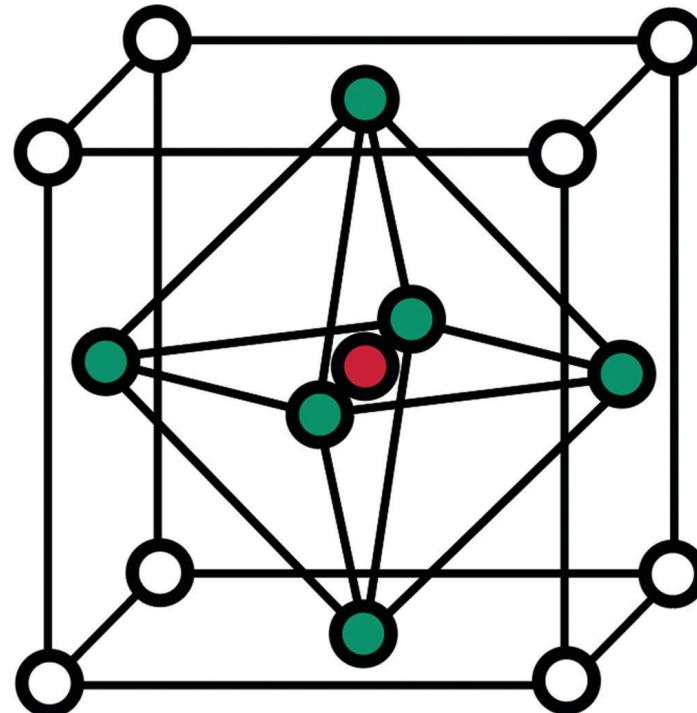


STRUCTURE II



MATE40004

Outline of Structure 1 Module

Aim: understanding of how materials are structured from the atomic to the micron scale

- **Crystallography:** Aron Walsh
- **Bonding:** Jason Reilly & Eleonora D'Eila
- **Defects:** Paul Franklyn
- **Polymers:** Theoni Georgiou
- **Phase Diagrams:** Milo Shaffer

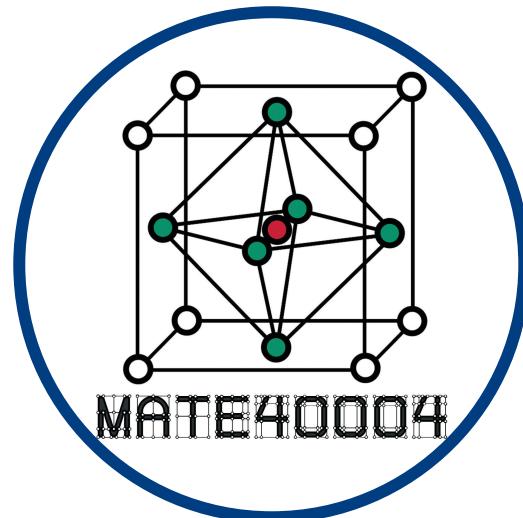
MATE40004 – Structure 1

Crystallography

A. Lattices

Professor Aron Walsh

Department of Materials
Imperial College London



<http://www.imperial.ac.uk/people/a.walsh>

What is Crystallography?

Crystallography: the science that examines the arrangement of atoms in solids

Over 25 Nobel prizes related to this topic!

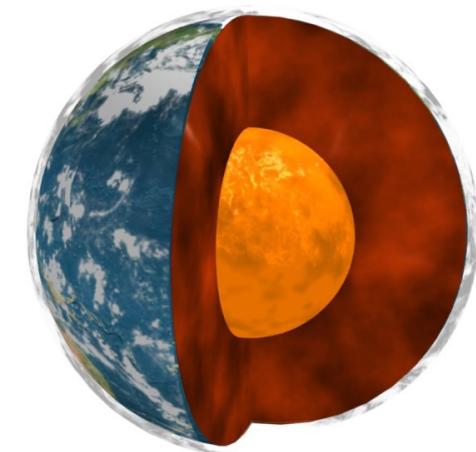
<https://www.iucr.org/people/nobel-prize>

X-ray spectrometer developed at the University of Leeds

W.H. Bragg and W.L. Bragg – Use of X-rays to determine crystal structure (1915 Nobel prize in Physics)

A World of Crystals

Crystalline materials can be found everywhere



Structure–Property Relationships

Knowledge of crystal structure allows us to engineer materials properties, including:

- **Mechanical:** metal alloys for aircraft
- **Electrical:** semiconductors for electrical devices
- **Magnetic:** high-density information storage
- **Optical:** lasers and light-emitting diodes
- **Chemical:** catalysts for fuel generation
- **Biological:** accelerated drug design

Outline of Crystallography

Mix of lectures & activities

- A. Lattices
- B. Symmetry
- C. Geometry
- D. Packing



Core concepts

Test 1 with feedback (12.5% of module)

- E. Crystals 1
- F. Crystals 2
- G. Diffraction



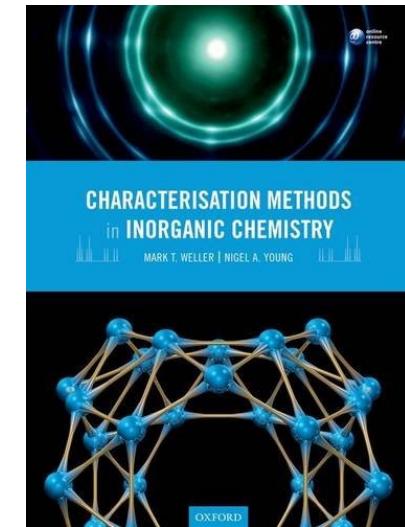
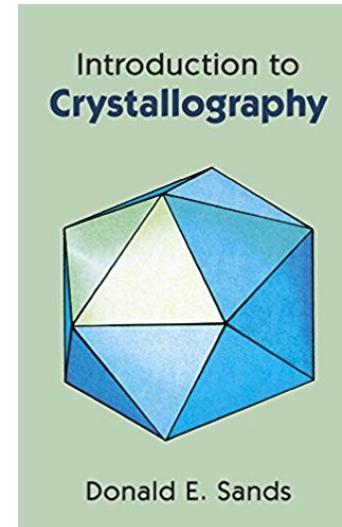
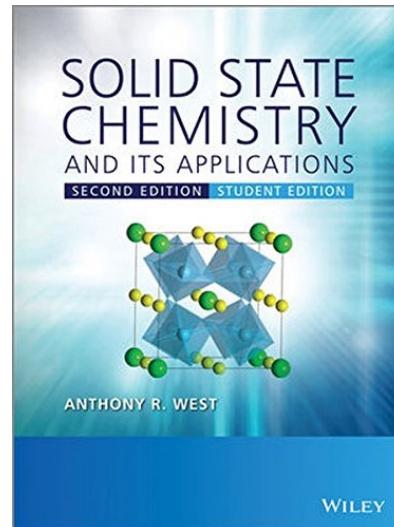
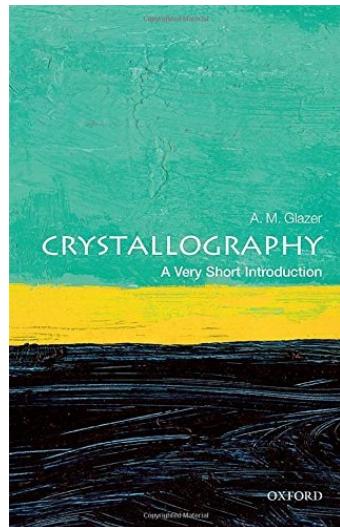
Real materials

Test 2 with feedback (12.5% of module)

