Crystal Systems and Space Groups

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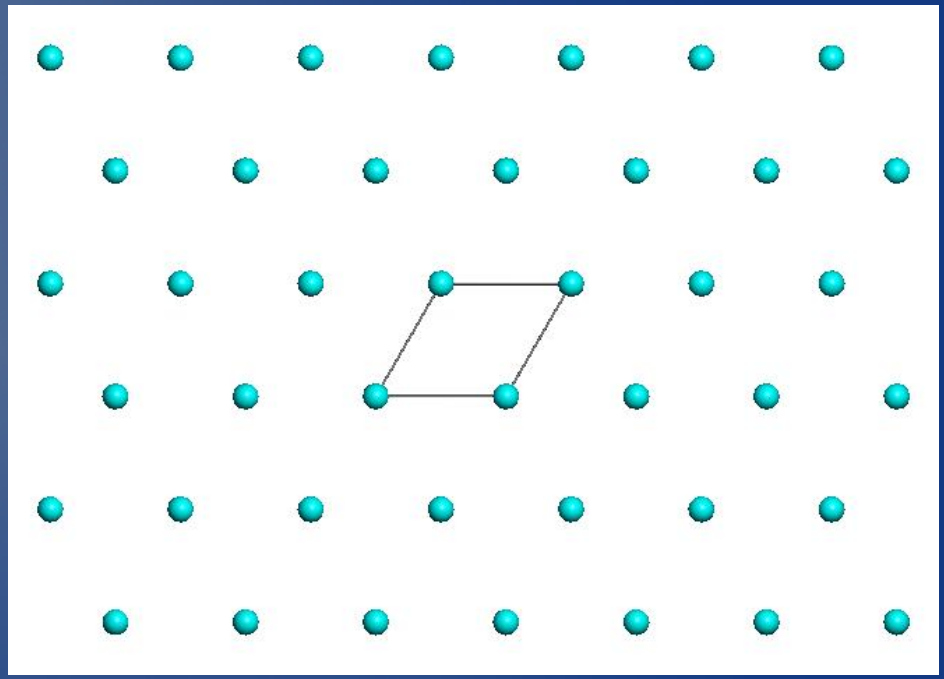
Lattices

- Lattices are a regular array of points
- We use **basis vectors** to describe the lattice
- The choice of basis vectors is not unique
- We choose the set of basis vectors which reflects the symmetry present in the lattice
- Transforming from one set of basis vectors does not change the lattice only our description of it



The Unit Cell

- Any 3 non-coplanar lattice translations may be used to define a unit cell (basis vectors)
- The basis vectors are referred to as **a**, **b**, **c**
- The angles between the vectors are referred to as α, β, γ

Primitive and Non-Primitive Unit Cells

- If the basis vectors are the 3 shortest lattice translations or if they describe a cell of equal volume, the lattice is referred to as a “primitive” lattice
- Lattice symbol is **P**
- A primitive lattice has one lattice point per unit cell
- “Non-primitive” lattices have more than one lattice point per unit cell

Non-primitive Lattice Translation Vectors

Designation	Extra lattice point(s)	Mnemonic Device	Centring Vector
A	bc face	Abc	(0, ½, ½)
B	ac face	aBc	(½, 0, ½)
C	ab face	abC	(½, ½, 0)
F	each face centre		(0, ½, ½); (½, 0, ½); (½, ½, 0)
I	body centre		(½, ½, ½)
R		(hexagonal setting)	(⅔, ⅓, ⅓); (⅓, ⅔, ⅔)

- Choosing a non-primitive vs. primitive lattice is a matter of convention and observable symmetry
- It is always possible to choose a primitive triclinic lattice
- Choose the lattice and crystal system which conforms to the observable symmetry

Different Unit Cells

- Buerger Cell: a unit cell comprised of the 3 shortest non-coplanar lattice vectors
- Niggli (or reduced) cell: a uniquely defined Buerger cell
- All primitive and non-primitive lattices can be reduced to their unique Niggli reduced cell
- Algorithm: Delaunay reduction gives the Niggli cell

Conventional Unit Cell

- Basis vectors define a right-handed system
- Unit cell edges lie along symmetry directions in the crystal
- Cell is the smallest cell compatible with conditions 1 and 2
- Niggli cells can always be transformed to a conventional setting (and vice versa)

Crystal Systems

There are 7 crystals systems and they are named: **Triclinic**, **Monoclinic**, **Orthorhombic**, **Tetragonal**, **Trigonal**, **Hexagonal**, and **Cubic**.

What differentiates one crystal system from another?

