})$ $(\bar{2}11)$ $(1\bar{2}1)$ $(\bar{1}12)$ $(2\bar{1}1)$ $(12\bar{1})$
3	<i>a</i>	<i>m</i>	Trigon Trigon (<i>d</i>)	or $(10\bar{1})$ $(\bar{1}10)$ $(0\bar{1}1)$ (101) (110) (011)
31m				
6	<i>b</i>	1	Ditrigon Truncated trigon (<i>d</i>)	(hki) (ihk) (kih) (khi) (ikh) (hik)
			Hexagon Hexagon	(101) (110) (011) (011) (101) (110)
3	<i>a</i>	<i>m</i>	Trigon Trigon (<i>c</i>)	or $(11\bar{2})$ $(\bar{2}11)$ $(1\bar{2}1)$ $(\bar{1}12)$ $(2\bar{1}1)$ $(12\bar{1})$
6				
6	<i>a</i>	1	Hexagon Hexagon (<i>d</i>)	(hki) (ihk) (kih) (khi) (ikh) (hik)
6mm				
12	<i>c</i>	1	Dihexagon Truncated hexagon (<i>f</i>)	(hki) (ihk) (kih) (khi) (ikh) (hik) $(\bar{h}\bar{k}\bar{i})$ $(\bar{i}\bar{h}\bar{k})$ $(\bar{k}\bar{i}\bar{h})$ $(\bar{k}\bar{h}\bar{i})$ $(\bar{i}\bar{k}\bar{h})$ $(\bar{h}\bar{i}\bar{k})$
6	<i>b</i>	<i>m</i>	Hexagon Hexagon (<i>e</i>)	$(10\bar{1})$ $(\bar{1}10)$ $(0\bar{1}1)$ (101) (110) (011)
6	<i>a</i>	<i>m</i>	Hexagon Hexagon (<i>d</i>)	$(11\bar{2})$ $(\bar{2}11)$ $(1\bar{2}1)$ $(\bar{1}12)$ $(2\bar{1}1)$ $(12\bar{1})$

Figure 4: 2-Dimensional point groups: a reproduction of Pages 768–769 of the ITC [2]

- **Reference frame:** All point groups are represented on a circle with thin lines through it. The fixed point is at the center of the circle. All symmetry-related points are at the same distance from the center (remember that symmetry operators are isometries), so the circle around the center locates symmetry-related points. The thin lines represent possible systems of coordinate axes (*crystal axes*) to locate the points. We have not introduced axes at this point, but we will note that the lines have the same symmetry of the pattern.
- **System:** Once again, this refers to the type of axes and choice of the unit length. The classification is straightforward.
- **Point group symbol:** It is listed in the top left corner, and it generally consists of 3 characters: a number followed by two letters (such as $6mm$). When there is no symmetry along a particular direction (see below), the symbol is omitted, but it could also be replaced by a "1". For example, the point group m can be also written as $1m1$. The first symbol stands for one of the allowed rotation axes perpendicular to the sheet (the "primary symmetry direction"). Each of the other two symbols represent elements defined by *inequivalent* symmetry directions, known as "secondary" and "tertiary", respectively. In this case, they are *sets of mirror lines that are equivalent by rotational symmetry* or, in short, different conjugation classes. The lines associated with each symbol are not symmetry-equivalent (so they belong to different conjugation classes). For example, in the point group $4mm$, the first m stands for two orthogonal mirror lines. The second m stands for two other (symmetry-inequivalent) orthogonal mirror lines rotated by 45° with respect to the first set. Note that all the symmetry directions are equivalent for the three-fold axis 3, so either the primary or the secondary direction must carry a "1" (see below).
- **General and special positions:** Below the point group symbol, we find a list of general and special positions (points), the latter lying on a symmetry element, and therefore having fewer "equivalent points". Note that the unique point at the center is always omitted. From left to right, we find:

Column 1 The **multiplicity**, i.e., the number of equivalent points.

Column 2 The **Wickoff letter**, starting with a from the bottom up. Symmetry-inequivalent points with the same symmetry (i.e., lying on symmetry elements of the same type) are assigned different letters.

Column 3 The **site symmetry**, i.e., the symmetry element (always a mirror line for 2D) on which the point lies. The site symmetry of a given point can also be thought as the **point group leaving that point invariant**. Dots are used to indicate which symmetry element in the point group symbol one refers to. For example, site b of point group $4mm$ has symmetry $.m$, i.e., lies on the *second* set of mirror lines, at 45° from the first set.

Column 4 Name of crystal and *point* forms (the latter in italic) and their "limiting" (or degenerate) forms. Point forms are easily understood as the polygon (or later polyhedron) defined by sets of equivalent points with a given site symmetry. Crystal forms are historically more important, because they are related to *crystal shapes*. They represent the polygon (or polyhedron) with sides (or faces) passing through a given point of symmetry and orthogonal to the radius of the circle (sphere). We shall not be further concerned with forms.

