Introduction to Crystallography

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Outline

1. Crystal structures, symmetry, lattices, unit cells and crystal systems.

2. Elements of point symmetry and point groups.

3. Elements of translation symmetry and space groups.

4. Crystal structures, symmetry operations, equivalent positions, special positions and site multiplicities.

5. Crystal planes, d-spacing, *hkl* indices and plan multiplicities.

What is a Crystal Structure?

- A crystal structure is a pattern of atoms which repeats periodically in three dimensions (3D).
- The pattern can be as simple as a single atom, or complicated like a large organic molecule or protein.
- The periodic repetition can be represented using a 3D lattice.
- The atomic pattern and the lattice generally both exhibit elements of symmetry.

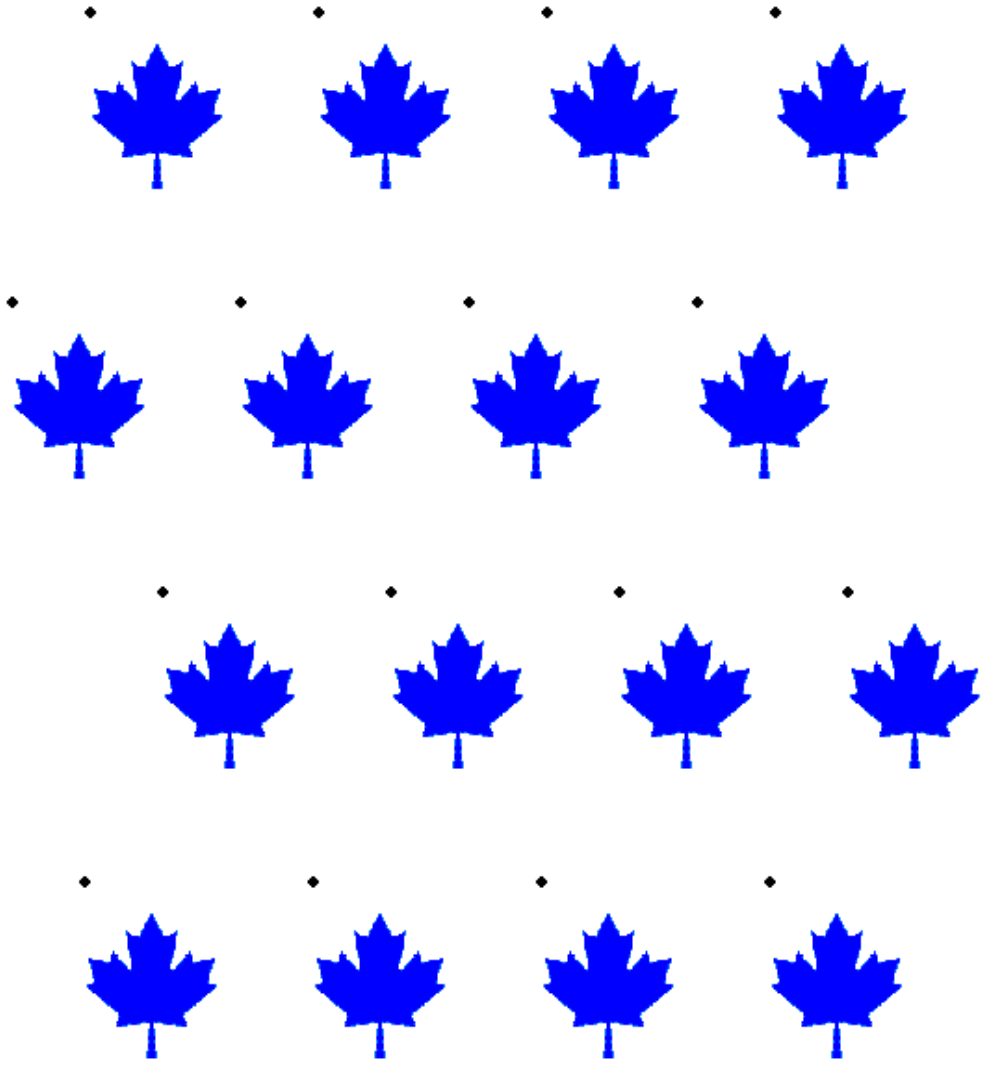
What is Symmetry?

- An object has symmetry if an operation or movement leaves the object in a position indistinguishable from the original position.

- Crystals have two types of symmetry we have to consider:
  - Point symmetry (associated with the atomic pattern).
  - Translational symmetry (associated with the crystal lattice).

What is a Lattice?

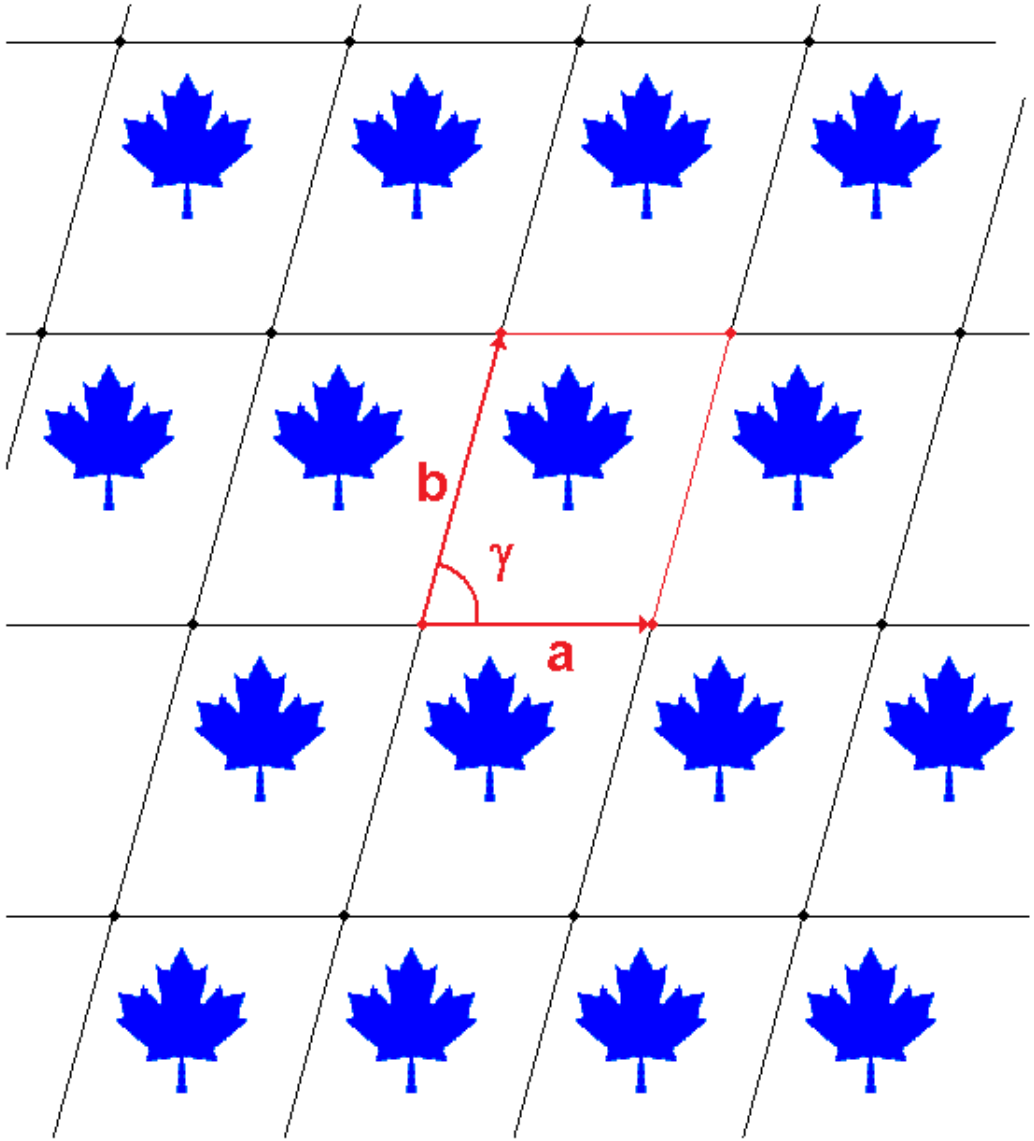
- Consider a periodic pattern in 2D.
- A system of points can be obtained by choosing a random point with respect to the pattern.
- All other points identical to the original point form a set of lattice points.



Lattice Points and Unit Cells

- By connecting our lattice points, we divide the area into parallelograms.

- Each parallelogram represents a **unit cell**, a basic building block which can be used to replicate the entire structure.

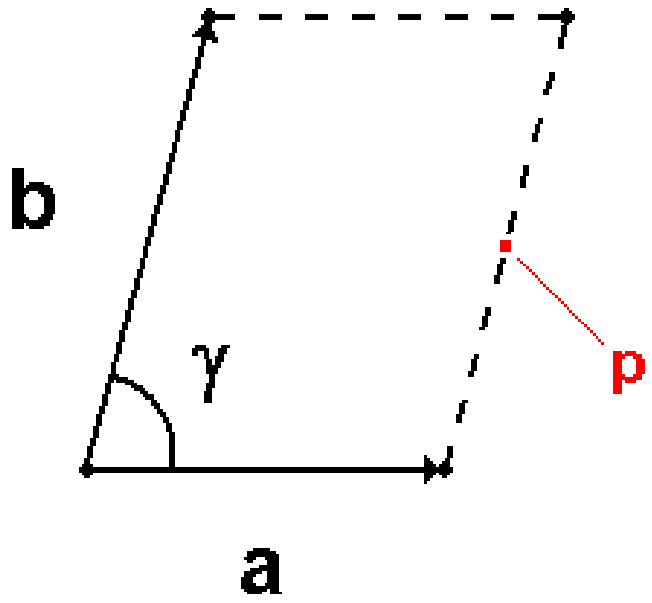


Unit Cell (2D)

- The size and shape of the unit cell can be described by **2 basis vectors** (two edge lengths, a & b, and the angle γ).
- Any position in the unit cell can be described in terms of the basis vectors with fractional coordinates:

  Point **p** → (1, ½) = 1 **a** + 0.5 **b**

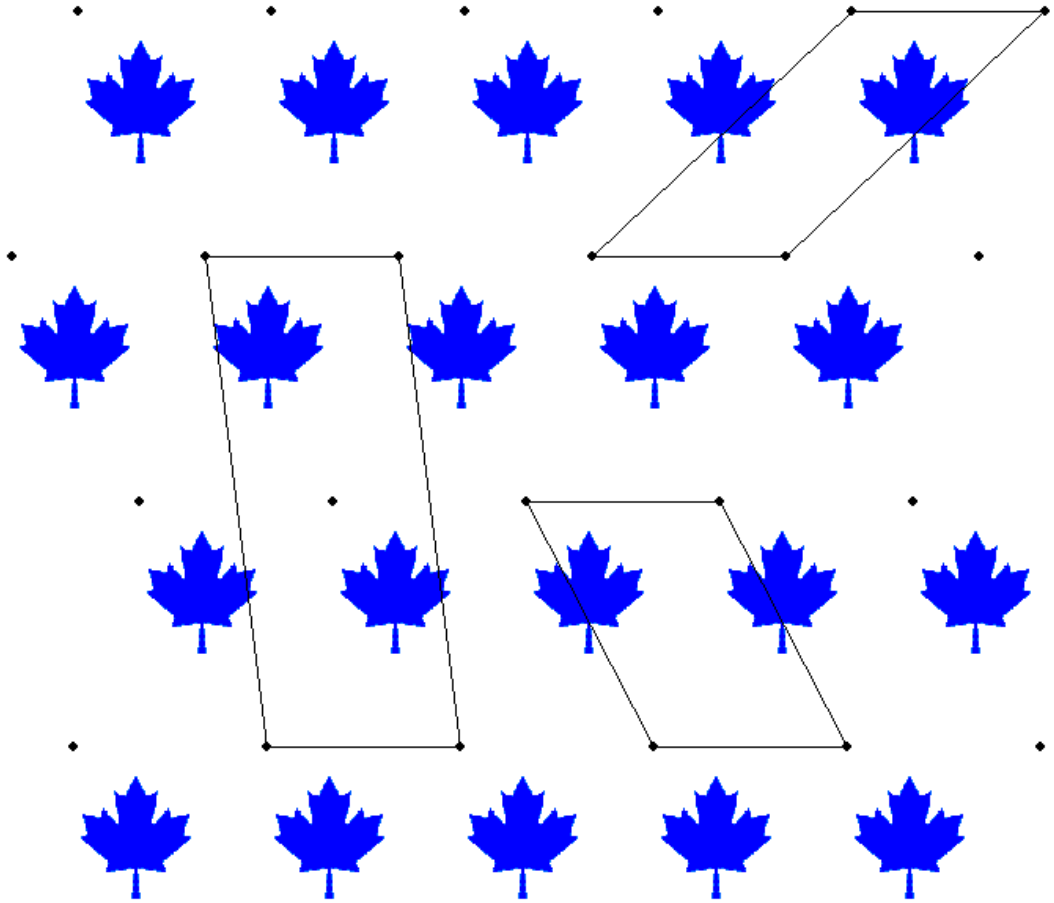
- Every lattice point can be generated by integer translations of the basis vectors (**t** = u**a** + v**b**, where u & v are integers).



