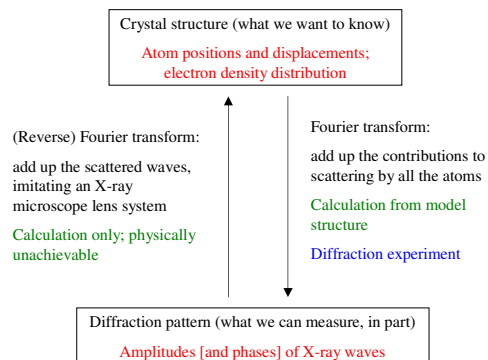# Introduction to symmetry and diffraction

Bill Clegg
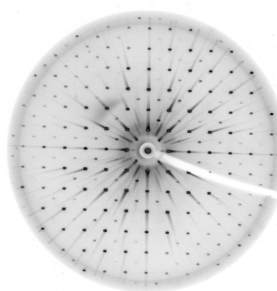
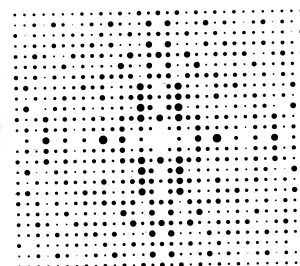## CCG course 2005

1.1 The relationship between a crystal structure and its diffraction pattern

Crystal structure (what we want to know)
Atom positions and displacements; electron density distribution

(Reverse) Fourier transform:

add up the scattered waves, imitating an X-ray microscope lens system

Calculation only; physically unachievable

Fourier transform:

add up the contributions to scattering by all the atoms

Calculation from model structure

Diffraction experiment

Diffraction pattern (what we can measure, in part)
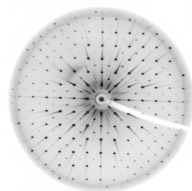Amplitudes [and phases] of X-ray waves

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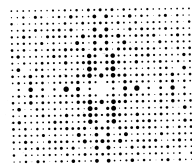Examples of diffraction patterns:

An actual X-ray photograph

A computer-generated reproduction

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3 obvious properties:

1. Geometry: regular arrangement of spots corresponding to directions of diffracted beams of X-rays

2. Symmetry: in positions and intensities of spots

3. Intensities: wide variation with no apparent pattern except symmetry

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Crystal structure

Unit cell geometry
(lattice parameters)

Crystal symmetry
(space group)

Unit cell contents
(atom positions etc.)

Diffraction pattern

Diffraction geometry
(directions, positions)

Diffraction symmetry
(Laue class)

Intensities
(amplitudes and phases)

1.2 Translation symmetry in crystalline solids

The characteristic property of the crystalline solid state is its high degree of internal order: molecules (or atoms, or ions) are arranged in a regular way in an effectively infinite 3D repeat pattern, like 3D wallpaper (theoretically, zero entropy).

This repetition is *translation symmetry*.

It is **always** present in crystalline solids. Other kinds of symmetry (rotation, reflection, inversion, improper rotation) **may** also be present.

A complete crystal structure can be specified by describing the contents of one repeat unit, together with the way in which this unit is repeated by translation symmetry.

Concepts: lattice

                   unit cell
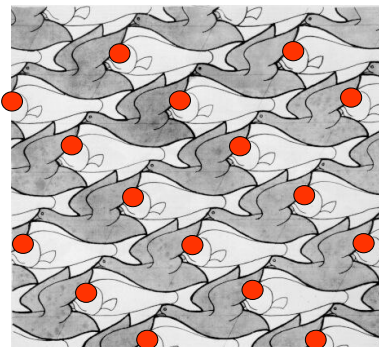
White fish and grey birds: a sort of 2D ionic structure?

[M. C. Escher]

All white fish are identical. All grey birds are identical.

