

Crystal Structure and Dynamics

Paolo G. Radaelli, Michaelmas Term 2015

Part 1: Symmetry in the solid state Lectures 1-5

Web Site:

<http://www2.physics.ox.ac.uk/students/course-materials/c3-condensed-matter-major-option>

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Contents

1 Lecture 1 — The translational and rotational symmetry of crystal in “real” space.	6
1.1 Introduction: crystals and their symmetry	6
1.2 Translational symmetry of crystals	7
1.2.1 Bravais Lattices	7
1.2.2 Crystallographic coordinates	9
1.2.3 More on fractional coordinates	11
1.2.4 Different choices of basis vectors and coordinate systems	12
1.2.5 Measuring distances and angles between atoms	12
1.2.6 The dot product between two position vectors: the metric tensor	13
1.3 Rotational symmetry of crystals	14
1.3.1 Crystal symmetry: an infinite “grid” of rotations/reflections	14
1.3.2 Crystallographic rotations (proper and improper) in 3D and their symbols	15
1.3.3 Proper and improper rotations expressed in terms of matrices and vectors	19
1.3.4 Rotations about points other than the origin	19
1.3.5 Normal form of the symmetry operators	20
1.3.6 The Seitz and ITC notations	21
2 Lecture 2 — An introduction to crystallographic groups	22
2.1 More on composition of operators	22
2.1.1 Compositions of operators in normal form	22
2.1.2 The inverse operator	22
2.1.3 Rotations around different origins vs Roto-translations .	23

2.2	Invariant points, lines and planes: special points and symmetry elements	25
2.2.1	Graphical representation of symmetry elements	26
2.2.2	“Companions” of general and special points	26
2.3	Some elements of group theory	27
2.3.1	Groups as mathematical sets	27
2.3.2	Full crystallographic groups (including translations)	28
2.3.3	Finite groups in crystallography: crystal classes and point groups	28
2.4	Point Groups in 2 and 3 dimensions	30
2.4.1	Graphical representations of point groups through symmetry elements	31
2.4.2	Notation of point groups	31
3	Lecture 3 —The symmetry of periodic crystals: space groups	34
3.1	Representation and notation of space groups	34
3.1.1	Graphical representation and symmetry elements	34
3.1.2	Notation for space groups	35
3.2	“Companions” revisited: site multiplicities	36
3.2.1	General and special multiplicities	36
3.2.2	Companions of special points of symmetry vs points of equal symmetry	37
3.2.3	Notation for general and special positions: multiplicity, Wyckoff letter and site symmetry	38
3.3	Summary: Understanding the International Tables of Crystallography	39
4	Lecture 4 — Symmetry in 2 dimensions: wallpaper groups.	43
4.1	Wallpaper vs space group symmetry	43
4.1.1	Bravais lattices in 2D	43

4.1.2	Rotations in 2D	43
4.1.3	Roto-translations in 2D	44
4.2	Construction and identification of the 17 wallpaper groups . . .	44
4.2.1	Point groups in 2D	44
4.2.2	Wallpaper groups	45
4.2.3	Identification of wallpaper groups	45
5	Lecture 5 — Reciprocal lattice and reciprocal space	47
5.1	Basic definitions	47
5.2	The reciprocal lattice	47
5.2.1	Dual basis in 3D	47
5.2.2	Centring extinctions	48
5.2.3	Dual basis — alternative definition <i>without</i> cross product	51
5.2.4	Dot products in reciprocal space	52
5.2.5	A very useful example: the hexagonal system in 2D . .	52
5.3	Fourier transform of lattice functions	53
5.4	Atomic-like functions	53
5.5	Centring extinctions	54
5.6	Extinctions due to roto-translations	54
5.7	The symmetry of $ F(\mathbf{q}) ^2$ and the Laue classes	55
6	Appendix I: Fourier transform of lattice functions	56
7	Appendix II: “Real” crystal structures	57
7.1	Cohesive forces in crystals — atomic radii	58
7.2	Close-packed structures	59
7.3	Packing spheres of different radii	60
7.4	Framework structures	61

7.5 Layered structures	62
7.6 Molecular structures	62

1 Lecture 1 — The translational and rotational symmetry of crystal in “real” space.

1.1 Introduction: crystals and their symmetry

In 1928, Swiss physicist Felix Bloch obtained his PhD at University of Leipzig, under the supervision of Werner Heisenberg. In his doctoral dissertation, he presented what we now call the quantum theory of crystals, and what a momentous occasion that was! Much of the technology around us — from digital photography to information processing and storage, lighting, communication, medical imaging and much more is underpinned by our understanding of the behavior of electrons in metals (like copper) and semiconductors (like silicon). Today’s contemporary physics also focuses on crystals, in particular on properties that cannot be described in terms of simple one-electron physics, such as high-temperature superconductivity.

One may ask what is special about a crystal as compared, for example, to a piece of glass. From previous introductory courses, you already know part of the answer: crystals have a *lattice*, i.e., atoms are found regularly on the corners of a 3-dimensional grid. You also know that some crystals have a *basis*, comprising several atoms within the *unit cell*, which is replicated by placing copies at all nodes of the lattice.

At a more fundamental level, crystals differ from glasses and liquids because they have fewer symmetries. In a liquid or glass, properties look identical *on average* if we move from any point A to any point B (translation) and if we look in any direction (rotation). By contrast in a crystal, properties vary in a periodic manner by translation, and are only invariant by certain discrete rotations. The theory of symmetries in crystals underpin all of the crystal physics we have mentioned and much more. Here, we will start by describing *translational symmetry* in a more general way than you might have seen so far, suitable for application to crystals with non-orthogonal lattices. We will then look at ways of classifying *rotational* symmetries systematically, and we will learn how to use the International Tables of Crystallography (ITC hereafter), an essential resource for condensed matter physics research.

Symmetry can be defined as the invariance of a system upon certain transformations. Intuitively, we understand for instance that a cube remains invariant by rotations through 90° around a face normal or through 120° around a cube diagonal. What we are doing here is to apply a *global transformation*, in which each point of the cube is made to rotate around an axis so that it moves from

the original position to a new position. Only for certain values of the rotation angle is the result the same as the starting configuration.

Unlike a solid polyhedron, which is generally invariant by a discrete set of rotations/reflections, crystals are invariant by *an infinite set of discrete global transformations* — translations, rotations, inversion and combinations thereof. These will be explored in the remainder of this lecture.

1.2 Translational symmetry of crystals

1.2.1 Bravais Lattices

Translational invariance, periodicity and the presence of a lattice are equivalent and interchangeable properties that characterise *all* crystals. The fact that a crystal can be thought as built up by unit cells means that the crystal is invariant by translation by any of the cell edges and their (infinite) combinations. Although this symmetry is exact only for an infinite crystal, a typical 1mm crystal of a metal is made up of $\sim 10^{-22}$ unit cell, making exact translational lattice symmetry a very good approximation, at least for the purpose of calculating scattering properties.

As you already know, in 3 dimensions there are 14 Bravais lattices (from 19-century French physicist Auguste Bravais) — see fig. 1. The lattices have distinct rotational symmetries, belonging to one of the 7 lattice systems (see below), and distinct topologies, since some lattice systems admit both *primitive* and *centred* lattices¹.

We recall that *primitive* lattices have nodes only at the corners of the unit cells, whereas *centred* lattices (or lattices with a basis) have nodes at other positions of the unit cell as well. The conventional notation is as follows:

Body-centred lattices (symbol I) have a 2-node basis at the corners and at the centre of the unit cell (positions $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). An example of this is the BBC lattice. The fractional vector² $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ (and equally in the examples below) is known as **centring vector**.

Single-face-centered lattices (symbols A, B, C) have a 2-node basis at the corners and at the centre of a pair of faces intersecting the a , b and c axes, respectively. So, for instance, the nodes of a C -centred lattice are at $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, 0$ etc.

¹The distinction between *lattice* systems and *crystal* systems is explained in sec. 2.4.2 below.

²See below for the square bracket notation.

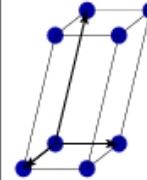
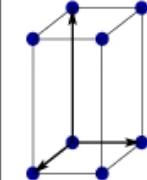
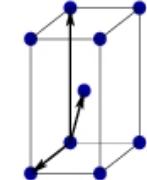
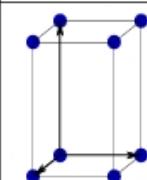
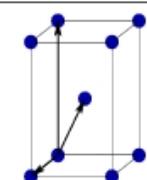
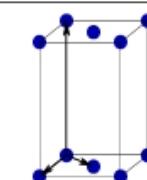
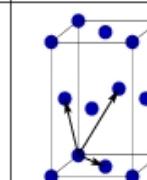
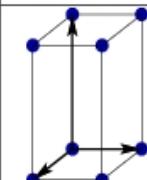
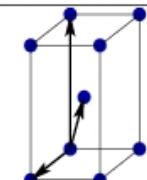
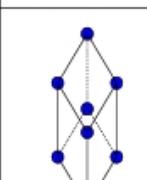
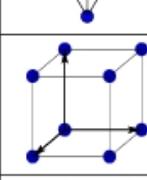
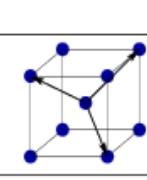
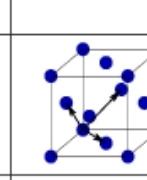
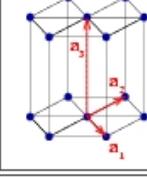
Lattice System	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Rhombohedral	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^\circ$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

Figure 1: The 14 Bravais lattices in 3D. The R-centred hexagonal cell can be used as a conventional cell for the rhombohedral lattice.

All-face-centred lattices (symbol F) have a 4-node basis at the centre of all faces, i.e., at $0, 0, 0$, $\frac{1}{2}, \frac{1}{2}, 0$, $0, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}, 0, \frac{1}{2}$. An example of this is the FCC lattice.

Rhombohedrally-centred lattices (symbol R) are hexagonal lattices with $a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$. R -centred lattices have a 3-node basis at $0, 0, 0$, $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$, and $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ (or, alternatively, at $0, 0, 0$, $\frac{1}{3}, \frac{2}{3}, \frac{1}{3}$, and $\frac{2}{3}, \frac{1}{3}, \frac{2}{3}$; the two alternatives are called *obverse* and *reverse* setting and are equivalent). R -centred lattices are a bit of an anomaly in that they are completely equivalent to rhombohedral (primitive) lattices (this is why they are not listed separately in fig. 1). However, the R -centred conventional unit cell is often more convenient to use than the trigonal primitive unit cell, which has $\alpha \neq \beta \neq \gamma$.

It is important to emphasise the fact that **it is always possible to choose a primitive cell to describe any lattice**. So, why does one bother with centred cells in the first place, and why do they occur only in certain lattice systems? The answer is that **conventional unit cells are chosen to have the full rotational symmetry of the lattice when primitive cells do not**.

1.2.2 Crystallographic coordinates

The symmetry of the unit cell affects the choice of the coordinate system that is used to define the position of atoms in the crystal. The logic is that if an atom exists at positions x, y, z , then the “companion atoms” of that atom in different unit cells will have coordinates $x+n_x, y+n_y, z+n_z$, where $[n_x, n_y, n_z]$ is a vector of integers or simple fractions (see below). **We don't use cartesian coordinates in crystallography.** More formally, these companion atoms are called *symmetry-equivalent atoms by translation*.

Let us start by looking at the cubic, tetragonal and orthorhombic lattices you should already be familiar with. The position of the nodes (i.e., unit cell origins and centring positions, when present) w.r.t. a chosen origin are expressed by means of position vectors³ of the form:

$$\mathbf{r}_n = a\hat{\mathbf{i}}\mathbf{n}_x + b\hat{\mathbf{j}}\mathbf{n}_y + c\hat{\mathbf{k}}\mathbf{n}_z \quad (1)$$

³Here, we will call *vector* an object of the form shown in eq. 2, containing both components and basis vectors. In this form, a vector is *invariant* by any coordinate transformation, which affect both components and basis vectors. Both basis vectors and components (coordinates) are written as *arrays* — see below. For a concise introduction to this kind of notation, see ITC volume B, chapter 1.

where a, b, c are the lattice constants ($a = b$ for the tetragonal lattice, $a = b = c$ for the cubic lattice) and $\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}$ are unit vectors along the x, y and z axes, while n_x, n_y and n_z are arbitrary integers (primitive lattices) or integers and half-integers (centred lattices). We can interpret these vectors as *invariant translation symmetry operators* — if points A and B are separated by one such vector, the properties of the crystal are identical in A and B. In particular, if there is an atom in A, there will be an identical “companion” atom in B.

By *symmetry operator* we mean a transformation of the coordinates (e.g., of an atom), which generates the coordinates of a *companion atom*.

The position vector of points in the crystal that are *not* on lattice nodes can be expressed as

$$\mathbf{r} = a\hat{\mathbf{i}}x + b\hat{\mathbf{j}}y + c\hat{\mathbf{k}}z \quad (2)$$

One can see the relation between x, y and z (which are *dimensionless*) and the usual Cartesian coordinates, which have dimensions. We can define the **basis vectors** (not to be confused with the unit cell basis) $\mathbf{a} = a\hat{\mathbf{i}}$, $\mathbf{b} = b\hat{\mathbf{j}}$ and $\mathbf{c} = c\hat{\mathbf{k}}$. In the cubic, tetragonal and orthorhombic lattices, the basis vectors are orthogonal, but this is not so in other most important cases — for example, that of hexagonal crystal like graphite, where the angle between $a = b \neq c$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. We can, however, generalise the notion of basis vectors so that it applies to cases such as this and even the most general (triclinic) lattice. In summary:

- In crystallography, we *do not* usually employ Cartesian coordinates. Instead, we employ a dimensionless coordinate systems associated with appropriate **basis vectors**.
- *Basis vectors* have the dimension of a *length*, and *coordinates* (position vector components) are *dimensionless*.
- We can denote the basis vectors as \mathbf{a}_i , where the correspondence with the usual crystallographic notation is

$$\mathbf{a}_1 = \mathbf{a}; \mathbf{a}_2 = \mathbf{b}; \mathbf{a}_3 = \mathbf{c} \quad (3)$$

- We will sometimes employ explicit array and matrix multiplication for clarity.

In this case, the array of basis vectors is written as a *row*⁴, as in $[\mathbf{a}] = [\mathbf{a}_1 \mathbf{a}_2 \mathbf{a}_3]$.

- With this notation, a generic position within the crystal will be defined by means of a *position* vector, written as

$$\mathbf{r} = \sum_i \mathbf{a}_i x^i = \mathbf{a}x + \mathbf{b}y + \mathbf{c}z \quad (4)$$

Points within the unit cell at the origin of the lattice have $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$ — the so-called *fractional coordinates*.

From eq. 4, we can re-write the position of the lattice points in the most general case as:

$$\mathbf{r}_n = \sum_i \mathbf{a}_i n^i = \mathbf{a}n_x + \mathbf{b}n_y + \mathbf{c}n_z \quad (5)$$

NOTATION: Real-space coordinates of an atom are usually written without any brackets. When the need for clarity arises, components of position vectors and in general of any vector defined in real space are **surrounded by square brackets**, so $[x, y, z]$ is the position vector w.r.t. the origin of an atom with coordinates x, y, z ⁵.

1.2.3 More on fractional coordinates

Fractional coordinates form the basis of the atomic-scale description of crystals. In fact, the position of *all* the atoms in the crystal is completely defined in terms of the fractional coordinates of the atoms in just one unit cell. Let an atom be at fractional coordinates x, y, z , with $0 \leq x \leq 1, 0 \leq y \leq 1, 0 \leq z \leq 1$. Then, all other “companion” atoms (i.e., atoms equivalent by translation) will be found at coordinates $x + n_x, y + n_y, z + n_z$, where $[n_x, n_y, n_z]$ is either an *integer vector* with positive or negative integral components (for primitive unit cells) or an *integer vector plus a centring vector of simple fractions* (for centred unit cells).