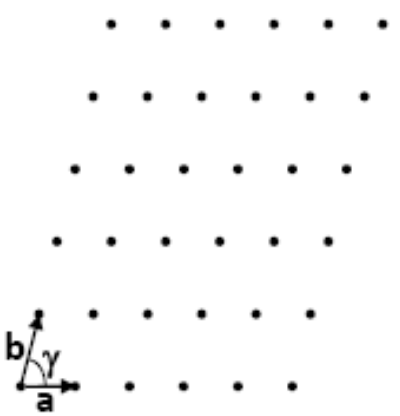
Choice of Unit Cell

- The choice of unit cell is not unique.

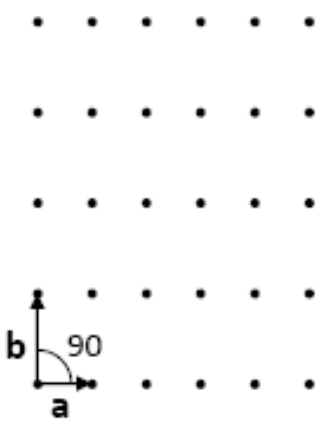
- A unit cell with lattice points only at the corners (1 lattice point per cell) is called **primitive**, while a unit cell with additional lattice points is called **centered**.



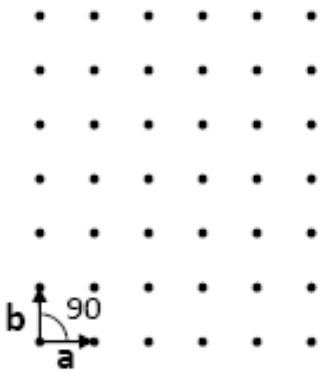
2D Planar Systems



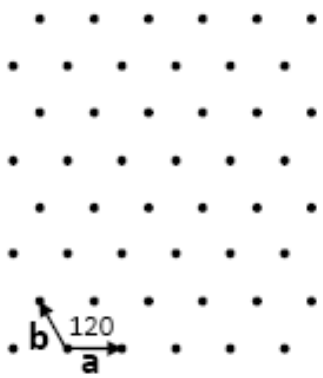
Oblique
(a, b, γ)
2-fold symmetry



Rectangular
(a, b, 90)
2-fold symmetry
Mirror symmetry



Square
(a, a, 90)
4-fold symmetry
Mirror symmetry

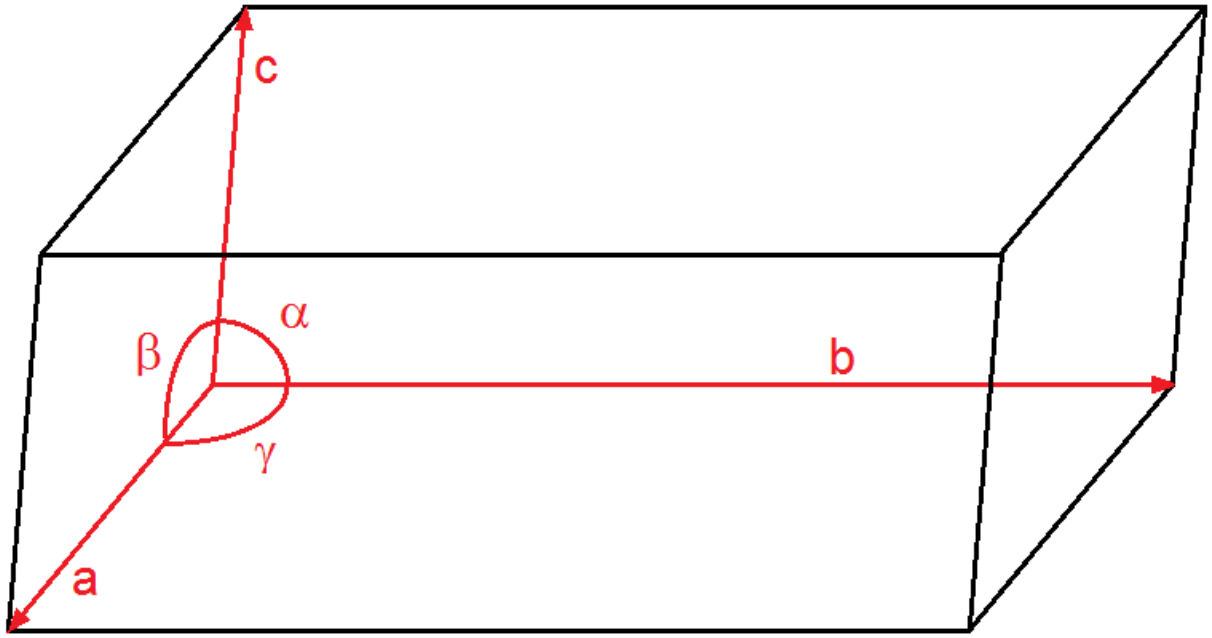


Hexagonal
(a, a, 120)
6-fold symmetry
Mirror symmetry

Figure courtesy of Michael Gharghouri.

Unit Cell (3D)

- The 3D unit cell size and shape can be fully described using **3 basis vectors** (three lengths a, b & c and three angles α, β & γ).

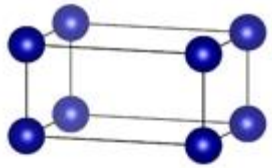


- The volume of the unit cell is given by:

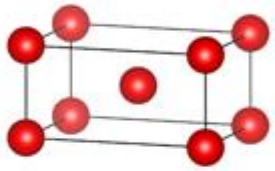
$$V = abc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}$$

3D Crystal Systems

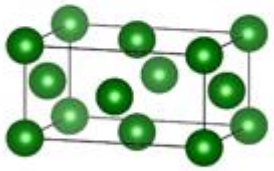
System	Lattice Parameter Restrictions	Bravais Lattices
Triclinic (Anorthic)	a, b, c, α, β, γ	aP
Monoclinic	a, b, c, 90, β, 90	mP, mC
Orthorhombic	a, b, c, 90, 90, 90	oP, oC, oI, oF
Trigonal	a, a, a, α, α, α a, a, c, 90, 90, 120	R hP
Hexagonal	a, a, c, 90, 90, 120	hP
Tetragonal	a, a, c, 90, 90, 90	tP, tI
Cubic	a, a, a, 90, 90, 90	cP, cI, cF



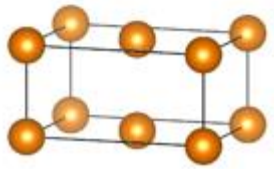
Primitive (P)



Body Centered (I)



Face Centered (F)



Base Centered (C)

Redundant Bravais Lattices

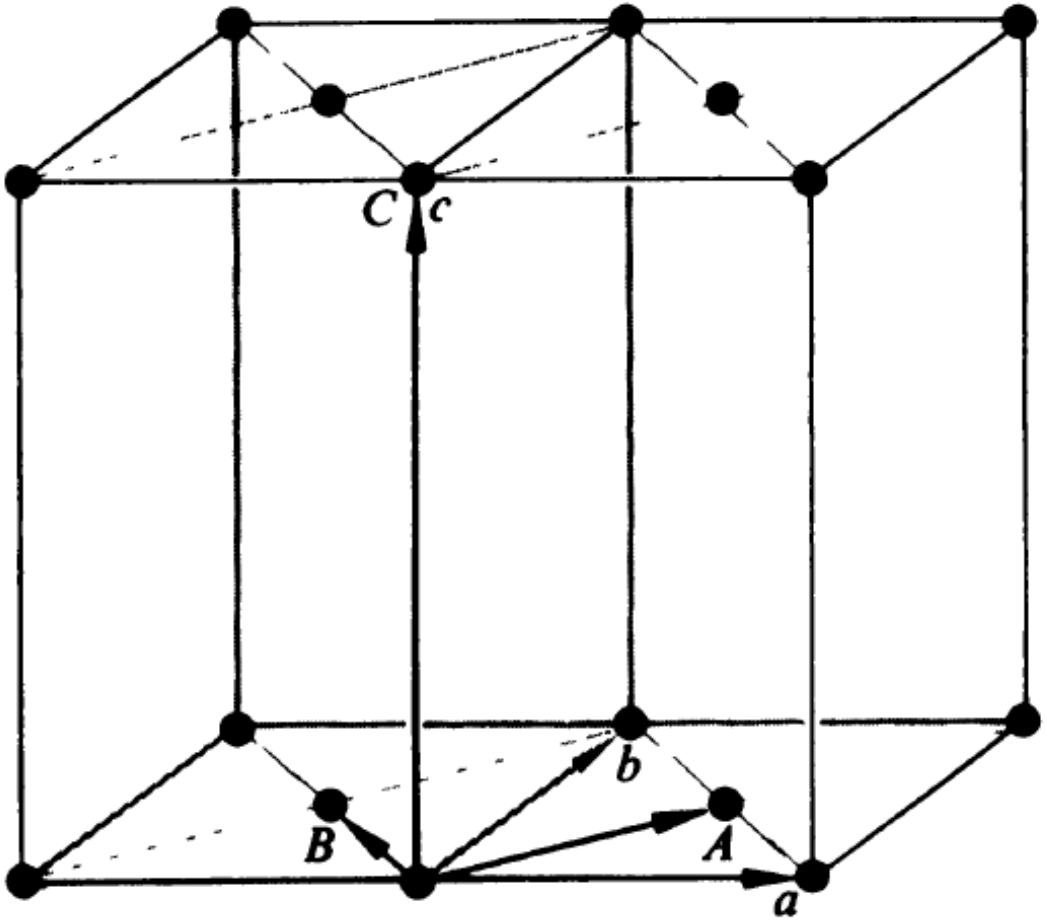
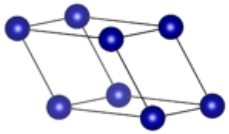
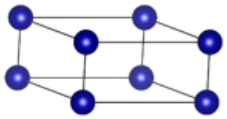
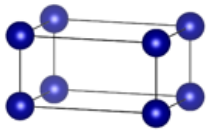
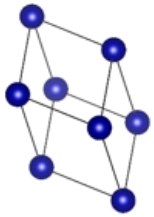
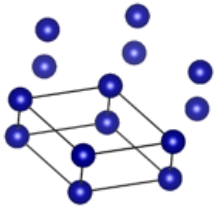
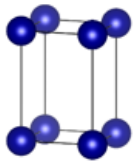
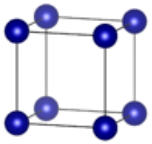
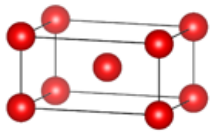
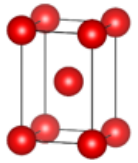
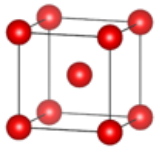
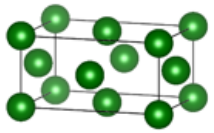
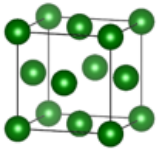
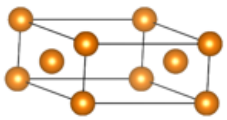
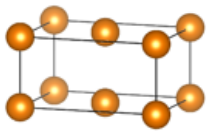


Figure taken from: Sands, D.E., Introduction to Crystallography. (Dover: New York, 1993)

Bravais Lattices

	Triclinic a ≠ b ≠ c, α ≠ β ≠ γ ≠ 90°	Monoclinic a ≠ b ≠ c, α = γ = 90°, β ≠ 90°	Orthorhombic a ≠ b ≠ c, α = β = γ = 90°	Rhombohedral a = b = c, α = β = γ ≠ 90°	Hexagonal a = b ≠ c, α = β = 90°, γ = 120°	Tetragonal a = b ≠ c, α = β = γ = 90°	Cubic a = b = c, α = β = γ = 90°
Primitive (P)							
Body Centered (I)							
Face Centered (F)							
Base Centered (C)							

Types of Symmetry

- The lattice and unit cell basis vectors describe aspects of the translational symmetry of the crystal structure.

- However, we also have to consider symmetry elements inherent to the atoms and molecules within the unit cell.