Basic structural unit is one bird plus one fish, repeated in a regular way in 2D to give the complete structure.
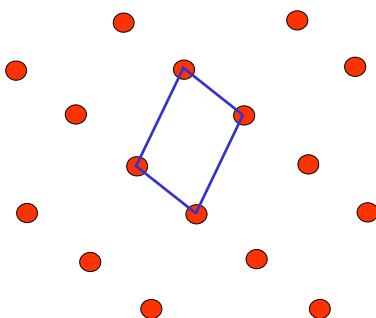
There is no other symmetry.

How do we specify the geometry of the repeat unit?

Choose any point, such as a fish's eye.

Then mark all the other equivalent points in the same way.

Now take away the original picture…

We are left with a regular pattern of dots, showing the geometrical form of the translation symmetry but not the detailed contents of the structure.

This is called the *lattice* of the structure.

How do we measure its geometry?

Join up four neighbouring lattice points to form a parallelogram (like a rectangle but with angles not equal to 90°).
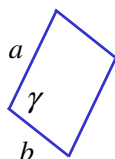
This is called the *unit cell* of the structure.
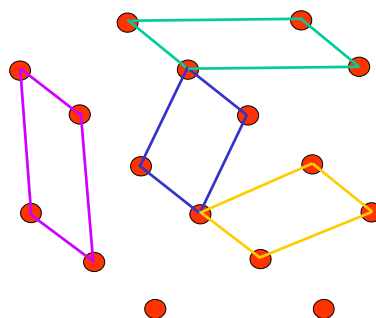
Many different unit cells could be chosen, all equally valid.

For convenience and by convention, the sides are made as short as possible, and the angles close to 90°.

Here, the blue unit cell is the best choice.

The unit cell geometry is fully described by giving the lengths of two sides and the angle between them (in 2 dimensions).
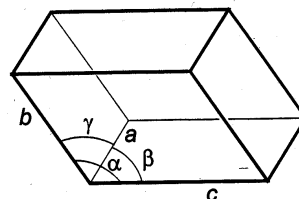
In three dimensions, a unit cell is a parallelepiped (like a brick, but with the angles not necessarily 90°).

To describe the unit cell geometry, we need three lengths (a, b, c) and three angles (α, β, γ); α is the angle between b and c, β between a and c, γ between a and b.

Alternatively, using vectors, the unit cell is specified by the three axis vectors: **a**, **b**, **c**.

In the absence of any rotation or reflection symmetry, the unit cell lengths are usually different from each other, and the angles do not have special values such as 90° or 120°.

In other words, pure translation symmetry imposes no restrictions on the values of unit cell parameters (lengths and angles).

Close approximation to equality or to such special values may fortuitously be found sometimes (and is one factor that can lead to twinning).

Translation symmetry is what gives rise to X-ray diffraction, the crystal acting as a 3D diffraction grating. Unit cell dimensions are comparable to the wavelengths of X-rays.

1.3 Symmetry of individual molecules, with relevance to crystalline solids

Symmetry element

A physically identifiable point, line, or plane in a molecule about which symmetry operations are applied.

Symmetry operation

Inversion through a point, rotation about a line, or reflection in a plane (or a special combination of two of these together), that leaves the molecule afterwards with an identical appearance; also included, for completeness, is the identity operation (doing nothing).

Each symmetry element provides a number (one or more) of possible symmetry operations.

For individual molecules, all symmetry operations can be classified as one of two types:

proper rotation – rotation by $360°/n$ about a rotation axis;

improper rotation – combination of a rotation about an axis and a simultaneous reflection in a perpendicular plane through the centre of the molecule.

This is the definition used in spectroscopy and bonding applications (Schoenflies convention).

Crystallography uses a different definition (Hermann-Maugin or international convention, for good reasons!):

proper rotation – rotation by $360°/n$ about a rotation axis;

improper rotation – combination of a rotation about an axis and a simultaneous inversion through a point at the centre of the molecule.

Reflection and inversion symmetry are just special cases of improper rotations.

Improper operations involve a change of hand; proper operations retain the same hand.

