

Crystal Systems and Crystallographic Point Groups

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Point Symmetry & Crystallography

- Symmetry is fundamental in crystallography
- Determines what properties a material can have:
 - Piezoelectricity
 - Non-linear optical properties
 - etc.
- Determines how we refine crystal structures and what conclusions we can draw from our structure determinations
 - Centrosymmetric or non-centrosymmetric
 - Polar or non-polar group, enantiomeric group
 - Absolute structure and absolute configuration

Hermann-Mauguin 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*
- Hermann-Mauguin notation is preferred for crystallography
 - Easier to add translational symmetry elements
 - Directions of symmetry axes are specified

Notes on Hermann-Mauguin Notation

- 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

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**

Lattices and Symmetry

- 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

3-fold Rotation in Different Coordinate Systems

- The coordinate system makes a difference how symmetry operations are expressed
- Using cartesian systems are more complicated in crystallography
- Involves calculation of transcendental functions

Cartesian Coordinate System

$$\begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Trigonal Coordinate System

$$\begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Crystal Systems

There are 7 crystal 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: “ \neq ” 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	$a \neq b \neq c$; $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$
Orthorhombic	mmm , $mm2$, 222	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$4/mmm$, $\bar{4}2m$, $4mm$, 422, $4/m$, $\bar{4}$, 4	$a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$
Trigonal rhombohedral setting hexagonal setting	$\bar{3}m$, 3m, 32, $\bar{3}$, 3	$a = b = c$; $\alpha = \beta = \gamma \neq 90^\circ$ $a = b \neq c$; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$
Hexagonal	$6/mmm$, $\bar{6}m\bar{2}$, $6mm$, 622, $6/m$, $\bar{6}$, 6	$a = b \neq c$; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$
Cubic	$m\bar{3}m$, $\bar{4}3m$, 432, $m\bar{3}$, 23	$a = b = c$; $\alpha = \beta = \gamma = 90^\circ$

Categories of Crystallographic Point Groups

- Centrosymmetric (11 of the 32 point groups)
- Non-centrosymmetric (non-exclusive categories)

Enantiomorphic: Point groups which contain only proper rotation axes

- Enantiopure compounds can only crystallize in crystals which have these point symmetries
- SHELXL hint: Flack parameter should be refined, absolute configuration determination is possible

Polar: Point groups which have a “polar” sense to them

- Polar groups are non-centrosymmetric, but may have symmetry elements of the second kind
- Samples which crystallize in these point group may be racemic
- SHELXL hint: Flack parameter should be refined, **absolute structure determination is possible but absolute configuration cannot be determined if point group contains symmetry elements of the second kind**

Laue Groups and Holohedries

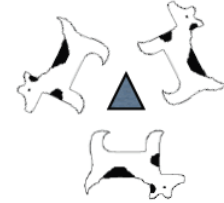
- **Laue groups:** the 11 centrosymmetric groups
 - Symmetry of the diffraction pattern as determined from the observed intensities
 - Matches the space group without any translations and adding a centre of symmetry
 - A crystal system can have more than one Laue group
- **Holohedry:** When the point 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

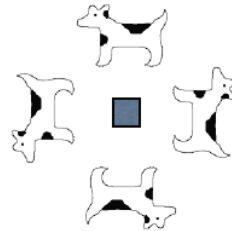
- Rotation about an axis by $360^\circ/n$.
- Symmetry operation of the first kind
- Doesn't change handedness of object



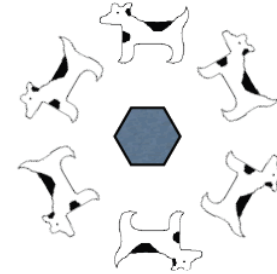
2 fold
'Diad'



3 fold
'Triad'



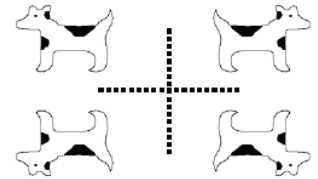
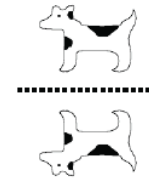
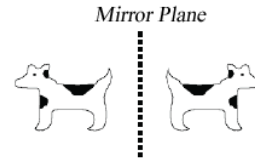
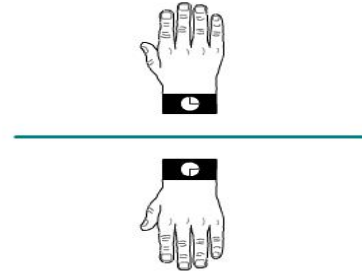
4 fold
'Tetrad'



6 fold
'Hexad'

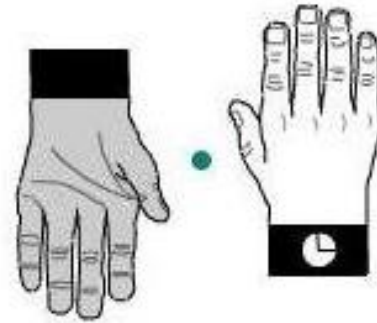
Mirror plane

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



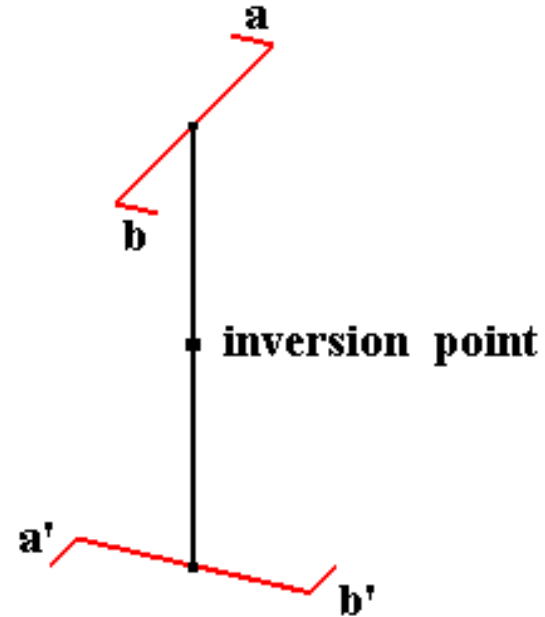
Inversion Centre

- 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 $360^\circ/n$ 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



Understanding Hermann-Mauguin Notation for Point Groups

- See next slide for your Hermann-Mauguin Secret Decoder Ring!

Crystal System	1 st Position	2 nd Position	3 rd 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 (<i>b</i> 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 [110]	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