- The symmetry elements of finite molecules are called point symmetry.

What is Point Symmetry?

- A point symmetry operation always leaves at least one point fixed (an entire line or plane may remain fixed).

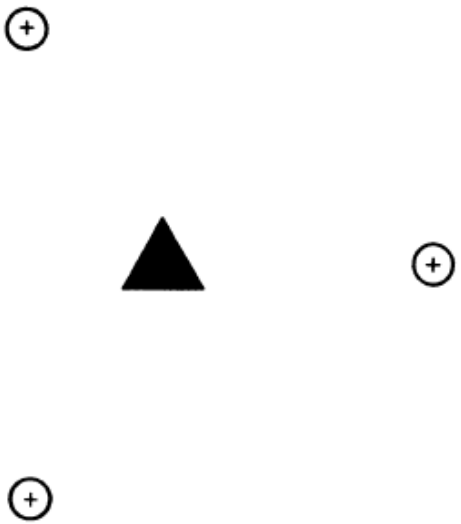
- Rotation axes, mirror planes, centers of symmetry (inversion points) and improper rotation axes are all elements of point symmetry.

- Collections of point symmetry elements describing finite molecules are called point groups.

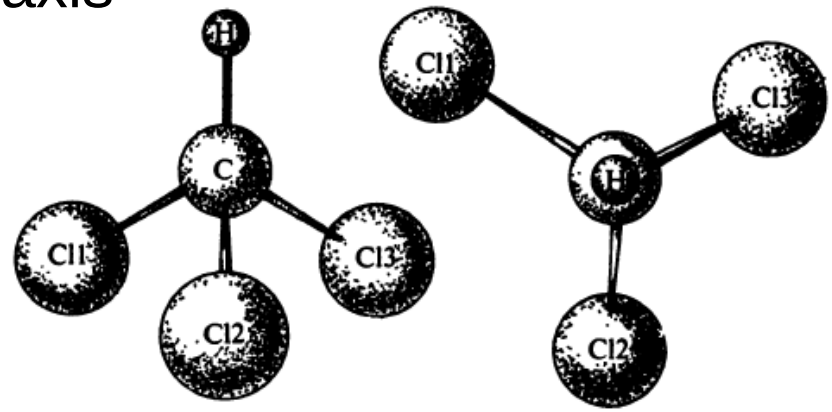
Rotation Axes

- A rotation of 360°/n is referred to with the symbols **n** (Hermann-Mauguin notation) or $\mathbf{C_n}$ (Schoenflies notation).

- Crystals are restricted (in 3D) to **1**, **2**, **3**, **4** & **6** rotation axes.



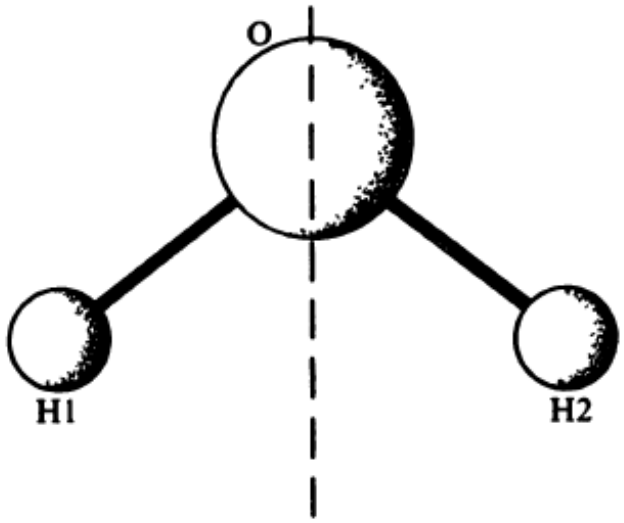
3 or C_3 axis

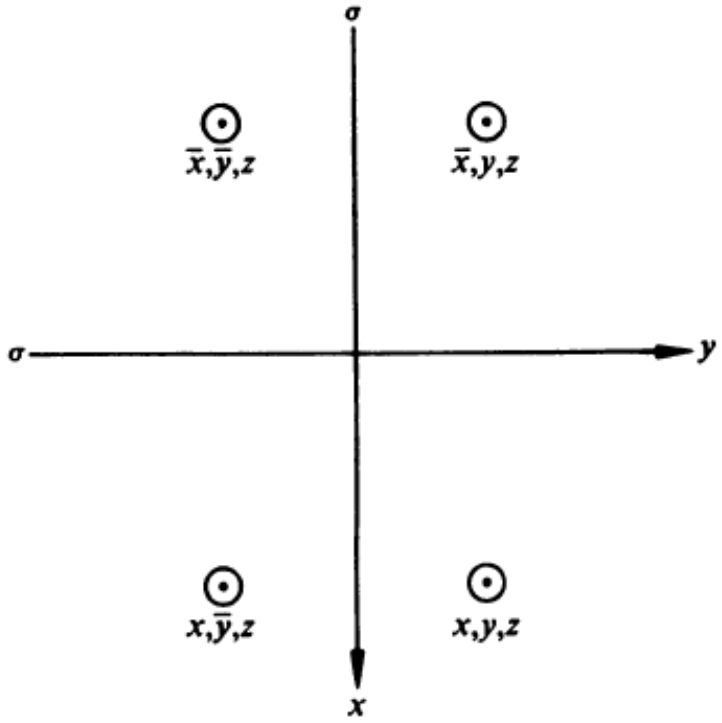


Figures taken from: Sands, D.E., Introduction to Crystallography. (Dover: New York, 1993)

Mirror Planes

- A mirror (or reflection) plane is referred to as **m** (Hermann-Mauguin) or **σ** (Schoenflies).





Figures taken from: Sands, D.E., Introduction to Crystallography. (Dover: New York, 1993)

Center of Symmetry (Inversion)

- A line drawn from any point though a center of symmetry arrives at an identical point an equivalent distance from the center (if the inversion center is the origin, a point at x, y, z is equivalent to a point at –x, -y, -z).

- Referred to with the symbols $\bar{1}$ (Hermann-Mauguin notation) or **i** (Schoenflies notation).

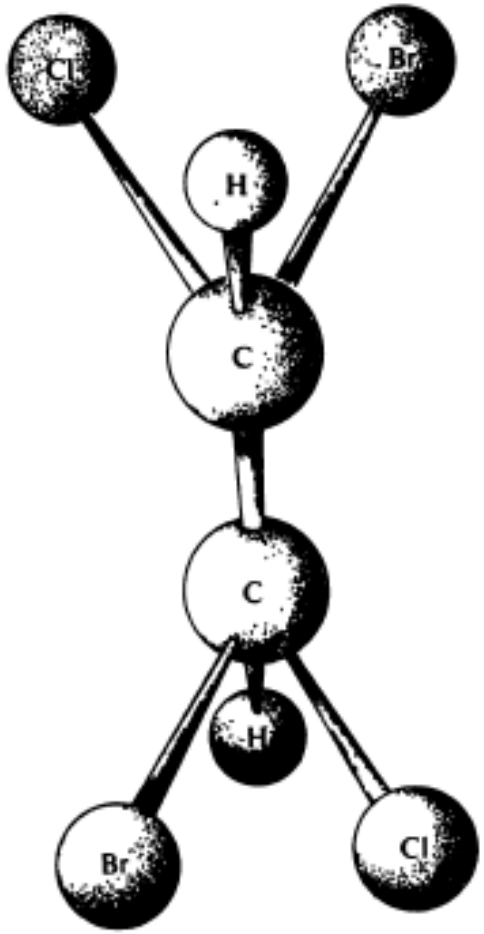
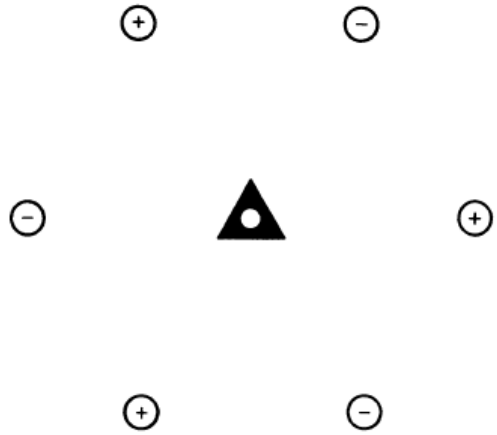


Figure taken from: Sands, D.E., Introduction to Crystallography. (Dover: New York, 1993)

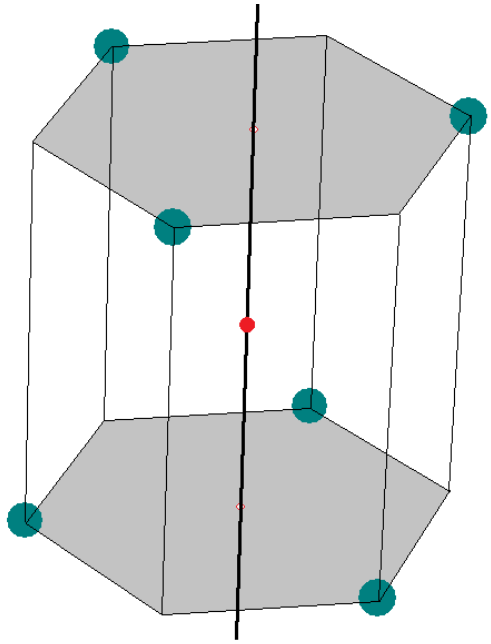
Improper Rotation Axes

- An improper rotation axis (rotoinversion or rotoreflection axis) combines two operations.

- A Hermann-Mauguin improper rotation (rotoinversion) axis, referred to with the symbol $\bar{n}$, is a combination of a rotation by 360°/n followed by inversion through a point.

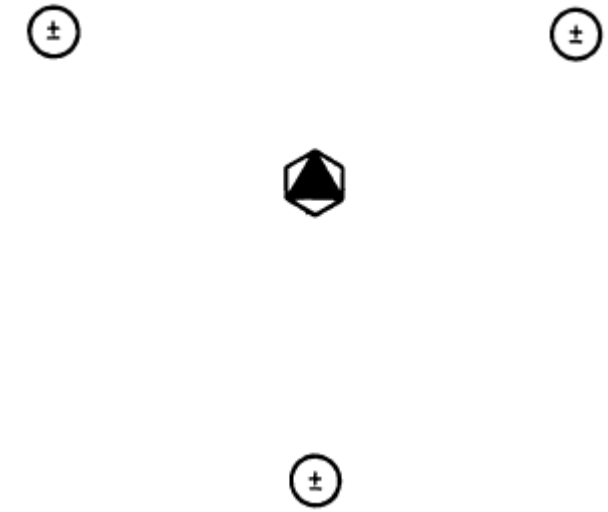


$\bar{3}$ axis



Improper Rotation Axes

- A Schoenflies improper rotation (rotoreflection) axis, referred to with the symbol $\mathbf{S_n}$, is a combination of a rotation by 360°/n followed by reflection in a plane normal to the axis.



- For odd values of n:

$$S_n = \overline{2n}$$
$$\bar{n} = S_{2n}$$

$$\boldsymbol{S_3 = \overline{6}}$$

Figure taken from: Sands, D.E., Introduction to Crystallography. (Dover: New York, 1993)

Elements of Point Symmetry

Element	Hermann-Mauguin Symbols	Schoenflies Symbols
Rotation Axis	1,2,3,4,6	C_1, C_2, C_3, C_4, C_6
Mirror Plane	m	σ
Identity	1	$E = C_1$
Center of Symmetry (Inversion)	$\bar{1}$	i
Rotary Inversion (or Reflection) Axis	$\bar{1}, \bar{2}, \bar{3}, \bar{4}, \bar{6}$	S_2, S_1, S_6, S_4, S_3

Point Groups

- The point group refers to the collection of point symmetry elements possessed by an atomic or molecular pattern.
- There are 32 point groups that are compatible with translational symmetry elements.
- With Hermann-Mauguin notation, each position in the symbol specifies a different direction.

Point Groups – Hermann-Mauguin

- Each component of the point group symbol corresponds to a different direction.

- The position of an **m** refers to a direction normal to a mirror plane.

- A component combining a rotation axis and mirror plane (i.e. **4/m** or “four over m”) refers to a direction parallel a rotation axis and perpendicular the mirror plane.

- Orthorhombic groups: The three components refer to the three mutually perpendicular crystal axes (x, y, z).

Point Groups – Hermann-Mauguin

- Tetragonal point groups: The 4-fold axis is parallel the z direction. The second component refers to the equivalent x and y directions, and the third component refers to directions in the xy plane bisecting the x and y axes.

- Hexagonal and Trigonal point groups: The second component refers to equivalent directions (120° or 60° apart) in the plane normal to the main 6-fold or 3-fold axis.