Symbols for symmetry operations and elements

Crystallography (Hermann-Maugin)	Spectroscopy (Schoenflies)	Notes
Proper rotations		
1	C_1 (or E)	identity operation
2	C_2	
3	C_3	
4	C_4	
6	C_6	
Improper rotations		
$\bar{1}$	$i\ (= S_2)$	inversion
$\bar{2}$ (or m)	$\sigma\ (= S_1)$	reflection
$\bar{3}$	S_6	
$\bar{4}$	S_4	
$\bar{6}$	$S_3\ (= C_3 + \sigma_h)$	

In individual molecules, other orders of rotation are possible (5, and 7 upwards) – though not common.
These are incompatible with an infinite lattice.

Point groups

Symmetry elements can be combined only in certain ways that are consistent with each other. For a single molecule, all symmetry elements must pass through a common point at the centre of the molecule.

The total collection of all the symmetry elements/operations for a molecule is called its point group. There are conventional symbols for point groups (again, two conventions).

Some symmetry elements are incompatible with translation symmetry and so can not occur in a crystal structure.

Only 32 point groups are relevant to crystallography.

In the absence of any rotation or reflection symmetry, the unit cell lengths are usually different from each other, and the angles do not have special values such as 90° or 120°.

In other words, pure translation symmetry imposes no restrictions on the values of unit cell parameters (lengths and angles).

Neither does inversion symmetry (the geometry of all lattices has inversion symmetry anyway).

The presence of **any** rotation or reflection symmetry in a 3D lattice imposes restrictions on unit cell parameters.

Look at 2D analogues again to illustrate this.

In 2D, two-fold rotation is just the same as inversion, and adds no extra restrictions.
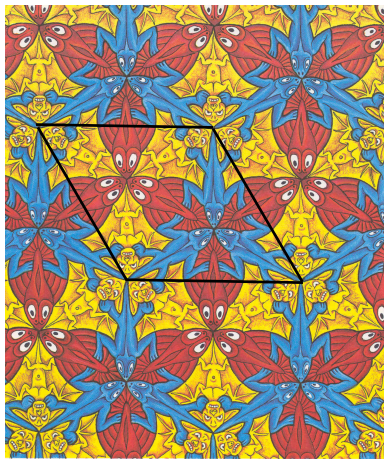
3-fold rotation symmetry

Choose lattice points and outline a unit cell.

This has equal sides ($a = b$) and the angle is exactly 120° as a direct consequence of the rotation symmetry.
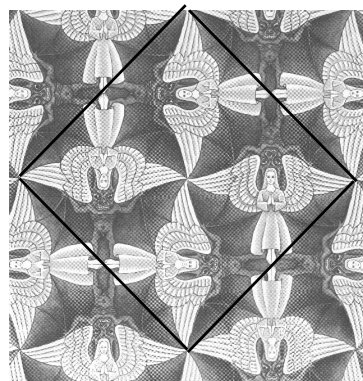
6-fold rotation symmetry generates the same unit cell restrictions as 3-fold rotation symmetry.

4-fold rotation symmetry

Choose lattice points and outline a unit cell.

This has equal sides ($a = b$) and the angle is exactly 90° as a direct consequence of the rotation symmetry. The unit cell is a perfect square.

The point at the centre of the unit cell is not identical to the corners! It has the opposite direction of rotation (look carefully). So it is not an equivalent lattice point. The unit cell drawn here is the smallest possible.
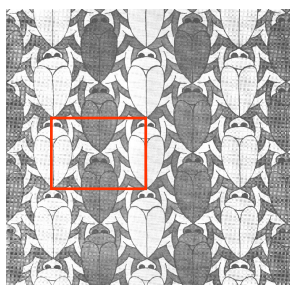
Reflection symmetry

Choose lattice points and outline a unit cell.

This is a rectangle: the sides are not equal, but the angle must be 90° because of the reflection lines (2D equivalent of reflection planes in 3D) that run vertically through the centres of all the beetles.

In 3 dimensions similar restrictions apply, in the presence of ANY rotation or reflection symmetry.

As a result, there are just 7 different possible types of unit cell shapes for 3D crystal structures, and these are called the seven *crystal systems*.

Each one has a characteristic minimum symmetry associated with it, and its own particular geometrical restrictions.