Source Material for Course

Most materials science / chemistry / physics textbooks cover the basics of this course

The slides are a skeleton, fleshed out with lectures, activities, and reading

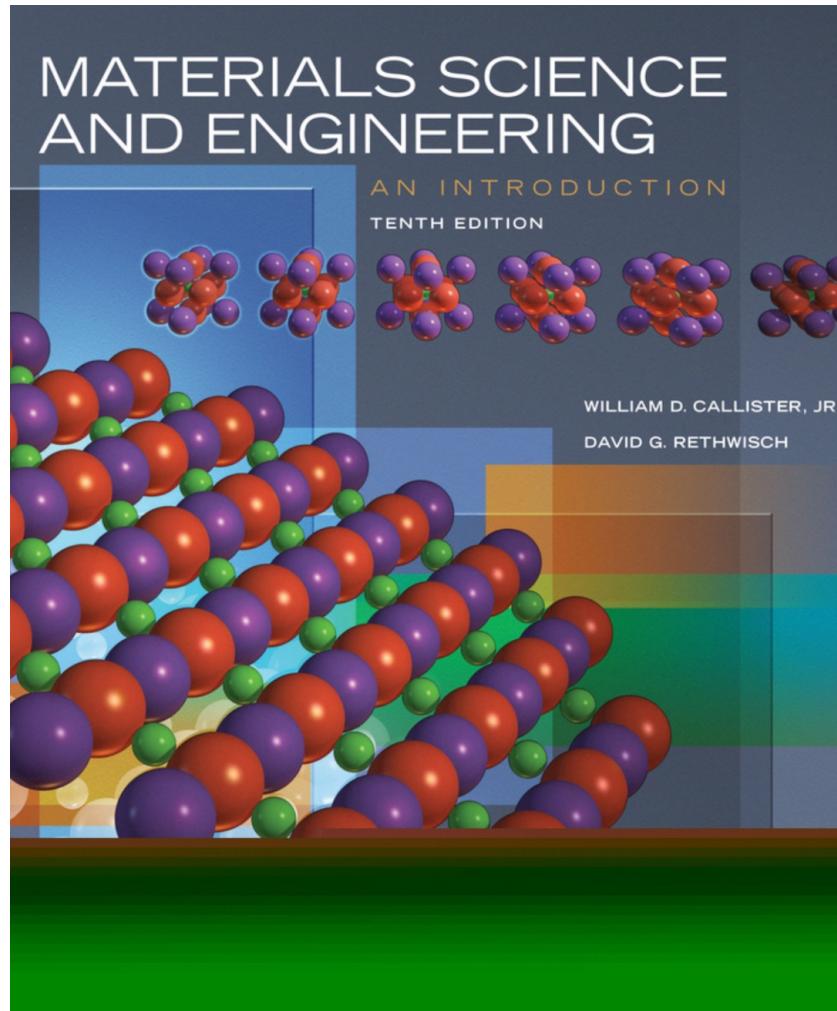


General

Specialist

Special thanks to Michael Rushton for sharing his images

Recommended General Textbook



(Any edition is fine) ICL Library Access: <https://bit.ly/3g8fflv>

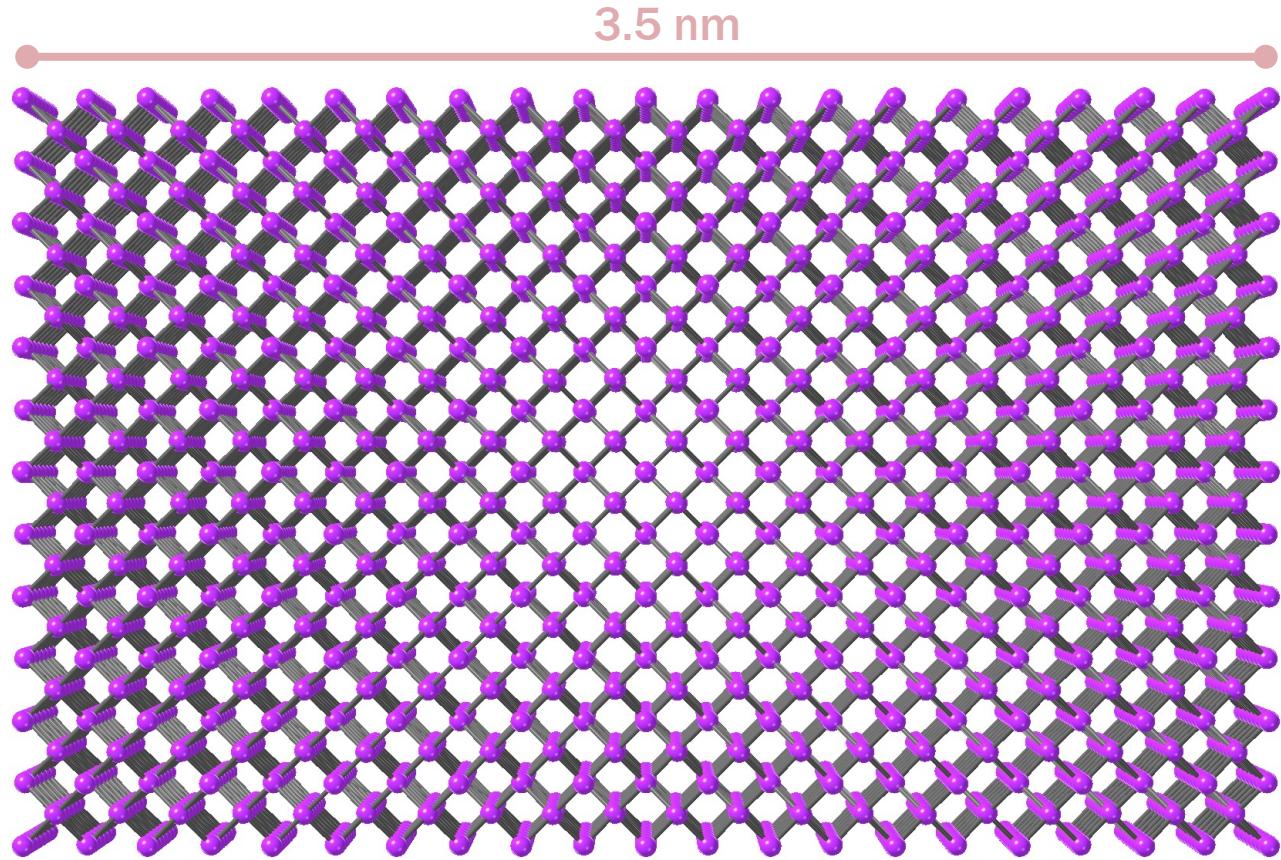
A Crystal is a Repeating Pattern

Crystalline material: atoms arranged in a pattern that repeats in three dimensions