- Cubic point groups: The first component refers to the cube axes, the second component (3) refers to the four 3-fold axes along the body diagonals, the third component refers to the face diagonals.

Point Groups

Crystal system	Schoenflies symbol	Hermann–Mauguin symbol	Order of group
Triclinic	C_1	1	1
	C_i	$\bar{1}$	2
Monoclinic	C_2	2	2
	C_s	m	2
	C_{2h}	$2/m$	4
Orthorhombic	D_2	222	4
	C_{2v}	$mm2$	4
	D_{2h}	mmm	8
Tetragonal	C_4	4	4
	S_4	$\bar{4}$	4
	C_{4h}	$4/m$	8
	D_4	422	8
	C_{4v}	$4mm$	8
	D_{2d}	$\bar{4}2m$	8
	D_{4h}	$4/mmm$	16
Trigonal	C_3	3	3
	C_{3i}	$\bar{3}$	6
	D_3	32	6
	C_{3v}	$3m$	6
	D_{3d}	$\bar{3}m$	12
Hexagonal	C_6	6	6
	C_{3h}	$\bar{6}$	6
	C_{6h}	$6/m$	12
	D_6	622	12
	C_{6v}	$6mm$	12
	D_{3h}	$\bar{6}m2$	12
	D_{6h}	$6/mmm$	24
Cubic	T	23	12
	T_h	$m3$	24
	O	432	24
	T_d	$\bar{4}3m$	24
	O_h	$m3m$	48

Table taken from: Sands, D.E., Introduction to Crystallography. (Dover: New York, 1993)

Crystal Systems

System	Lattice Parameter Restrictions	Bravais Lattices	Minimum Symmetry Elements
Triclinic (Anorthic)	a, b, c, α, β, γ	aP	None
Monoclinic	a, b, c, 90, β, 90	mP, mC	One 2-fold axis
Orthorhombic	a, b, c, 90, 90, 90	oP, oC, oI, oF	Three perpendicular 2-fold axes
Trigonal	a, a, a, α, α, α a, a, c, 90, 90, 120	R hP	One 3-fold axis
Hexagonal	a, a, c, 90, 90, 120	hP	One 6-fold axis
Tetragonal	a, a, c, 90, 90, 90	tP, tI	One 4-fold axis
Cubic	a, a, a, 90, 90, 90	cP, cI, cF	Four 3-fold axes

Trigonal System

- The trigonal system has two distinct types of lattices:

1. A primitive cell can be chosen with a = b, α = β = 90°, γ = 120°. This type is identical to the hexagonal lattice except the trigonal cell has a 3-fold rather than a 6-fold axis.

2. A primitive cell can be chosen with a = b = c, α = β = γ ≠ 90°, this lattice type is called rhombohedral (R).

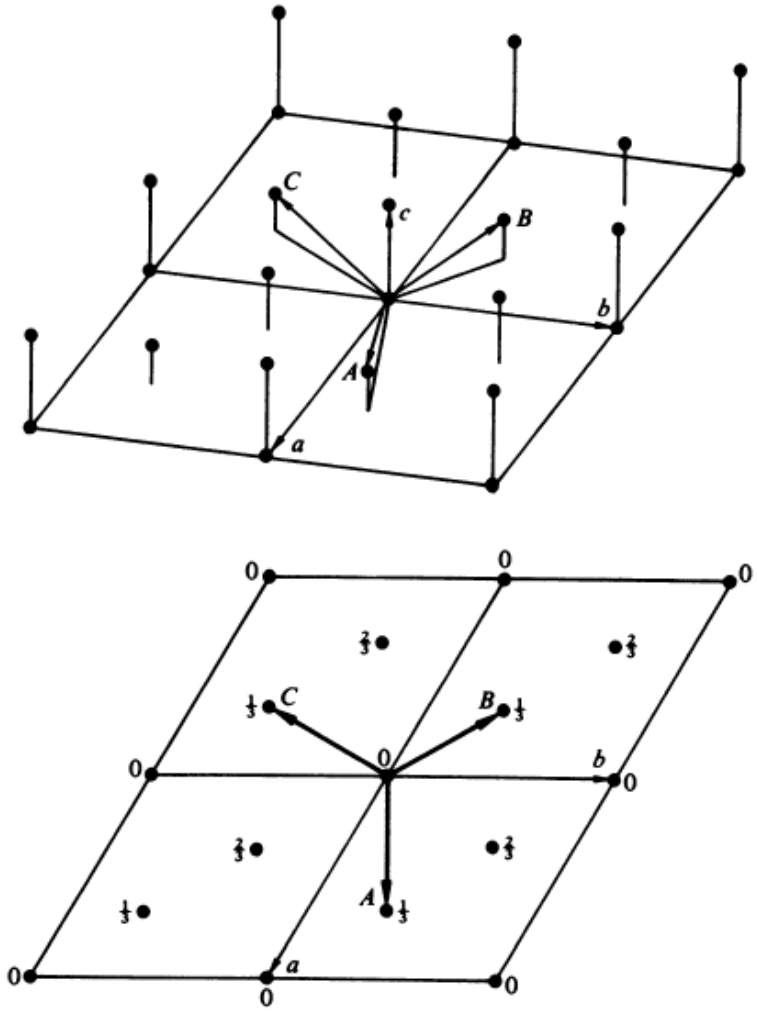
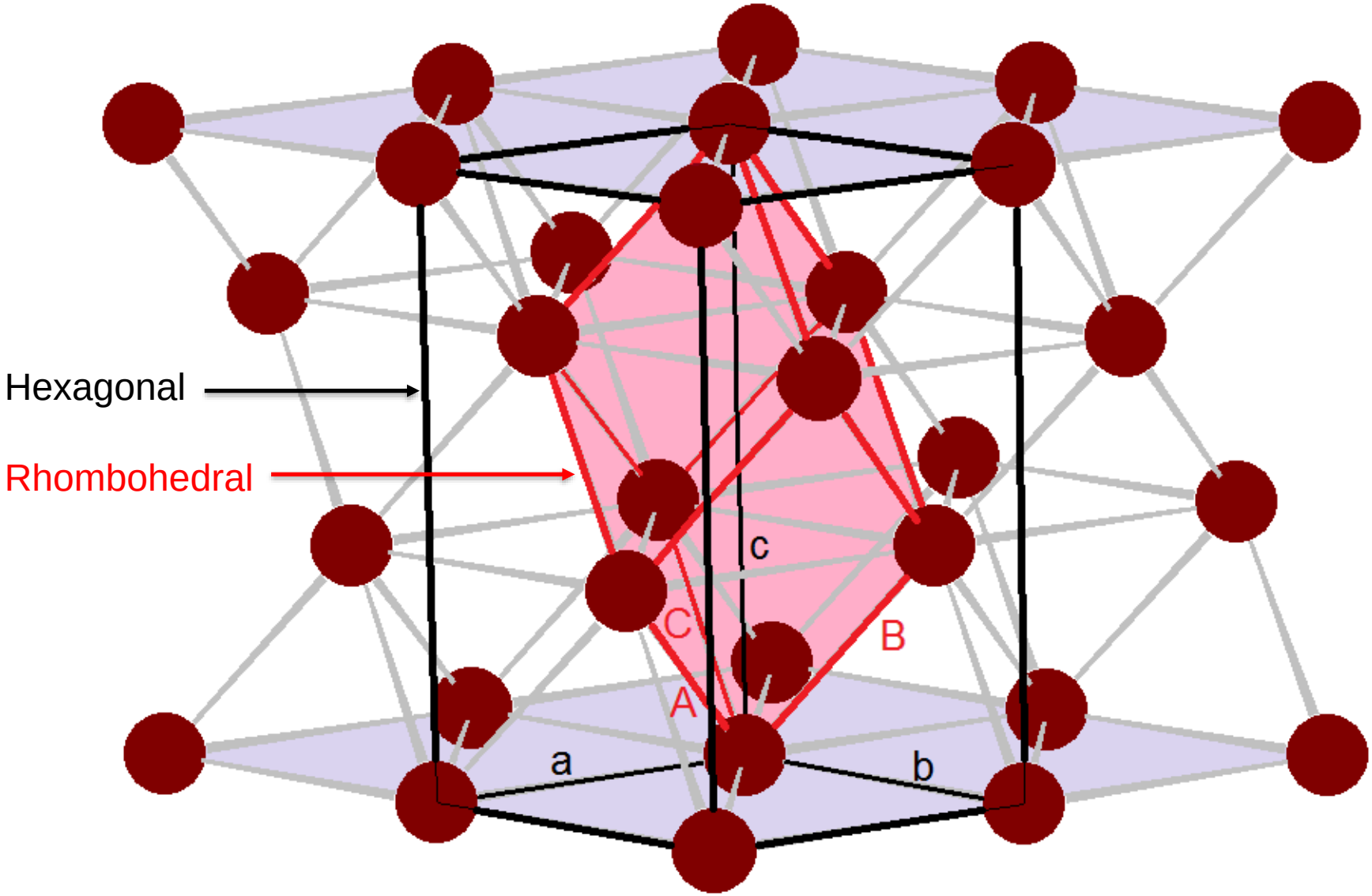


Figure taken from: Sands, D.E., Introduction to Crystallography. (Dover: New York, 1993)

Hexagonal and Rhombohedral Lattices



Point Groups & Space Groups

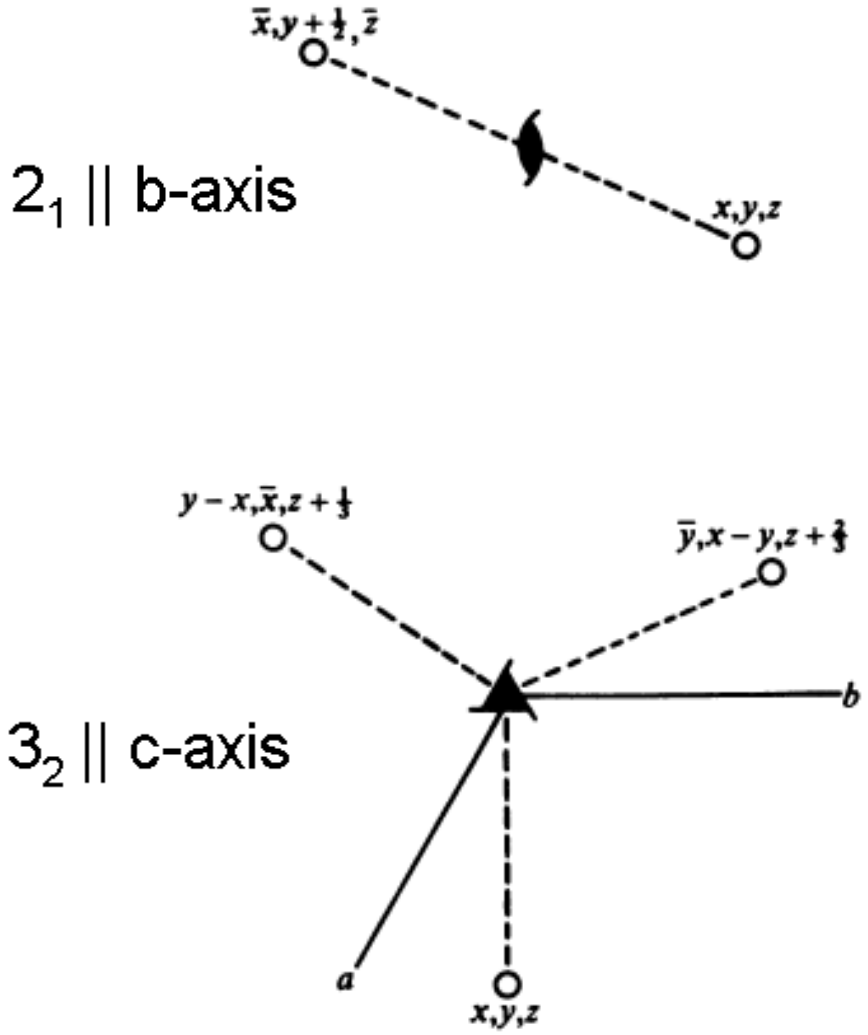
- The 32 point groups cover all the possible point symmetry elements which occur in finite molecules

- To fully describe the symmetry of crystal structures, we need to include two symmetry elements which combine rotation and reflection with the translational symmetry of the lattice (called **screw axes** and **glide planes** respectively).

- Groups which include both the point symmetry elements of finite molecules and the translational elements of a crystal are called **space groups**.