The order of its principal or characteristic symmetry

Crystal Systems & Their Symmetries

Crystal System	**Lattice & point symmetries**	**Metric Constraints** NOTE: "≠" means "not constrained to be equal to" rather than "not equal to"
Triclinic	**$\bar{1}$**, 1	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$
Monoclinic	**2/m**, 2, m	$a \neq b \neq c$; $\alpha = \gamma = 90^o$, $\beta \neq 90^o$
Orthorhombic	**mmm**, mm2, 222	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90^o$
Tetragonal	**4/mmm**, $\bar{4}$2m, 4mm, 422, 4/m, $\bar{4}$, 4	$a = b \neq c$; $\alpha = \beta = \gamma = 90^o$
Trigonal rhombohedral setting hexagonal setting	**$\bar{3}$m**, 3m, 32, $\bar{3}$, 3	 $a = b = c$; $\alpha = \beta = \gamma \neq 90^o$ $a = b \neq c$; $\alpha = \beta = 90^o$, $\gamma = 120^o$
Hexagonal	**6/mmm**, $\bar{6}$m$\bar{2}$, 6mm, 622, 6/m, $\bar{6}$, 6	$a = b \neq c$; $\alpha = \beta = 90^o$, $\gamma = 120^o$
Cubic	**m$\bar{3}$m**, $\bar{4}$3m, 432, m$\bar{3}$, 23	$a = b = c$; $\alpha = \beta = \gamma = 90^o$

Crystallographic Point Symmetries

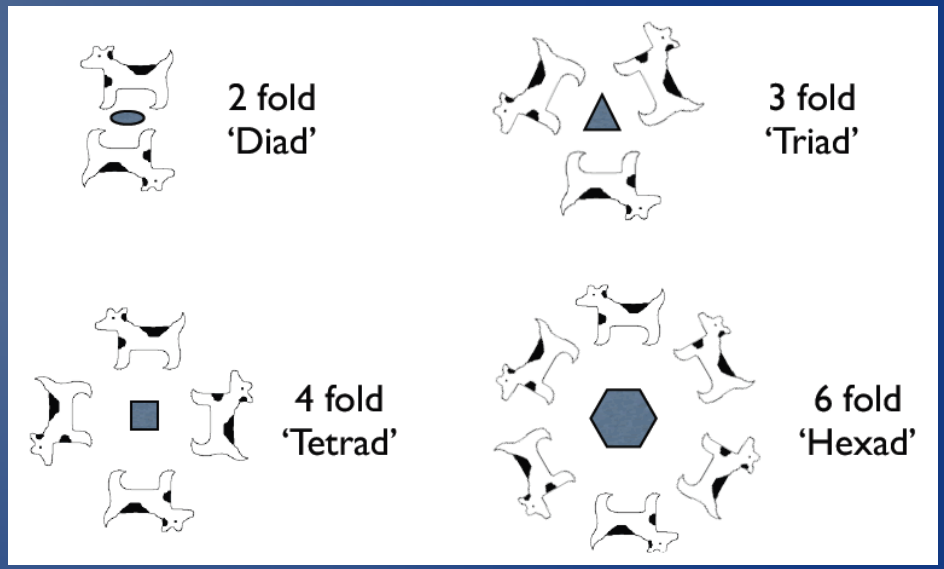
- Point symmetries are symmetries which all pass through a given point and this point does not change with the application of a symmetry operation
- The symmetry elements which constitute the crystallographic point groups are:
  - Proper rotation axes (n)
  - Mirror planes (m)
  - Inversion centre ($\bar{1}$, or no explicit symbol)
  - Rotary inversion axes ($\bar{n}$)
- Only n-fold axes where n = 1, 2, 3, 4, 6 are allowed for space filling 3 dimensional objects
- 32 unique crystallographic point groups are obtained from combining the various allowed rotation axes, mirror planes, and inversions
- 11 of the 32 crystallographic point groups are ***centrosymmetric***

Laue Groups and Holohedries

- **Laue groups:** the 11 centrosymmetric groups
  - Symmetry of the diffraction pattern as determined from the observed intensities
  - Matches the space group without any translations and adding a centre of symmetry
  - A crystal system can have more than one Laue group
- **Holohedry:** When the point group of a crystal is identical to the point group of its lattice
  - There are 7 holohedral point groups which correspond to the 7 crystal systems
  - Holohedries are always centrosymmetric
- All holohedries are Laue groups, but not all Laue groups are holohedries

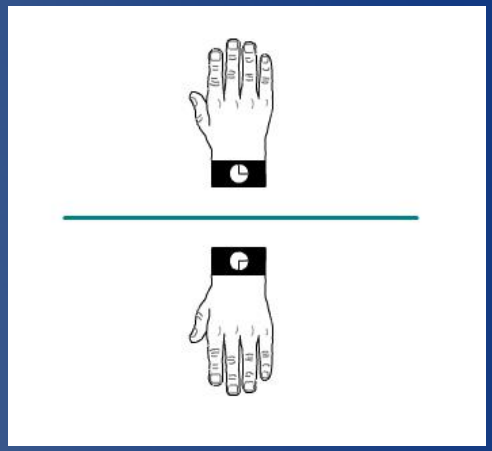
Proper Rotation Axes

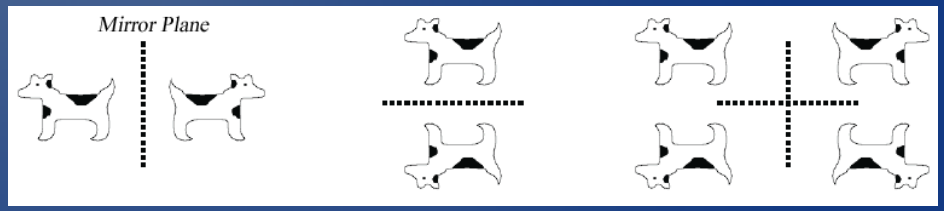
- Rotation about an axis by 360º/n.
- Symmetry operation of the first kind
- Doesn't change handedness of object