The seven crystal systems

Crystal system	Essential symmetry	Restrictions on unit cell
triclinic	none	none
monoclinic	2 and/or *m* for one axis	$\alpha = \gamma = 90°$
orthorhombic	2 and/or *m* for three axes	$\alpha = \beta = \gamma = 90°$
tetragonal	4 for one axis	$a = b; \alpha = \beta = \gamma = 90°$
trigonal	3 for one axis	$a = b; \alpha = \beta = 90°; \gamma = 120°$
hexagonal	6 for one axis	$a = b; \alpha = \beta = 90°; \gamma = 120°$
cubic	3 for four directions	$a = b = c; \alpha = \beta = \gamma = 90°$

For some crystal structures with rotation and/or reflection symmetry, it is convenient to choose a unit cell that has lattice points not only at the corners but also in the centres of some faces or at the body centre of the cell, because this gives the conventional shape for the crystal system, revealing the type of symmetry present. These are called *centred* unit cells, as opposed to *primitive* unit cells with lattice points only at the corners.
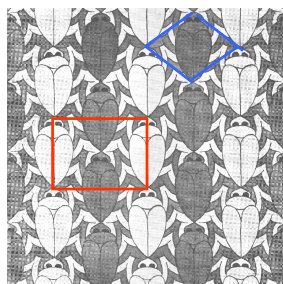
If all beetles are considered the same regardless of colour, the smallest unit cell is the blue one, with lattice points only at the corners. However, this does not have the 90° angle characteristic of reflection symmetry. If we use the rectangular red unit cell, then this is twice the size and has a lattice point right in the middle. This is a centred unit cell (and is conventional), while the blue one is a primitive cell.

4

Centred unit cells

2 dimensions:
        primitive (*p*) for all 4 unit cell shapes (oblique, rectangular, square, hexagonal)
        centred (*c*) for the rectangular shape only (unnecessary for other shapes)

3 dimensions:
        primitive (*P*) for all 7 crystal systems
        centred on one pair of faces (*A*, (*B*), *C*) for monoclinic, orthorhombic
        centred on all faces (*F*) for orthorhombic, cubic
        centred at the unit cell centre (*I*) for orthorhombic, tetragonal, cubic
        rhombohedral unit cell on hexagonal/trigonal axes has 3 lattice points per unit
                cell (*R*)

A centred unit cell is larger by a factor of 2 (*A*, *C*, *I*), 3 (*R*), or 4 (*F*) than the corresponding *P* cell.
Therefore the related reciprocal unit cell is smaller by the same factor, and a corresponding fraction of its corners do not lie on reflection positions.

The seven crystal systems

| Crystal system	Essential symmetry	Restrictions on unit cell	"Lattice types"
triclinic	none	none	*P*
monoclinic	2 and/or *m* for one axis	$\alpha = \gamma = 90°$	*P, C (I)*
orthorhombic	2 and/or *m* for three axes	$\alpha = \beta = \gamma = 90°$	*P, C (A), I, F*
tetragonal	4 for one axis	$a = b; \alpha = \beta = \gamma = 90°$	*P, I*
trigonal	3 for one axis	$a = b; \alpha = \beta = 90°; \gamma = 120°$	*P (R)*
hexagonal	6 for one axis	$a = b; \alpha = \beta = 90°; \gamma = 120°$	*P*
cubic	3 for four directions	$a = b = c; \alpha = \beta = \gamma = 90°$	*P, I, F*

1.4 Symmetry in the solid state

The limited possibilities for rotation axes in crystalline solids might make it seem that symmetry is very restricted in solids.

However, crystalline solids can have symmetry elements that are impossible in individual objects such as single molecules.

These combine rotation with translation (to produce *screw axes*) or combine reflection with translation (to produce *glide planes*).