Column 5 Miller indices. For point groups, Miller indices are best understood as related to crystal forms, and represent the inverse intercepts along the crystal axes. By the well-known "law of rational indices", real crystal faces are represented by integral Miller indices. We also note that for the hexagonal system 3 Miller indices (and 3 crystal axes) are shown, although naturally only two are needed to define coordinates.

- **Projections:** For each point group, two diagrams are shown. It is worth noting that for 3D point groups, these diagrams are *stereographic projections* of systems of equivalent points. The diagram on the **left** shows the projection circle, the crystal axes as thin lines, and a set of equivalent general positions, shown as dots. The diagram on the **right** shows the symmetry elements, using the same notation we have already introduced.
- **Settings** We note that one of the 10 2D point groups is shown twice with a different notation, $3m1$ and $31m$. By inspecting the diagram, it is clear that the two only differ for the position of the crystal axes with respect of the symmetry elements. In other words, the difference is entirely conventional, and refers to the choice of axes. We refer this situation, which reoccurs throughout the ITC, as two different *settings* of the same point group.
- Unlike the case of other groups, the **group-subgroup relations** are not listed in the group entries but in a separate table.

6 Wallpaper groups

6.1 A few new concepts for Wallpaper Groups

- **Translations.** This is a new symmetry that we did not encounter for point groups, since, by definition they had a fixed point, whereas translations leave no point fixed. In all 2D (Wallpaper) and 3D (Space) group, there exist fundamental ("primitive") translations that defines the repeated pattern.
- **Repeat unit or unit cell.** A minimal (but never unique, i.e., always conventional) part of the pattern that generates the whole pattern by application of the *pure translations*.

- **Asymmetric unit.** A minimal (but never unique) part of the pattern that generates the whole pattern by application of all the operators. It can be shown that there is always a simply connected choice of asymmetric unit.
- **Multiplicity.** It is the number of equivalent points *in the unit cell*.
- **Points of special symmetry.** These are points that are invariant by application of one or more operator, and have therefore reduced multiplicity with respect to “general positions”. This is analogous to the case of the point groups. They are essentially the graphs of generalized rotations and their intersections. The generalized rotation operators intersecting in each given point define a *point group*, known as the *local symmetry group* for that point.
- **Crystal class** This is a *point group* obtained by combining all the *rotational parts* of the operators in the group. The same definition is valid for wallpaper and space groups.
- **Glides.** This is a composite symmetry, which combines a translation with a *parallel* reflection, neither of which on its own is a symmetry. In 2D groups, the glide is indicated with the symbol g . *Twice* a glide translation is *always* a symmetry translation: in fact, if one applies the glide operator twice as in $g \circ g$, one obtains a pure translation (since the two mirrors cancel out), which therefore must be a symmetry translation.

6.2 Lattices and the “translation set”

The symmetry of the translation set must be “compatible” with that of the other operators of the group. In other words, if one applies a rotation to one of the primitive translation vectors (remember that this means transforming the translation by *graph symmetry*, one must find another primitive translation. This is best seen by introducing the concept of *lattices*.

Lattices are an alternative representation of the translation set. They are sets of points generated from a single point (*origin*) by applying all the translation operators.

The symmetry of the lattice (known as the *holohedry*) must be at least as high as the *crystal class*, supplemented by the inversion (180° rotation in 2 dimensions). This result is also valid in 3 dimensions

6.3 Bravais lattices in 2D

Bravais lattices, named after the French physicist Auguste Bravais (1811–1863), define all the translation sets that are mutually compatible with crystallographic point groups. There are 5 of

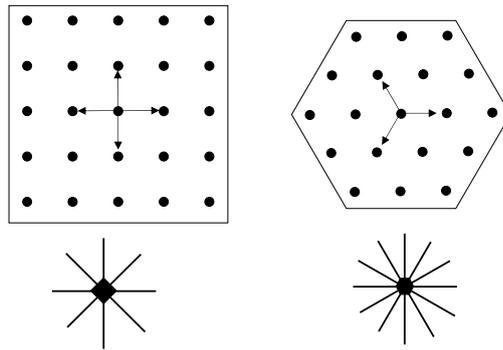


Figure 5: Portions of the square and hexagonal lattices, with their respective point symmetry groups. Note that the symmetry of the lattice is *higher* than that of the minimal point group needed to construct them from a single translation (4 and 3, respectively)

them: "Oblique", "*p*-Rectangular", "*c*-Rectangular", "Square" and "Hexagonal". They can all be generated constructively in simple ways.