Mirror plane

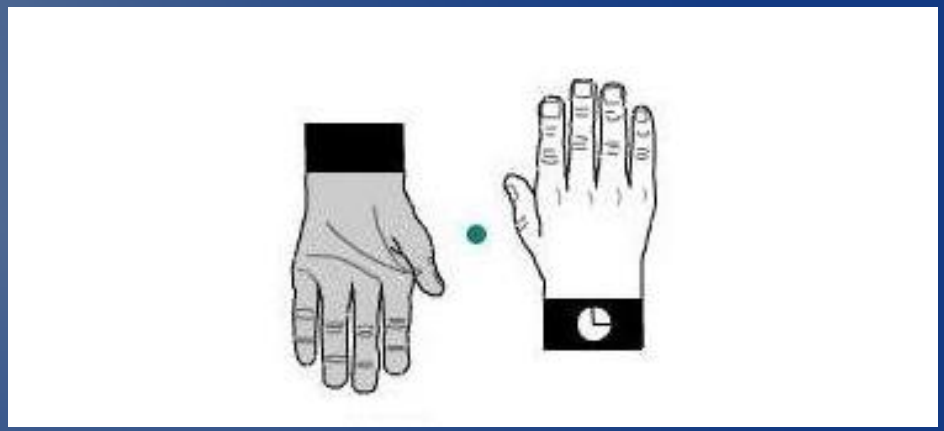
- Creates a reflected object
- Symmetry element of the second kind
- Changes handedness of object





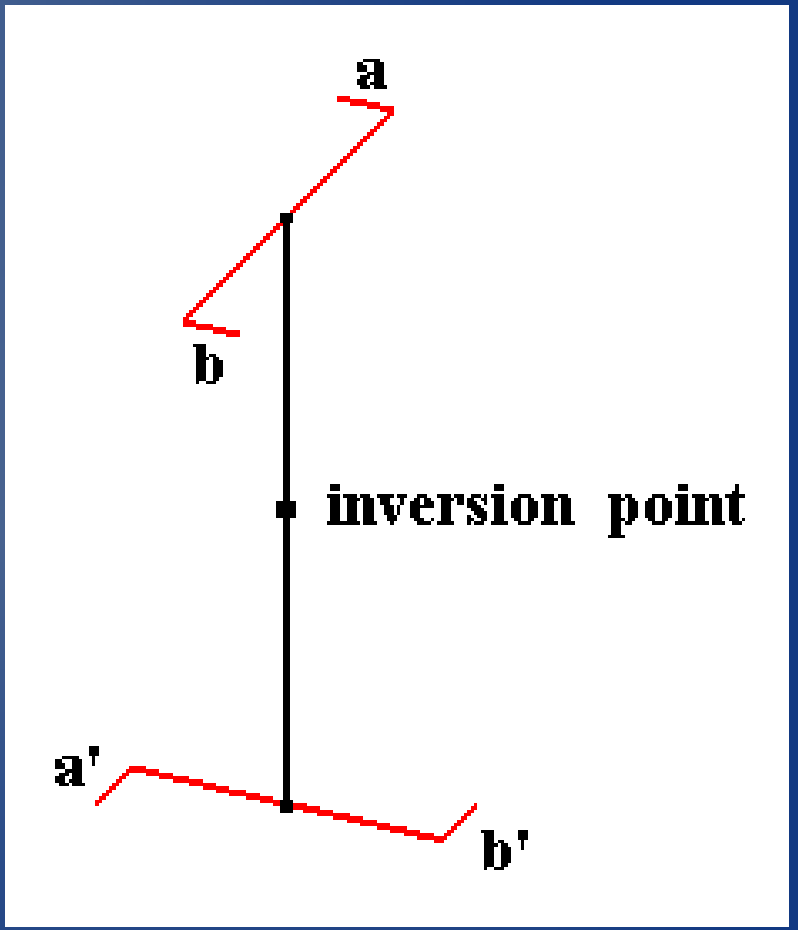
Inversion Centre

- Transforms x, y, z into $\bar{x}$, $\bar{y}$, $\bar{z}$
- Symmetry element of the second kind
- Changes handedness of object



Rotary Inversion Axis

- Rotation of 360º/n followed by inversion
- Symmetry element of the second kind
- Changes handedness of object
- $\bar{1}$ is equivalent to an inversion centre
- $\bar{2}$ is equivalent to a mirror plane



Symmetry Notation

- Spectroscopists use Schoenflies notation to describe symmetry (*e.g.* C_{2v}, D_{4h})
- Crystallographers use Hermann-Mauguin notation (International notation)
- Was introduced by Carl Hermann in 1928, modified by Charles-Victor Mauguin in 1931
- Adopted for the 1935 edition of the *International Tables for Crystallography*