For an illustration, return to a 2D analogue of a glide plane (a glide line).
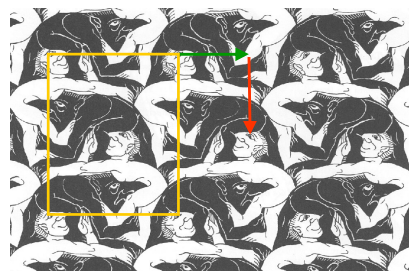
There is obviously some kind of reflection symmetry here: all the white figures are identical or mirror images; all the black figures are identical or mirror images. But mirror images are not directly in line (eye-to-eye). The operation relating them is a combination of reflection across a vertical line with translation half a unit cell upwards or downwards. Repeating this operation does not come back to the original position (a normal reflection), but finishes exactly one unit cell away (a pure translation operation). This is possible in the solid state, but not in individual non-polymeric molecules.

In 3D, we have glide planes instead of glide lines.

Imagine a glide plane perpendicular to the *b* axis (common in the monoclinic crystal system). Reflection across this plane is combined with translation equal to half a unit cell repeat. This translation may be parallel to the a axis, parallel to the c axis, or both of these simultaneously, *i.e.* along a unit cell face diagonal. The symbols for these glide planes are the single letters *a*, *c*, and *n*, respectively, replacing the letter *m* for a simple mirror plane.

For unit cells in some crystal systems, it is also possible to have glide planes with a translation component of one-quarter of a unit cell repeat, and the symbol for these is *d*; they are not common.

Translation can also be combined with rotation axes, the translation always being along the direction of the rotation axis and by an amount equal to a multiple of 1/*n* of the lattice repeat in that direction (*n* is the order of the rotation axis). This produces screw axes. Some of them, in which the translation is not half a lattice repeat, are chiral, like screw threads. For example, a 4_1 axis is equivalent to a right-handed screw thread, while a 4_3 axis is the left-handed equivalent.

Symmetry elements with translation components

Rotations (screw axes)

Two-fold	2_1
Three-fold	$3_1 \ 3_2$
Four-fold	$4_1 \ 4_2 \ 4_3$
Six-fold	$6_1 \ 6_2 \ 6_3 \ 6_4 \ 6_5$

Reflections (glide planes)

Translation parallel to cell axes	*a b c*
Translation parallel to diagonals	*n*
Translation half-way to centring lattice point	*d*

The combination of all the symmetry elements/operations in a crystalline solid structure (including translation) is called the *space group* of the structure, in the same way as we have *point groups* for individual molecules.

There are exactly 230 different space groups, *i.e.* different possible ways of putting symmetry elements together in the crystalline solid state. All their descriptions and properties are given in *International Tables for Crystallography*, Volume A.

Point groups

All symmetry elements pass through one point,
      which remains unchanged by any symmetry operation.
Repeated use of any symmetry operation eventually returns the molecule
      to the original orientation exactly (not just an equivalent form).
Any proper or improper rotation is possible,
      but only certain combinations are allowed.

Space groups

Identical symmetry elements are arranged parallel
      at intervals of half a unit cell edge,
      so they do not all pass through one point.
Repeated use of any symmetry operation may eventually return to the original
      point, or to an equivalent one in a different unit cell.
Only 1, 2, 3, 4, 6-fold proper and improper rotations are possible,
      but there are also screw axes and glide planes;
      only certain combinations are allowed (230 in total).

Notation for space groups

A single capital letter for the unit cell centring (one of *P*, *A*, *C*, *I*, *F*, *R*)

followed by a combination of numbers and lower-case letters to show the presence of rotation, reflection and inversion symmetry in the structure.

The combination of some symmetry operations necessarily implies the presence of others as well, so not all the symmetry needs to be indicated in every case; there are conventions about which take precedence.

The rules are different for each of the crystal systems, as shown in the lecture notes.

Number of space groups in each crystal system

Triclinic	2
Monoclinic	13
Orthorhombic	59
Tetragonal	68
Trigonal	25
Hexagonal	27
Cubic	36

Choice of unit cell origin (selection of positions of lattice points)

In principle, this is arbitrary.

By convention in most space groups, the origin is chosen to lie on a symmetry element.