⁴By writing basis vectors as rows and coordinates or components as columns, vectors become the usual product of a row and a column array. Moreover, upon coordinate transformations, the transformation matrices for basis vectors and components are inverse of one another. The subscript and superscript notation also emphasises this.

⁵Although this is the most commonly used convention, the ITC Vol A does not always follow it, and uses, for example, $t(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ to indicate the translation vector $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$.

For example, in the case of the I -centred unit cell, companion atoms to x, y, z will be found at $x + n_x, y + n_y, z + n_z$ and $x + n_x + \frac{1}{2}, y + n_y + \frac{1}{2}, z + n_z + \frac{1}{2}$, with $[n_x, n_y, n_z]$ being an integer vector and $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ being the I -centring vector.

1.2.4 Different choices of basis vectors and coordinate systems

There are many possible choices of primitive unit cells/basis vectors, as well as many possible choice of the origin of the coordinate system, and consequently *there exist many equivalent coordinate systems*. In fact, coordinate transformations are the bane of crystallography, and a lot of effort has been devoted, to the extent that this is possible, to define universal conventions. This subject will not be discussed further, except for the following general points.

- In order to describe the same lattice, the two *transformation matrices* converting one basis set to the other and vice versa must be integer matrices. This is obvious, since the new basis vectors connect lattice points, and must be expressible with integral coordinates on the old basis.
- This implies that the determinant of these matrices is exactly 1 or -1 (depending on the relative handedness of the basis sets), because the determinant of an integer matrix is an integer and the determinant of the inverse matrix is the inverse of the original determinant.
- One can show that the inverse of an integer matrix M is again an integer matrix if and only if the determinant of M is exactly 1 or -1. Therefore, all integer unimodular matrices define valid coordinate transformations for primitive cells.

1.2.5 Measuring distances and angles between atoms

Measuring distances between nearby atoms is clearly very important, for example, to determine whether such atoms are *chemically bonded* and the strength of the bond. Likewise, angles between bonds are very important, since they define the *coordination* of each atom. We know, for example, that in diamond each C atom is surrounded by a tetrahedron of C atoms, which means that the angle between bonds linking to the same atom is the tetrahedral angle — 109.5° . Therefore, once we know the *fractional coordinates* of all the atoms, we want to be able to measure distances and angles. This is clearly best done by calculating dot products of the *relative position vectors*

between two atoms, the components of which are simply the difference of the fractional coordinates. This can be straightforwardly extended to atoms in different unit cells by using their coordinates (fractional plus appropriate integer vectors) as explained above.

1.2.6 The dot product between two position vectors: the metric tensor

- The dot product between two position vectors is given explicitly by

$$\begin{aligned}
 \mathbf{r}_1 \cdot \mathbf{r}_2 &= \mathbf{a} \cdot \mathbf{a} x_1 x_2 + \mathbf{b} \cdot \mathbf{b} x_1 x_2 + \mathbf{c} \cdot \mathbf{c} z_1 z_2 + \\
 &\quad + \mathbf{a} \cdot \mathbf{b} [x_1 y_2 + y_1 x_2] + \mathbf{a} \cdot \mathbf{c} [x_1 z_2 + z_1 x_2] + \mathbf{b} \cdot \mathbf{c} [y_1 z_2 + z_1 y_2] = \\
 &= a^2 x_1 x_2 + b^2 x_1 x_2 + c^2 z_1 z_2 + ab \cos \gamma [x_1 y_2 + y_1 x_2] \\
 &\quad + ac \cos \beta [x_1 z_2 + z_1 x_2] + bc \cos \alpha [y_1 z_2 + z_1 y_2]
 \end{aligned} \tag{6}$$

- The quantities in square bracket represent the elements of a **symmetric matrix**, known as the **metric tensor**. The metric tensor elements have the dimensions of *length square*.

$$G_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j \tag{7}$$

Calculating lengths and angles using the metric tensor

- You are generally given the **lattice parameters** a , b , c , α , β and γ . In terms of these, the metric tensor can be written as

$$\mathbf{G} = \begin{bmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{bmatrix} \tag{8}$$

- To measure the **length** v of a vector \mathbf{v} :

$$v^2 = |\mathbf{v}|^2 = [v^1 \ v^2 \ v^3] \mathbf{G} \begin{bmatrix} v^1 \\ v^2 \\ v^3 \end{bmatrix} \tag{9}$$

- To measure the **angle** θ between two vectors \mathbf{v} and \mathbf{u} :

$$\cos \theta = \frac{1}{uv} [u^1 \ u^2 \ u^3] \mathbf{G} \begin{bmatrix} v^1 \\ v^2 \\ v^3 \end{bmatrix} \tag{10}$$

1.3 Rotational symmetry of crystals

We have seen how in all crystals “companion atoms” to an atom in a given unit cell are generated by translation, i.e., by adding appropriate integer and centring vectors to their coordinates. In addition to these symmetry-equivalent atoms by translations, **most crystals also include symmetry-equivalent atoms by rotation, inversion and reflection, as well as combinations of these with non-lattice translations** (see below). This is very convenient, because it often enables us to define the crystal fully with a much smaller number of atoms than those contained in one unit cell.

However, it is worth emphasising from the outset the profound difference between the rotation/reflection symmetry of a simple polyhedron (say, a cube or a dodecahedron) and that of a crystal. The symmetry of the polyhedra consists of a finite set of rotations/reflections that always leave the centre of the polyhedron invariant. This is called a **point-group symmetry**, and as we shall see is also very important in crystallography. By contrast, the full symmetry of a crystal **always contains an infinite number of elements**. Notably, if there is even a single symmetry axis of rotation or a single mirror plane, then there is always an infinite number of them. Intuitively, this must be the case because of the lattice translational symmetry: if there is a rotation axis in one unit cell, there also must be one in all the other unit cells. However, there are actually more rotations that one would expect purely based on this argument.

1.3.1 Crystal symmetry: an infinite “grid” of rotations/reflections

Let us see how this comes about. Consider a simple two-fold rotation axis around the origin, parallel to the b axis. This means that an atom at position x, y, z will have a symmetry-equivalent companion atom at $-x, y, -z$ (or \bar{x}, y, \bar{z} to use standard crystallographic notation). Both atoms will also have an infinite set of companions by translation, as explained above. So, for instance, the second atom will have a companion at $1 - x, y, \bar{z}$, which logically will be a companion of the original atom at x, y, z . **This is an example of composition of symmetries**, i.e., of the sequential application of symmetry operators. The position vectors of atoms 1 and 3 will be related as follows:

$$\begin{bmatrix} 1-x \\ y \\ -z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} + \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad (11)$$

This can be re-written:

$$\begin{bmatrix} 1-x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x - \frac{1}{2} \\ y \\ z \end{bmatrix} + \begin{bmatrix} \frac{1}{2} \\ 0 \\ 0 \end{bmatrix} \quad (12)$$

One can see immediately that eq. 12 **represent a rotation around a two-fold axis parallel to b shifted so that it passes through position $\frac{1}{2}, 0, 0$ rather than through the origin.** It is worth noting that this axis is *not* a companion by translation to the original rotational axis (such companions occur at $1, 0, 0$ etc.).

This is *completely general* to any translation vector and also to any kind of rotation, reflection or inversion (with appropriate modifications). The presence of one such rotation/inversion/reflection operators, together with the composition of symmetries with the lattice translation, generates an *infinite grid of rotations/inversions/reflections* around different points of the crystal.

The process is illustrated in fig. 2. The whole construction has the periodicity of the lattice, so all the unit cells are identical, as one would expect, but there are 2-fold axes generated in this way also in the centre of the unit cell and at the mid-points of the edges, as made clear from eq. 12.

1.3.2 Crystallographic rotations (proper and improper) in 3D and their symbols

We have just seen an example of crystallographic symmetry consisting of *lattice translations* and an infinite set of two-fold rotations around different points of the unit cell. Rotations other than two-fold are of course possible, but there is a limited number of them, because **the lattice is required to be symmetrical (invariant) by all the symmetry rotations.** We recall that *improper rotations* arise from the *composition* of an ordinary (proper) rotation with the inversion. Each proper rotations has a corresponding improper rotation. The proper rotation corresponding to the inversion is the identity. In 3 dimensions, the following proper and improper rotations are compatible with some crystallographic lattices (see fig. 3 for the graphic symbols used in the ITC — see the next lectures for further explanations of these symbols):

Proper rotations

- Identity (letter symbol 1) (*all lattices*). This is a “null” operators that leaves things unaltered.

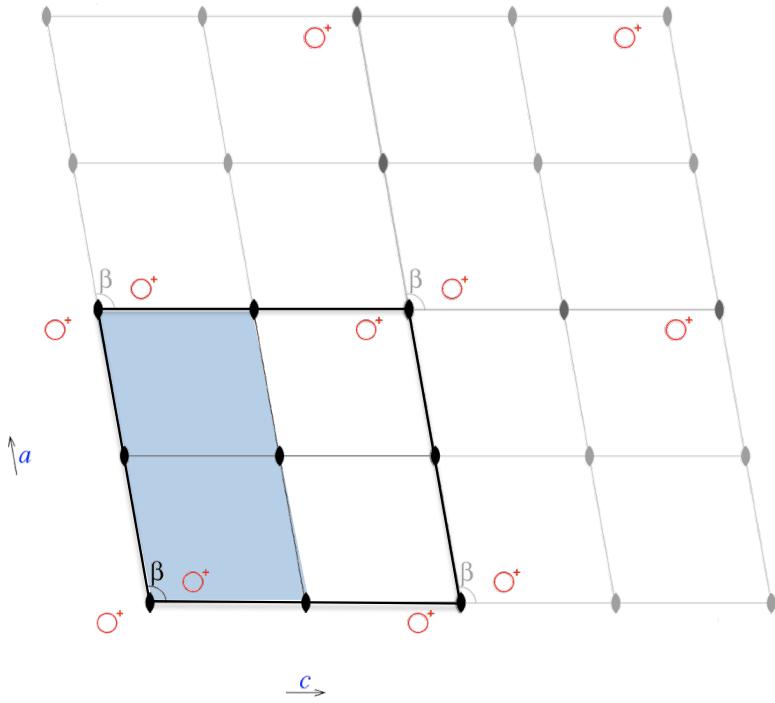


Figure 2: b -axis projection of the infinite grid of 2-fold axes in Space Group $P2$ (number 3 in the ITC). The thick black lines define the boundaries of the unit cell. The shaded area is the asymmetric unit cell (see text). The circles are symmetry-equivalent “companion” atoms.

- Two-fold rotation (letter symbol 2) (*monoclinic, orthorhombic, tetragonal, hexagonal and cubic lattices*).
- Three-fold rotation (letter symbol 3) (*trigonal, hexagonal and cubic lattices*).
- Four-fold rotation (letter symbol 4) (*tetragonal and cubic lattices*).
- Six-fold rotation (letter symbol 6) (*hexagonal lattice*).

Improper rotations

- Inversion (letter symbol $\bar{1}$) (*all lattices*). The inversion by the origin corresponds to a change in sign of all coordinates in all coordinate systems.
- Mirror plane (letter symbol m) (*monoclinic, orthorhombic, tetragonal, hexagonal and cubic lattices*). It is a *composition* of a two-fold rotation with the inversion, and could therefore be written as $\bar{2}$.
- “Three-bar” operator (letter symbol $\bar{3}$) (*trigonal, hexagonal and cubic lattices*). It is a *composition* of a three-fold rotation with the inversion
- “Four-bar” operator (letter symbol $\bar{4}$) (*tetragonal and cubic lattices*). It is a *composition* of a four-fold rotation with the inversion
- “Six-bar” operator (letter symbol $\bar{6}$) (*hexagonal lattice*).

The effect of the “three-bar” ($\bar{3}$), “four-bar”($\bar{4}$) and “six-bar” ($\bar{6}$) improper rotations may be somewhat unfamiliar, and is therefore illustrated in fig. 4.

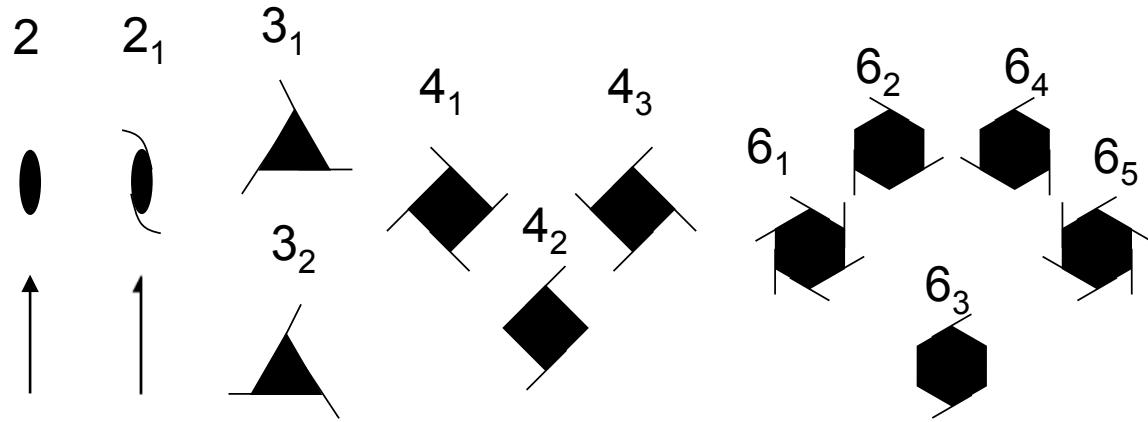
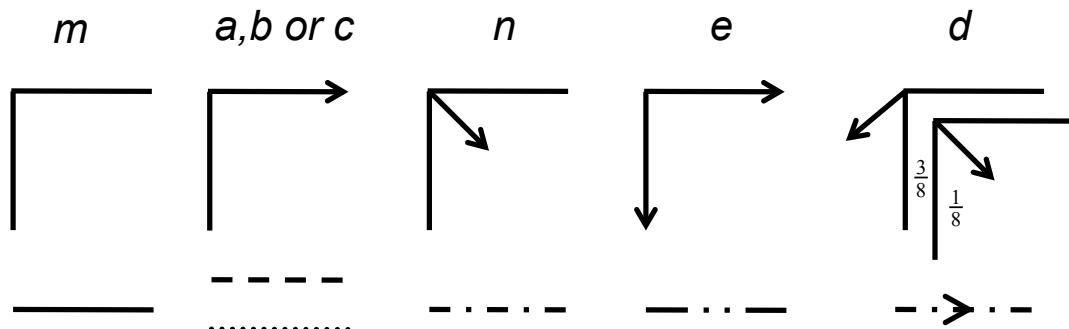
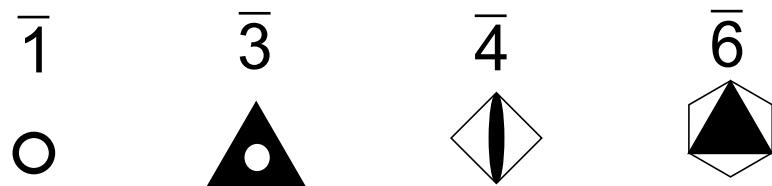


Figure 3: The most important symbols for symmetry elements (see sec. 2.2.1 for a definition) employed in the ITC to describe 3D space groups. Fraction next to the symmetry element indicate the height (z coordinate) with respect to the origin.

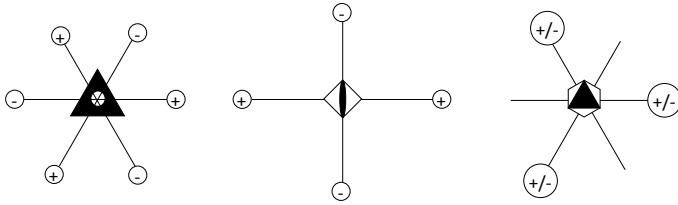


Figure 4: Action of the $\bar{3}$, $\bar{4}$ and $\bar{6}$ operators and their powers. The set of equivalent points forms a trigonal antiprism, a tetragonally-distorted tetrahedron and a trigonal prism, respectively. Points marked with "+" and "-" are above or below the projection plane, respectively. Positions marked with "+/—" correspond to pairs of equivalent points above and below the plane. Starting from any of these points, multiple applications of these improper rotations generate all the other points both above and below the plane.