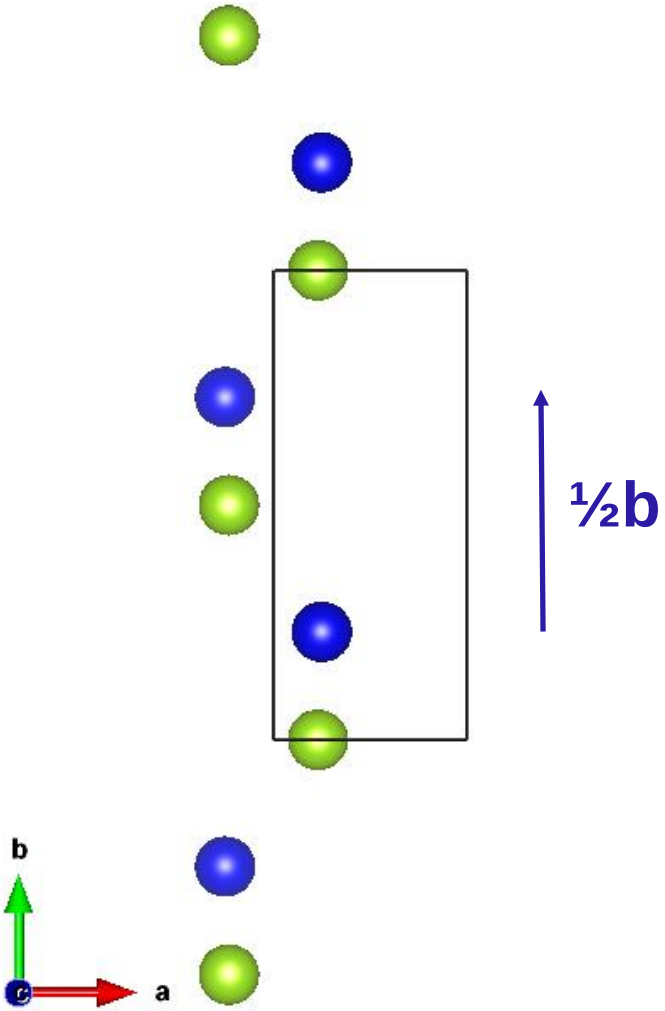
Screw Axes

- A screw axis, referred to with the symbol $\mathbf{n_p}$, combines two operations; a rotation of **360°/n** followed by a translation of **p/n** in the direction of the axis.

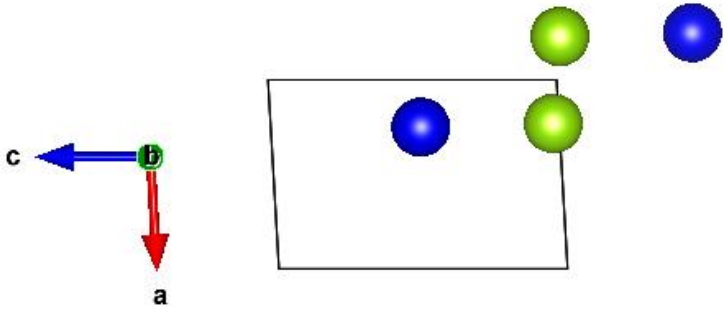


Figures taken from: Sands, D.E., Introduction to Crystallography. (Dover: New York, 1993)

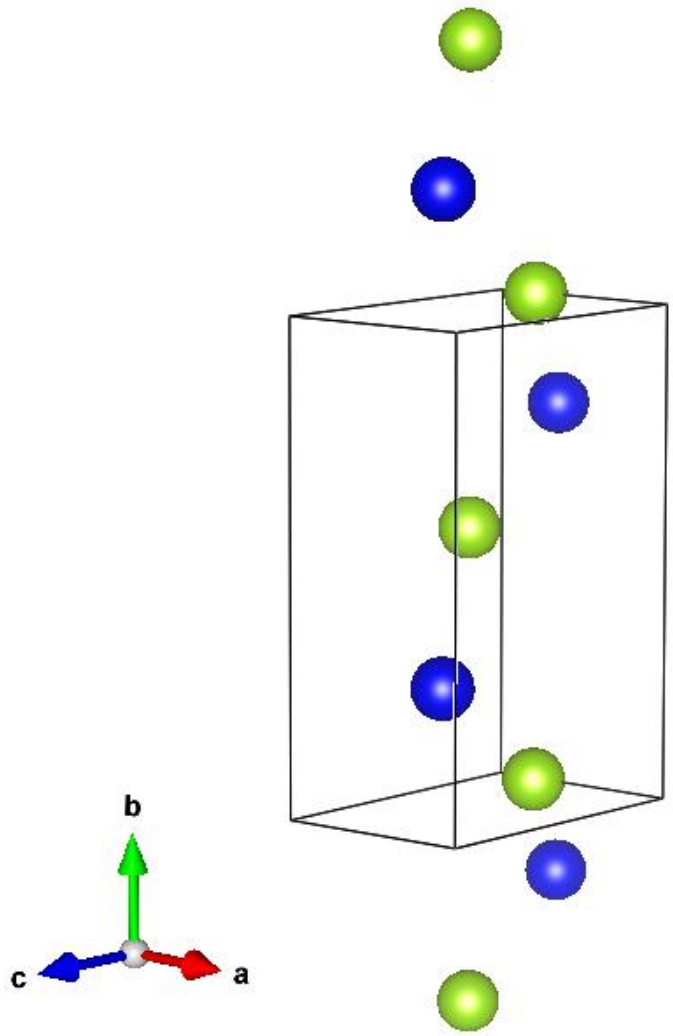
2_1 Screw Axis Parallel the b-axis



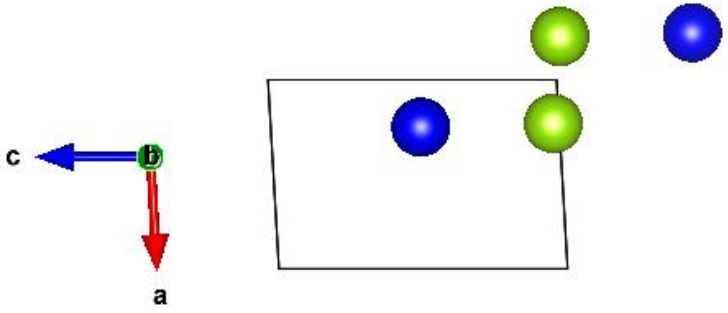
2_1 || b-axis



2_1 Screw Axis Parallel the b-axis



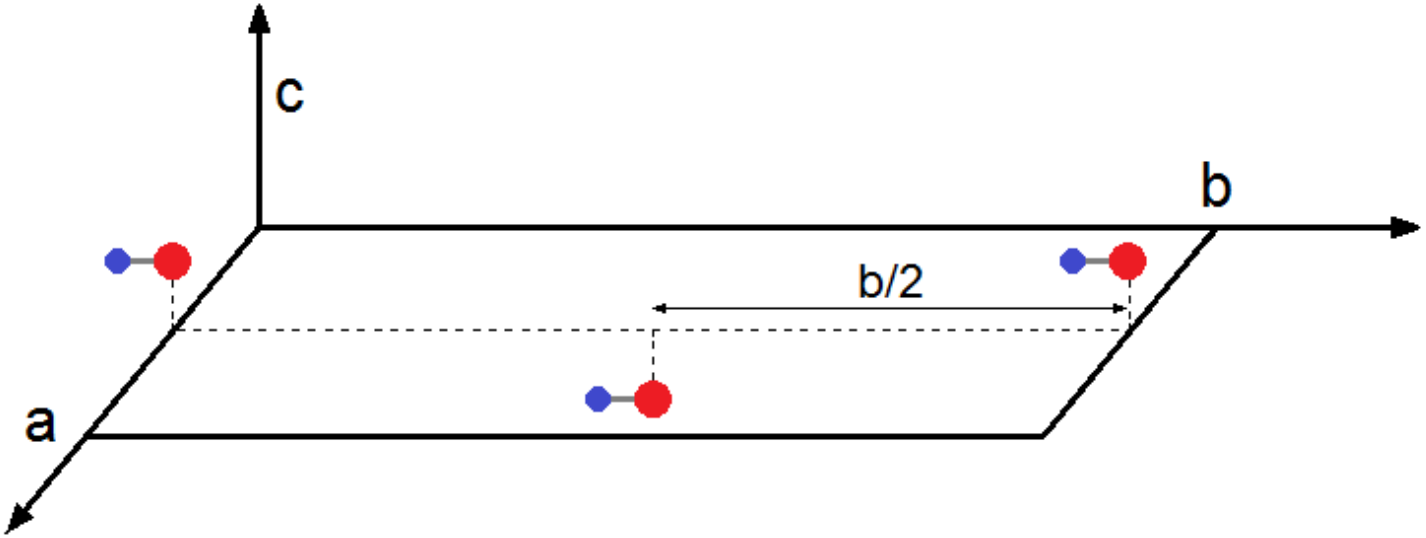
2_1 || b-axis



Glide Planes

- A glide plane combines two operations, reflection in a plane followed by translation parallel the plane.

- A glide parallel the b-axis would be referred to with the symbol **b**, and consist of a reflection followed by a translation of b/2.



Diagonal Glide Planes

- A glide plane parallel the a-b axes diagonal would be referred to with the symbol **n**, and consist of a reflection in the a-b plane followed by a translation of (a+b)/2.

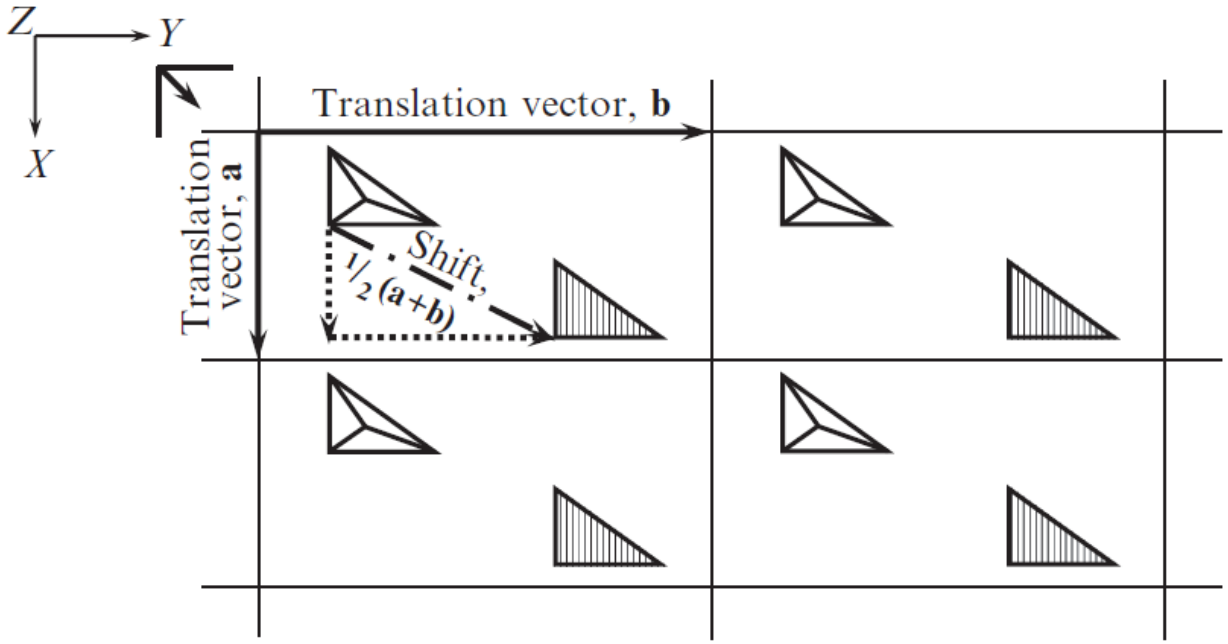


Figure taken from: Pecharsky, V. K. & Zavaliy, P. Y., Fundamentals of Powder Diffraction and Structural Characterization of Materials, 2nd edition. (Springer: Berlin, 2009).

Space Groups

- By combining the point groups, Bravais lattices and translation symmetry elements (screw axes and glide planes), 230 unique space groups are obtained.