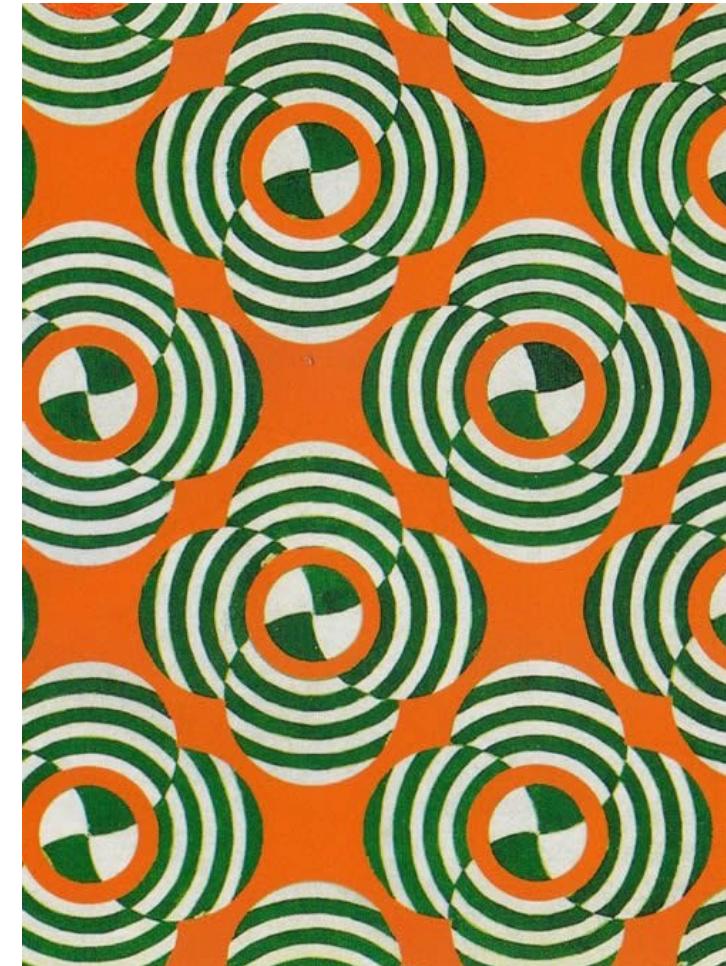
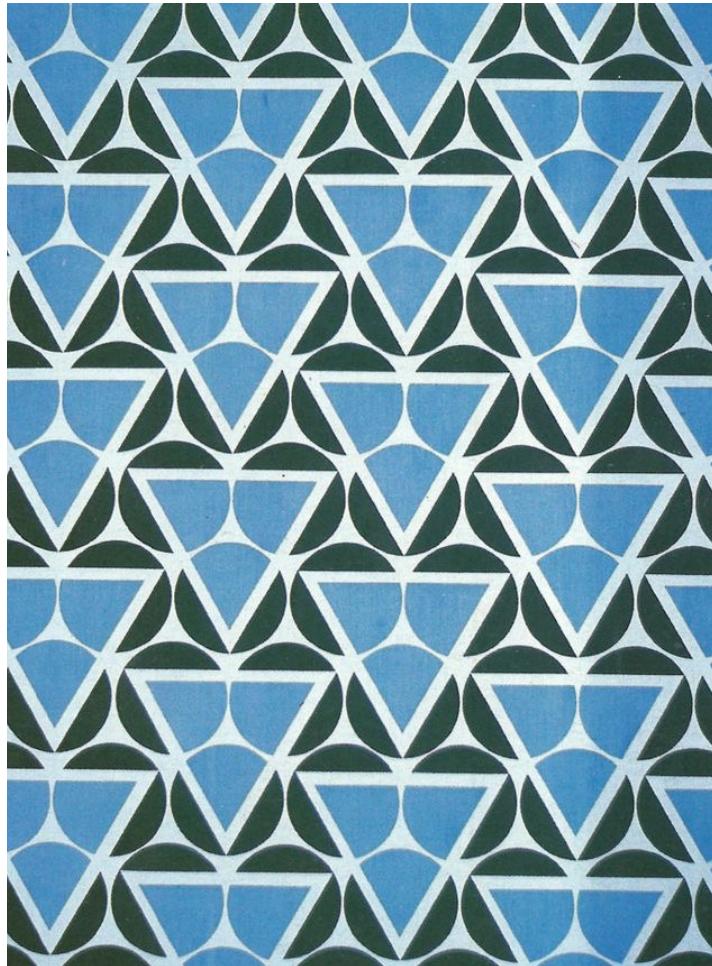
3.5 cm



3.5 nm



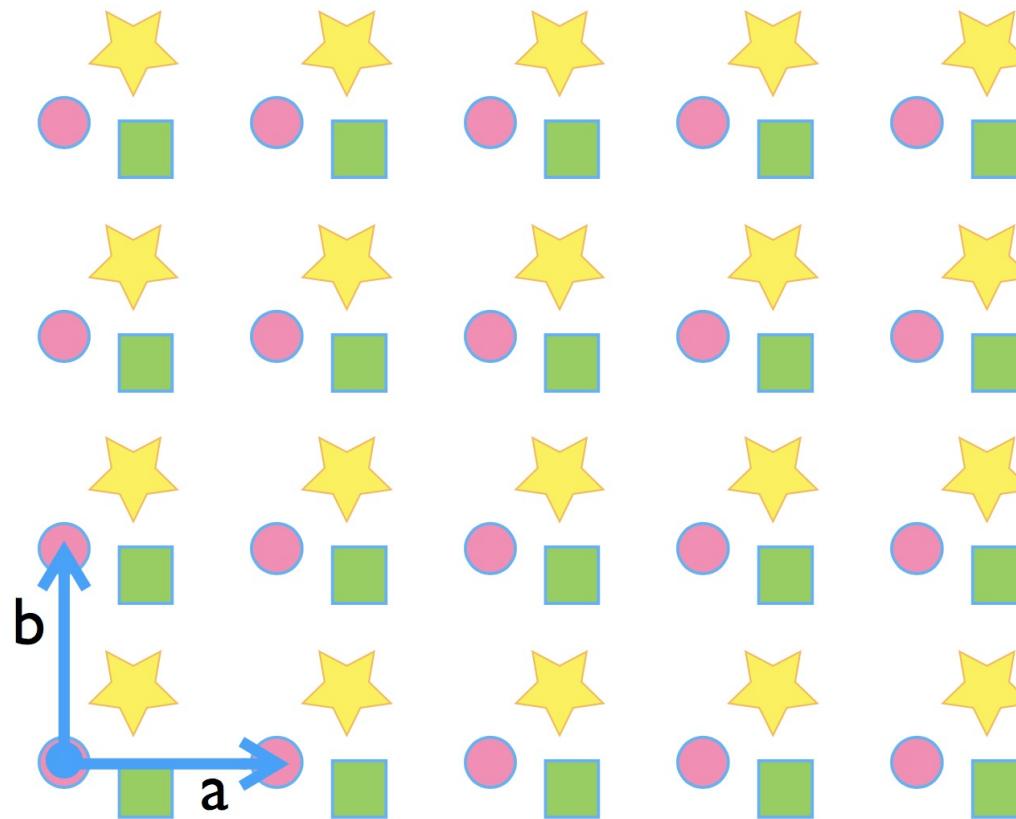
A Crystal is a Repeating Pattern



Textiles designs from Russian artist Varvara Stepanova (1894–1958)