Features of Hermann-Mauguin Notation

- Hermann-Mauguin notation is preferred for crystallography
  - Easier to add translational symmetry elements
  - Directions of symmetry axes are specified
- Quick things to note:
  - Interpretation of Hermann-Mauguin symbols depends on the crystal system
  - “n/m” notation means mirror plane perpendicular to n-fold axis
  - Hermann-Mauguin symbols have both “long” and “short” forms
  - Not all symmetry elements present are symbolized, some are left implicit

Brief Detour: Specifying Directions in a Crystal

- Miller Indices, h, k, l
- Specify a plane in a crystal by indexing the reciprocals of where the plane intersects the axes
- Example: a plane has axial intercepts at (-¼, ½, ⅓) the Miller index is ($\bar{4}$23)
- Planes, vectors, reciprocal lattice points, and forms may be specified using Miller indices
  - Plane: (hkl)
  - Vector: [hkl]
  - Reciprocal lattice point: hkl
  - Forms {hkl}
- In this lecture we will be using (hkl) and [hkl] often

Understanding Hermann-Mauguin Notation for Point Groups

Crystal System	1st Position	2nd Position	3rd Position	Point Groups
Triclinic	Only one position, denoting all directions in crystal			$\bar{1}$, 1
Monoclinic	Only 1 symbol: 2 or $\bar{2}$ ‖ to Y (*b* is principal axis)			**2/m**, 2, m
Orthorhombic	2 and/or $\bar{2}$ ‖ to X	2 and/or $\bar{2}$ ‖ to Y	2 and/or $\bar{2}$ ‖ to Z	**mmm**, mm2, 222
Tetragonal	4 and/or $\bar{4}$ ‖ to Z	2 and/or $\bar{2}$ ‖ to X and Y	2 and/or $\bar{2}$ ‖ to [110]	**4/mmm**, $\bar{4}$2m, 4mm, 422, 4/m, $\bar{4}$, 4
Trigonal	3 and/or $\bar{3}$ ‖ to Z	2 and/or $\bar{2}$ ‖ to X, Y, U		**$\bar{3}$m**, 3m, 32, $\bar{3}$, 3
Hexagonal	6 and/or $\bar{6}$ ‖ to Z	2 and/or $\bar{2}$ ‖ to X, Y, U	2 and/or $\bar{2}$ along [1$\bar{1}$0]	**6/mmm**, $\bar{6}$m$\bar{2}$, 6mm, 622, 6/m, $\bar{6}$, 6
Cubic	2 and/or $\bar{2}$ ‖ to X, Y, Z	3 and/or $\bar{3}$ ‖ to [111]		m$\bar{3}$, 23
	4 and/or $\bar{4}$ ‖ to X, Y, Z		2 and/or $\bar{2}$ along face diagonals	**m$\bar{3}$m**, $\bar{4}$3m, 432

Choosing the Correct Crystal System

- Do not assume the metric relations indicate the correct point group and crystal system!!!
- Correctly identify the Laue group symmetry of the diffraction pattern (equivalent intensities, R_{sym})
- The Laue symmetry indicates the crystal system of your sample
- Correct Laue group assignment narrows space group choices

Space Groups

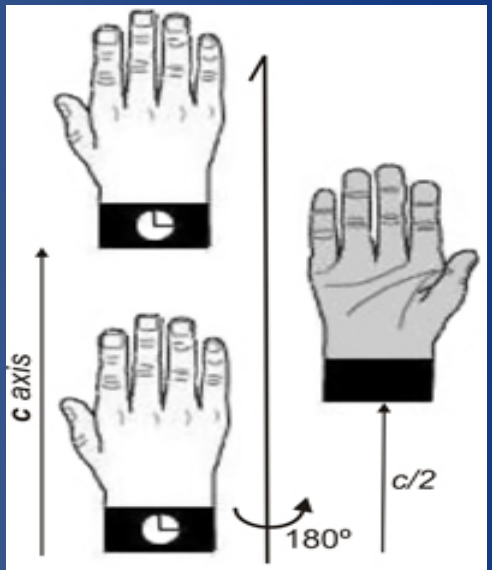
- Space groups vs Point groups
  - Point groups describe symmetry of isolated objects
  - Space groups describe symmetry of infinitely repeating space filling objects
- Space groups include point symmetry elements
- Space groups include additional *translational symmetry elements*
- The presence of translational symmetry elements causes systematic absences in the diffraction pattern