1.3.3 Proper and improper rotations expressed in terms of matrices and vectors

Rotations about the origin

In Cartesian coordinates, a rotation about the origin is expressed as:

$$\begin{bmatrix} x(2) \\ y(2) \\ z(2) \end{bmatrix} = \mathbf{R} \begin{bmatrix} x(1) \\ y(1) \\ z(1) \end{bmatrix} \quad (13)$$

where $x(1), y(1), z(1)$ are the coordinates of the original point, $x(2), y(2), z(2)$ are the coordinates of the companion point and \mathbf{R} is an orthogonal matrix with $\det(\mathbf{R}) = +1$. Matrices with $\det(\mathbf{R}) = -1$ represent *improper rotations*.

In crystallographic (non-Cartesian) coordinates, eq. 13 is modified as:

$$\begin{bmatrix} x(2) \\ y(2) \\ z(2) \end{bmatrix} = \mathbf{D} \begin{bmatrix} x(1) \\ y(1) \\ z(1) \end{bmatrix} \quad (14)$$

where in general \mathbf{D} is a non-orthogonal matrix, which, however, still has $\det(\mathbf{D}) = \pm 1$. In any coordinate systems, the inversion through the origin is represented by *minus the identity matrix* (change of sign of all coordinates).

1.3.4 Rotations about points other than the origin

As we have seen, the internal rotational symmetry of crystals always includes rotations around an infinite number of points that are not the origin. In Carte-

sian coordinates, the expression for a proper or improper rotation through the point x_0, y_0, z_0 , is

$$\begin{aligned} \begin{bmatrix} x(2) \\ y(2) \\ z(2) \end{bmatrix} &= \mathbf{R} \begin{bmatrix} x(1) - x_0 \\ y(1) - y_0 \\ z(1) - z_0 \end{bmatrix} + \begin{bmatrix} x_0 \\ y_0 \\ z_0 \end{bmatrix} \\ &= \mathbf{R} \begin{bmatrix} x(1) \\ y(1) \\ z(1) \end{bmatrix} + \begin{bmatrix} t_x \\ t_y \\ t_z \end{bmatrix} \end{aligned} \quad (15)$$

where

$$\begin{bmatrix} t_x \\ t_y \\ t_z \end{bmatrix} = \begin{bmatrix} x_0 \\ y_0 \\ z_0 \end{bmatrix} - \mathbf{R} \begin{bmatrix} x_0 \\ y_0 \\ z_0 \end{bmatrix} \quad (16)$$

for example, a mirror plane *perpendicular* to the x axis and located at $x = 1/4$ will produce the following transformation:

$$\begin{bmatrix} x(2) \\ y(2) \\ z(2) \end{bmatrix} = \begin{bmatrix} -x(1) + 1/2 \\ y(1) \\ z(1) \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x(1) \\ y(1) \\ z(1) \end{bmatrix} + \begin{bmatrix} 1/2 \\ 0 \\ 0 \end{bmatrix} \quad (17)$$

Note that when using non-Cartesian coordinates the form of symmetry operators about a point other than the origin remains the same:

$$\begin{bmatrix} x(2) \\ y(2) \\ z(2) \end{bmatrix} = \mathbf{D} \begin{bmatrix} x(1) \\ y(1) \\ z(1) \end{bmatrix} + \begin{bmatrix} t_x \\ t_y \\ t_z \end{bmatrix} \quad (18)$$

In general, \mathbf{D} is not orthogonal, but its determinant is still ± 1 .⁶

1.3.5 Normal form of the symmetry operators

Symmetry operators written in the form of eq. 15 are said to be in **normal form**. They are written as the *composition* (application of two operators in succession) of a rotation (proper or improper) — the *rotational part*, followed by a translation — the *translational part*. **Every crystallographic symmetry**

⁶We will use \mathbf{R} in the remainder to indicate rotation matrices in any coordinate system.

operator can be written in normal form, including proper and improper rotations about any point and other compositions of rotations and translations, as described in more detail in the next lecture.

1.3.6 The Seitz and ITC notations

The Seitz notation is a shorthand notation used in crystallography to denote operators in normal form. The generic notation of eq. 18 is $\{R | t\}$, where R is the rotational part and t is the translational part (let us not forget that *the rotation is always applied first!*). The rotational part R is usually represented by its letter symbol (see sec. 1.3.2) with a subscript to indicate its orientation rather than by the corresponding matrix. For example, the Seitz notation of the operator in eq. 17 is $\{m_x | \frac{1}{2}00\}$. The Seitz notation of a pure (lattice) translation is $\{1 | t_xt_yt_z\}$, where the identity operator (proper rotation of 0 degrees) 1 is represented by the identity matrix $\mathbb{1}$ in all coordinate systems.

Although the Seitz notation for operators is the most useful to describe the theory of crystallographic groups, the ITC use a different notation that shows explicitly the point(s) about which the operator acts with respect to the origin of the coordinate systems. For example, the ITC notation of the same operator in eq. 17 is $m \frac{1}{4}, y, z$, meaning that the points of the mirror plane about which we are reflecting have coordinates $\frac{1}{4}, y, z$.

2 Lecture 2 — An introduction to crystallographic groups

2.1 More on composition of operators

2.1.1 Compositions of operators in normal form

As we have seen at the end of the previous lecture, all crystallographic symmetry operators (i.e., transformation of coordinates to generate companion atoms) can be expressed in *normal* form. We have also seen that *operator composition* corresponds to the application of two symmetry operators, one after another. In the remainder, composition will be indicated with the symbol \circ , so that $O_2 \circ O_1$ corresponds to the application of O_1 *first*, followed by the application of O_2 . Let's ask the following question: assume that $O_1 = \{\mathbf{R}_1 \mid t_1\}$ and $O_2 = \{\mathbf{R}_2 \mid t_2\}$ are both in normal form. What is the normal form of $O_2 \circ O_1$? This is easily deduced from eq. 15:

$$\begin{aligned} \begin{bmatrix} x(2) \\ y(2) \\ z(2) \end{bmatrix} &= \mathbf{R}_1 \begin{bmatrix} x(1) \\ y(1) \\ z(1) \end{bmatrix} + \begin{bmatrix} t_{1x} \\ t_{1y} \\ t_{1z} \end{bmatrix} \\ \begin{bmatrix} x(3) \\ y(3) \\ z(3) \end{bmatrix} &= \mathbf{R}_2 \begin{bmatrix} x(2) \\ y(2) \\ z(2) \end{bmatrix} + \begin{bmatrix} t_{2x} \\ t_{2y} \\ t_{2z} \end{bmatrix} \\ &= \mathbf{R}_2 \mathbf{R}_1 \begin{bmatrix} x(1) \\ y(1) \\ z(1) \end{bmatrix} + \mathbf{R}_2 \begin{bmatrix} t_{1x} \\ t_{1y} \\ t_{1z} \end{bmatrix} + \begin{bmatrix} t_{2x} \\ t_{2y} \\ t_{2z} \end{bmatrix} \end{aligned} \quad (19)$$

whence we deduce the very important relation:

$$\{\mathbf{R}_2 \mid t_2\} \circ \{\mathbf{R}_1 \mid t_1\} = \{\mathbf{R}_2 \mathbf{R}_1 \mid \mathbf{R}_2 t_1 + t_2\} \quad (20)$$

2.1.2 The inverse operator

Suppose that operator $O = \{\mathbf{R} \mid t\}$ (in normal/Seitz form) connect the coordinates of an atom at x_1, y_1, z_1 with those of its companion point x_2, y_2, z_2 . What is the Seitz form of the *inverse* operator O^{-1} that connects x_2, y_2, z_2 to x_1, y_1, z_1 ? Since $O^{-1} \circ O = O \circ O^{-1}$ must be the identity operator, and since the Seitz notation of the identity operator clearly is $\{1 \mid 000\}$, from eq. 20 it must be:

$$\begin{aligned} \mathbf{R}_2 \mathbf{R}_1 &= \mathbb{1} \\ \mathbf{R}_2 t_1 + t_2 &= [0 \ 0 \ 0] \end{aligned} \tag{21}$$

whence

$$O^{-1} = \{\mathbf{R}^{-1} \mid -\mathbf{R}^{-1}t\} \tag{22}$$

Test your understanding: using this result, prove that the operator $\{m_x \mid \frac{1}{2}00\}$ (see sec. 1.3.6) is the inverse of itself. This should be obvious, since applying a mirror symmetry operator twice, no matter where the plane of the mirror is, is equivalent to doing nothing at all.

2.1.3 Rotations around different origins vs Roto-translations

All proper and improper rotations about the origin have Seitz notation $\{\mathbf{R} \mid 000\}$. As we have seen, proper and improper rotations about a point other than the origin have Seitz notation $\{\mathbf{R} \mid t\}$, where t is an appropriate translation vector (usually *not* a lattice vector). However, not all symmetry operators of the form $\{\mathbf{R} \mid t\}$ are proper/improper rotations about a point other than the origin. If we apply such an operator n times, were n is the order of the axis or of the improper rotation, we must necessarily obtain the identity. By looking at eq. 20 we can see that, in order for this to be the case, t *must not have any component that is left invariant by \mathbf{R}* .

Consider for instance the composition of a lattice translation along the a axis with a rotation around the a axis (rotation applied first):

$$\{1 \mid 100\} \circ \{2_x \mid 000\} = \{2_x \mid 100\} \tag{23}$$

This is clearly not a rotation about an axis, since no point is left invariant by it. Another example of this is the composition of a lattice translation along the $[110]$ direction with a mirror plane perpendicular to the c axis (mirror applied first):

$$\{1 \mid 110\} \circ \{m_z \mid 000\} = \{m_z \mid 110\} \tag{24}$$

Operators of this kind are called proper and improper **roto-translation**. As we have just seen, an infinite set of roto-translations are generated “automat-

ically” by composition of rotations and lattice translations. However, a special class of symmetries in crystallography is represented by proper or improper rotations *followed by a non-lattice translation*.

There are **strong restrictions** on both the rotational and the translational parts of proper and improper roto-translation operators, as follows:

- The *rotational part* of a roto-translation operator must leave either a *line* or a *plane* invariant. Compositions of an improper rotation leaving a single point invariant with a translation are always improper rotations about a point other than the origin. Therefore, **only 2, 3, 4, 6 (invariant lines) and m (invariant plane) can form roto-translations.** Roto-translations where the rotational part is a proper rotation are called **screw operators**. Roto-translations where the rotational part is a mirror plane are called **glide operators**.
- The *translational part* of a roto-translation operator must be a vector in the invariant *line* or a *plane*, i.e., $Rt = t$. Adding a translation vector perpendicular to the line or plane results in a shift of origin of the roto-translation (see below for more details).
- The **translational part must be equal to a lattice translation divided by the order of the rotation.** This is easy to see by applying the roto-translation multiple times:

$$\begin{aligned} \{\mathbf{R} | t\} \circ \{\mathbf{R} | t\} &= \{\mathbf{RR} | Rt + t\} = \{\mathbf{RR} | 2t\} \\ \{\mathbf{R} | t\} \circ \{\mathbf{R} | t\} \circ \{\mathbf{R} | t\} &= \{\mathbf{RRR} | 3t\} \\ &\dots \end{aligned} \tag{25}$$

where we have exploited the fact that $Rt = t$. Applying a roto-translation a number of times equal to the order of the rotation results in a *pure translation*. So, for instance, $\{3 | t\} \circ \{3 | t\} \circ \{3 | t\} = \{1 | 3t\}$, and this must *necessarily* be a **lattice translation**. Symbols are used to represent roto-translations with the same rotational part and different translations parts *to within a lattice translation* (see below for further clarifications).

Screw axes

Screw axes are *proper* roto-translation operators, the rotational part of which is a proper rotation, i.e., 2, 3, 4, 6. The translational part, called *screw vector*,

is parallel to the direction of the rotation axis, and, as stated before, must be equal to a lattice translation divided by n , where n is the order of the rotation. Having decided that we will assign unique symbols to roto-translations with screw vectors within a primitive unit cell, for a rotation of order n one needs $n - 1$ distinct symbols, with screw vectors $t_l/n, 2t_l/n, \dots, (n - 1)t_l/n$, where t_l is a simple lattice translation — usually [100], [010], [001], [110] etc. The corresponding symbol are 2_1 for two-fold screws, 3_1 and 3_2 for three-fold, 4_1 , 4_2 , 4_3 for four-fold etc., as illustrated in fig. 3.

Glide planes

Glide planes are *improper* roto-translation operators, the rotational part of which is a mirror plane m , while the translational part t — the *glide vector* — is a non-lattice vector in the mirror plane. Since $m \circ m = 1$, the glide vector is always *half* of a lattice translation, i.e., $t = t_l/2$. Glide planes have different names depending on the orientation of the glide vector — see tab. 1. The graphical representation of glides planes depends on whether they are shown flat or edge-on in the projection — see fig. 3.

Table 1: Nomenclature for glide planes. The glide vector is $t_l/2$, where t is a lattice vector.

symbol	t_l (glide vector is $t_l/2$)	Notes
g	[10] or [01] along the glide line	In two dimensions only
a	[100]	
b	[010]	
c	[001]	
n	[110] or [101] or [011]	
e	[100] and [010]	Indicates two symmetry-related families of parallel planes. Occurs only in face centred orthorhombic groups 39, 41, 64, 67, 68.
d	$[\frac{1}{2}\frac{1}{2}0]$ and equivalent or $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$	F and I centred lattices only, where these t_l are lattice vectors.

2.2 Invariant points, lines and planes: special points and symmetry elements

From the previous paragraphs, it should already be clear that some points within the unit cell are **special points**, by virtue of being left invariant by certain symmetry operators. By contrast, **general points** are only left invariant by the identity operator. **A set of special points left invariant by the same**

operator (or set of operators) is called a *symmetry element*. Symmetry elements can be:

- A *single point*, for operators $\bar{1}$, $\bar{3}$, $\bar{4}$, $\bar{6}$.
- A *line of points*, for operators 2, 3, 4, 6
- A *plane of points*, for operator m .

Roto-translations do not give rise to special points, because no point is left invariant by them. However, points on a glide plane or a screw axis are transformed into other points on the same glide plane or screw axis, so in this weaker sense they are distinct from all other points. Such points are also said to be the *symmetry element* associated with the glide plane/screw axis.

If a point/line/plane is the symmetry element associated with a certain proper/improper rotation/roto-translation $\{R \mid t\}$, it is necessarily also the symmetry element of $\{R \mid t\} \circ \{R \mid t\}$, $\{R \mid t\} \circ \{R \mid t\} \circ \{R \mid t\}$ and so on for all the *powers* of that operator.

2.2.1 Graphical representation of symmetry elements

Looking back at fig. 2 and at a few example pages of the ITC, we can see many examples of *symmetry elements* drawn within the unit cell with the special symbols shown in fig. 3. The symbols give an intuitive representation of how the operator and, in some cases its powers (repeated applications), act. For example, the symbol for $\bar{4}$ contains the symbol of a 2-fold axis, because $\bar{4} \circ \bar{4} = 2$.

2.2.2 “Companions” of general and special points

Special points of symmetry, i.e., point lying on symmetry elements *other than roto-translations*, **have fewer companions by rotation than general points**. This follows from the fact that some symmetry operators transform special points into themselves, and therefore do not generate companions. The following question arise naturally from this consideration: **How many companion points does each general or special point have in the unit cell in each type of symmetry?** In order to answer this question rigorously, we have to introduce a few element of the mathematical theory of groups.

2.3 Some elements of group theory

2.3.1 Groups as mathematical sets

As we have seen, if two symmetry operators are known to exist in a crystal, say O_1 and O_2 , then we can construct a third symmetry operator by applying O_1 and O_2 one after the other. This means that the set of all symmetry operators is *closed by composition*. Likewise, we can always create the *inverse* of an operator, e.g., by reversing the sense of rotation and the direction of translations etc. These considerations indicate that the set of all symmetry operators of a crystal has the *mathematical structure of a group*. More rigorously, a group is defined as a set of elements with a defined binary operation known as *composition*, which obeys the following rules.