- Many space groups have multiple settings (and/or choices of origin based on the site symmetry chosen for the origin):
  - Space group number 62 (orthorhombic)
  - Standard setting: Pnma
  - Alternate settings: Pnam, Pmcn, Pcmn, Pbnm, Pmnb

- Two very useful websites for space group information:

  http://img.chem.ucl.ac.uk/sgp/mainmenu.htm

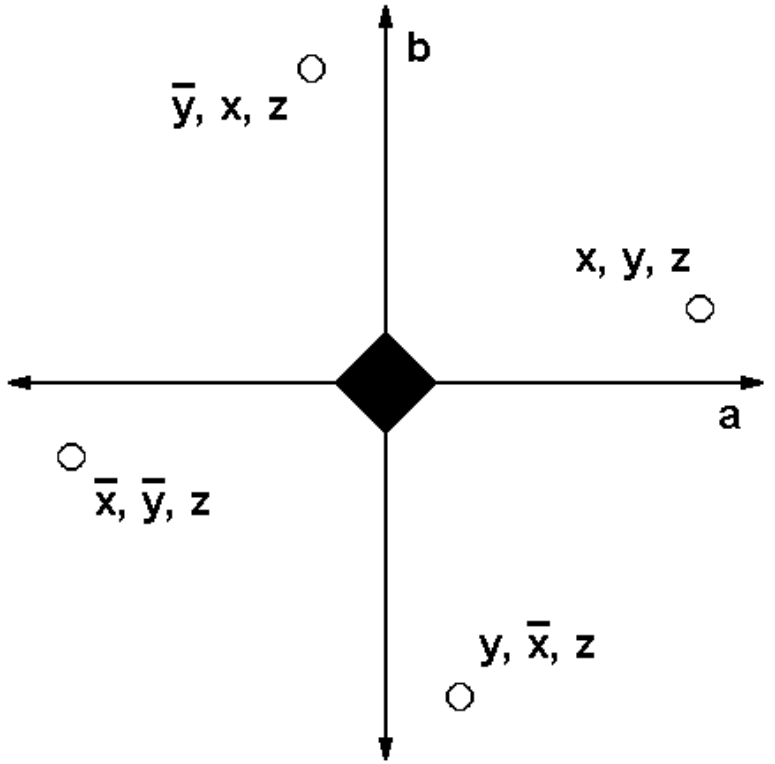
  http://www.cryst.ehu.es/

Equivalent Positions

- The symmetry operations associated with a space group can be used to generate positions which are symmetrically equivalent. Consider tetragonal space group P4/m (#83):

- For a general point (with coordinates x, y, z), the **4** axis parallel **c** generates three new points.

- Each of these four points is then reflected in the z=0 plane (z → -z).



Special Positions (space group P4/m)

Multiplicity	Wyckoff	Site Symmetry	Equivalent Positions
8	l	1	x, y, z; -y, x, z; -x, -y, z; y, -x, z; x, y, -z; -y, x, -z; -x, -y, -z; y, -x, -z
4	k	m	x, y, ½ ; -y, x, ½; -x, -y, ½; y, -x, ½
4	j	m	x, y, 0; -y, x, 0; -x, -y, 0; y, -x, 0
4	i	2	0, ½, z; ½, 0, z; 0, ½, -z; ½, 0, -z
2	h	4	½, ½, z; ½, ½, -z
2	g	4	0, 0, z; 0, 0, -z
2	f	2/m	0, ½, ½; ½, 0, ½
2	e	2/m	0, ½, 0; ½, 0, 0
1	d	4/m	½, ½, ½
1	c	4/m	½, ½, 0
1	b	4/m	0, 0, ½
1	a	4/m	0, 0, 0

Example Structures - Perovskite

Cubic (T = 1720 K)

Formula: $CaTiO_3$ (Z=1)

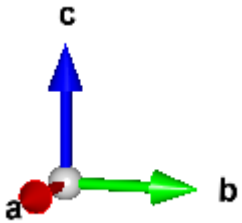
Space Group: $Pm\bar{3}m$ (#221)

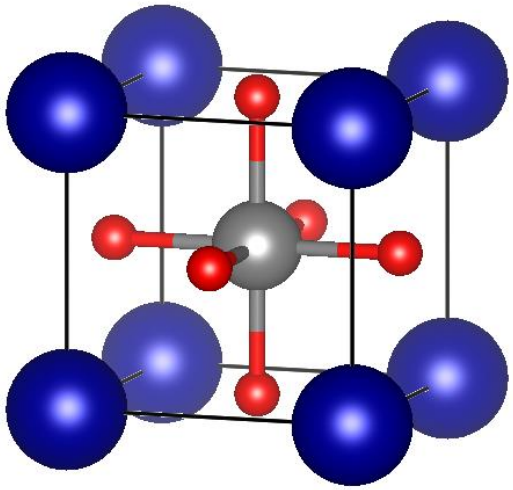
Lattice Parameter: a = 3.8967 Å

Atoms: Ca in 1a (0,0,0)

Ti in 1b (½,½,½)

O in 3c (½,½,0), (½,0,½), (0,½,½)





Tetragonal (T = 1598 K)

Formula: $CaTiO_3$ (Z=4)

Space Group: $I4/mcm$ (#140)

Lattice Parameters: a = 5.4984 Å, c = 7.7828 Å

Atoms: Ca in 4b (0,½,¼), (½,0,¼), (0,½,¾), (½,0,¾)

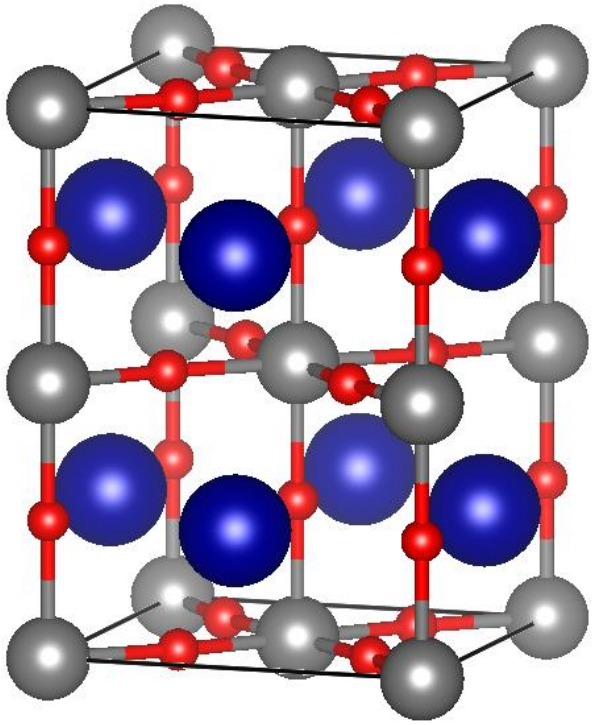
Ti in 4c (0,0,0), (0,0,½), (½,½,½), (½,½,0)

O in 4a (0,0,¼), (0,0,¾), (½,½,¾), (½,½,¼)

O in 8h (x,x+½,0), (-x+½,x,0), (-x,-x+½,0),

(x+½,-x,0) + (½,½,½)

where x = 0.2284



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Example Structures - Perovskite

Orthorhombic (T = 296 K)

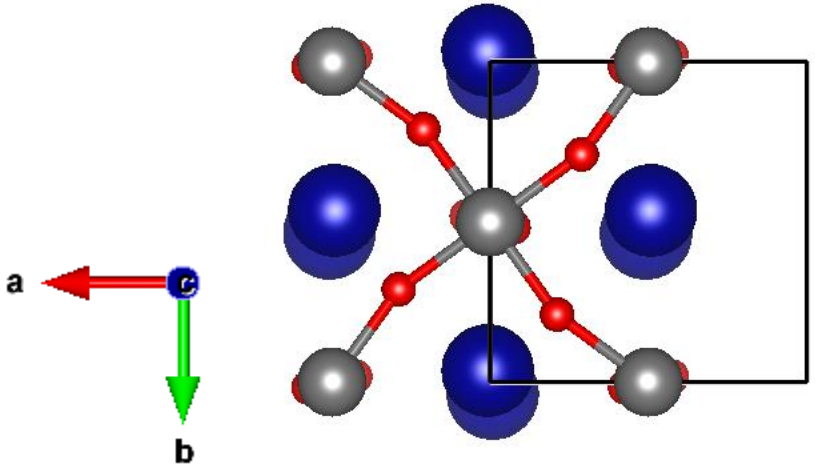
Mineral Name: Perovskite

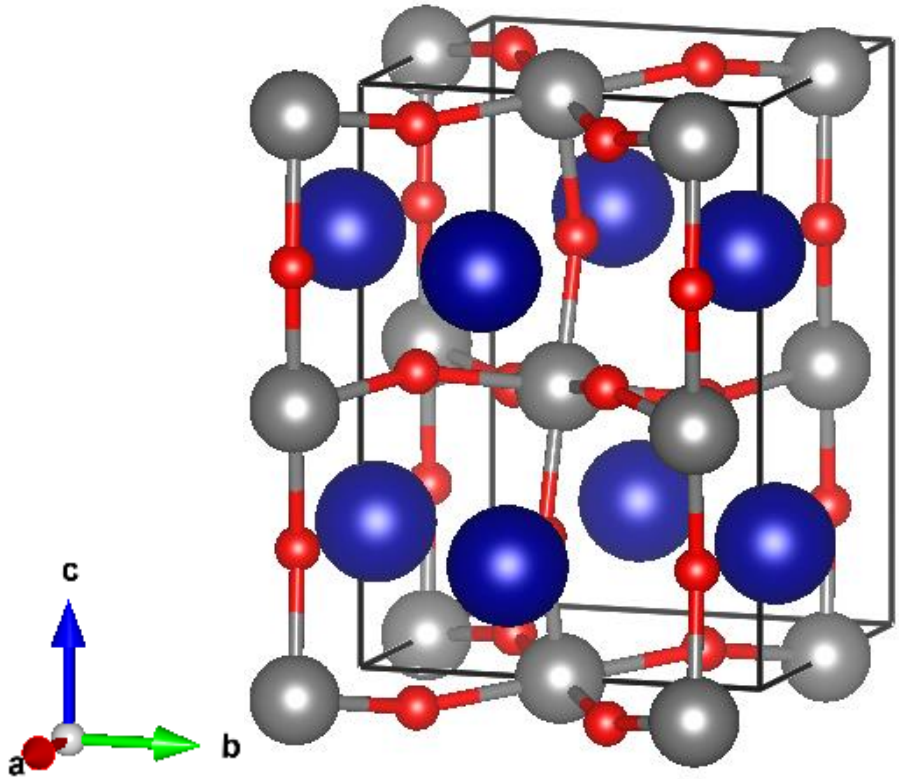
Formula: $CaTiO_3$ (Z=4)

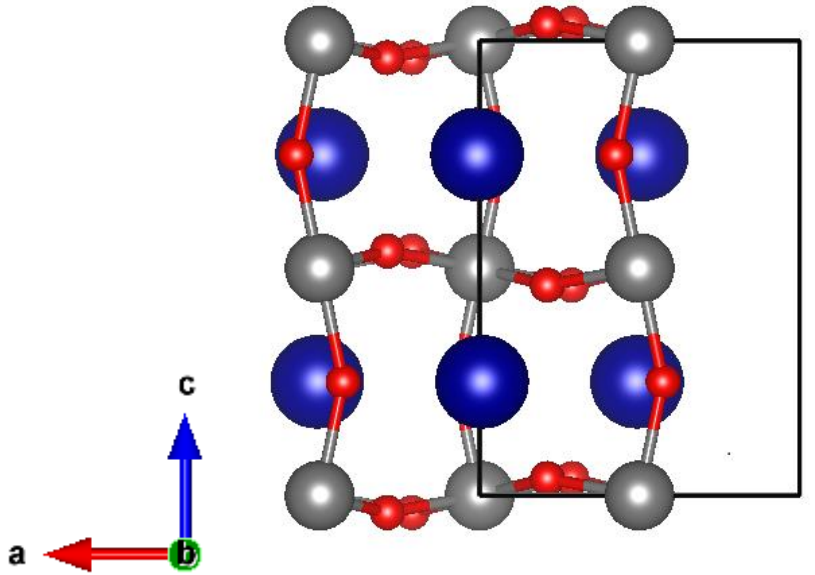
Space Group: $Pbnm$ (#62)

