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

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

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: "≠" means "not constrained to be equal to" rather than "not equal to"
Triclinic	$\mathbf{\bar{1}}$, 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	$\mathbf{\bar{3}m}$, 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	$\mathbf{m\bar{3}m}$, $\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***

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

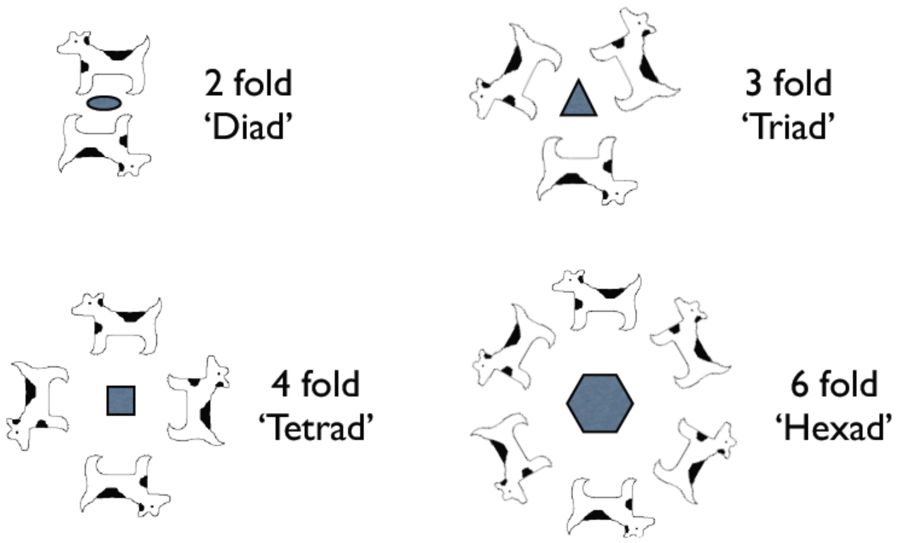
- Polar groups are non-centrosymmetric, but may have symmetry elements of the second kind
- Samples which crystallize in these point group may be racemic
- SHELXL hint: Flack parameter should be refined, **absolute structure determination is possible but <u>absolute configuration</u> cannot be determined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

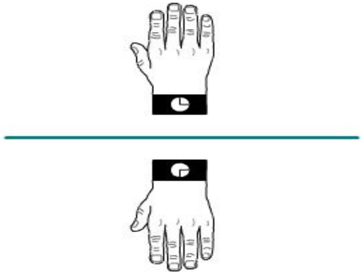
Proper Rotation Axes

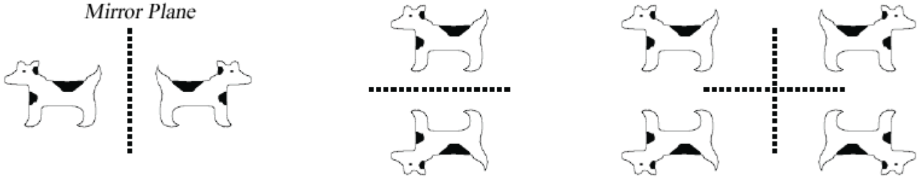
- Rotation about an axis by 360º/n.
- Symmetry operation of the first kind
- Doesn't change handedness of object



Mirror plane

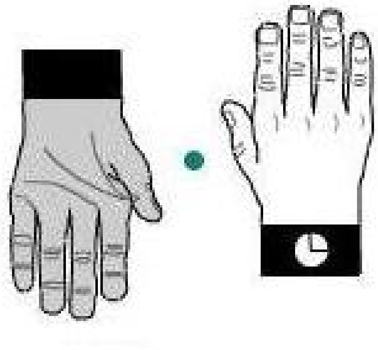
- Creates a reflected object
- Symmetry element of the second kind
- Changes handedness of object





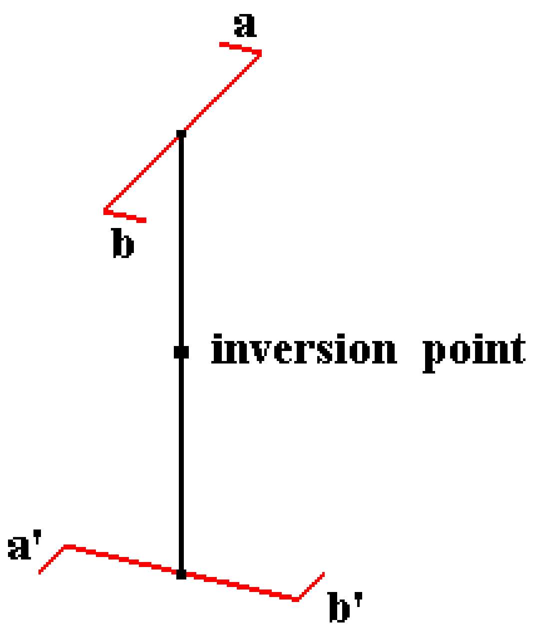
Inversion Centre

- 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*
- 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

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			m$\bar{3}$, 23

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