6.3.1 Oblique system

Here, each translation is symmetry-related to its opposite only, so there is no restriction on the length or orientation of the translations. The resulting lattice is a tiling of parallelograms.

6.3.2 Rectangular system

Here we have two cases (Fig. 6):

- A simple tiling of rectangles, known as a "*p*-Rectangular" (primitive rectangular) lattice.
- A rectangular lattice with nodes at the centers of the rectangles, known as a "*c*-Rectangular" (centered rectangular) lattice.

6.3.3 Square system

There are two point groups in this system: 4 and $4mm$. They both generate simple square lattices. In the latter case, as we have already shown, the nodes must lie on the mirror planes (Fig. 5).

6.3.4 Hexagonal system

There are four point groups in this system: 3, $3m1$ (or $31m$), 6 and $6mm$. They all generate simple hexagonal lattices. In the case of $6mm$, the nodes must lie on the mirror planes (Fig. 5), whereas in the case of $31m$ they must lie either on the mirror planes (setting $31m$) or exactly in between (setting $3m1$). Note that here the distinction is real, and will give rise to two different wallpaper groups.

6.4 Primitive, asymmetric and conventional Unit cells in 2D

Primitive unit cells Minimal units that can generate the whole pattern by translation.

Asymmetric unit cells Minimal units that can generate the whole pattern by application of all symmetry operators.

Conventional unit cells In the case of the *c*-rectangular lattice, the primitive unit cell is either a rhombus or a parallelogram and does not possess the full symmetry of the lattice. It is therefore customary to introduce a so-called *conventional centered* rectangular unit cell, which has double the area of the primitive unit cell (i.e., it always contains two lattice points), but has the full symmetry of the lattice and is defined by orthogonal translation vectors, known as **conventional translations** (Fig. 8).

6.5 The 17 wallpaper groups

Table 1: The 17 wallpaper groups. The symbols are obtained by combining the 5 Bravais lattices with the 10 2D point groups, and replacing *g* with *m* systematically. Strikeout symbols are duplicate of other symbols.

crystal system	crystal class	wallpaper groups
oblique	1	$p1$
	2	$p2$
rectangular	m	pm, cm, pg, eg
	$2mm$	$p2mm, p2mg (=p2gm), p2gg, c2mm, e2mg, e2gg$
square	4	$p4$
	$4mm$	$p4mm, p4gm, p4mg$
hexagonal	3	$p3$
	$3m1-31m$	$p3m1, p3mg, p31m, p31g$
	6	$p6$
	$6mm$	$p6mm, p6mg, p6gm, p6gg$

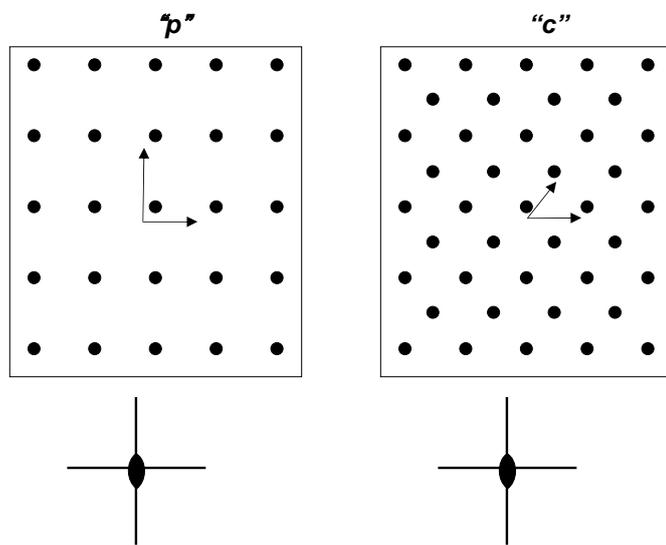


Figure 6: The two types of rectangular lattices ("p" and "c") and their construction.

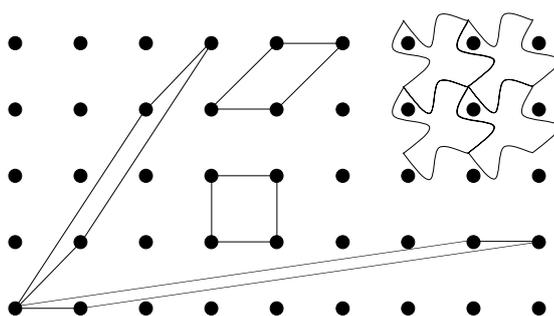


Figure 7: Possible choices for the primitive unit cell on a square lattice.

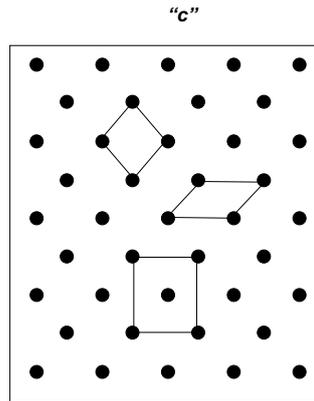


Figure 8: Two primitive cells and the conventional unit cell on a c -centered rectangular lattice.