Lattice Parameters:

a = 5.3789 Å, b = 5.4361 Å, c = 7.6388 Å







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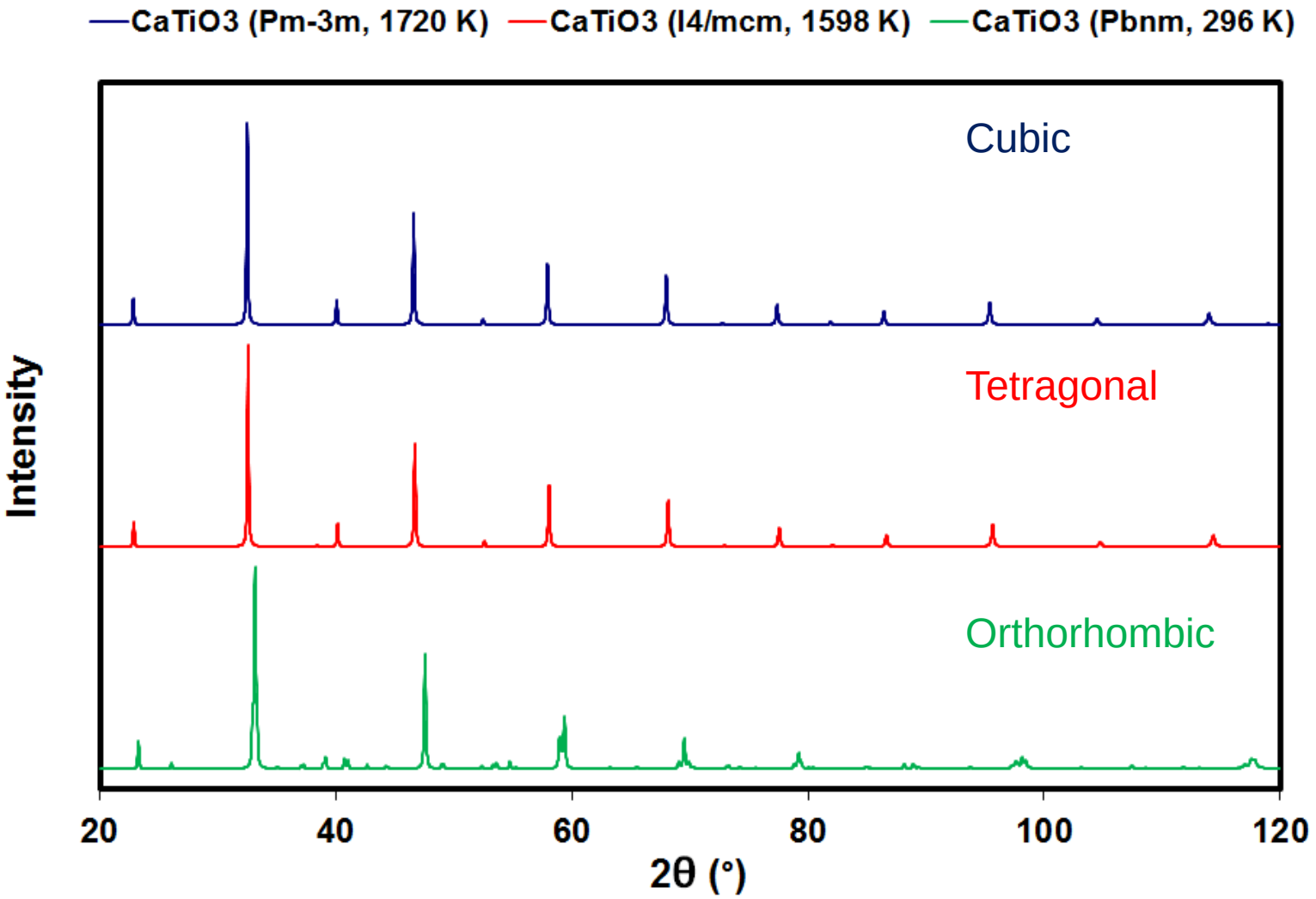
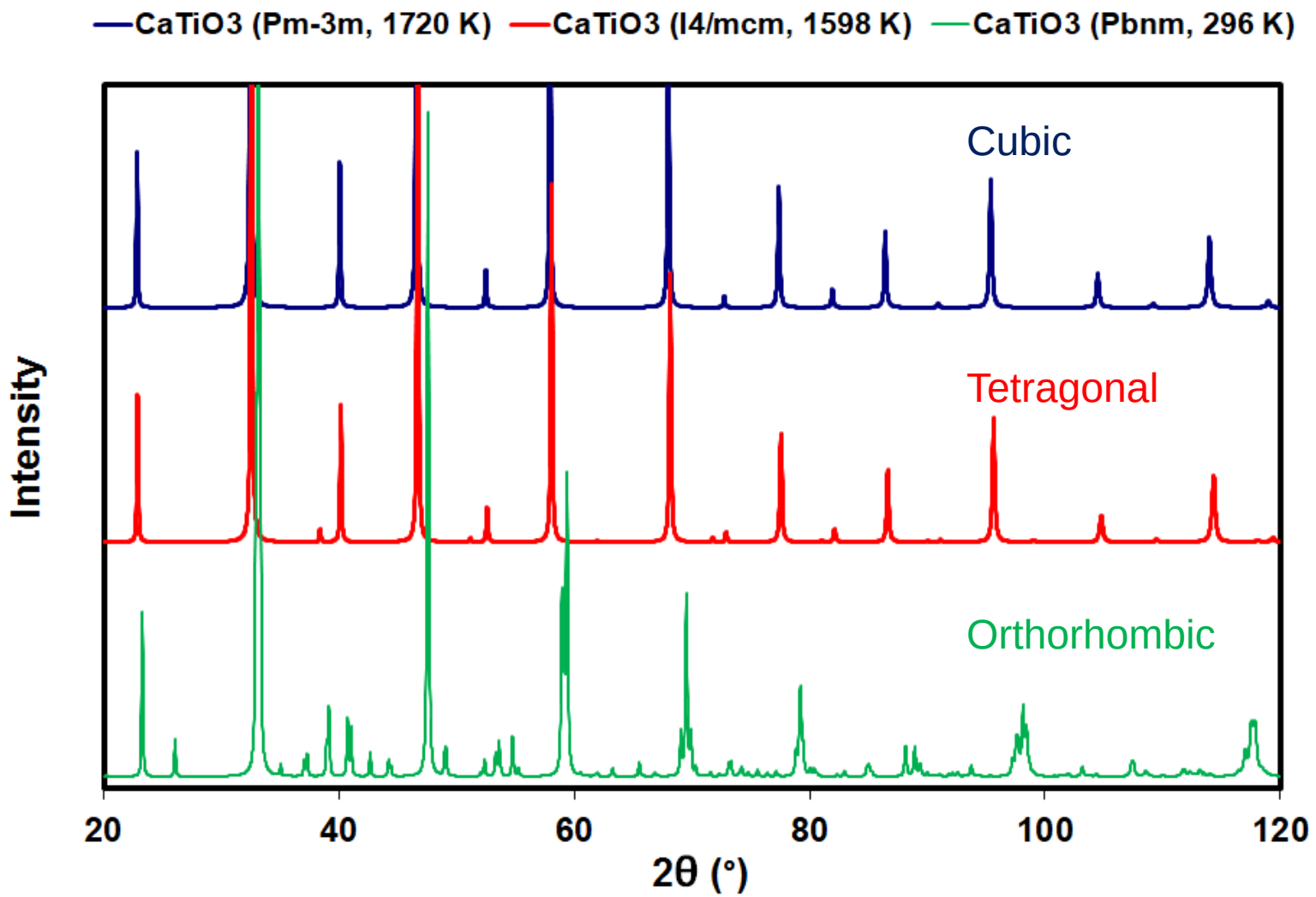
Powder Patterns - Perovskite



For more details on this system, see: Ali, R. & Yashima, M. J. Solid State Chem. 178 (2005) 2867-2872.

Powder Patterns - Perovskite



For more details on this system, see: Ali, R. & Yashima, M. J. Solid State Chem. 178 (2005) 2867-2872.

Reflection Positions - Bragg's Law

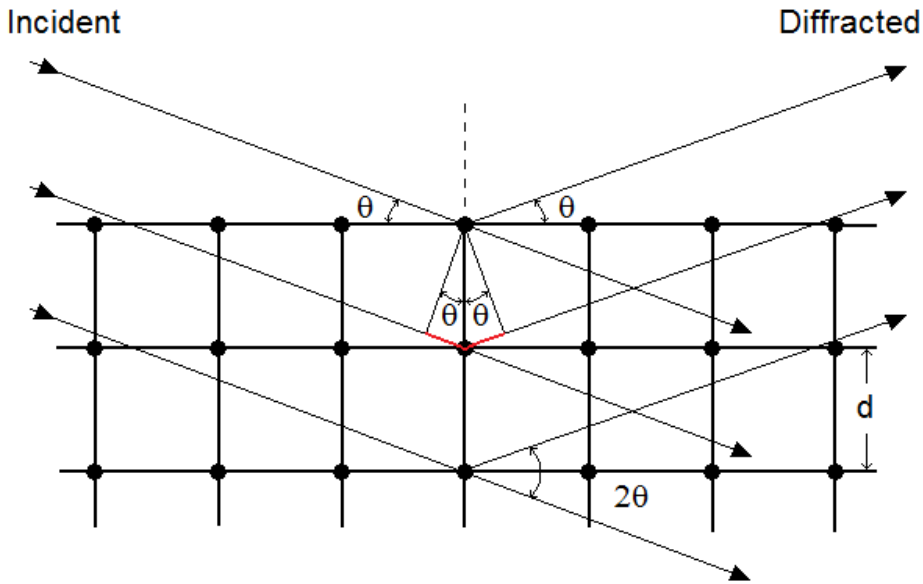
- Bragg's law tells us where a diffraction peak will be located (its 2θ position, in degrees, or °)

- The peak position depends on the X-ray wavelength (λ) and the d-spacing between crystal planes (d_{hkl}).

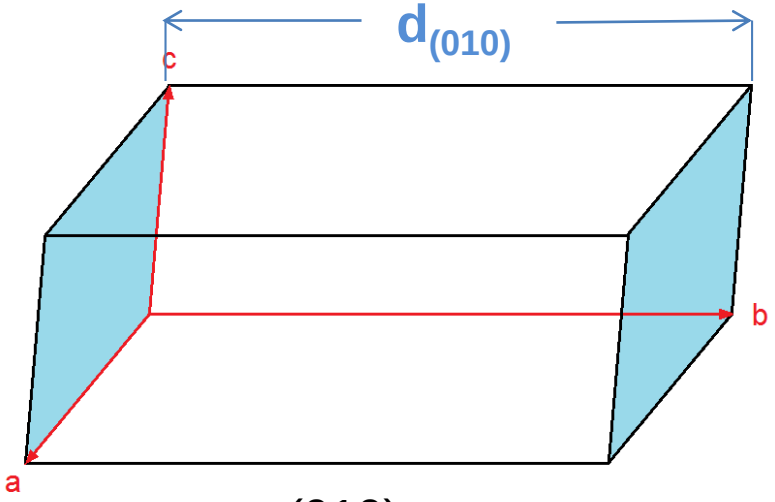
- The d-spacing (d_{hkl}) depends on the Miller indices of the crystal plane (*hkl*) and lattice parameters of the unit cell.

$$\lambda = 2d_{hkl} \sin\theta$$

$$2\theta_{calc} = 2 \sin^{-1}\left(\frac{\lambda}{2d_{hkl}}\right)$$

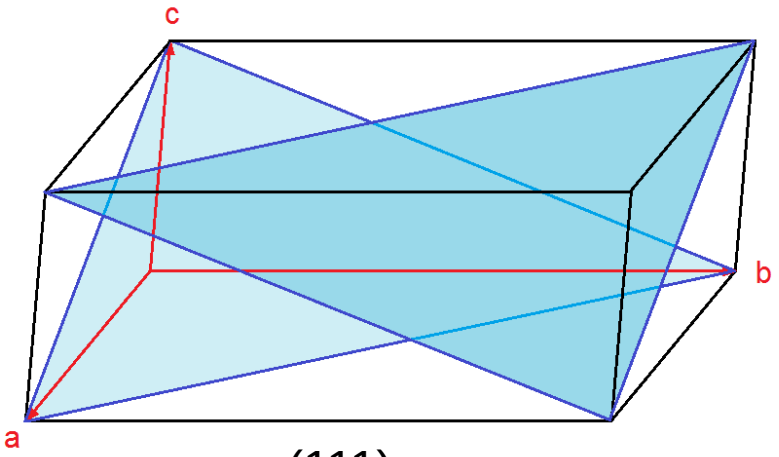


Crystal Planes & Interplanar Spacing

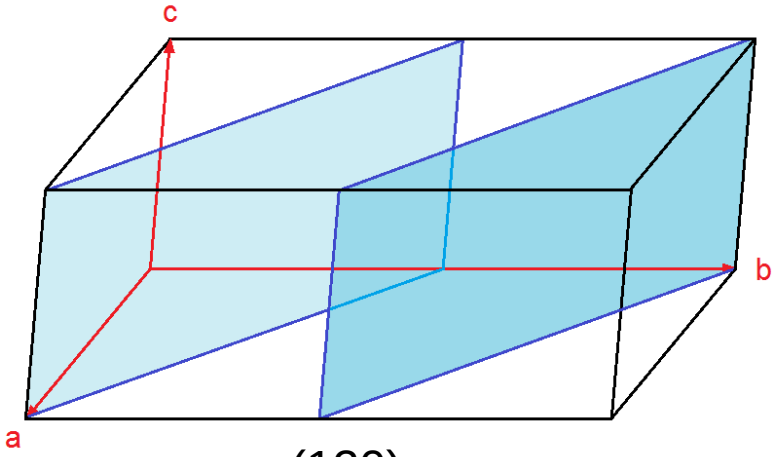


(010)

- Diffraction is analogous to reflection of X-rays from planes in the unit cell of the crystal.
- The position of peaks in a diffraction pattern depend on the distance (d-spacing) between crystalline planes.