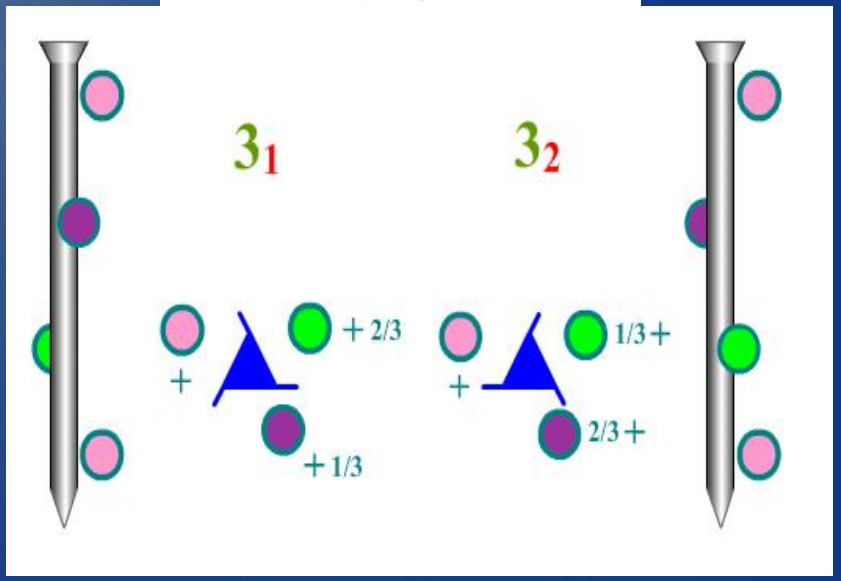
Translational Symmetry Elements

- Lattice Translations
  - Trivial unit cell translations
  - Translations due to centring vectors from non-primitive Bravais lattices
- Screw Axes – combine a rotation with translation
- Glide Planes – combine a reflection with translation

Screw Axes

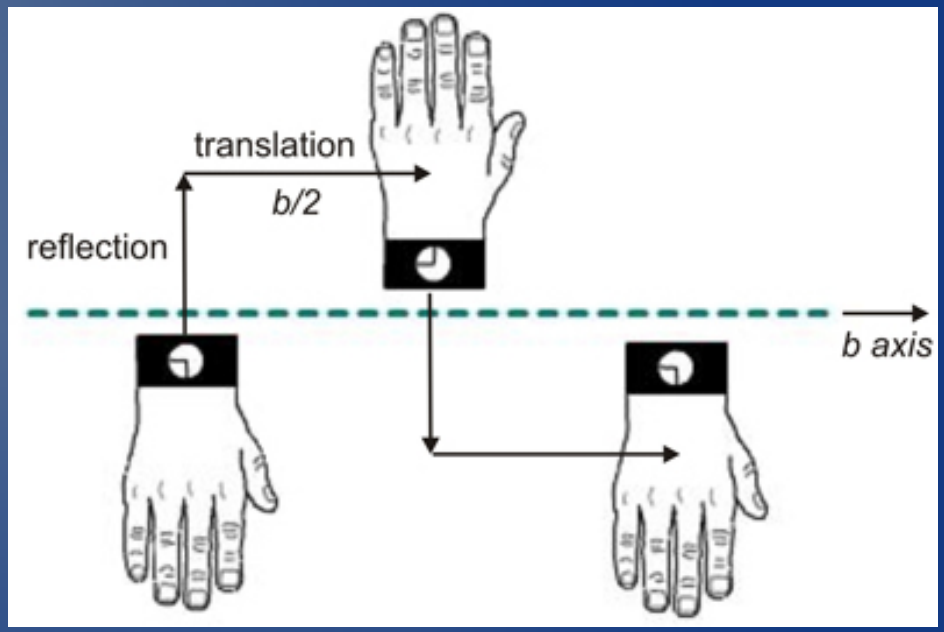
- Combines rotation and translation
- Designated as n_m (*e.g.* 2_1, 4_1, 3_2, 4_3)
- Rotation as 360º/n
- Symmetry element of the first kind
- Translation as m/n of a unit cell (n > m)
- Orientation of the screw axis given by its place in the H-M symbol
- Causes systematic absences in axial (h00,0k0,00l) reflections
- Certain pairs of screw axes correspond to right and left handed screws (*e.g.* 3_1 and 3_2) and are enantiomorphs





Glide Planes

- Combine reflection with translation
- Symmetry element of the second kind
- Designated as *a*, *b*, *c*, *d*, *n* and letter gives direction of translational component
- Orientation of reflection plane given by place in the H-M symbol
- Cause systematic absences in zero layers (0kl, h0l, and hk0) of the diffraction pattern