6.6 Analyzing wallpaper and other 2D art using wallpaper groups

The symmetry of a given 2D pattern can be readily analyzed and assigned to one of the wallpaper groups, using one of several schemes. One should be careful in relying too much on the lattice symmetry, since it can be often higher than the underlying pattern (especially for true wallpapers). Mirrors and axes are quite easily identified, although, once again, one should be careful with pseudo-symmetries. Fig. 9 shows a decision-making diagram that can assist in the identification of the wallpaper group. Here, no reliance is made on the lattice, although sometimes centering is easier to identify than glides.

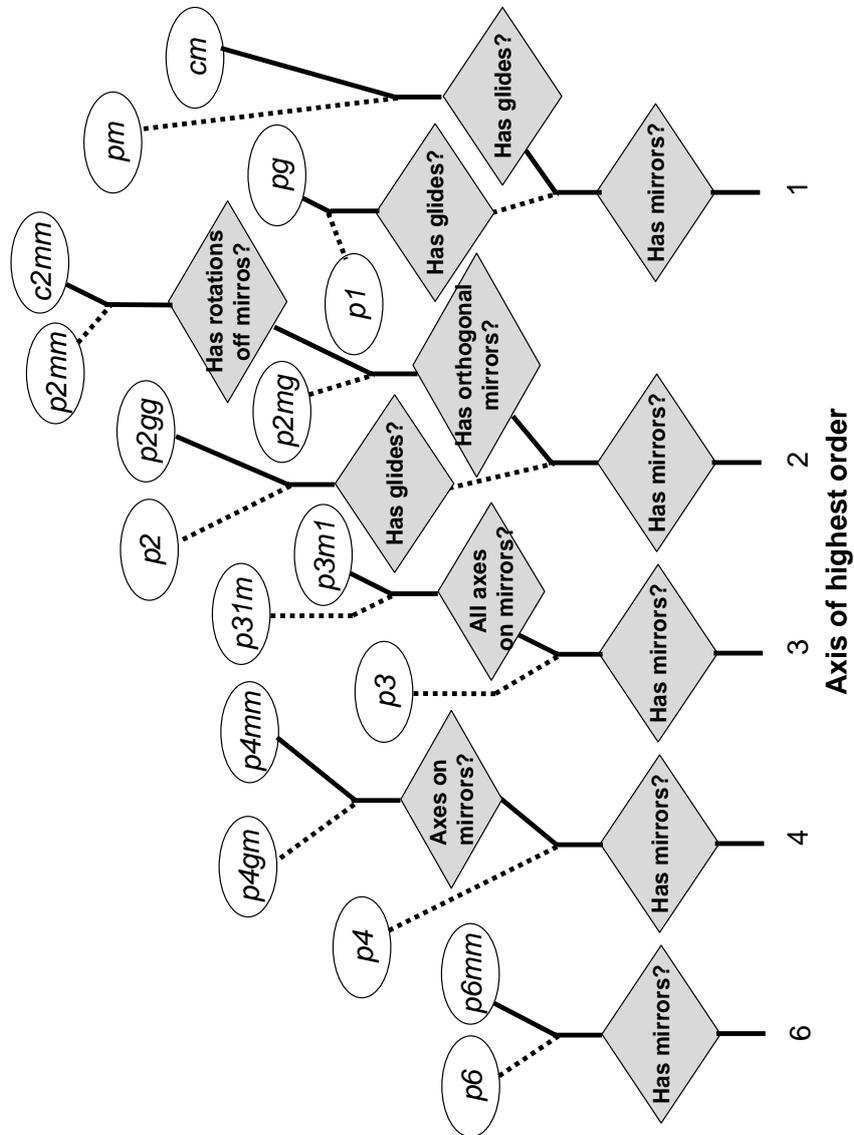


Figure 9: Decision-making tree to identify wallpaper patterns. The first step (bottom) is to identify the axis of highest order. Continuous and dotted lines are "Yes" and "No" branches, respectively. Diamonds are branching points.

7 Bibliography

P.G. Radaelli, “Symmetry in Crystallography: Understanding the International Tables ” [1], contain much of the same materials covering lectures 1-3, but in an extended form.

The International Tables for Crystallography [2] is an indispensable text for any condensed-matter physicist. It currently consists of 8 volumes. A selection of pages is provided on the web site. Additional sample pages can be found on <http://www.iucr.org/books/international-tables>.

C. Giacovazzo, “Fundamentals of crystallography” [3] is an excellent book on general crystallography, including some elements of symmetry.

References

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