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

$$f \circ (g \circ h) = (f \circ g) \circ h \quad (26)$$

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

$$g \circ E = E \circ g = g \quad (27)$$

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

$$g \circ g^{-1} = g^{-1} \circ g = E \quad (28)$$

- A **subgroup** is a subset of a group that is also a group. We state the following without proof: **for finite groups, the number of elements (known as the order) of a subgroup is always a divisor of the order of the main group.**
- A **set of generators** is a subset of the group (not usually a subgroup) that can generate the whole group by composition. Infinite groups (e.g., the set of all lattice translations) can have a finite set of generators (in this example, the primitive translations).

- **Composition is in general *not commutative***, i.e., $g \circ f \neq f \circ g$ for some pairs of elements. Groups for which all compositions commute are known as *Abelian groups*. Although translations always commute, a few examples of applications of eq. 20 should clarify that many operators in Seitz form do not commute. Therefore, most crystallographic groups are non-Abelian.

2.3.2 Full crystallographic groups (including translations)

By applying eq. 20 and 22, one can easily become convinced that **all the symmetry operators of a given crystal must form a group as defined above**. By employing the Seitz notation, one can explicitly test associativity (eq. 26) and the fact that right and left inverse are the same (eq. 28), with the neutral element being $\{1 | 000\}$. The set of pure lattice translations, which are expressed as $\{1 | t\}$, is clearly a group and is always a subgroup of any crystal symmetry group. Therefore, **crystal symmetry groups are infinite groups**.

- In **3 dimensions**, crystal symmetry groups are known as **space groups**. As we shall see, there are 230 such groups.
- In **2 dimensions**, crystal symmetry groups are known as **planar (or wallpaper) groups**, the second name referring to the fact that these groups describe all possible symmetries of a wallpaper (excluding colour symmetry). There are 17 wallpaper groups.
- The seven **frieze groups** describe all the possible symmetries of 1-dimensional patterns.

2.3.3 Finite groups in crystallography: crystal classes and point groups

Although the full symmetry of a crystal is always described by an *infinite* group, *finite* groups have a very important place in crystallography. These are groups of *proper and improper rotations around the origin*, and are completely equivalent and isomorphic to *groups of matrices* used to describe these rotations, e.g., in Cartesian coordinates. There are two important uses of these finite groups in crystallography:

Crystal classes

Crystal classes are groups formed by **all rotational parts of all symmetry operators** of a given space or wallpaper group. As one can see from eq.

20, the rotational parts of symmetry operators in Seitz form are simply multiplied by each other upon composition, in the usual sense of rotation matrix multiplication. Also, the rotational part of the inverse operator is the inverse rotational matrix (eq. 22). It is therefore evident that all the rotational parts of all operators in a given symmetry, considered in isolation from the associated translations, form a finite group, known as the **crystal class** of that space or wallpaper group.

Site symmetry groups

Let us consider a generic point in a crystal, shift the origin of the coordinate system onto that point and consider all operators of Seitz form $\{R \mid 000\}$ in that coordinate system, i.e., all operators describing proper and improper rotations around that point. There is always at least one such operators, i.e., $\{1 \mid 000\}$. For points of special symmetry, the **site symmetry group**⁷ is the set of operators that leave that point invariant. Remembering the discussion in sec. 2.2, we conclude that the *symmetry elements* (excluding roto-translations) of the site symmetry group operators at a certain point all pass through that point. **Roto-translations are never associated with any site symmetry group**, because they can never be written as $\{R \mid 000\}$, regardless of the choice of origin.

The equivalence between site symmetry groups and crystal classes

From the definitions above, it should not be difficult to convince oneself that **site symmetry groups at any point in the crystal are subgroups of the crystal class of the space/wallpaper group**. However, **in many space and wallpaper groups, there is no point in the crystal with a point group symmetry equal to the crystal class**. Groups in which this is the case are called *symmorphic groups*. It turns out that there is at least one symmorphic group for each crystal class⁸, so that, for classification purposes, the set of all possible crystal classes is equal to the set of all possible site symmetry groups. In the remainder, we will discuss the (which are 10 in 2 dimensions, 32 in 3 dimensions), keeping in mind that this refers both to possible site symmetry groups and to crystal classes.

⁷I call “site symmetry group” the symmetry around a fixed point in the crystal, since “point group” is used as a more general term that also denotes crystal classes — see below.

⁸in fact, there are many more symmorphic groups (73 in 3 dimensions) than crystal classes (32 in 3 dimensions) For example, *Pmmm*, *Cmmm*, *Fmmm* and *Immm* are all symmorphic groups of the crystal class *mmm*.

2.4 Point Groups in 2 and 3 dimensions

Point groups are groups of symmetry operators that leave one point invariant, and correspond to the symmetries of simple polygons and polyhedra. Although there is an infinite number of point groups, the number of *crystallographic* point groups is rather small, since only axes of order 2, 3, 4 and 6 are allowed (other axes are not compatible with a crystal lattice)⁹. There are **10 crystallographic point groups in 2 dimensions and 32 in 3 dimensions**. Crystallographic point groups are listed in the ITC vol A from page 763 (green edition). The relevant pages are linked through from the course web site. The entry for point group $6mm$ is shown in fig. 5 .

				Equivalent points for general position (here 12 c)	Symmetry elements representation
			Primary symmetry direction Secondary symmetry direction Tertiary symmetry direction		
6	m				
12	c	1	Dihexagon Truncated hexagon (<i>f</i>)	(<i>hki</i>) (<i>hki</i>) (<i>khi</i>) (<i>khi</i>) (<i>kh</i>) (<i>kh</i>)	
6	b	$.m.$	Hexagon Hexagon (<i>e</i>)	(101) (101)	(110) (110)
6	a	$.m.$	Hexagon Hexagon (<i>d</i>)	(112) (112)	(011) (011)
			Site symmetry Wychoff letter Site multiplicity	(112) (211) (211)	(121) (211) (121)

Figure 5: An explanation of the most important symbol in the Point Groups subsection of the International Tables for Crystallography. All the 10 2D point groups (11 if one counts $31m$ and $3m1$ as two separate groups) are reproduced in the ITC (see lecture web site). The graphical symbols are described in fig. 3. Note that primary, secondary and tertiary symmetries are never equivalent by symmetry (see text).

⁹For example, the well-known icosahedral point groups 235 and $m\bar{3}\bar{5}$ are not crystallographic point groups because they have 5-fold axes.

2.4.1 Graphical representations of point groups through symmetry elements

The most intuitive way to represent a point group is through its *symmetry elements*, which all intersect at the point that is left invariant by that point group. Allowed symmetry elements of a point group are all pure proper and improper rotations shown fig. 3. *Roto-translations are obviously not allowed*, because they leave no point invariant. An example of the ITC point group entries is shown in 5, and the symmetry elements representation is shown in more details in 6 . One point worth emphasising is that *some symmetry elements are related to each other by symmetry* (e.g., the group of mirror planes marked with “1” are related to each other by the 6-fold rotations), whereas others are not (the mirror planes marked with “1” and “2” are not related to each other by any symmetry)¹⁰. This has important consequences in understanding the letter notation of point groups (sec. 2.4.2).

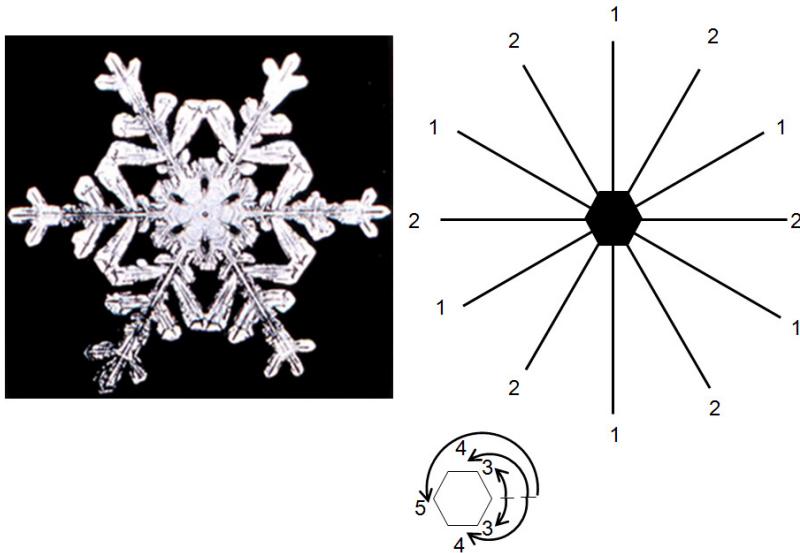


Figure 6: **Left.** A snowflake by by Vermont scientist-artist Wilson Bentley, c. 1902. **Right** The symmetry group of the snowflake, $6mm$ in the ITC notation. The number identifies groups of operators that are equivalent by symmetry.

2.4.2 Notation of point groups

In the notation employed by the ITC, known as Hermann–Mauguin notation¹¹, point groups are also described using up to 4 symmetry operator symbols for

¹⁰This is formalised in the theory of *conjugation classes of group elements*, which is not discussed here.

¹¹There is an alternative notation for point groups, known as the Schoenflies notation, which is very popular in older physics articles and books. Schoenflies symbols are listed in the ITC together with the Hermann–Mauguin notation.

pure proper and improper rotations (fig. 3). The following bullet points provide a key to understand point group symbols.

- When the first symbol is 2, 4 or 6 and the second symbols is m , they can be joined by a slash, as in $2/m$ and $(4/m)mm$ (pronounced “two over m” and “four over m-mm”), forming a compound symbol. This has the meaning of a 2-fold, 4-fold or 6-fold axis with a mirror plane *perpendicular* to it.
- Each symbol or compound symbol is oriented along a particular symmetry direction in the crystal. A symmetry direction is simply the direction of a symmetry element; remembering that $m \equiv \bar{2}$, the symmetry direction of a mirror plane is *perpendicular* to the plane. In 3 dimensions, there are up to 3 *inequivalent* (see here below) symmetry directions, known as primary, secondary and tertiary.
- Symmetry directions listed in point group symbols *are never equivalent by symmetry*. In other words, the symbols never lists symmetry-equivalent symmetry elements (see discussion in sec. 2.4.1).

Tab. 2 lists the symmetry directions and possible point groups for each of the 7 *crystal systems*¹².

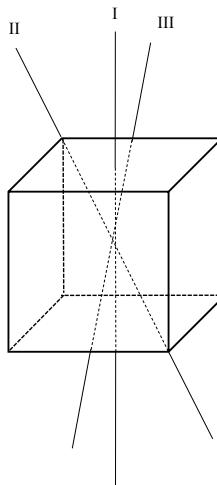


Figure 7: The primary, secondary and tertiary symmetry directions for cubic groups.

¹²Roughly speaking, the 7 crystal systems are set of point groups/crystal classes sharing the same axis of highest order and the same symmetry directions. They map onto the 7 lattice systems (fig. 1 with one exception: the trigonal crystal system, which is characterised by the presence of a 3-fold axis of highest order, can give rise to crystals with rhombohedral (*R*-centred hexagonal) or primitive hexagonal lattices

Table 2: Crystal systems, symmetry directions and point groups in 3 dimensions. Although the notion of basis vectors is not intrinsic to point groups, secondary and tertiary symmetry directions in the *tetragonal*, *trigonal* and *hexagonal* systems are referred to a basis , with the *secondary* direction (second symbol) always chosen along the *a* axis. This creates pairs of point groups which are geometrically the same but are rotated with respect to each other in a fixed basis frame.

Crystal system	Symmetry directions	Point groups	notes
Triclinic	None	$1, \bar{1}$	
Monoclinic	Unique symmetry direction	$2, m, 2/m$	Conventionally along <i>b</i> or <i>c</i> axis
Orthorhombic	3 orthogonal symmetry directions	$222, 2mm, mmm$	Various axis choices
Tetragonal ,,	4 or $\bar{4}$ or $4/m$ axis There can be two additional 2-fold symmetry directions in the orthogonal plane, at 45° to each other	$4, \bar{4}, 4/m$ $422, 4mm, \bar{4}m2, 4/mmm$	4-fold axis along <i>c</i> Reference to basis vectors creates a distinction between $\bar{4}m2$ and $\bar{4}2m$, which are rotated by 45° .
Trigonal ,,	3 or $\bar{3}$ axis There can be one additional 2-fold symmetry direction in the orthogonal plane	$3, \bar{3}$ $32, 3m, \bar{3}m$	3-fold axis along <i>c</i> Reference to basis vectors creates the pairs $32 \rightarrow 312/321$, $3m \rightarrow 31m/3m1$ and $\bar{3}m \rightarrow \bar{3}1m/\bar{3}m1$, which are rotated by 30° .
Hexagonal ,,	6 or $\bar{6}$ or $6/m$ axis There can be two additional 2-fold symmetry directions in the orthogonal plane, at 30° to each other)	$6, \bar{6}, 6/m$ $622, 6mm, \bar{6}m2, 6/mmm$	6-fold axis along <i>c</i> Reference to basis vectors creates a distinction between $\bar{6}m2$ and $\bar{6}2m$, which are rotated by 30° .
Cubic ,,	2-fold and 3-fold symmetry direction along cube faces and diagonals 2-fold along cube faces becomes 4-fold, additional 2-fold symmetry direction along cube edges	$23, m\bar{3}$ $432, \bar{4}3m, m\bar{3}m$	See fig. 7 for symmetry directions

3 Lecture 3 —The symmetry of periodic crystals: space groups

3.1 Representation and notation of space groups

3.1.1 Graphical representation and symmetry elements

As we have seen in sec. 2.4.1, point groups can be represented by a collection of symmetry elements, each oriented along one of up to 3 inequivalent symmetry directions. We have also seen (sec. 2.3.3) that the rotational parts of the symmetry operators of a space group for a group, which is one of the 32 (3D) point groups¹³. It follows logically that **the symmetry elements of a space group are proper or improper rotations and roto-translations, with rotational parts corresponding to the elements of the crystal class and different origins and/or glide/screw vectors. These operators are oriented in the same way as the elements of the crystal class.**

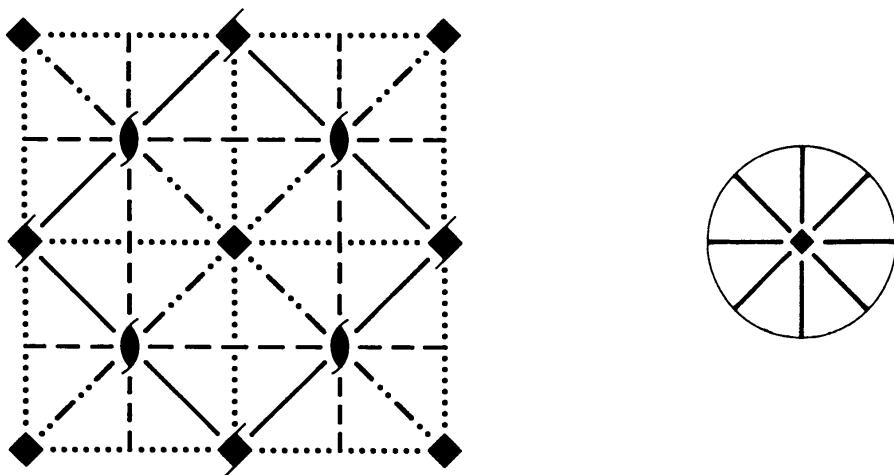


Figure 8: Symmetry elements in the unit cell of space group $I4cm$ (**left**) and of its crystal class $4mm$ (**right**).

An example of this for space group $I4cm$ (no. 108) is illustrated in fig. 8. The crystal class of $I4cm$ is $4mm$ (right panel), which has 8 group elements: 7 are shown as symmetry elements — remember that the symmetry element for 4^+ (rotation by 90°) is the same as that for $4^+ \circ 4^+ = 2$ and $4^+ \circ 4^+ \circ$

¹³Here, we are specifically discussing space groups, although, as we shall see in the next lecture, the concepts and notations are very similar also for wallpaper groups (2D).