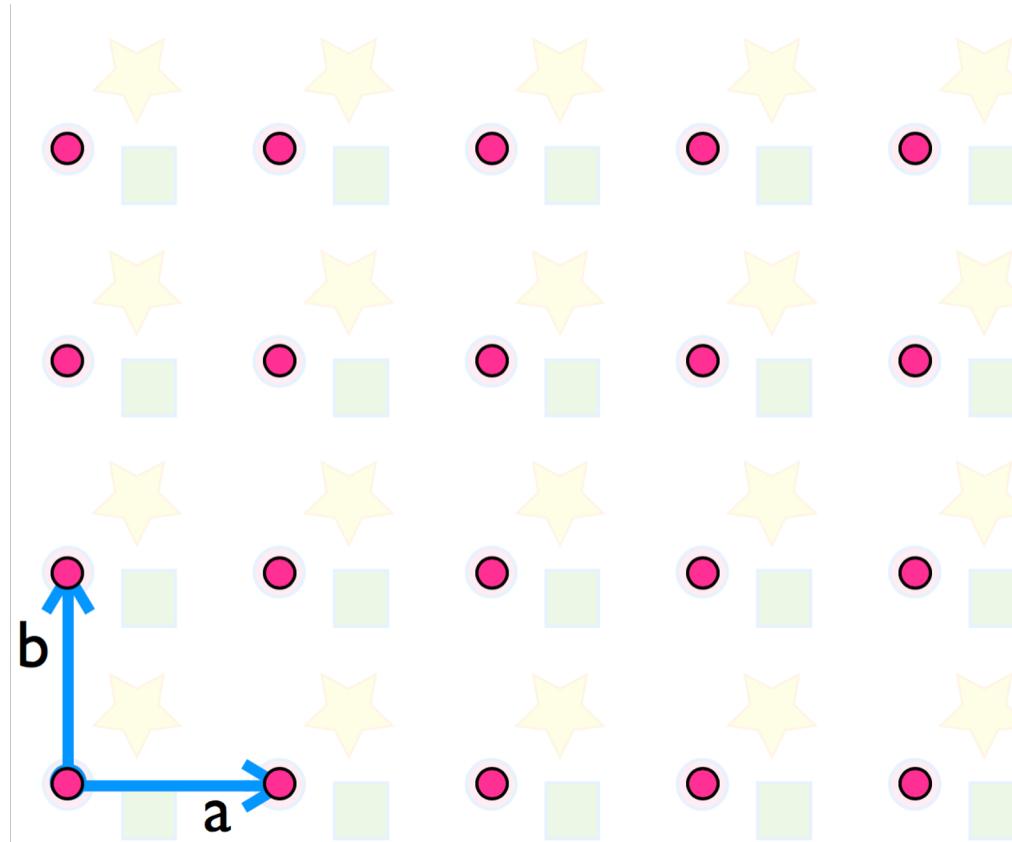
A Crystal is a Repeating Pattern

Crystalline material: atoms arranged in a pattern that repeats in multiple dimensions



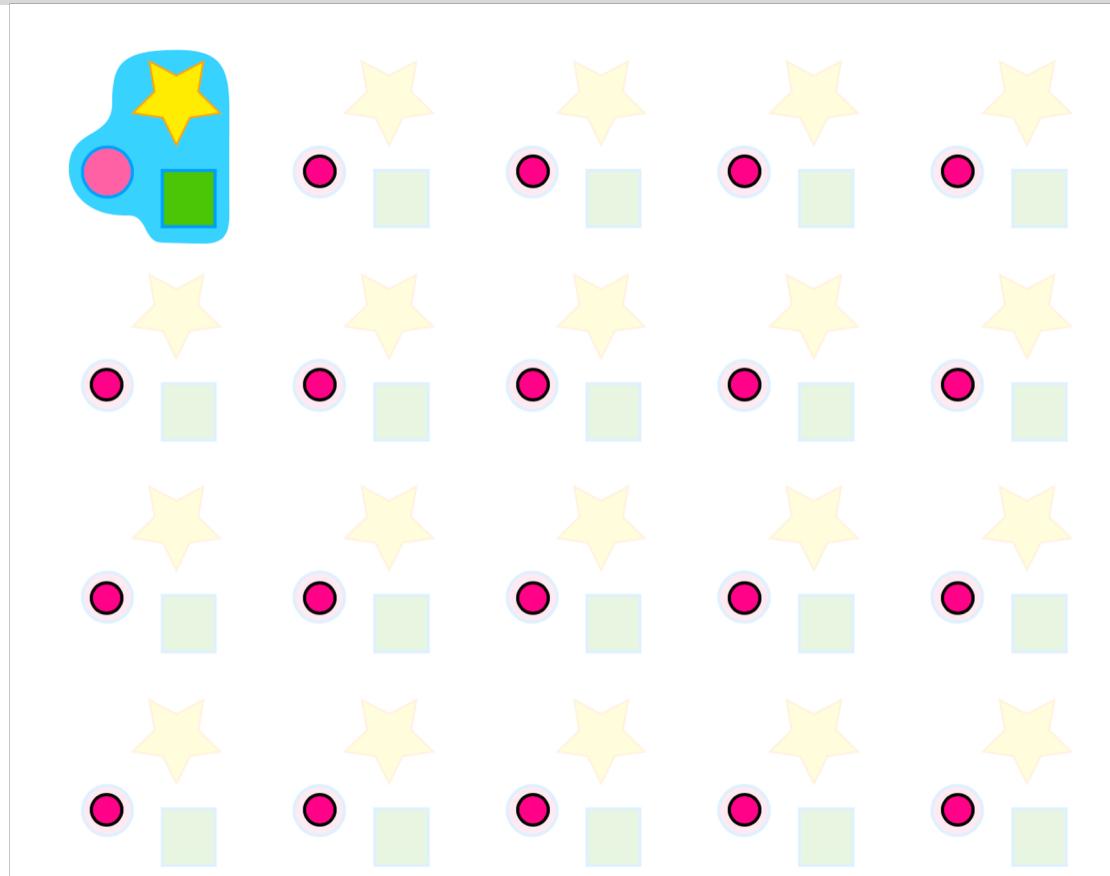
A Crystal is a Repeating Pattern

Lattice: an infinite array of points in space with each point having identical surroundings



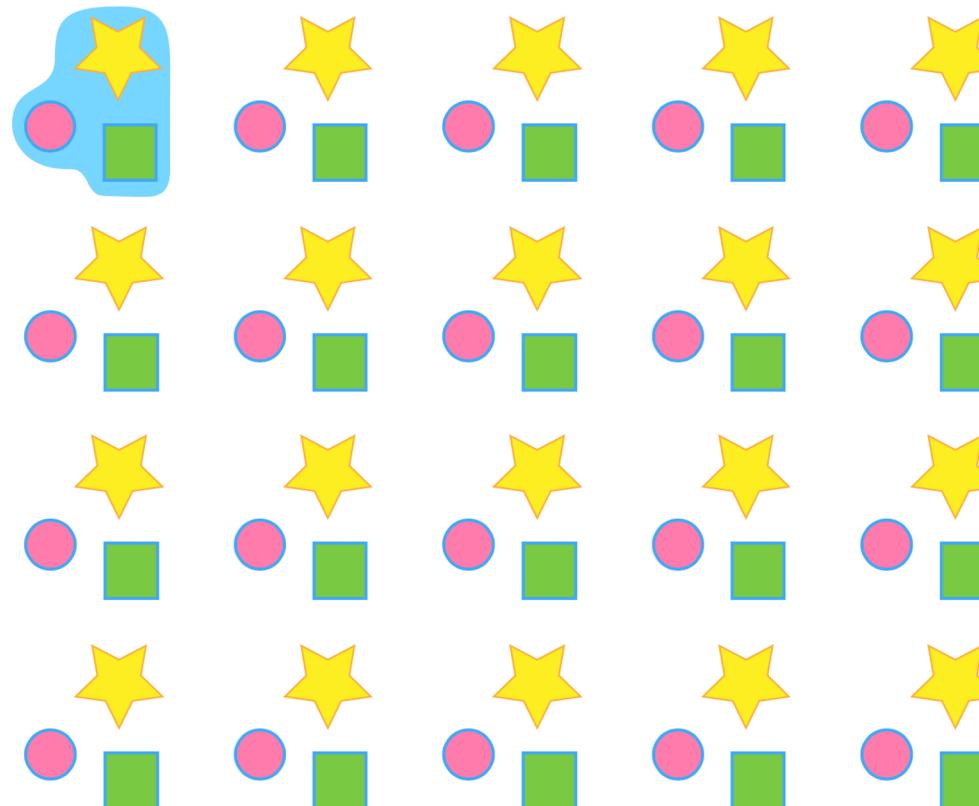
A Crystal is a Repeating Pattern

Basis: a motif consisting of an arrangement of atoms (or molecules) at each lattice point



A Crystal is a Repeating Pattern

Crystal: a combination of a lattice and a basis
 $C = L \otimes B$ (convolution operation)



Translational Symmetry

Symmetry associated with translation in space

1D Rod

$$R = ua$$

2D Net

$$R = ua + vb$$

An infinite array of points (R) generated by an integer number (u) of vectors (\mathbf{a})

3D Lattice

$$R = ua + vb + wc$$

What do the resulting arrays of points look like?

