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 to another basis 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: "≠" 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	$a = b = c$; $\alpha = \beta = \gamma = 90^o$

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

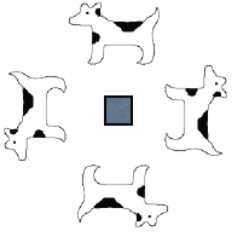
- **Laue groups:** the 11 centrosymmetric groups
  - Symmetry of the diffraction pattern as determined from the observed intensities
  - Matches the space group without any translations and adding a centre of symmetry
  - A crystal system can have more than one Laue group
- **Holohedry:** When the point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

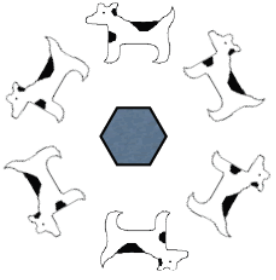
- Rotation about an axis by 360º/n.
- Symmetry operation of the first kind
- Doesn't change handedness of object

2 fold
'Diad'

3 fold
'Triad'



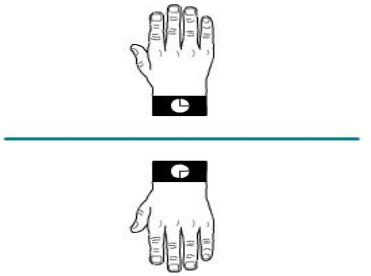
4 fold
'Tetrad'

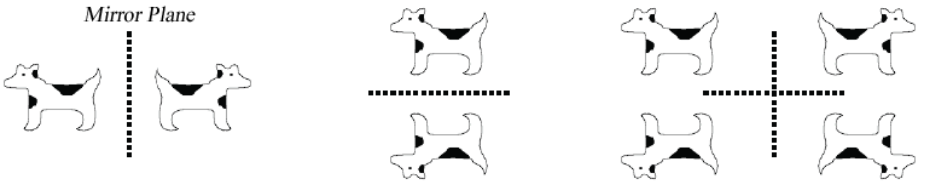


6 fold
'Hexad'

Mirror plane

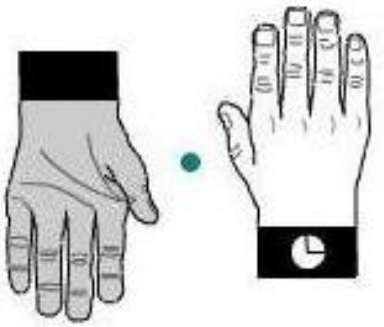
- Creates a reflected object
- Symmetry element of the second kind
- Changes handedness of object





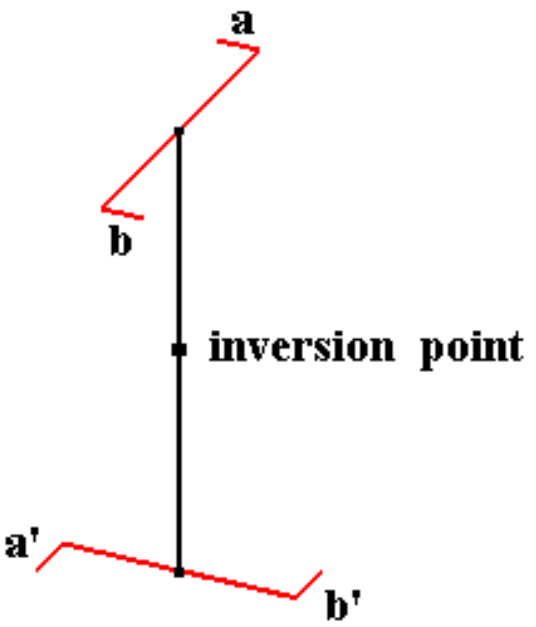
Inversion Centre

- 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 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



Understanding Hermann-Mauguin Notation for Point Groups

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

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

How do symmetry operators work numerically (i.e. in real life)?