For centrosymmetric space groups, the origin is usually placed on an inversion centre (because this simplifies the mathematics of Fourier calculations).

In most crystal structures, symmetry elements lie between molecules, rather than inside molecules, so atoms do not usually lie on lattice points.

The main exception is for high-symmetry inorganic crystal structures such as simple ionic salts, in which ions lie in special positions of high symmetry.

1.5 Diffraction and symmetry

How is the symmetry of a diffraction pattern related to the symmetry of the crystal structure?

A diffraction pattern has a central point, corresponding to the reflection with indices 0,0,0, so its symmetry is expressed in terms of a point group.

The symmetry of the crystal structure is expressed in terms of a space group.

In the absence of anomalous scattering (anomalous dispersion, or resonant scattering), every diffraction pattern has inversion symmetry, whether or not the crystal structure is centrosymmetric: Friedel's Law.

Thus, of the 32 crystallographic point groups, only 11 are possible as the symmetry of a diffraction pattern, and these are called the 11 Laue classes.

Each space group (230) has a corresponding point group (32), and a corresponding Laue class (11).

Space group → corresponding point group

Ignore the initial capital letter

Replace all screw axes by corresponding pure rotation axes

Replace all glide planes by simple mirror planes

Examples

$P2_1/c$	→	$2/m$
$Aba2$	→	$mm2$
$I4_1/acd$	→	$4/mmm$

Point group → corresponding Laue class

Add an inversion centre if there is not already one

Examples

$P2_1/c$	→	$2/m$	→	$2/m$
$Aba2$	→	$mm2$	→	mmm
$I4_1/acd$	→	$4/mmm$	→	$4/mmm$

For each of the triclinic, monoclinic and orthorhombic systems, there is only one Laue class. For each of the other systems, there are two.

Crystal systems, point groups, and Laue classes

System	Laue class	Other point groups	Corresponding Schoenflies	
triclinic	$\bar{1}$	1	C_i	C_1
monoclinic	$2/m$	2, m	C_{2h}	C_2, C_s
orthorhombic	mmm	$mm2$, 222	D_{2h}	C_{2v}, D_2
tetragonal	$4/m$	4, $\bar{4}$	C_{4h}	C_4, S_4
	$4/mmm$	$4mm$, 422, $\bar{4}m2$	D_{4h}	C_{4v}, D_4, D_{2d}
trigonal	$\bar{3}$	3	S_6	C_3
	$\bar{3}m$	32, $3m$	D_{3d}	D_3, D_{3d}
hexagonal	$6/m$	6, $\bar{6}$	C_{6h}	C_6, C_{3h}
	$6/mmm$	$6mm$, 622, $\bar{6}m2$	D_{6h}	C_{6v}, D_6, D_{3d}
cubic	$m\bar{3}$	23	T_h	T
	$m\bar{3}m$	432, $\bar{4}3m$	O_h	O, T_d

Symmetry in crystallography: a summary

Metric symmetry
Symmetry of the unit cell shape, ignoring contents
6 (7) possible shapes

Laue symmetry
Symmetry of the diffraction pattern, assuming Friedel's law (centrosymmetric)
11 possible Laue classes

Space group symmetry
Symmetry of the complete crystal structure
230 possible space groups

Point groups
Metric symmetry (unit cell shapes)
Laue classes
Crystal shapes
Molecules and their environments: general and special positions

Table 5 shows a summary of all 32 crystallographic point groups

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Miscellaneous further points

Asymmetric unit
The symmetry-independent part of the structure
A rational fraction of the unit cell
Related to other parts of the unit cell by space group symmetry operations
May be one molecule, more than one molecule, or a fraction of a molecule

General position
Not on a pure rotation axis, a mirror plane, or an inversion centre
Point group site symmetry = 1

Special position
On a pure rotation axis, a mirror plane, or an inversion centre,
 or more than one of these intersecting
Point group symmetry depends on the symmetry element(s) here
One or more coordinates with special values (e.g. 0, ½) or related (e.g. $x = y$)
Some coordinates and displacement parameters may need constraints