$4^+ = 4^-$), to which one has to add the identity. The symmetry elements of $I4cm$ all correspond to those of $4mm$ in their rotational part, but have different translational parts, which is reflected by their different origin and in some cases by the glide/screw vectors. For example, along the c axis there are both 4-fold rotations and 4-fold screws (4_2), as well as 2_1 screws; perpendicular to the horizontal axis there are two types of glide planes (c and b); perpendicular to the $[110]$ and $[1\bar{1}0]$ direction there are both proper mirrors (m) and glides (e).

3.1.2 Notation for space groups

The notation for space groups may appear to be daunting, but is actually rather simple if one has understood the point group notation in sec. 2.4.2.

- The **first symbol** is always the lattice symbol, one of the 14 Bravais lattice.
- There is a precise correspondence between the symbol of the **crystal class** (e.g., $4mm$ in the example above) and the **remaining symbols** if the space groups (e.g., $I4cm$ (no. 108)), whereby symbols in the crystal are either kept as such or replaced by a *roto-translation symmetry operator with the same rotational part*. Therefore, the symbol 2 in the crystal class can remain 2 or replaced by 2_1 ; m can be replaced by g (2D wallpaper groups only), a , b , c , d , n and e ; 3 can be replaced by 3_1 or 3_2 etc. It is therefore extremely easy to deduce the crystal class from the space group symbol: for example $P\bar{4}c2$ (No. 166) $\rightarrow \bar{4}m2$.
- As explained above, in each space group there are usually several operators with the same rotational part but different translational parts, often a mixture of rotations and roto-translations. Therefore, an **order of priority** must be established to decide which of these operators to list in the space group symbol. As a rule, **pure proper/improper rotations are listed if they exist**, in preference to roto-translations.
- The symbol of a symmorphic group is always the lattice symbol followed by the crystal class symbol, e.g., $I4/mmm$.

3.2 “Companions” revisited: site multiplicities

3.2.1 General and special multiplicities

Armed with some knowledge of group theory and of the crystallographic point groups, we can now revisit and answer the question posed in sec. 2.2.2: **How many companion points does each general or special point have in the unit cell in each space or wallpaper group symmetry?** We shall first state an important theorem (the proof is given in the footnote¹⁴).

Theorem: if companions p_1' and p_2' to a generic point p are generated by two operators having the same rotational part, then either $p_1' = p_2'$ or p_1' and p_2' are in different *primitive* unit cells.

General multiplicity The consequence of this theorem is that each element of the crystal class generates to each generic point exactly one companion point in the *primitive* cell. Therefore, the number of equivalent points to a generic point in the primitive unit cell is the **order (number of elements) of the crystal class**. The **general multiplicity** (or multiplicity of the general positions) is defined as the number of equivalent points to a generic point in the *conventional* unit cell. ***The general multiplicity of a space (or wallpaper) group is the order of its crystal class times the number of nodes in the basis (see sec. 1.2.1).***

Example (see later for the interpretation of these symbols), for space group $Ia\bar{3}$ (no. 206 in the ITC, page 632 in the "green edition") has crystal class $m\bar{3}$ (page 787 in the ITC), which has order 24. The general multiplicity is the order of the crystal class times the number of nodes in the basis, in this case 2, since this is an I -centred lattice. The multiplicity (number of equivalent sites in the conventional unit cell) of a generic point x, y, z for $Ia\bar{3}$ is therefore 48 (see top of page 633).

Multiplicity of special positions

As we have discussed in sec. 2.2.2, special points of symmetry have fewer companions than general positions, because certain operators bring that point into itself. But how many companions will remain? This can be determined rigorously using more advanced group theory (the so-called *cosets* and *quotient groups*). The answer is stated below, and an intuitive explanation is

¹⁴In fact, let $p_1' = \{\mathbf{R} \mid t_1\} p$ and $p_2' = \{\mathbf{R} \mid t_2\} p$. We can write $p = \{\mathbf{R}^{-1} \mid -\mathbf{R}^{-1}t_1\} p_1'$ and $p_2' = \{\mathbf{R} \mid t_2\} \circ \{\mathbf{R}^{-1} \mid -\mathbf{R}^{-1}t_1\} p_1' = \{1 \mid -t_1 + t_2\} p_1'$. Therefore p_1' and p_2' are related by a translation, which is necessarily a lattice translation if these are generic points. We conclude that they are either the same point (the translation being [000]) or are in different primitive cells.

given in the footnote¹⁵.

The multiplicity of a special point (\equiv number of companions in the conventional unit cell) is the general multiplicity of that space (or wallpaper) group divided by the order (\equiv number of elements) of the point group at that point. Note that, as stated in sec. 2.3.1, the order of the point group is a divisor of the order of the crystal class, because site symmetry groups are subgroups of the crystal class (sec. 2.3.3).

Example Continuing on the example above, let us consider the special position marked 8 b on page 633 of the ITC, which has a point group symmetry $\bar{3}$ (page 777). The order of this point group is 6. Consequently, the multiplicity of the 8 b special position is $48/6 = 8$, which is indicated by the number 8 in 8 b.

3.2.2 Companions of special points of symmetry vs points of equal symmetry

Let's look again carefully at fig. 2 to illustrate a very important but rather subtle point. Fig. 2 shows a typical grid of symmetry elements for one of the simplest space groups ($P2$). One can see that there are *four* 2-fold axes in the unit cell, one at the origin, two on the centre of the edges and one in the centre of the cell (it is easy to see that there are 4 axes by shifting a little bit the origin of the unit cell). Points on these 2-fold axes have the same point group symmetry, i.e., 2. Could these points be companions of each other in the sense illustrated above? *The answer is clearly no.* In fact, the crystal class is also 2 and the number of nodes in the basis is 1 (primitive lattice), so the multiplicity of points on 2-fold axes is 1 — these points have no companions.

This example illustrates an important point: there can be different special points of symmetry in the unit cell having the same point-group symmetry, without them being necessarily companions of each other. We will illustrate this later on the Escher symmetry drawings.

¹⁵Consider a general point very close to our special position. The elements of the point group of the special position leave it invariant, but will generate a number of general points around it, equal to the order of the point group, say m . If the order of the crystal class is n and the number of nodes in the basis is b , there will be a total of $n \times b$ such general points in the unit cell, which merge in groups of m as the generic point is brought close to the special position. We can conclude that the number of such groups is $n/m \times b$, and this is the number of the companions of the special point itself.

3.2.3 Notation for general and special positions: multiplicity, Wyckoff letter and site symmetry

In the ITC Volume A, each space/wallpaper group entry lists the general and all the special positions in the unit cell. Positions that are symmetry equivalent to each other are listed in on the same line (or group of lines if there are many such companions). We therefore often encounter non-equivalent sites with the same multiplicity and the same site symmetry, each listed on a separate line. In order to distinguish them from each other, each entry is given a unique letter, known as **Wyckoff letter**. The letter *a* is assigned to the site with the highest point-group symmetry and so on, until the general position (which has always site symmetry 1) is assigned the highest letter. In the ITC Vol A, positions are listed listed in order of *decreasing multiplicity*. The structure of the positions entries is as follows:

- Multiplicity (see sec. 3.2.1).
- Wyckoff letter (see here above). When referring to a site, e.g., in a paper, one always uses both the multiplicity and the Wyckoff letter, as in $2b$ or $8j$.
- Site symmetry (see sec. 2.3.3). The notation for the site symmetry is slightly modified from that of standard point group notation¹⁶.
- Coordinates of the equivalent positions. Note that these coordinates will not necessarily fall within the unit cell (primitive or conventional). To shorten notation, the minus sign is replaced by a bar above the coordinate (e.g., $\bar{x}, \bar{y}, z \equiv -x, -y, z$).
- In the case of non-primitive lattices, the **centring vectors** are listed at the top of the list of coordinates. For example, *I*-centred space groups would list $(0, 0, 0)+$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$, meaning that the number of equivalent positions in the *conventional* unit cell is to be doubled by adding the two vectors to each position.

¹⁶The main difference is that the site symmetry symbol often contains dots (.) to indicate missing symmetry operators. As you will recall, the site symmetry group is a subgroup of the crystal class, so some operators in the crystal class may be missing in the site symmetry group. These are indicated with dots. Sometimes there are additional symbols that would have been implied in the crystal class but are no longer so because some other operator is missing. For example, in space group $P\bar{4}c2$ (No. 116 — crystal class $\bar{4}m2$), $2a$ and $2b$ sites have both site symmetry $2.22 \equiv 222$. The two symmetry operators after the dots, at 90° from each other, would have been equivalent (and therefore are not listed) in $\bar{4}m2$ but are no longer equivalent in 222

3.3 Summary: Understanding the International Tables of Crystallography

The ITC have been designed to enable scientists with minimal understanding of group theory to work with crystal structures and diffraction patterns. Most of the ITC entries, except for the graphical symbols that we have already introduced, are self-explanatory (see fig. 9 and 10). In the lecture, we will discuss the case of Ag_2O_2 , a simple oxide that crystallise in space group $P2_1/c$ (no. 14) — see fig. 11 .

By using the ITC, one can (amongst other things):

- Given the coordinates of one atom, determine the number and coordinates of all companion atoms. This greatly simplifies the description of crystal structures.
- Determine the local *point-group* symmetry around each atom, which is the same as the symmetry of the electron density and is connected to the symmetry of the atomic wavefunction. This is particularly important for certain types of spectroscopy.
- Determine the *crystal class*. Crystal classes are associated with the presence or absence of certain macroscopic properties, such as optical activity, piezoelectricity, ferroelectricity etc. (see later part of this course).

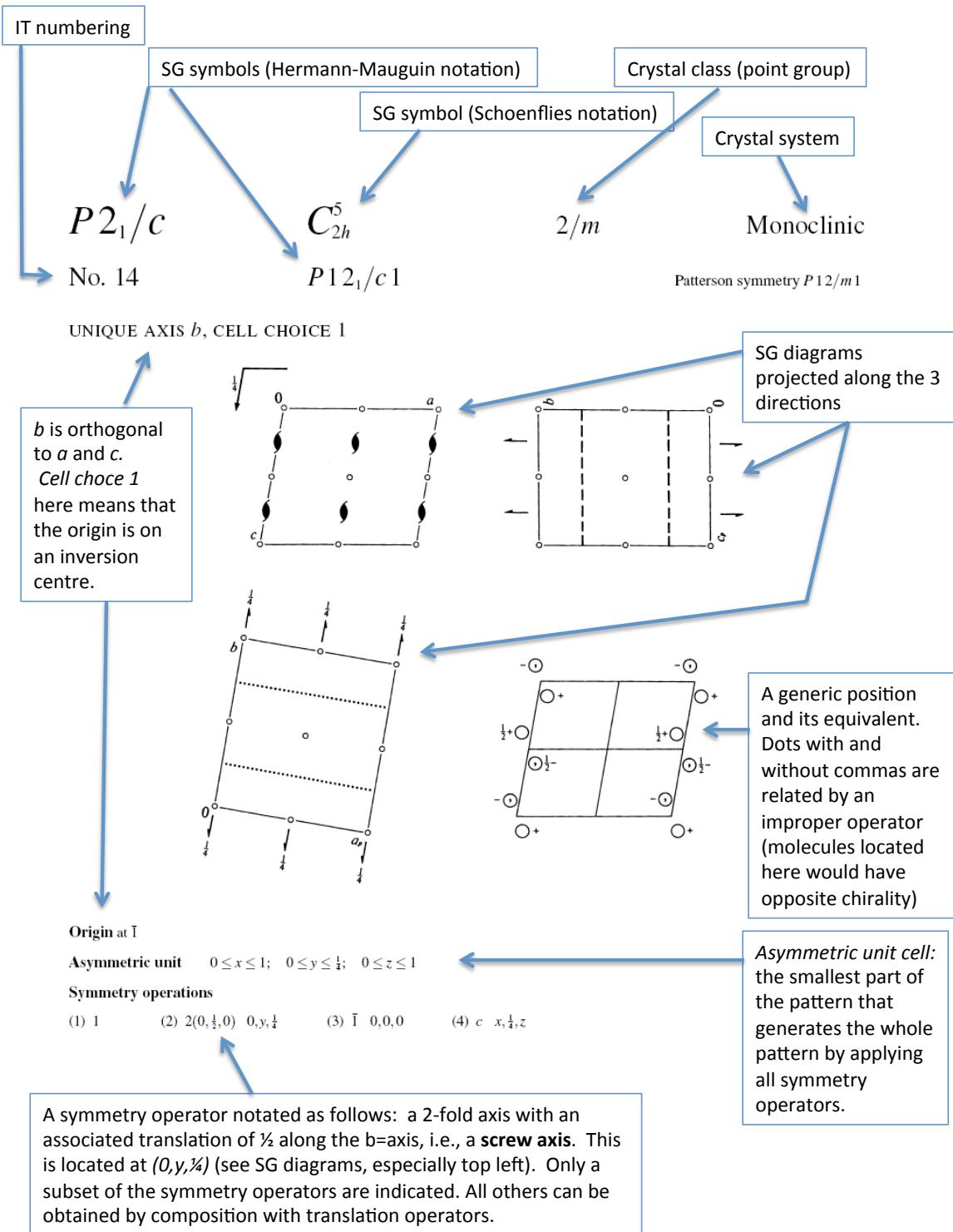


Figure 9: Explanation of the most important symbols and notations in the Space Group entries in the International Tables. The example illustrated here is SG 14: $P\bar{2}_1/c$.

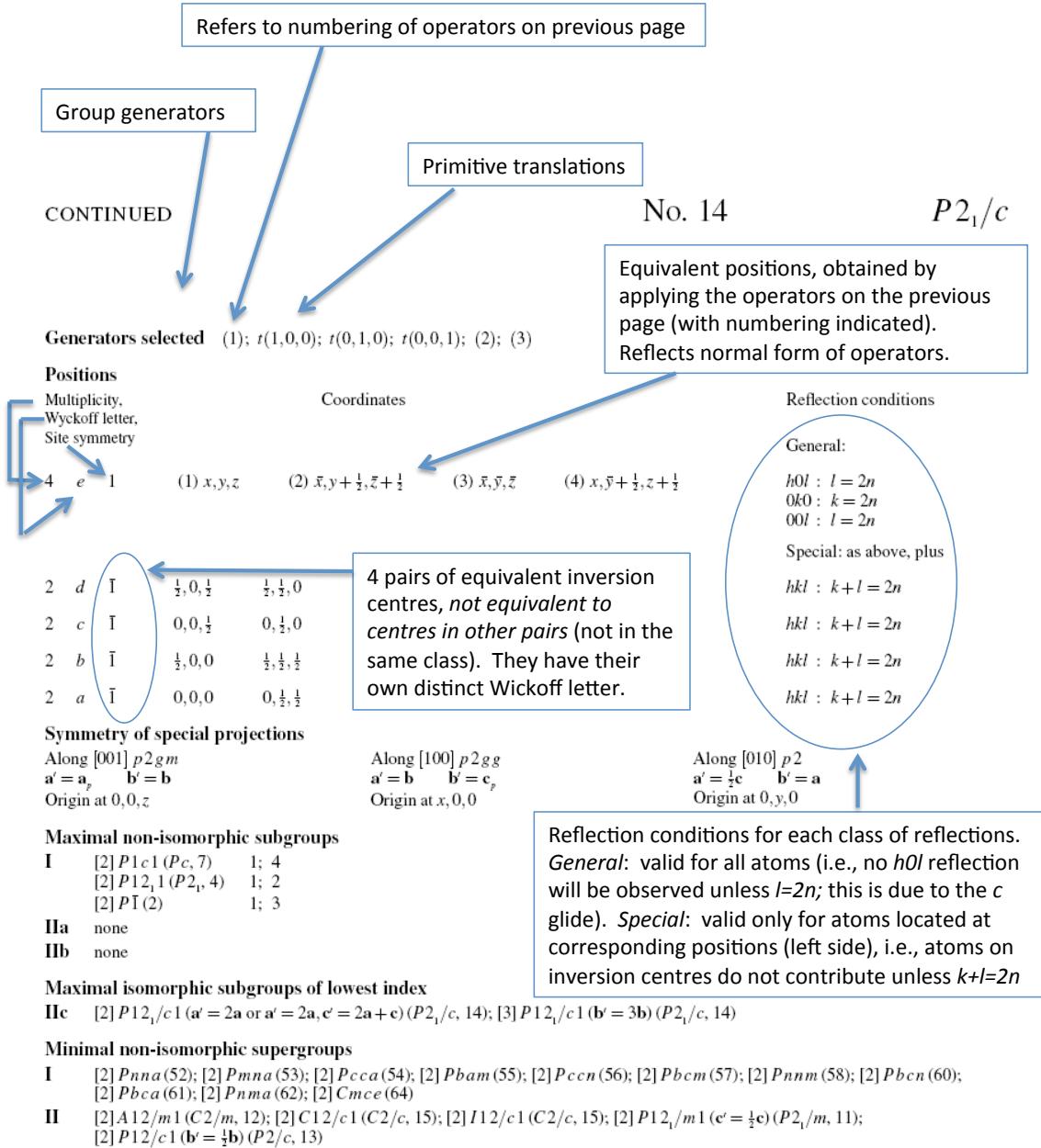


Figure 10: IT entry for SG 14: $P2_{1}/c$ (page 2).