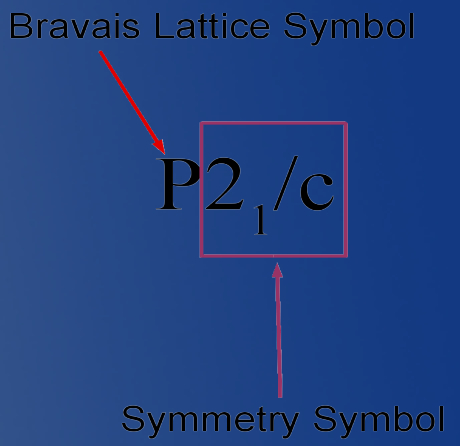


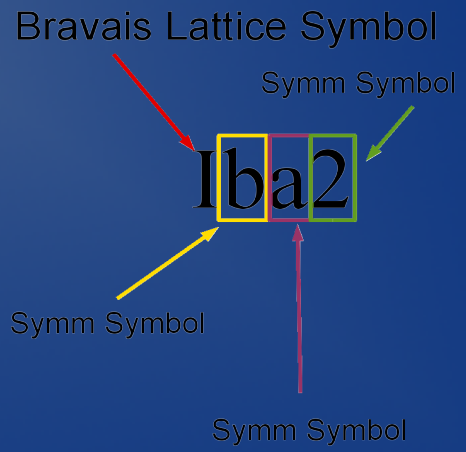
n and *d* Glide Planes

- *n* glides translate along face diagonals, (a+b)/2, (a+c)/2, or (b+c)/2
- *d* glides only occur F and I centred lattices
- *d* glides translate along face diagonals at ¼ along each direction, *i.e.* (a+b)/4, (a+c)/4, or (b+c)/4
- After 2 (or 4 for d glides) consecutive glide operations the point is identical to the original point plus a unit translations along 2 axes

Interpretation of Space Group Symbols

- Space group symbols consist of several parts
  - Bravais lattice type
  - List of symbols denoting type and orientation of symmetry elements
- Must know the Crystal System in order to correctly interpret the space group symbol





Interpretation of Space Group Symbols

- Perform the following steps:
  - Identify the point group of the crystal
    - Remove Bravais lattice type symbol
    - Iba2 →”ba2”
    - Convert all translational symmetry elements to their point counterparts (glides →mirror; screw axes → rotation axes)
    - “ba2” → mm2
  - Look up crystal system which corresponds to that point group (mm2 → orthorhombic)
  - Use Hermann-Mauguin rules for that crystal system

Interpretation of Iba2 Space Group Symbol

- Continue with Iba2 example
- Body centred
- *b* glide reflecting across (100)
- *a* glide reflecting across (010)
- 2-fold proper rotation parallel to [001]
- mm2 is an acentric point group. Therefore, Iba2 is an acentric space group

Notable Features of Space Groups

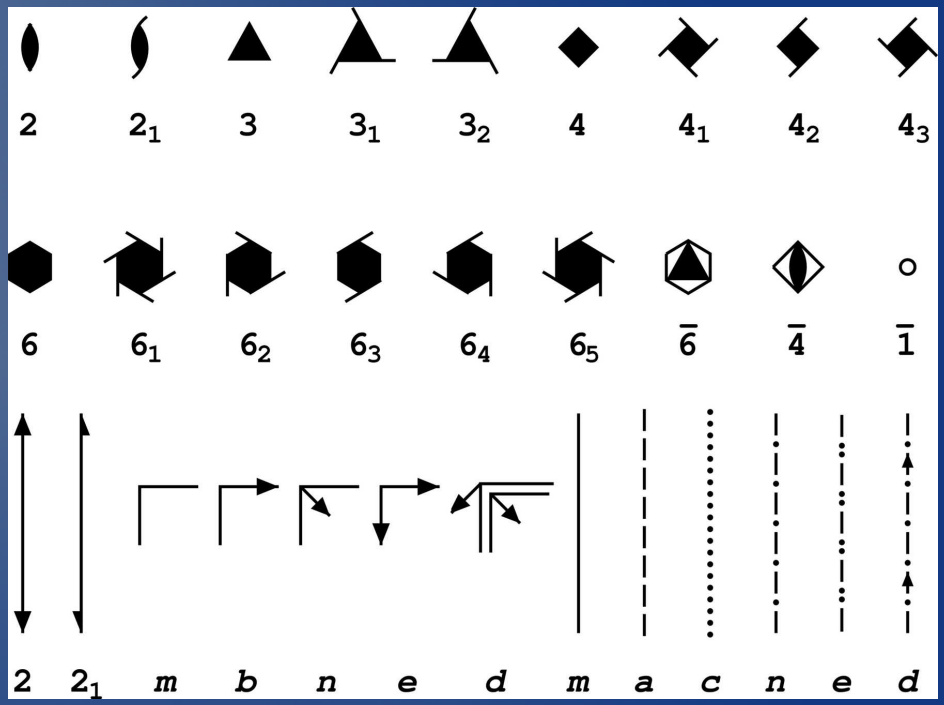
- Combining point symmetry and translational symmetry elements with the 14 Bravais lattices yields 230 unique space groups
- 73 of these are symmorphic space groups. These have no translational symmetry elements (*e.g.* P222, F23, Immm)
- 11 enantiomorphous pairs. If a (+) chiral molecule crystallizes in one of these space groups, the (-) enantiomer will crystallize in the other of the pair. *E.g.* $P6_122$ and $P6_522$
- Enantiopure compounds will crystallize in space groups which only contain symmetry elements of the first kind. There are 65 of these space groups

Representations of Symmetry

- Graphical Representation
  - Qualitative and Symbolic
  - Non-mathematical
  - Visually intuitive (for the most part)
- Equivalent positions (x,y,z)
  - Simple algebraic expressions
  - Good for humans
- Matrix Representation
  - Easy to transform
  - Numerically oriented
  - Good for computers
- ORTEP Representation
  - Compact notation of symmetry operation and unit cell translations
  - Related representations found in PLATON, XP, and CIF