Lattice Vectors in 3D

All lattice points (R) can be generated from three lattice vectors (a, b, c) by translation

$$R = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

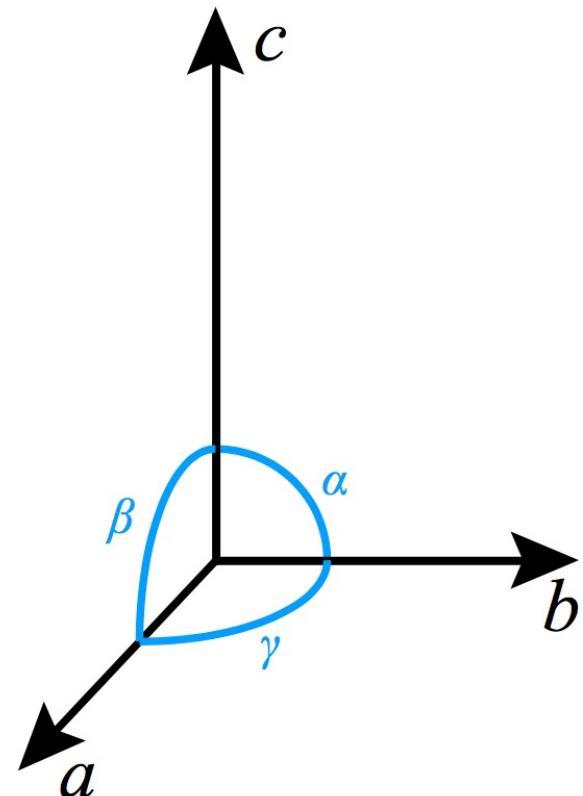
Vectors: $\mathbf{a}, \mathbf{b}, \mathbf{c}$

Vector lengths: a, b, c

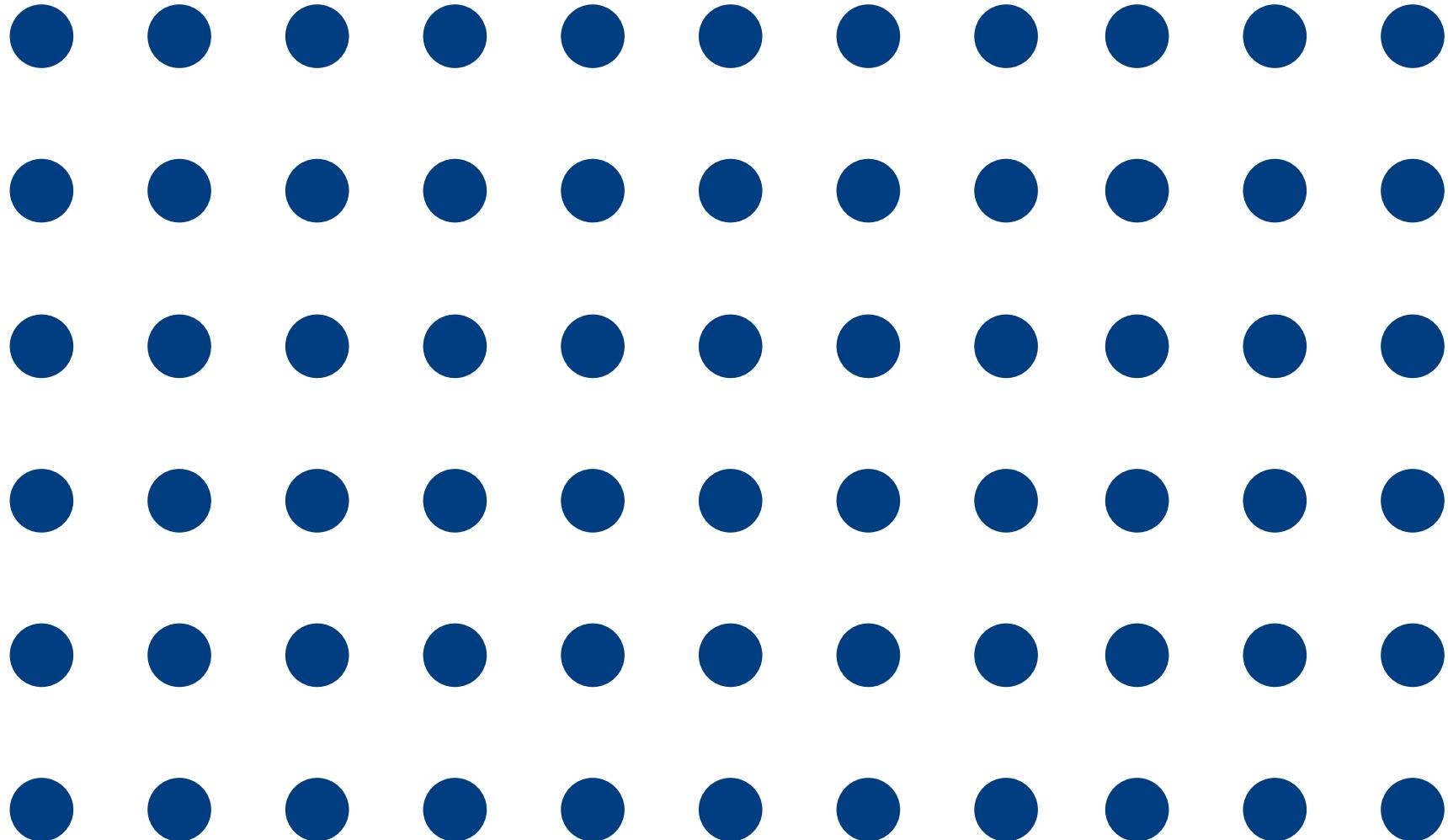
Vector angles: α, β, γ

Vector matrix:

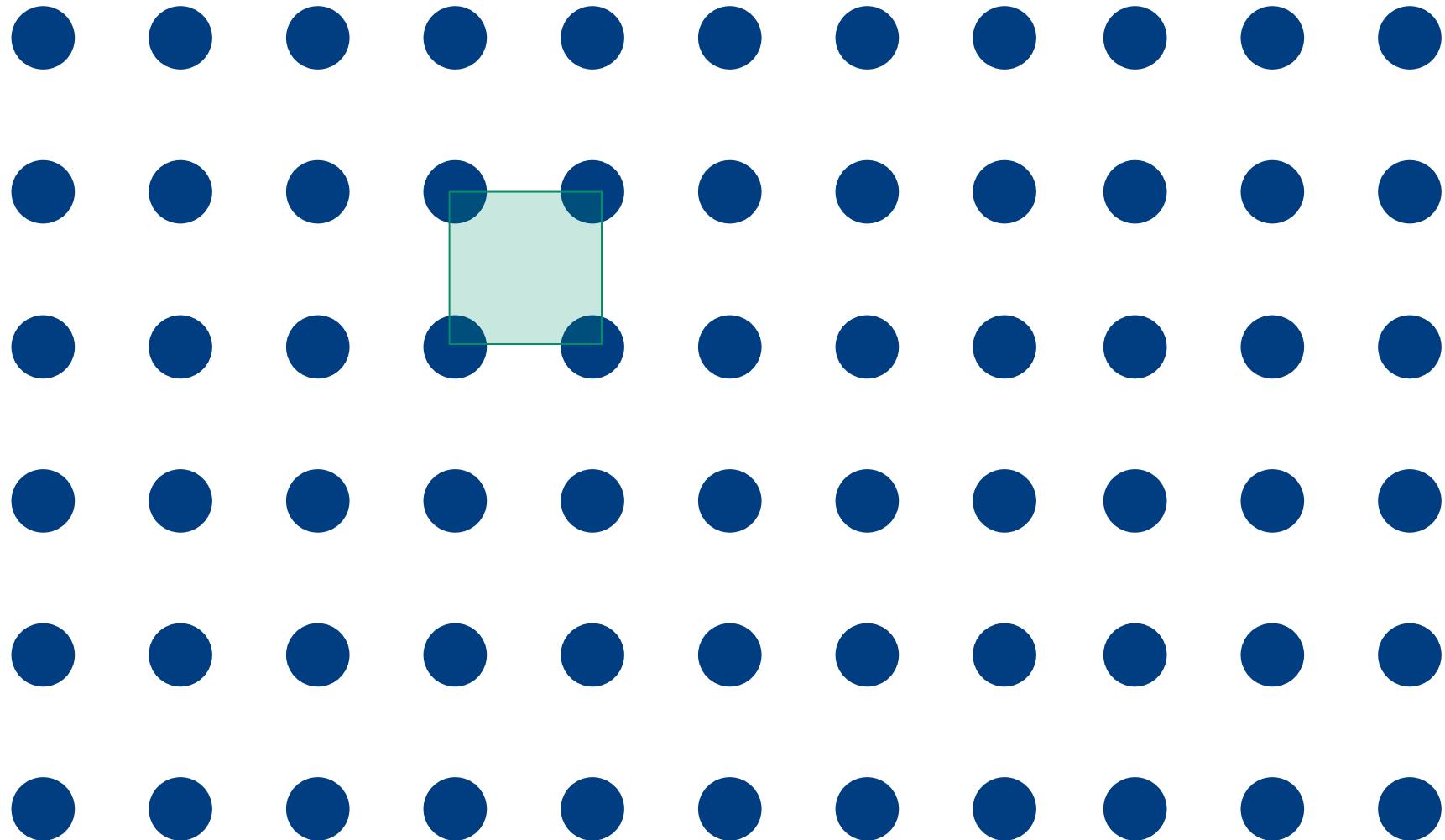
$$\begin{bmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{bmatrix}$$