Collection Code 69095

Summary			
Struct.formula	Ag ₂ O ₂	Author	Brese, N.E.; O'Keeffe, M.; Ramakrishna, B.L.; von Dreele, R.B.
Space Group	P 1 21/c 1(14)	Title of Article	Low-temperature structures of CuO and AgO and their relationships to those of MgO and PdO
Unit Cell	5.8517(3) 3.4674(2) 5.4838(3) 90. 107.663(3) 90.	Reference	Journal of Solid State Chemistry (1990) 89, p184-p190
Cell Volume	106.02 Å ³	Formula Units per Cell	2
Temperature	9 K	Pressure	atmospheric
PDF-numbers	01-080-1269	R-value	0.033
Remark			
Export CIF File MyBaseFileName		Feedback to the ICSD Editor	

Details							
Expand All Collapse All <ul style="list-style-type: none"> ▶ Visualization ▶ Chemistry ▼ Published Crystal Structure Data 							
Cell Parameters 5.8517(3) 3.4674(2) 5.4838(3) 90. 107.663(3) 90.							
Volume	106.02	Formula Units per Cell	2	Calc. Dens.	7.76		
Space Group	P 1 21/c 1(14)	Pearson Symbol	mP8	Meas. Dens.			
Crystal System	monoclinic	Crystal Class	2/m	Laue Class	2/m		
Wyckoff Sequence	e d a	Structure Type	AgO				
Axis Ratios	a/b 1.6876	b/c 0.6323	c/a 0.9371				
Remark							
EL	Lbl	OxState	WyckSymb	X	Y	Z	U
Ag	1	+1.00	2a	0	0	0	0.0013(5)
Ag	2	+3.00	2d	0.5	0	0.5	0.0017(5)
O	1	-2.00	4e	0.2949(3)	0.3470(5)	0.2187(4)	0.0010(4)

[Top](#)

Figure 11: Crystal structure data for silver (I,III) oxide (Ag₂O₂), space group *P2₁/c* (no. 14). Data are from the Inorganic Crystal Structures Database (ICSD), accessible free of charge from UK academic institutions at <http://icsd.cds.rsc.org/icsd/>.

4 Lecture 4 — Symmetry in 2 dimensions: wallpaper groups.

It is extremely useful to apply what we have learned about space groups to the much simpler case of wallpaper groups in 2D. First of all, compared with the 3D case, in 2D there is a much smaller number of point groups (10 vs 32) and wallpaper groups (17 vs 230), and the latter can essentially all be built by hand (see below). Secondly, wallpaper groups can be employed to analyse the symmetry of real 2D periodic patterns, including the beautiful Escher symmetry drawings (see course web site), in a way that is much simpler and more intuitive than the 3D analogues.

4.1 Wallpaper vs space group symmetry

4.1.1 Bravais lattices in 2D

In 2D, there are 5 types of lattices: *oblique*, *p-rectangular*, *c-rectangular*, *square* and *hexagonal* (see Fig. 12). In the c-rectangular lattice, no primitive cell has the full symmetry of the lattice, as in the 3D centred lattices. It is therefore convenient to adopt a non-primitive *centred* cell having double the area of the primitive cell. As in the 3D case, the *origin* of the unit cell is to a large extent arbitrary. It is convenient to choose it to coincide with a symmetry element.

4.1.2 Rotations in 2D

Each rotation in 2D may correspond to either a proper rotation or an improper rotation in the “embedding” 3D space. For example, the 2D inversion, technically a proper rotation because the determinant of the corresponding matrix is +1, may correspond to either the 3D inversion (improper) or the 3D rotation about z (proper). The convention is to consider rotations about z as proper operators, and reflections about lines in the planes as improper operators (mirrors). In summary:

- **Rotations about z** , symbols 2, 3, 4, 6
- **Reflections in the plane**, symbol m .

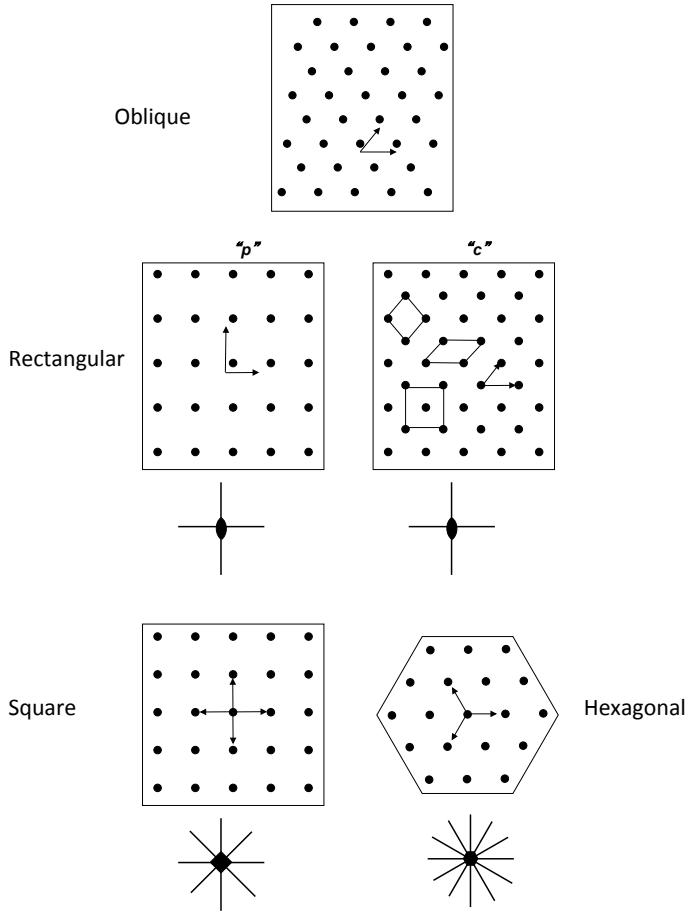


Figure 12: The 5 Bravais lattices in 2 dimensions.

4.1.3 Roto-translations in 2D

There is a single roto-translation operator in 2D, the **glide line** (symbol g), which is the roto-translation corresponding to the mirror line m . As in the 3D case, *twice* a glide translation is *always* a lattice 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 lattice translation.

4.2 Construction and identification of the 17 wallpaper groups

4.2.1 Point groups in 2D

The 10 point groups in 2D, which correspond to both *2D crystal classes* and *2D site symmetries*, are listed in the middle column of tab. 3. They are a subset of the 32 3D point groups, and can be thought as those 3D point

groups that do not change the value of the z coordinate.

4.2.2 Wallpaper groups

The 17 Plane (or Wallpaper) groups describing the symmetry of all periodic 2D patterns are listed in tab. 3, right column, next to their crystal class. As in the 3D case, their symbols are obtained from the crystal class symbol by replacing systematically rotations with roto-translations. However, since there is a single roto-translation operation in 2D (g , which can only replace m), the procedure is straightforward and is shown in tab. 3. One often obtains the same wallpaper group twice with a different symbol, corresponding to an exchange of axes or by a different priority convention. Can you explain why, for example, cg is not distinct from cm ? (hint: look at set of parallel symmetry element in the wallpaper group representation — see web site).

Table 3: 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	$p3$
	$3m1-31m$	$p3m1, p3g1, p31m, p31g$
	6	$p6$
	$6mm$	$p6mm, p6mg, p6gm, p6gg$

4.2.3 Identification of wallpaper groups

When observing a 2D periodic pattern, the decision tree in fig. 13 can be used to identify the corresponding wallpaper group. It is instructive (and quite fun) to apply the decision tree to the Escher symmetry drawings (see web site).

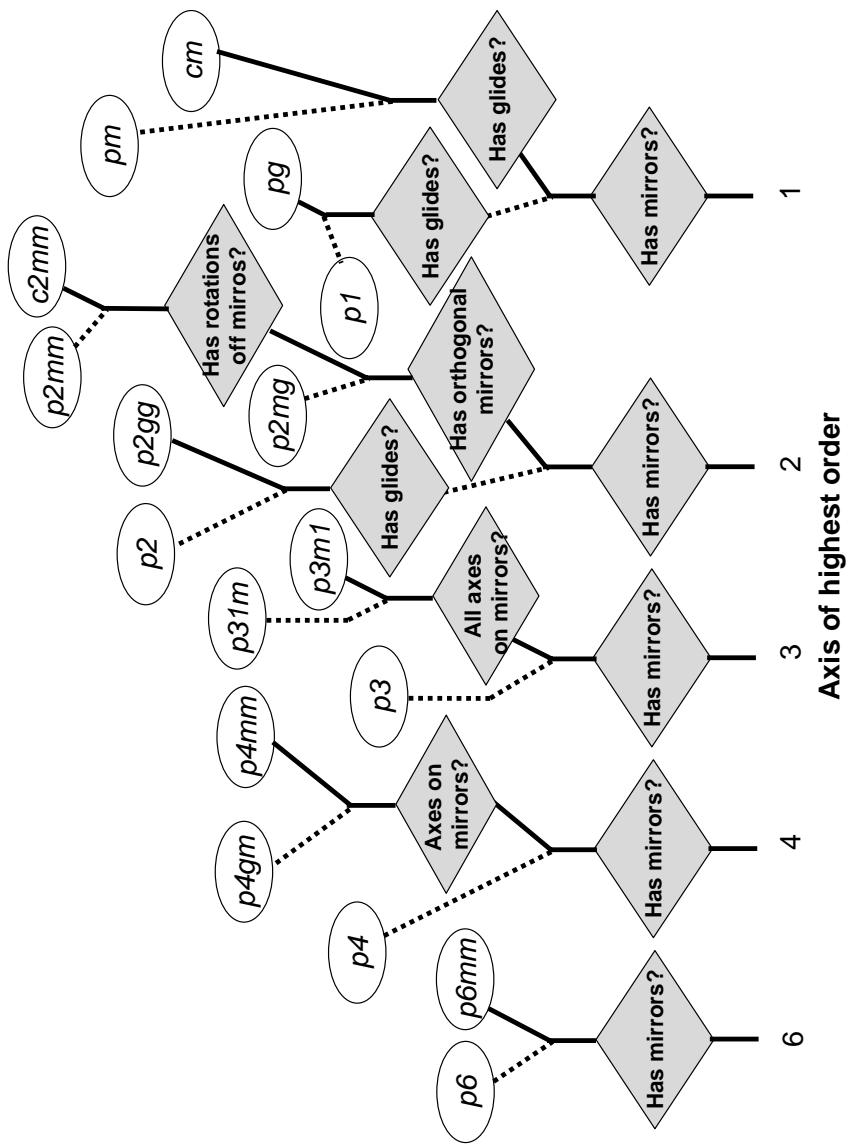


Figure 13: Decision-making tree to identify wallpaper patterns. The first step (bottom) is to identify the axis of highest order. Continuous and dotted lines are "Yes" and "No" branches, respectively. Diamonds are branching points.

5 Lecture 5 — Reciprocal lattice and reciprocal space

5.1 Basic definitions

- The **reciprocal lattice** is a constructed from an infinite set of vectors chosen in such a way that the dot product of any of these vectors with any of the “real” lattice vectors is an integer multiple of 2π . We recall that the real lattice vectors are the position vectors of the nodes of the real lattice with respect to an arbitrary “origin” node. Note that since the dimensions of vectors of the real lattice is (*length*), the dimension of the reciprocal lattice vectors is (*length*⁻¹)
- The **reciprocal lattice vectors** are constructed as a linear combination of **reciprocal basis vectors** (a.k.a. **dual basis vectors**) with integer coefficients. As you have already seen in previous years, reciprocal lattice vectors are orthogonal to families of nodal planes in real space, and in this context, their integer coefficients are known as *Miller indices* (usually h , k and l).
- The **reciprocal space** is a space of vectors defined by linear combinations of **reciprocal basis vectors** with dimensionless components.

5.2 The reciprocal lattice

5.2.1 Dual basis in 3D

In 3 dimensions, you have already seen the following to calculate the dual basis vectors, which makes use of the properties of the vector product:

$$\begin{aligned}\mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \\ \mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \\ \mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}\end{aligned}\tag{29}$$

With this definition of the dual basis, we have

$$\mathbf{a}_i \cdot \mathbf{b}^j = 2\pi \delta_i^j\tag{30}$$

Note that

$$v = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = abc \left(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma\right)^{1/2} \quad (31)$$

is the **unit cell volume**.

In crystallographic textbooks, the dual basis vectors are often written as \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* .

Using this definition of the dual basis, the dot product between vectors in real space (expressed on the real-space basis), and vectors in reciprocal space (expressed on the dual basis) is:

$$\mathbf{q} \cdot \mathbf{v} = 2\pi \sum_i q_i v^i \quad (32)$$

For this definition of dual basis to conform to our original definition of reciprocal lattice, we must have for every h, k, l integers:

$$\begin{aligned} (n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3) \cdot (h \mathbf{b}_1 + k \mathbf{b}_2 + l \mathbf{b}_3) &= \\ = 2\pi(h n_1 + k n_2 + l n_3) &= 2\pi \sum_i h_i n^i = 2\pi m \end{aligned} \quad (33)$$

where m is an integer. We can see that this is always true if n_1, n_2, n_3 are also integers, that is, if $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ is a *primitive* basis. It can be easily shown that all equivalent primitive bases in real space define equivalent primitive dual bases and reciprocal space lattices¹⁷.

On the contrary, if $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ is a *conventional* basis, *some* vectors expressed as $(h \mathbf{b}_1 + k \mathbf{b}_2 + l \mathbf{b}_3)$ will **not belong to the reciprocal lattice**.

5.2.2 Centring extinctions

If a **conventional** real-space basis is used to construct the dual basis, **only certain reciprocal-lattice vectors will yield a $2\pi m$ dot product with all real-lattice vectors** — a necessary (but not sufficient, see below) condition to

¹⁷This is due to the fact that the transformation matrix of the dual basis is the *inverse matrix* of the transformation matrix of the real-space basis. In this course, I will shy away from a full treatment of crystallographic coordinate transformations — a huge subject in itself, but one that at this level does not add much to the comprehension of the subject.

observe Bragg scattering at these points. These reciprocal-lattice vectors **are exactly those generated by one of the corresponding primitive bases**. All other Miller indices will not generate reciprocal-lattice vectors. There will never be scattering intensities at these points, which are therefore said to be *extinct by centring*. This is illustrated with an example in fig. 14 (in 2D). One can see that the conventional reciprocal-space unit cell (associated with the dual basis a_c^* and b_c^*) is *smaller* than the primitive reciprocal-space unit cell (a_p^* and b_p^*), and therefore generates more reciprocal lattice points. Bragg scattering is never observed at these points, for the reasons explained here below — we will say that they are *extinct by centering*.