Graphical Representation of Symmetry Elements

- Proper rotations depicted as symbols with the number of vertices which corresponds to n
- Screw axes have same symbol, but have “tails”
- Enantiomeric pairs of screw axes (*e.g.* 6_1 and 6_5) are mirror images of each other



Equivalent Position Representation

- Simple algebraic expressions
- Good for humans

- $P2_1/c$ example
  - (1) x, y, z
  - (2) $\bar{x}$, y + ½, $\bar{z}$ + ½
  - (3) $\bar{x}$, $\bar{y}$, $\bar{z}$
  - (4) x, $\bar{y}$ + ½, z + ½

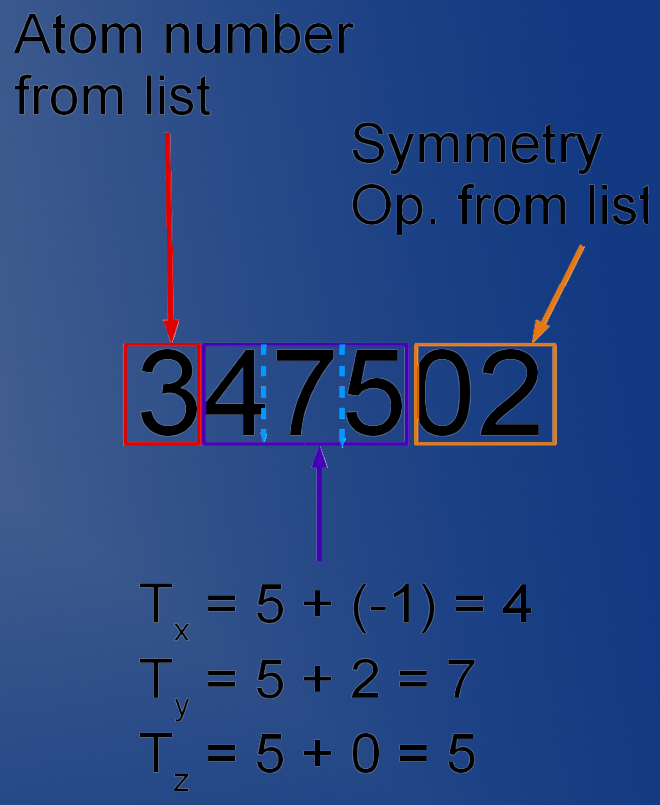
Matrix Representation of Symmetry

- Symmetry operator can be partitioned into a rotational part and a translational part
- Rotations can be described as simple 3x3 matrices. Matrix elements are either 1, 0, or -1
- Translations described as 3x1 matrix
- v' = Rv + t where v = [x,y,z]
- For example, in $P2_1/c$ the equivalent position: $\bar{x}$, y+ ½, $\bar{z}$ + ½ looks like this in matrix representation:

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} + \begin{bmatrix} 0 \\ 1/2 \\ 1/2 \end{bmatrix}$$

ORTEP Symmetry Representation

- Early days of computing memory was expensive
- Needed compact way to depict symmetry equivalent atomic positions including translations
- Avoid negative numbers in unit cell translations
- “5” is the new “0”
- Example: 347502
- Depends on lists of atoms and symmetry operators elsewhere in the file or the program



PLATON, XP, and CIF Symmetry Codes

- Derived and modified from original ORTEP scheme, maintains compactness
- PLATON: [sym_op][$T_x T_y T_z$].[residue]
  - *e.g.* 2565.01
- XP: [sym_op][$T_x T_y T_z$]
  - *e.g.* 2565
- CIF: [sym_op]_[$T_x T_y T_z$]
  - *e.g.* 2_565
- All depend on a list of symmetry operators being defined somewhere else in the file or the software

International Tables for Crystallography

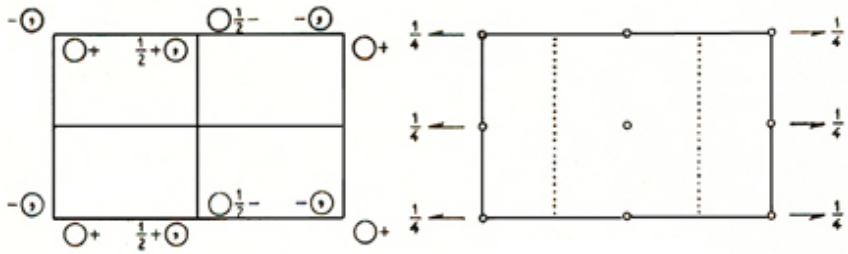
- Information on crystallographic symmetry and related topics has been codified and published in the *International Tables for Crystallography*
- Originally published in 1935, the work has been revised and expanded to include all sorts of topics relevant to X-ray Crystallography
- We will only concern ourselves with material related to space groups (Volume A)

Using the International Tables for X-ray Crystallography

- The *International Tables* (IT) contain information on all space groups
- Most common information used by crystallographers:
  - Graphical depictions
  - Equivalent positions
  - Special positions and site symmetries
  - Systematic absence conditions