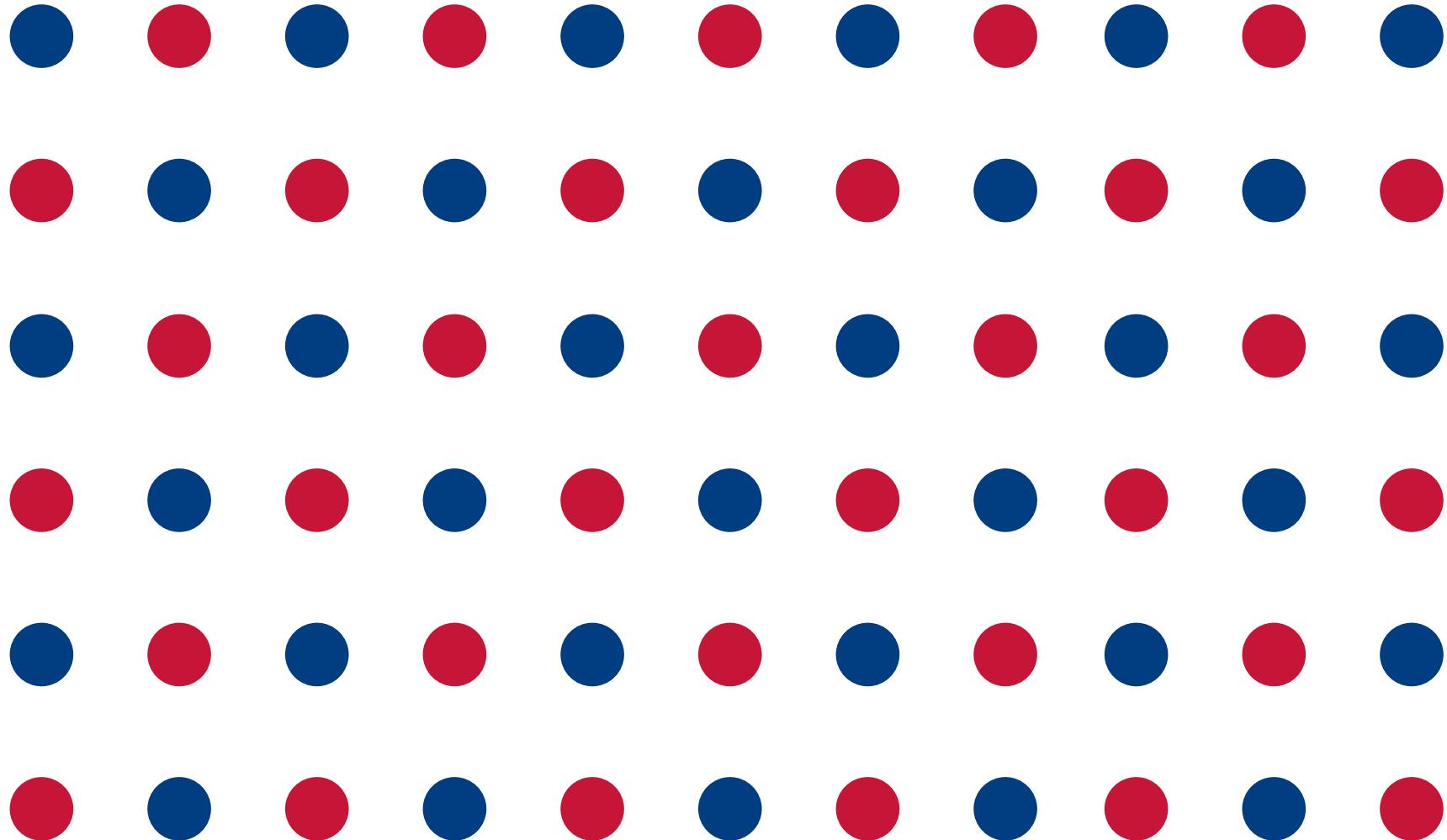
Identifying a Unit Cell



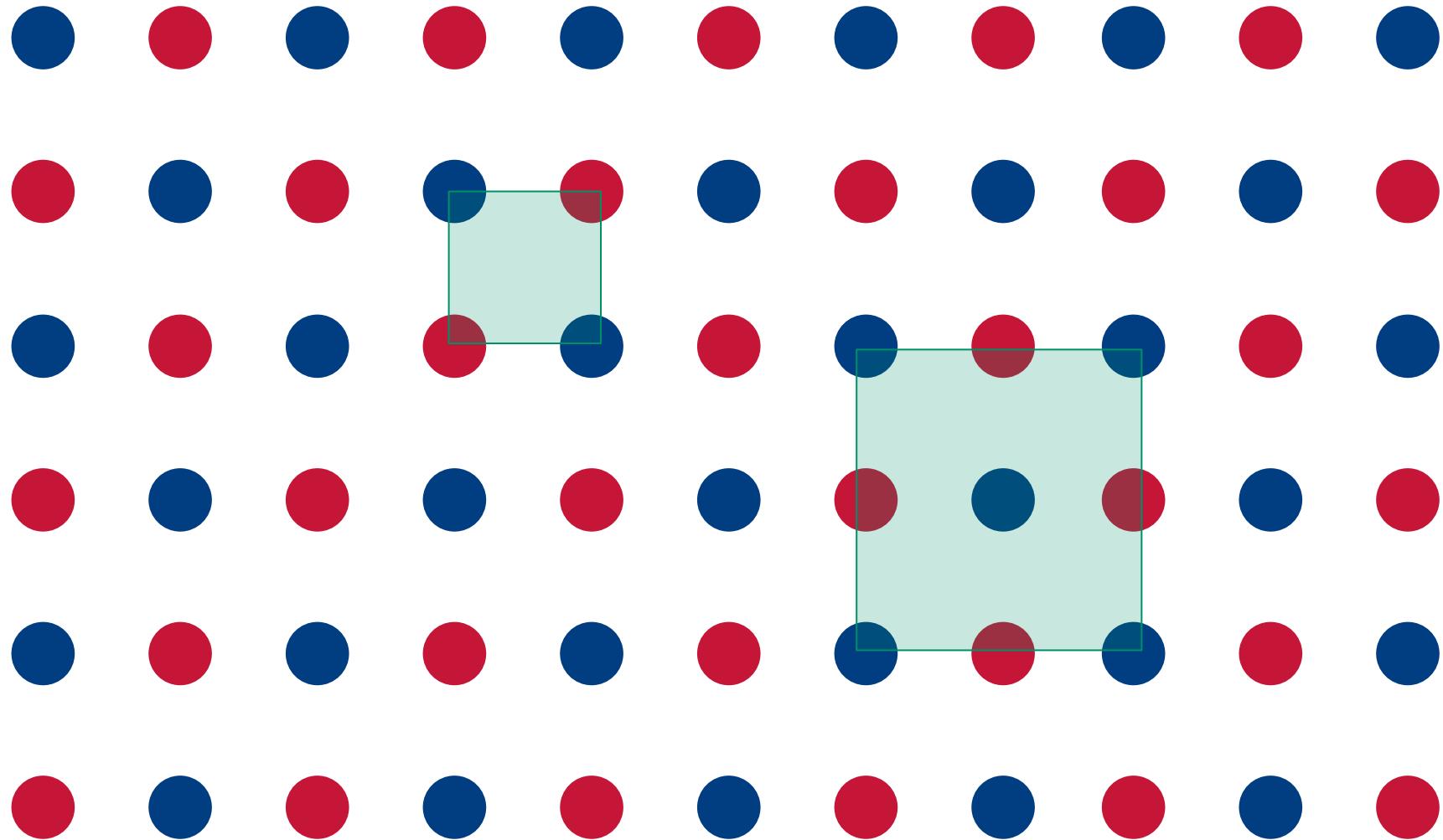
Identifying a Unit Cell



Identifying a Unit Cell



Identifying a Unit Cell



Identifying a Unit Cell

Unit cell: the simplest portion of a structure that fills all space when repeated by translation

There is an infinite number of possible cells, but there are crystallographic guidelines, including:

- Lattice points should be at the corners of the cell
- Edges of the cell connect equivalent points
- The 3D unit cell is a parallelepiped (opposite faces are parallel)
- Simplest repeating unit of a crystal (smallest volume and number of atoms)

Auguste Bravais (1811-1863)

Born in France. Research in crystallography, magnetism, astronomy. Published on “Bravais Lattices” in 1850

LES SYSTÈMES FORMÉS PAR DES POINTS

DISTRIBUÉS RÉGULIÈREMENT SUR UN PLAN OU DANS L'ESPACE;

PAR M. A. BRAVAIS,

Lieutenant de vaisseau, Professeur à l'École Polytechnique.

(Présenté à l'Académie des Sciences, le 11 décembre 1848.)

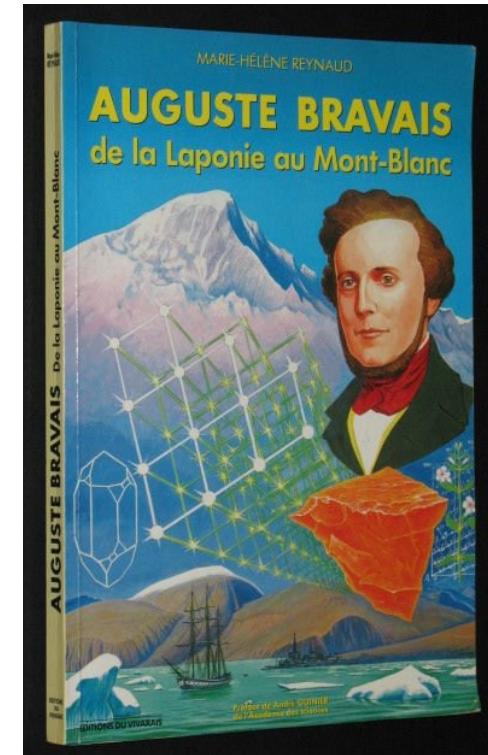
§ I. — DÉFINITIONS PRÉLIMINAIRES.

Pour obtenir un système de points distribués régulièrement dans l'espace, prenons deux points arbitrairement, et joignons-les l'un à l'autre par une ligne droite que nous prolongerons indéfiniment dans les deux sens. Chargeons cette droite d'une série illimitée d'autres points, tous équidistants entre eux, et séparés par un intervalle constant, égal à la distance des deux points primordiaux. Le système rectiligne de ces points équidistants recevra, dans le cours de ce Mémoire, le nom de *Rangée*. L'intervalle fondamental qui sépare deux points voisins sera désigné sous le nom de *paramètre de la Rangée*.

Prenons une deuxième Rangée de même paramètre ; plaçons-la parallèlement à la précédente, dans une situation relative arbitrairement choisie, et joignons entre elles ces deux Rangées par un plan géométrique qui, de sa

XXXII^e Cahier.

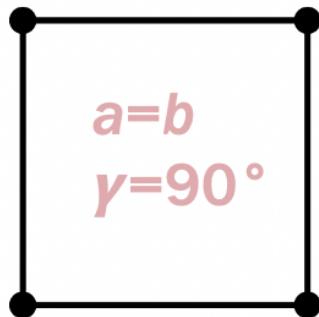
1



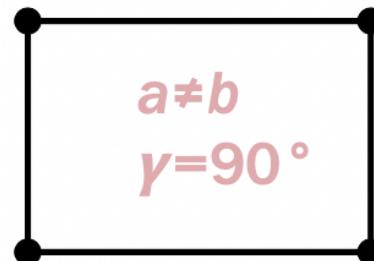
1848 Paper: <http://gallica.bnf.fr/ark:/12148/bpt6k4336880/f4.image>

Bravais Lattices in 2D

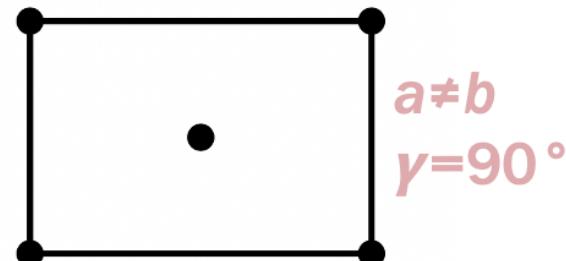
A parallelogram (two pairs of parallel sides)