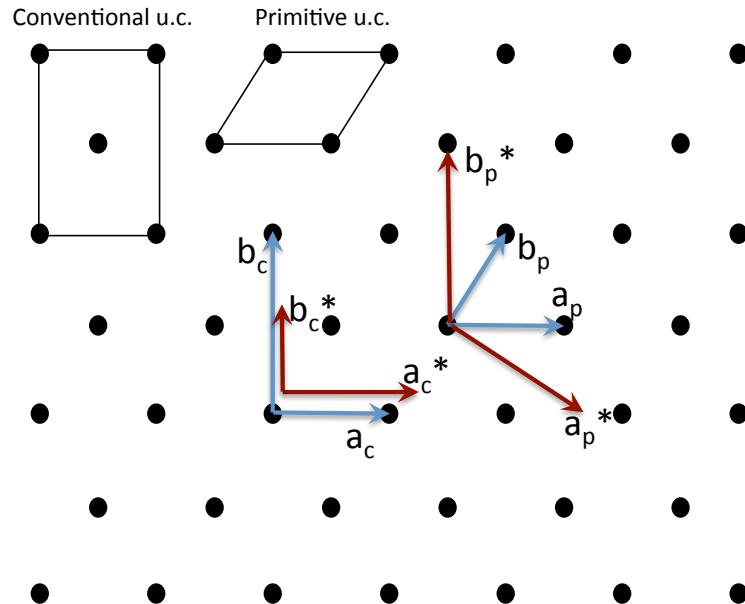
- Each non-primitive lattice type has centring extinctions, which can be expressed in terms of the Miller indices hkl (see table 4).

Table 4: Centering extinction and scattering conditions for the centered lattices. The “Extinction” columns lists the Miller indices of reflections that are **extinct by centering**, i.e., are “extra” RLV generated as a result of using a conventional basis instead of a primitive one. The complementary “Scattering” column corresponds to the listing in the International Tables vol. A, and lists the Miller indices of “allowed” reflections. “ n ” is any integer (positive or negative).

Lattice type	Extinction	Scattering
P	none	all
A	$k + l = 2n + 1$	$k + l = 2n$
B	$h + l = 2n + 1$	$h + l = 2n$
C	$h + k = 2n + 1$	$h + k = 2n$
F	$k + l = 2n + 1$ or $h + l = 2n + 1$ or $h + k = 2n + 1$	$k + l = 2n$ and $h + l = 2n$ and $h + k = 2n$
I	$h + k + l = 2n + 1$	$h + k + l = 2n$
R	$-h + k + l = 3n + 1$ or $-h + k + l = 3n + 2$	$-h + k + l = 3n$

- The non-extinct reciprocal lattice points also form a lattice, which is naturally one of the 14 Bravais lattices. For each real-space Bravais lattice, tab. 5 lists the corresponding *RL* type.

Real Space



Reciprocal Space

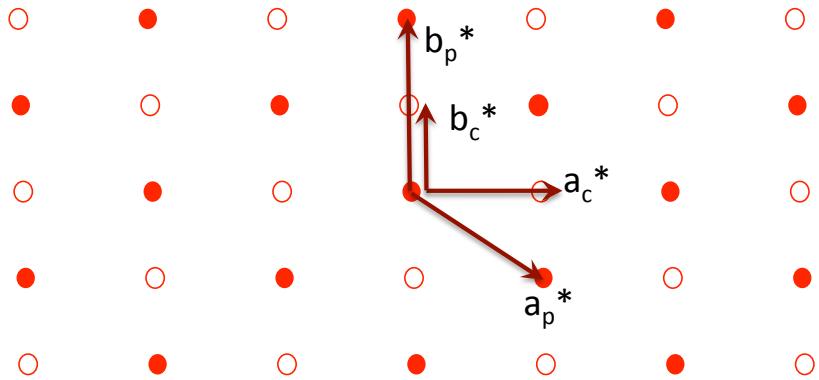


Figure 14: C-centred cells: construction of reciprocal basis vectors on the real-space lattice (**top**) and corresponding reciprocal lattice (**bottom**). One can see that the *primitive* reciprocal basis vectors generate fewer points (closed circles) than the *conventional* reciprocal basis vectors (open and closed points). Only closed points correspond to observed Bragg peaks, the others are *extinct by centring*.

Table 5: Reciprocal-lattice Bravais lattice for any given real-space Bravais lattice (BL).

Crystal system	Real-space BL	Reciprocal-space BL
Triclinic	P	P
Monoclinic	C	C
Orthorhombic	P	P
	A or B or C	A or B or C
	I F	F I
Tetragonal	P	P
	I	I
Trigonal	P	P
	R	R
Hexagonal	P	P
Cubic	P	P
	I	F
	F	I

5.2.3 Dual basis — alternative definition *without* cross product

Let us assume a basis vector set \mathbf{a}_i for our vector space as before, and let us consider the following set of *new* vectors.

$$\mathbf{b}^i = 2\pi \sum_k \mathbf{a}_k (G^{-1})^{ki} \quad (34)$$

From Eq. 7 follows:

$$\mathbf{a}_i \cdot \mathbf{b}^j = \mathbf{a}_i \cdot 2\pi \sum_k \mathbf{a}_k (G^{-1})^{ki} = 2\pi \sum_k G_{ik} (G^{-1})^{kj} = 2\pi \delta_i^j \quad (35)$$

This is exactly the same as eq. 30, so this new definition of the dual basis must be equivalent to the one given in eq. 29.

Recap of the key formulas for the dual basis

- From **direct** to **dual** bases (eq. 34)

$$\mathbf{b}^i = 2\pi \sum_k \mathbf{a}_k (G^{-1})^{ki}$$

- Dot product relation between the two bases (eq. 35)

$$\mathbf{a}_i \cdot \mathbf{b}^j = 2\pi \delta_i^j$$

- Dot product between vectors expressed on the two *different* bases (eq. 32):

$$\mathbf{q} \cdot \mathbf{v} = 2\pi \sum_i q_i v^i$$

5.2.4 Dot products in reciprocal space

As we shall see later, it is very useful to calculate the dot product between two vectors in reciprocal space. This can be tricky in non-Cartesian coordinate systems. A quick way to do this is to determine the *reciprocal-space metric tensor*, which is related to the real-space one. The reciprocal-space metric tensor is $\tilde{\mathbf{G}} = (2\pi)^2 \mathbf{G}^{-1}$, so that, for two reciprocal-space vectors \mathbf{q} and \mathbf{r} :

$$\mathbf{q} \cdot \mathbf{r} = \sum_{i,j} \tilde{G}^{ij} q_i r_j \quad (36)$$

5.2.5 A very useful example: the hexagonal system in 2D

- The hexagonal system in 2D has a number of important applications in contemporary solid-state physics problems, particularly for carbon-based materials such as graphene and carbon nanotubes.
- By crystallographic convention, the real-space basis vectors form an angle $\mathbf{a} \wedge \mathbf{b}$ of 120° (this is also true in 3D).
- The *real-space metric tensor* is therefore:

$$G = a^2 \begin{bmatrix} 1 & -1/2 \\ -1/2 & 1 \end{bmatrix} \quad (37)$$

- From eq. 36, we can find the *reciprocal-space metric tensor*:

$$\tilde{G} = \frac{(2\pi)^2}{a^2} \frac{4}{3} \begin{bmatrix} 1 & 1/2 \\ 1/2 & 1 \end{bmatrix} \quad (38)$$

- It follows, for example, that the length of a vector in reciprocal space is given by:

$$q = \frac{2\pi}{a} \sqrt{\frac{4}{3}(h^2 + hk + k^2)} \quad (39)$$

5.3 Fourier transform of lattice functions

As you have already seen in previous years (see also Appendix I), the Fourier transform of a function $f(\mathbf{r})$ (real or complex) with the periodicity of the lattice can be written as:

$$\begin{aligned} F(\mathbf{q}) &= \frac{1}{(2\pi)^{\frac{3}{2}}} \sum_{n_i} e^{-2\pi i \sum_i q_i n^i} \int_{u.c.} d\mathbf{x} f(\mathbf{x}) e^{-i\mathbf{q}\cdot\mathbf{x}} \\ &= \frac{v_0}{(2\pi)^{\frac{3}{2}}} \sum_{n_i} e^{-2\pi i \sum_i q_i n^i} \int_{u.c.} dx^i f(x^i) e^{-2\pi i \sum_i q_i x^i} \end{aligned} \quad (40)$$

where v_0 is the volume of the unit cell

The triple infinite summation in $n_i = n_x, n_y, n_z$ is over all positive and negative integers. The $q_i = q_x, q_y, q_z$ are reciprocal space coordinates on the dual basis. The $x_i = x, y, z$ are real-space crystallographic coordinates (this is essential to obtain the $q_i n^i$ term in the exponent). The integral is over one unit cell. $F(\mathbf{q})$ is non-zero only for \mathbf{q} belonging to the primitive RL. In fact, if \mathbf{q} belongs to the primitive reciprocal lattice, then by definition its dot product to the symmetry lattice translation is a multiple of 2π , the exponential factor is 1 and the finite summation yields N (i.e., the number of unit cells). If \mathbf{q} does not belong to the primitive reciprocal lattice, the exponential factor will vary over the unit circle in complex number space and will always average to zero.

It is the *periodic* nature of $f(\mathbf{r})$ that is responsible for the *discrete* nature of $F(\mathbf{q})$.

5.4 Atomic-like functions

Although the result in eq. 51 is completely general, in the case of scattering experiments the function $f(x)$ represents either the density of nuclear scat-

tering centres (neutrons) or the electron density (x-rays, electrons). These functions are sharply pointed around the atomic positions, and it is therefore convenient to write:

$$f(x) = \sum_j f_j(x) \quad (41)$$

where the summation is over all the atoms in the unit cell, and $f_j(x)$ is (somewhat arbitrarily) the density of scatterers assigned to a particular atom (see next lectures for a fully explanation). With this, eq. 51 becomes:

$$\begin{aligned} F(\mathbf{q}) &= \frac{v_0}{(2\pi)^{\frac{3}{2}}} \sum_{n_i} e^{-2\pi i \sum_i q_i n^i} \sum_j e^{-2\pi i \sum_i q_i x_j^i} \int_{u.c.} dx^i f_j(x^i) e^{-2\pi i \sum_i q_i (x^i - x_j^i)} = \\ &= \frac{v_0}{(2\pi)^{\frac{3}{2}}} \sum_{n_i} e^{-2\pi i \sum_i q_i n^i} \sum_j e^{-2\pi i \sum_i q_i x_j^i} f_j(q) \end{aligned} \quad (42)$$

When evaluated on reciprocal lattice points, the rightmost term is now the structure factor F_{hkl} .

5.5 Centring extinctions

In particular, we can show that those “conventional” RLV that we called *extinct by centring* are indeed extinct, that is, $F(\mathbf{q}) = 0$. For example, in the case of an I -centrel lattice, we have:

$$F_{hkl} = \sum_j e^{-2\pi i (hx + ky + lz)} \left(1 + e^{-2\pi i (\frac{h}{2} + \frac{k}{2} + \frac{l}{2})} \right) f_j(q) \quad (43)$$

and this is = 0 for $h + k + l \neq 2m$, which precisely identifies the non-primitive RL nodes.

5.6 Extinctions due to roto-translations

Similarly, the presence of roto-translation operators (glide planes and screw axes) produces extinction conditions, which, however, do not affect whole RL sub-lattices but only certain sections of it. In the case of *glides*, there are *planes* of hkl 's in which some of the reflections are extinct. In the case of *screws*, there are *lines* of hkl 's in which some of the reflections are extinct.

Here, I will show only one example, that of a glide plane \perp to the x axis and with glide vector along the y direction, which generates the two companions x, y, z and $-x, y + \frac{1}{2}, z$. We have:

$$F_{hkl} = \sum_j e^{-2\pi i(ky+lz)} \left(e^{-2\pi ihx} + e^{-2\pi i(-hx+\frac{k}{2})} \right) f_j(q) \quad (44)$$

We can see that, within the plane of reflections having $h = 0$, all reflections with $k \neq 2m$ are extinct.

5.7 The symmetry of $|F(\mathbf{q})|^2$ and the Laue classes

- It is very useful to consider the symmetry of the RL when $|F(\mathbf{x})|^2$ is associated with the RL nodes. In fact, this corresponds to the symmetry of the diffraction experiment, and tells us how many unique reflections we need to measure.
- Translational invariance is *lost* once $|F(\mathbf{x})|^2$ is associated with the RL nodes.
- Let \mathbf{R} be the rotational part and \mathbf{t} the translational part of a generic symmetry operators. One can prove that

$$F(\mathbf{q}) = \frac{N}{(2\pi)^{\frac{3}{2}}} \int_{u.c.} d(\mathbf{x}) f(\mathbf{x}) e^{-i(\mathbf{R}^{-1}\mathbf{q}) \cdot \mathbf{x}} e^{-i\mathbf{q} \cdot \mathbf{t}} = F(\mathbf{R}^{-1}\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{t}} \quad (45)$$

Eq. 45 shows that the reciprocal lattice weighed with $|F(\mathbf{q})|^2$ has the full point-group symmetry of the crystal class.

- This is because the phase factor $e^{-i\mathbf{q} \cdot \mathbf{t}}$ clearly disappears when taking the modulus squared. In fact, there is more to this symmetry when $f(\mathbf{x})$ is *real*, i.e., $f(\mathbf{x}) = f^*(\mathbf{x})$: in this case

$$\begin{aligned} F^*(\mathbf{q}) &= \frac{N}{(2\pi)^{\frac{3}{2}}} \int_{u.c.} d\mathbf{x} f^*(\mathbf{x}) e^{i\mathbf{q} \cdot \mathbf{x}} \\ &= \frac{N}{(2\pi)^{\frac{3}{2}}} \int_{u.c.} d\mathbf{x} f(\mathbf{x}) e^{i\mathbf{q} \cdot \mathbf{x}} = F(-\mathbf{q}) \end{aligned} \quad (46)$$

- Consequently, $|F(\mathbf{q})|^2 = F(\mathbf{q}) F(-\mathbf{q}) = |F(-\mathbf{q})|^2$ is *centrosymmetric*. As we shall shortly see, the lattice function used to calculate non-resonant scattering cross-sections is *real*. Consequently, the $|F(\mathbf{q})|^2$ -weighed RL

(proportional to the Bragg peak intensity) has the symmetry of the crystal class *augmented by the center of symmetry*. This is necessarily one of the 11 centrosymmetric point groups, and is known as the *Laue class* of the crystal.

Fridel's law

For normal (non-anomalous) scattering, the reciprocal lattice weighed with $|F(\mathbf{q})|^2$ has the *full point-group symmetry of the crystal class supplemented by the inversion*. This symmetry is known as the *Laue class* of the space group.

In particular, for normal (non-anomalous) scattering, **Fridel's law holds**:

$$|F(hkl)|^2 = |F(\bar{h}\bar{k}\bar{l})|^2 \quad (47)$$

Fridel's law is violated for non-centrosymmetric crystals in anomalous conditions. Anomalous scattering enables one, for example, to determine the *orientation of a polar crystal* or the *chirality of a chiral crystal* in an absolute way.