(111)



(120)

Miller Indices and Interplanar Spacing

- Crystallographic planes are described using **Miller indices (*hkl*)**, which are derived from the intercepts of the plane with the crystal axes.

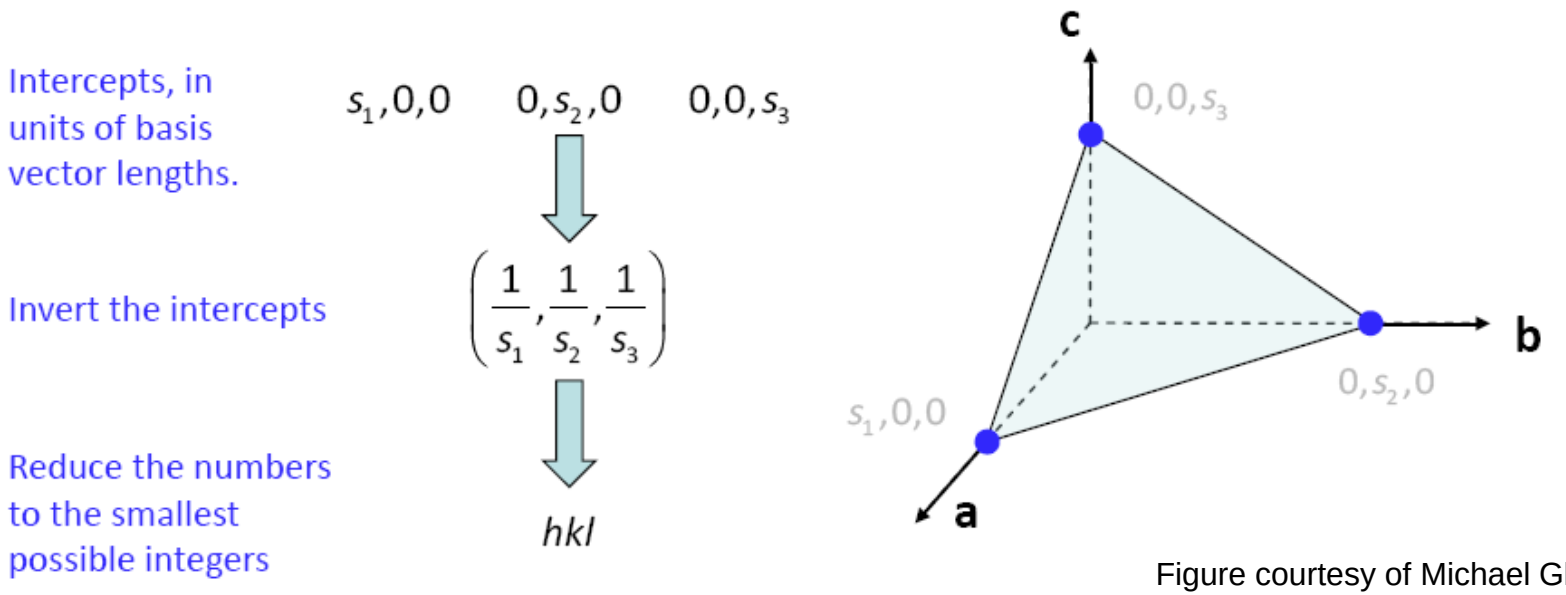


Figure courtesy of Michael Gharghouri.

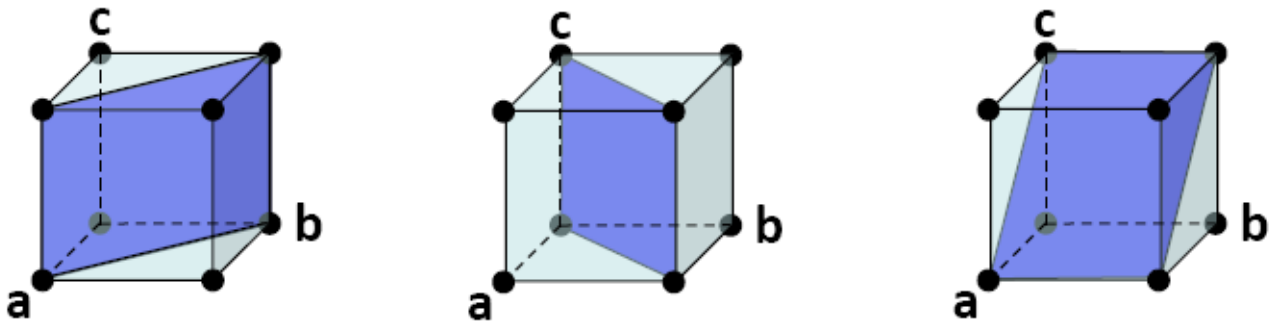
- The distance between lattice planes (**d-spacing**) is given by:

$$d_{hkl} = V[h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta + l^2a^2b^2\sin^2\gamma + 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta)$$

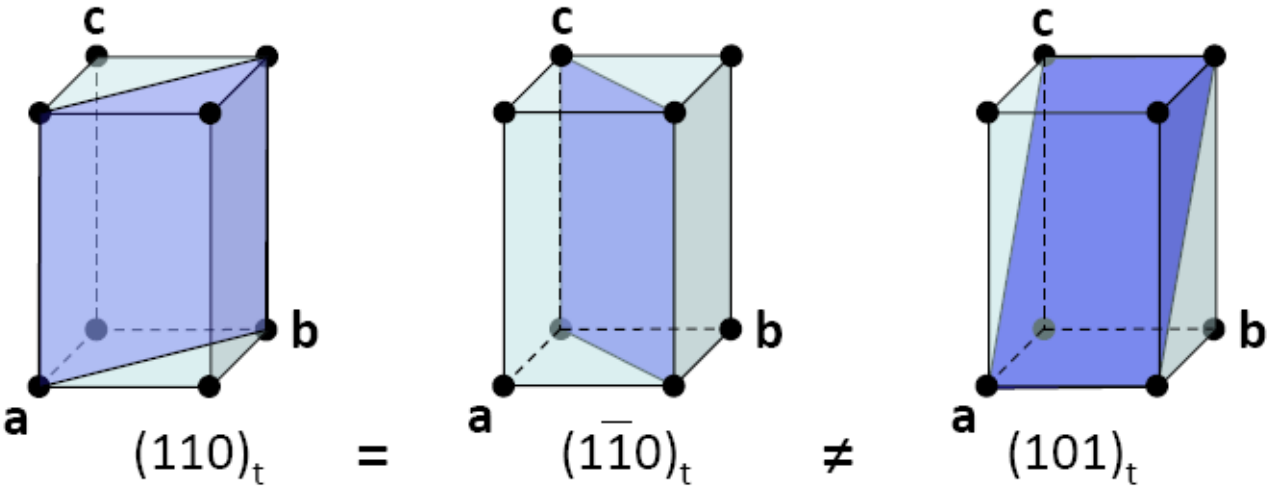
Families of Planes

Cubic

$(110)_c = (1\bar{1}0)_c = (101)_c \Rightarrow \{110\}_c$



Tetragonal



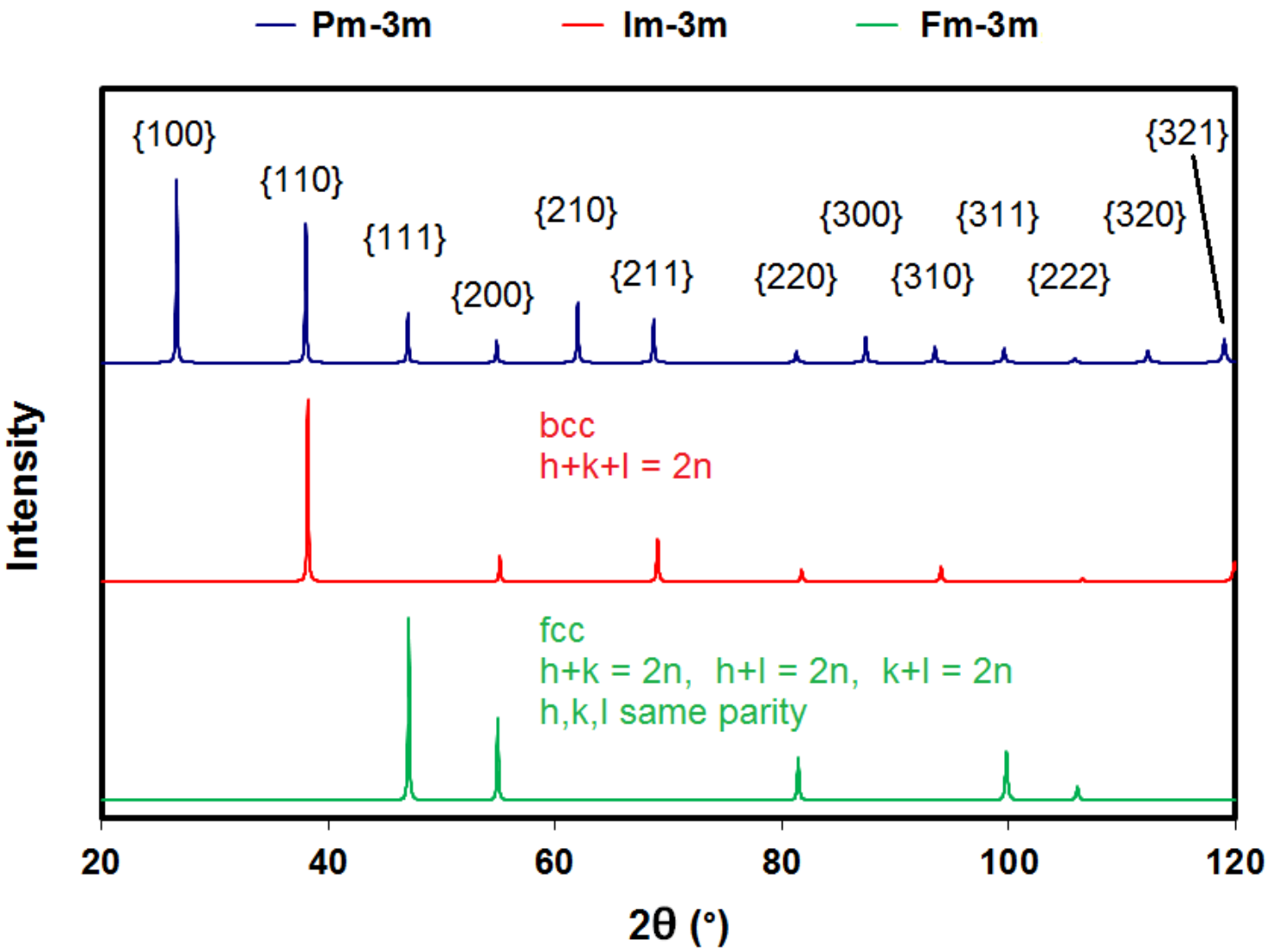
$(110)_t = (1\bar{1}0)_t \neq (101)_t$

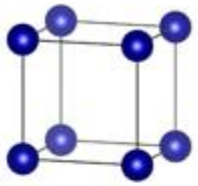
$\{110\}_t$

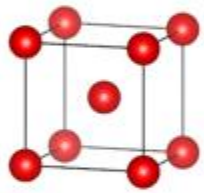
$\{101\}_t$

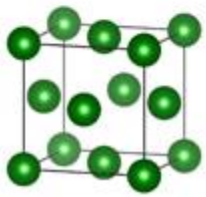
Figure courtesy of Michael Gharghouri.

Systematic Absences









Summary

- You don’t need to be an expert in crystallography, but a basic understanding is important to properly interpret your powder diffraction data and perform more complicated analysis like Rietveld refinement and pair distribution function (PDF) analysis.

Acknowledgements

- A sincere thank you to Jim Kaduk, John Faber, Michael Gharghouri, Pam Whitfield, Pawel Grochulski & Michel Fodje for the liberal use of their figures, ideas, knowledge & suggestions.

Further Reading - Crystallography

- Sands, D.E. **Introduction to Crystallography**.
  Dover: New York, 1993.

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  Dover: New York, 2002.

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  Oxford: New York, 2002.

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