Example of International Tables Entry ($P2_1/c$)

Monoclinic $2/m$ — $P\,1\,2_1/c\,1$ — No. 14 — $P\,2_1/c$ — C_{2h}^5



Origin at $\bar{1}$; unique axis b — 2ND SETTING

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions	Conditions limiting possible reflections
				General:
4	e	1	x,y,z; $\bar{x},\bar{y},\bar{z}$; $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$; $x,\frac{1}{2}-y,\frac{1}{2}+z$.	hkl: No conditions $h0l$: $l=2n$ $0k0$: $k=2n$
				Special: as above, plus
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$.	hkl: $k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$; $0,\frac{1}{2},0$.	hkl: $k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.	hkl: $k+l=2n$
2	a	$\bar{1}$	$0,0,0$; $0,\frac{1}{2},\frac{1}{2}$.	hkl: $k+l=2n$

Symmetry of special projections

(001) pgm; $a'=a$, $b'=b$ — (100) pgg; $b'=b$, $c'=c$ — (010) $p2$; $c'=c/2$, $a'=a$

Experimental Determination of Space Group

- Space groups are determined primarily through the examination of systematic absences
- Some space groups are uniquely determined by the systematic absences, others are not
- For ambiguous cases, very often the choice is between a centric and acentric space group, *e.g.* $Pca2_1$ and Pbcm

Systematic Absences due to Non-Primitive Lattices

- Non-primitive lattices exhibit systematic absences in the general hkl class of reflection

Centring	Absence Condition for hkl reflections
A	k+l = odd
B	h+l = odd
C	h+k = odd
F	k+l = odd, h+l = odd, h+k = odd
I	h+k+l = odd

Screw Axis Absences

- Screw axes affect the classes of axial reflections: h00, 0k0, and 00l
- The type of screw axis is determined by examining the pattern of the absence
- Example: consider 6 fold screws along c axis:
  - 6_1 or 6_5, 00l: l = 6n + 1, 2, 3, 4, 5 (not divisible by 6)
  - 6_2 or 6_4, 00l: l = 3n+1, 2 (not divisible by 3)
  - 6_3, 00l: l = 2n+1 (not divisible by 2)

Orientation of Glide Planes

- When a glide plane is present one can determine the orientation and type of glide plane from the affected class(es) of reflections
- The 0 index of the affected layer indicates the orientation of the glide's reflection plane
  - 0kl: glide reflects across (100)
  - h0l: glide reflects across (010)
  - hk0: glide reflects across (001)

Identification of Glide Planes

- The translational component identifies the type of glide plane
- The translational component causes absences along the affected axes
- 0kl:
  - k = odd → b glide; l = odd → c glide; k+l = odd → n glide
- h0l:
  - h = odd → a glide; l = odd → c glide; h+l = odd → n glide
- hk0:
  - h = odd → a glide; k = odd → b glide; h+k = odd → n glide

Conventional Settings

- Space group symbols depend on choice of axes
- Minimize ambiguity by following established conventions (unless there is a reason to break from convention)
- *International Tables* gives conventional settings
  - Lots of different rules
  - Learn through experience
- Some examples (conventional setting **bold**):
  - $P2_1/a$ is the same $\mathbf{P2_1/c}$
  - Pcab is the same as **Pbca**
  - $Pc2_1b$ is the same as $\mathbf{Pca2_1}$

Space Group Ambiguities

- Sometimes space group extinctions do not uniquely identify the space group
- In these cases, use some rules of thumb
  - Centric groups are more common than acentric groups. Therefore, try solving with the centric group first
  - Alternative approach: start with acentric group and look for missing symmetry after structure solution

Problems with Systematic Absences

- Sometimes systematic absences which should be there are violated for a couple of reasons
  - Twinning:
    - reflections from an alien lattice occur where absences from primary lattice should be
    - Twinning can cause a mis-indexing of lattice and upset the systematic absence patterns
  - Renninger effect (“double diffraction”) can cause apparent violations of systematic absence conditions
- Systematically weaker reflections due to pseudotranslational effects are missed and counted as absences when they should not be. *E.g.* mistaking a primitive cell to be a centred cell

Subtleties in Space Group Determination

- Space groups P$\bar{3}$m1, P$\bar{3}$1m, P3m1, and P31m are symmorphic space groups (no translational symmetry elements)
- Can we differentiate them in some way to identify the space group?
- P$\bar{3}$m1, P$\bar{3}$1m are distinguishable on the basis of their Laue symmetry equivalent intensities
- We cannot distinguish P$\bar{3}$m1 from P3m1 nor P$\bar{3}$1m from P31m (centric/acentric pairs of space groups)
- Similarly we can differentiate P6/m from P6/mmm on the basis of Laue intensity distributions

Conclusion

- Understanding symmetry in general and space groups in particular is essential to successful structure determination
- Incorrect assignment of crystal system and space group constitute serious errors in crystal structure analysis
- Thoughtfulness and experience are essential to becoming proficient in space group assignment