6 Appendix I: Fourier transform of lattice functions

In this section, we will consider a generic **real** or **complex** function $f(\mathbf{r})$ defined over the real space, \mathbf{r} being a position vector from an appropriately defined origin). We assume that $f(\mathbf{r})$ has the symmetry properties defined by one of the 230 space groups. We will calculate the Fourier transform of this function, $F(\mathbf{q})$, over the *whole* space. As we shall see in the next lectures, $F(\mathbf{q})$ corresponds to the diffraction **structure factor**. We have:

$$F(\mathbf{q}) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int d\mathbf{r} f(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \quad (48)$$

where the integral extends to the whole space. We now exploit the *lattice* periodicity of the function $f(\mathbf{r})$, which we can express by writing $\mathbf{r} = \mathbf{r}_0 + \mathbf{x}$ and

$$f(\mathbf{r}_0 + \mathbf{x}) = f(\mathbf{x}) \quad (49)$$

The \mathbf{r}_0 are the symmetry translation vectors, and \mathbf{x} is a position vector **within the first unit cell**, i.e., $x, y, z < 1$. We can also decompose the integral in Eq. 48 in integrals over the unit cells:

$$\begin{aligned}
F(\mathbf{q}) &= \frac{1}{(2\pi)^{\frac{3}{2}}} \sum_{\mathbf{r}_0} \int_{u.c.} d\mathbf{x} f(\mathbf{x}) e^{-i\mathbf{q}\cdot(\mathbf{r}_0+\mathbf{x})} \\
&= \frac{1}{(2\pi)^{\frac{3}{2}}} \sum_{\mathbf{r}_0} e^{-i\mathbf{q}\cdot\mathbf{r}_0} \int_{u.c.} d\mathbf{x} f(\mathbf{x}) e^{-i\mathbf{q}\cdot\mathbf{x}}
\end{aligned} \tag{50}$$

where the integral is now over a *single* unit cell. We now introduce a set of coordinates that are appropriate for the symmetry¹⁸ and recall that in these coordinates the symmetry translation vectors are expressed as $[n^i]$, i.e., a set of three integers. By using the relation $d\mathbf{x} = dx dy dz (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c} = v_0 dx dy dz$, v_0 being the volume of the unit cell, eq. 50 becomes:

$$F(\mathbf{q}) = \frac{v_0}{(2\pi)^{\frac{3}{2}}} \sum_{n_i} e^{-2\pi i \sum_i q_i n^i} \int_{u.c.} dx^i f(x^i) e^{-2\pi i \sum_i q_i x^i} \tag{51}$$

The sum is now over *all* the symmetry translations, i.e., over all the positive and negative values of the $[n^i]$. The $[n^i]$ are integers or simple fractions (for centering translations). We will perform the infinite summation by summing over a finite number N real-lattice vectors first, and then letting $N \rightarrow \infty$. The following statements is now clear by inspecting Eq. 51:

$F(\mathbf{q})$ is non-zero only for \mathbf{q} belonging to the primitive RL.

In fact, if \mathbf{q} belongs to the *primitive* reciprocal lattice, then by definition its dot product to the symmetry lattice translation is a multiple of 2π , the exponential factor is 1 and the *finite* summation yields N (i.e., the number of unit cells). Conversely, if \mathbf{q} does *not* belong to the *primitive* reciprocal lattice, the exponential factor will vary over the unit circle in complex number space and will *always* average to zero. In particular, $F(\mathbf{q})$ is *zero* for the conventional RLV that are **extinct by centering** (as we anticipated — this explains the terminology "extinction" we just introduced). For non-extinct RL vectors, the infinite summation yields ∞ .

7 Appendix II: “Real” crystal structures

Having discussed at length the symmetries of periodic “patterns” in 2 and 3 dimensions, we will devote the last part of this lecture to looking at “real”

¹⁸In this section, it should become absolutely clear why we do not use Cartesian coordinates.

crystal structures. This is in itself a vast subject that cannot be exhausted in such a short space. An interesting set of lectures devoted to the subject can be found in [?]. It is also worth pointing out to the interested student the existence of several very useful Crystal Structure Databases. The Inorganic Crystal Structures Database (ICSD), freely accessible on-line from the UK [?], can be searched for names, chemical formulas, crystallographic data and more, to display the resulting crystal structures in 3D and even to plot their powder diffraction patterns. The Cambridge Structural Database is the corresponding source for small-molecule structures. Here, we will outline a few basic principles that should provide a starting point to understand “real” crystal structures.

7.1 Cohesive forces in crystals — atomic radii

A number of different forces contribute to the cohesion of crystals, including:

- The **Coulomb interaction** between charged ions.
- **Chemical bonding** and **metallic bonding**.
- The **Van der Waals** (dipole-dipole) interaction.
- **Hydrogen bonding**.

These forces, which often coexist within the *same* crystal structure, are of very different strength. Another crucial difference is the **directionality** of these forces. **Chemical bonding** (both ionic and covalent) **is usually strongly directional**, and leads to the formation of specific **coordination polyhedra** (e.g., octahedra, tetrahedra) within the crystals. Conversely, most other interactions are poorly directional.

One useful way to understand many crystal structures, particularly those of inorganic compounds of greater interest for physicists, is that of considering them as **packings of spheres of different sizes**. Within this very simplistic picture, each ion is characterised by a **radius**. Atomic radii are not completely unique to each species, but vary depending on several factors:

- The **valence** state of the ion.
- The **spin** state of the ion.
- The number of neighbours (**coordination number**).

- Whether the bonding is **ionic** or **covalent**.

The standard reference for covalent and ionic radii was compiled by R.D. Shannon and can be found in¹⁹. Several versions of this table can be found on line.

Over most of the periodic tables, ionic and covalent radii vary between 0.5 Å and 2 Å. Typical interatomic distances are therefore of the order of 1.5–2.5 Å. This sets the length-scale of the probes (X-rays, neutrons, electrons) that can be most profitably used to study these structures.

7.2 Close-packed structures

When all the “spheres” are of equal size and the interactions between them are not strongly directional, the most common arrangement is one of the **close packed structures** (fig. 15):

CCP i.e., **Cubic Close-Packed**, which has a face-centered cubic (**FCC**) lattice (space group $Fm\bar{3}m$). Many metals, including all those of the Cu and Ni groups, adopt this structure.

HCP Hexagonal Close-Packed, which has a hexagonal lattice with two atoms per unit cell (space group $P6_3/mmc$). Metals such as Co, Zn, Cd, Hg, Mg and others adopt this structure.

Several metals, including Fe, Cr and its group, V and its group and all the alkaline metals adopt the **BCC (Body Centered Cubic) structure** — space group $Im\bar{3}m$, which is **not close-packed**.

Close-packed and BCC structures are also adopted by much more complex systems — for instance C_{60} (“Buckyballs”) and even viruses (fig. 16) — clearly with much larger inter-sphere distances. Here we have roughly spherical objects with strong internal bonding, which are weakly bonded among themselves.

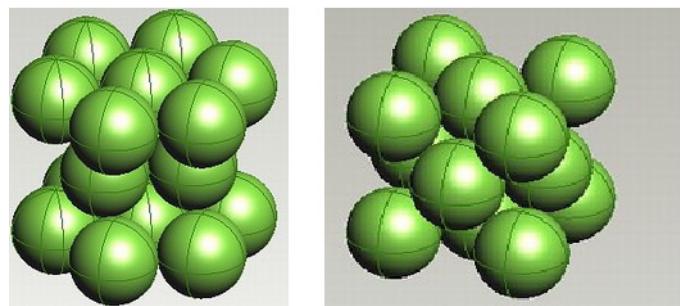


Figure 15: The close-packed structures of rigid spheres: HCP (**left**) and CCP (**right**).

¹⁹R. D. Shannon, *Acta Cryst. A* **32** 751-767(1976)

7.3 Packing spheres of different radii

Many simple binary or ternary compounds are made of ionic species with different radii. In these cases, their crystal structures can often be thought of as being close-packed arrangements of the *larger* spheres, with the *smaller* spheres located in the “interstices” or “vacancies” between the larger spheres. Both CCP and HCP structures have vacancies of this type, surrounded by four spheres (**tetrahedral vacancies**) or six spheres (**octahedral vacancies**).

Because of the geometry of the vacancies, this structural arrangement is suitable for ions with **strongly directional bonding**. When strong directional bonding is present, compounds with ions with similar radii and even mono-atomic compounds can adopt these structures. Among the structures that can be described in this way are:

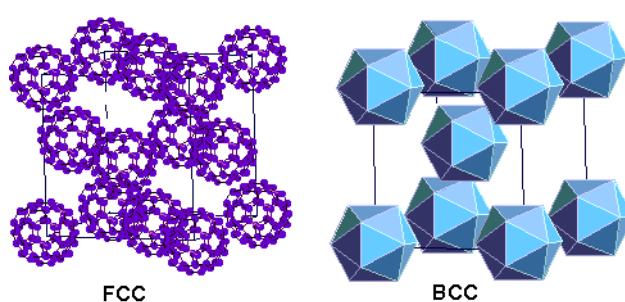


Figure 16: Simple arrangements of complex objects: (left) the CCP structure of C_{60} (“Buckyballs”) and (right) the BCC structure of the foot-and-mouth virus.

The NaCl structure (space group $Fm\bar{3}m$) where Na fills *all* the octahedral holes of the CCP structure.

The fluorite structure (prototype compound CaF_2 , space group $Fm\bar{3}m$), where the F atoms fill *all* the tetrahedral holes of the CCP structure (fig. 17).

The zinc blende structure (prototype compound ZnS , space group $F4\bar{3}m$), where the Zn ions fill *half* of the tetrahedral holes of the CCP structure.

The perovskite structure (prototype compound $CaTiO_3$, space group $Pm\bar{3}m$). In this interesting ternary example, the CCP array is formed by *both* Ca^{2+} (positively charged) *and* O^{2-} (negatively charged). The smaller Ti ion fills *a quarter* of the octahedral vacancies.

The corundum structure (Al_2O_3 , space group $R\bar{3}c$). Here, the oxygen ions form a HCP structure, and the much smaller Al ions fit into 2/3 of the octahedral vacancies (1/3 of the vacancies are empty). The **ilmenite** ($FeTiO_3$, space group $R\bar{3}$) is a variant with two metal ions instead of one.

The diamond structure is adopted, among others, by C and Si. It is identical to the zinc blende structure but with two identical, strongly-bonded

atoms.

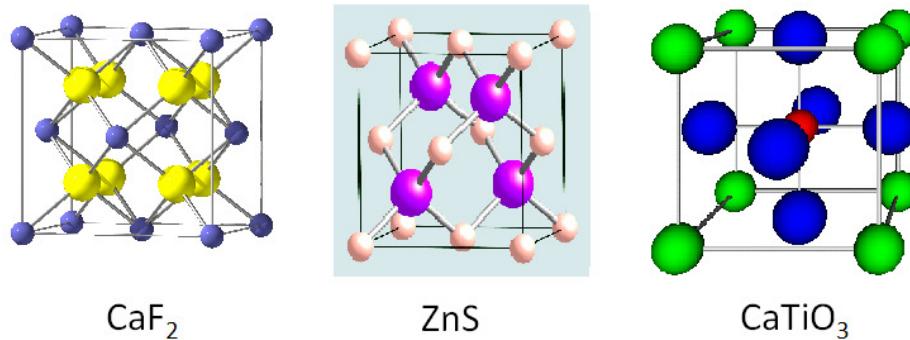


Figure 17: Three cubic structures obtaining by inserting ions in the “interstices” of the CCP structure. **Left** the fluorite structure ; **center** the zinc blende structure; **right** the perovskite structure.

7.4 Framework structures

Many crystal structures cannot be simply thought of in terms of close packing. One notable example is given by **framework structures** — structures built out of very rigid polyhedra (most often tetrahedra) with rather “flexible” connections to each other. Framework structures are low-density structures, and can often collapse rather easily to higher-density forms upon application of pressure.

The structure of **quartz** (SiO_2) consists of corner-sharing SiO_4 tetrahedra so that each Si is bonded to four oxygens, and each oxygen is bonded to two silicon atoms. The resulting structure forms an open three-dimensional framework, and it is quite flexible, so that different crystal variants exist (α - and β -quartz, crystobalite, trydimite etc.) When cooled rapidly, the quartz structure is unable to “choose” between these variants and forms a **glass**. An even more extreme example of silicate framework structure is provided by **zeolite** (SiO_2 , fig. 18), where the tetrahedral frame-

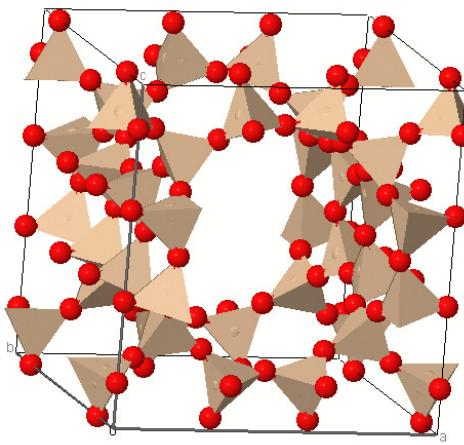


Figure 18: The structure of zeolite β (space group $P4_2/mmc$). Note the complex framework of SiO_4 tetrahedra, defining a large cavity in the middle of the unit cell. Many silicate and alumino-silicate zeolites exist, both natural and synthetic.

work encompasses large cavities. Zeolite is the prototype of a large family of silicates and alumino-silicates, collectively known as “zeolites”, which have wide-ranging applications in catalysis.

7.5 Layered structures

Many crystal structures have a pronounced 2-dimensional character, with strong covalent or ionic bonding in 2 dimensions and weaker (typically Van der Waals) bonding in the third. A well known example of this is **graphite** (space group $P6_3/mmc$ with two atoms per unit cell). Due to the weak inter-layer forces, the layers can “slip” onto each other, so that structures of this types are often employed as lubricants. Other examples of this kind are provided by the **clays**, such as vermiculite (fig. 19), and by the delafossite family (prototype CuFeO_2 , space group $R\bar{3}m$ or $P6_3/mmc$). Less extreme examples of 2D structures are provided by the **high- T_c superconducting cuprates** (fig 20).

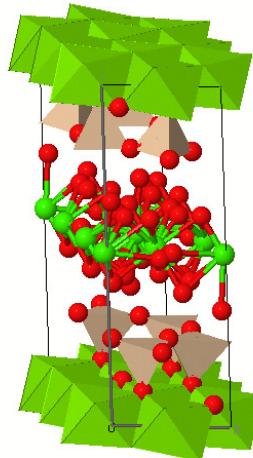


Figure 19: The structure of the vermiculite clay (chemical formula $A_3B_4O_{10} \cdot (H_2O)_n$, with $A=\text{Mg, Fe, Al}$, $B=\text{Al, Si}$; space group $C2/m$) is highly 2-dimensional. The A site forms triangular layers with formula AO_2 , connected to “rings” of BO_2 tetrahedra. These layers are widely separated and weakly interacting, and, as typical of clays, can accommodate large amounts of rather disordered water molecules.

7.6 Molecular structures

All the structures we have defined up to this point are built of infinite “networks” of atoms, either in 3D or in 2D. By contrast, molecular structures are

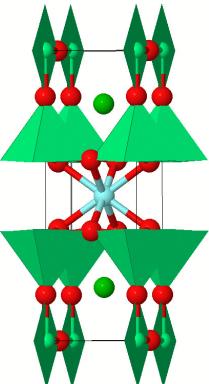


Figure 20: The structure of the 90 K-high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ or YBCO is also 2-dimensional, but with a less pronounced 2D *structural* character compared to clays. The central ion, Y, is ionically bonded to oxygen, so the structure does not exfoliate like that of graphite. Nevertheless, the electronic structure is highly 2D. Note that Cu exists both in square-pyramidal (“planes”) and in square-planar (“chains”) coordinations.

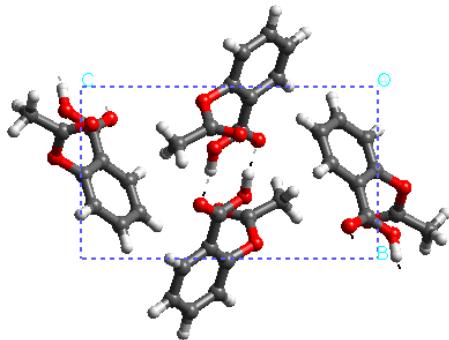


Figure 21: The molecular crystal structure of aspirin. The individual molecules are easily identifiable, and are linked to each other by hydrogen bonds (dotted lines).

built out of well defined “molecules”, with strong internal covalent bonding but weakly interacting with each other. A simple example is the structure of **ice**, with covalent bonding within the H_2O molecule and weak hydrogen bonding between molecules. Ordinary ice is known as “ice 1h”, and has space group $P6_3/mmc$. However, due to the particular geometry of the molecules, ice is **highly polymorphic** as a function of temperature and pressure, with 15 known different crystallographic structures being known to date. Molecular structures are adopted by most small molecules (such as drugs) and macromolecules (such as proteins). The molecule itself has rigid components (such as benzene rings) connected to each other by “joints” having some degree of flexibility. Therefore, the same molecule can often adopt different crystal structures (polymorphism), having different molecular configurations and packing of different molecules within the unit cell.