- Fractional atomic coordinates are actually vectors
- Symmetry operators operate on vectors to give a new vector
- **v’** = **Sv**
- where **S** is a 3x3 matrix and **v** is a 3x1 column vector

```
julia> using LinearAlgebra

julia> three_fold_rotation = [ 0 -1 0; 1 -1 0; 0 0 1]
3×3 Matrix{Int64}:
 0  -1  0
 1  -1  0
 0   0  1

julia> v = [ 0.127; -0.229; 0.352]
3-element Vector{Float64}:
  0.127
 -0.229
  0.352

julia> v_new = three_fold_rotation * v
3-element Vector{Float64}:
 0.229
 0.356
 0.352
```

Caveat!

- Symmetry operators in reciprocal space (i.e. in the diffraction pattern) are different than direct space operators
- $S^* = \overline{S}^{-1}$
- Important for trigonal and hexagonal point groups

```
julia> using LinearAlgebra

julia> three_fold_rotation = [ 0. -1. 0.; 1. -1. 0.; 0. 0. 1.]
3×3 Matrix{Float64}:
 0.0  -1.0  0.0
 1.0  -1.0  0.0
 0.0   0.0  1.0

julia> recip_three_fold_rotation = transpose( inv( three_fold_rotation ) )
3×3 transpose(::Matrix{Float64}) with eltype Float64:
 -1.0  -1.0  0.0
  1.0   0.0  0.0
 -0.0   0.0  1.0
```

Characterizing Point Symmetry Rotation Matrices

- Rotation matrices can be characterized using some elementary matrix operations
  - Determinant
  - Trace
- Calculation of rotation angle
- Eigenvalues and Eigenvectors are used to give the orientation of the rotation axis

Determinant and Trace of a Matrix

- Determinant
  - Characterizes some property of a matrix
  - For crystallographic symmetry rotation matrices the values the determinant are +1 or -1
  - +1 means the symmetry operation maintains the handedness of the object (symmetry operation of the first kind)
  - -1 means the symmetry operation changes the handedness of the object (symmetry operation of the second kind)
- Trace
  - The sum of the diagonal values of a matrix
  - The order of the rotation axis (n) can be derived from the trace

Using Determinant and Trace to Characterize Symmetry Matrices

Symmetry Element	Determinant	Trace
1	1	3
2	1	-1
3	1	0
4	1	1
6	1	2
$\bar{1}$	-1	-3
$\bar{2}$	-1	1
$\bar{3}$	-1	0
$\bar{4}$	-1	-1
$\bar{6}$	-1	-2

The combination of the determinant and the trace determines the order of the rotation and whether it is a proper or improper rotation

Calculation of Rotation Angle from Determinant and Trace

$$\phi = \cos^{-1}\left(0.5\left(\frac{t}{d} - 1.0\right)\right)$$

Eigenvalues and Eigenvectors of Crystallographic Symmetry Rotation Matrices

- One of the eigenvectors gives the orientation of the rotation axis
- A 3x3 matrix can have 3 eigenvalues and 3 eigenvectors (can be real or complex quantities). How to choose the correct eigenvalue/eigenvector pair?
- Criteria:
  - Choose the **real** eigenvalue which has the **same sign** as the determinant
  - Choose the eigenvector which corresponds to the chosen eigenvalue

Worked Example of Determining Orientation of Rotation Axis

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

```
julia> three_fold_axis
3×3 Matrix{Int64}:
 0  -1  0
 1  -1  0
 0   0  1

julia> det(three_fold_axis)
1.0

julia> tr(three_fold_axis)
0

julia> eigvals(three_fold_axis)
3-element Vector{ComplexF64}:
 -0.49999999999999994 - 0.8660254037844386im
 -0.49999999999999994 + 0.8660254037844386im
                  1.0 + 0.0im

julia> eigvecs(three_fold_axis)
3×3 Matrix{ComplexF64}:
 -0.707107-0.0im        -0.707107+0.0im        0.0+0.0im
 -0.353553-0.612372im   -0.353553+0.612372im   0.0+0.0im
       0.0-0.0im              0.0+0.0im        1.0+0.0im

julia>
```

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