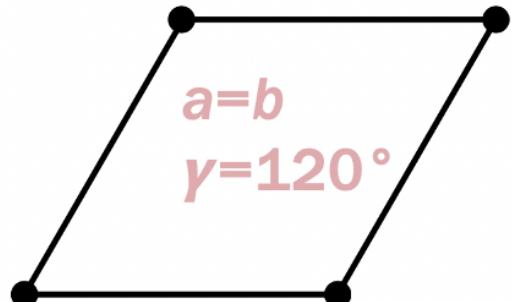
Square p-lattice



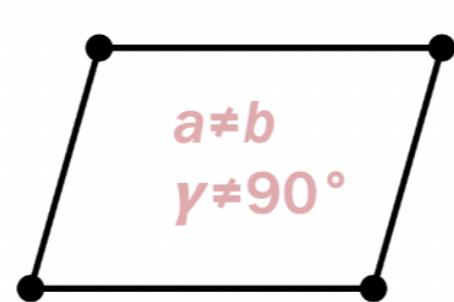
Rectangular p-lattice



Rectangular c-lattice



The hexagonal p-lattice



Oblique p-lattice

Note 1: A primitive (p) cell contains one lattice point only

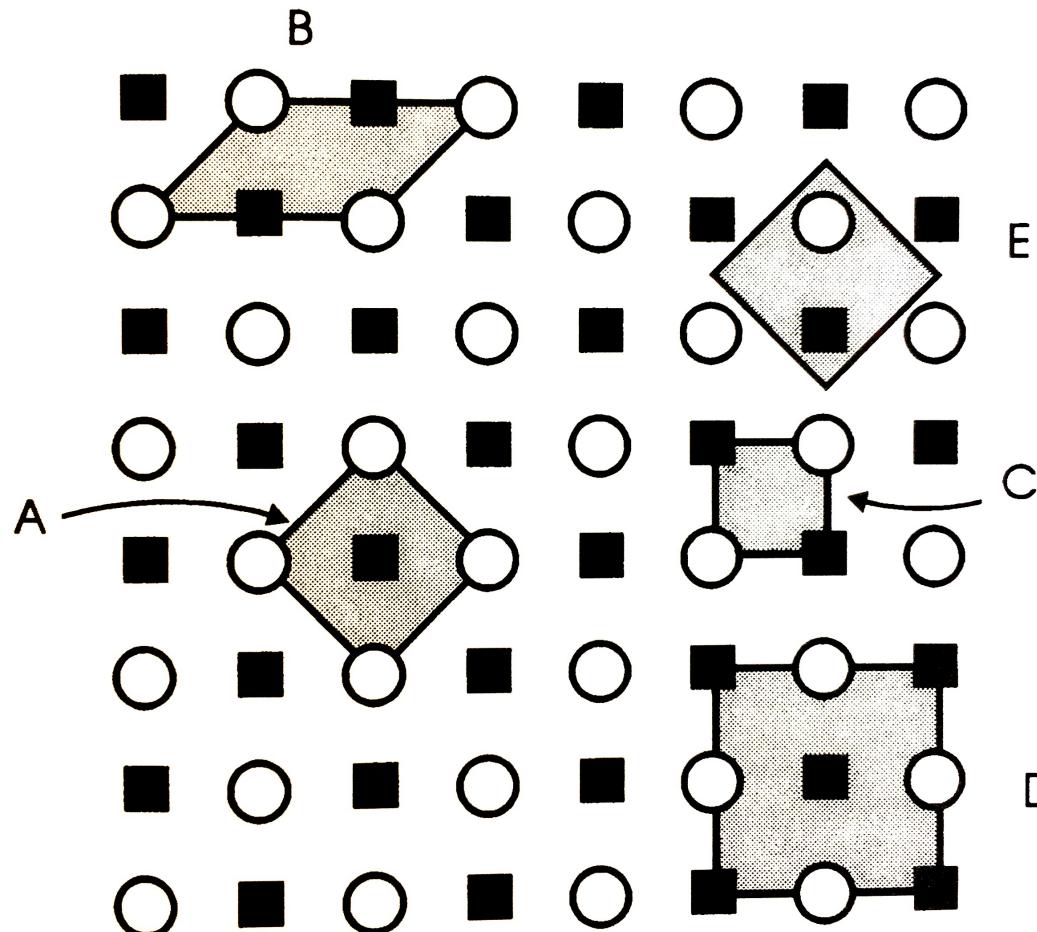
Note 2: A centered (c) cell contains two lattice points

Which 2D Bravais Lattice?

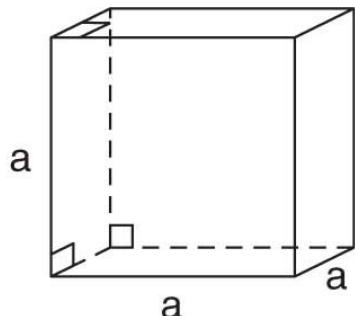


Drawing Unit Cells

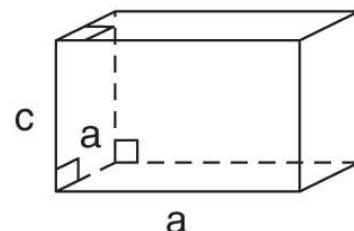
Which are valid unit cells for this 2D lattice?



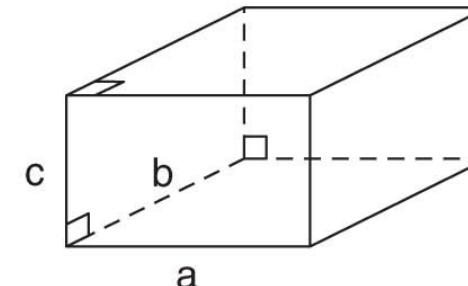
7 Crystal Systems in 3D



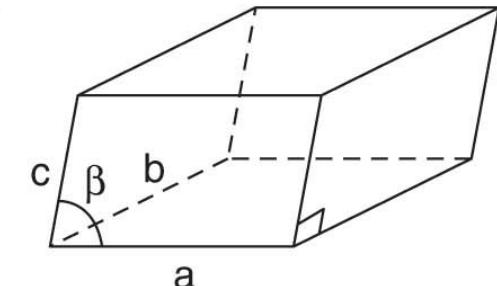
Cubic



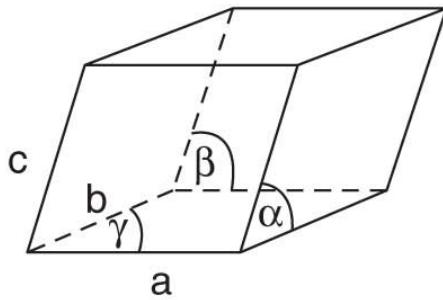
Tetragonal



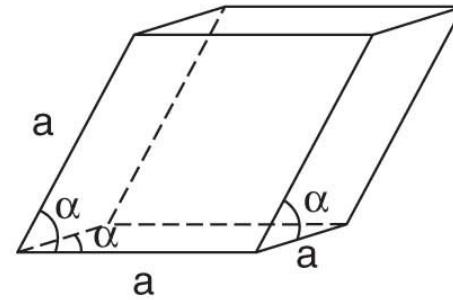
Orthorhombic



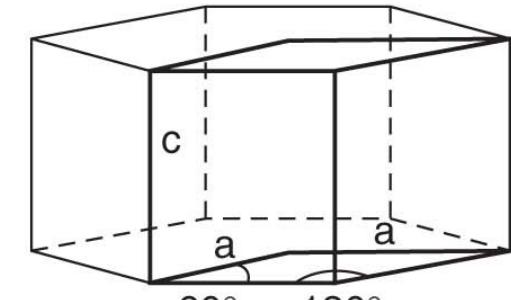
Monoclinic



Triclinic



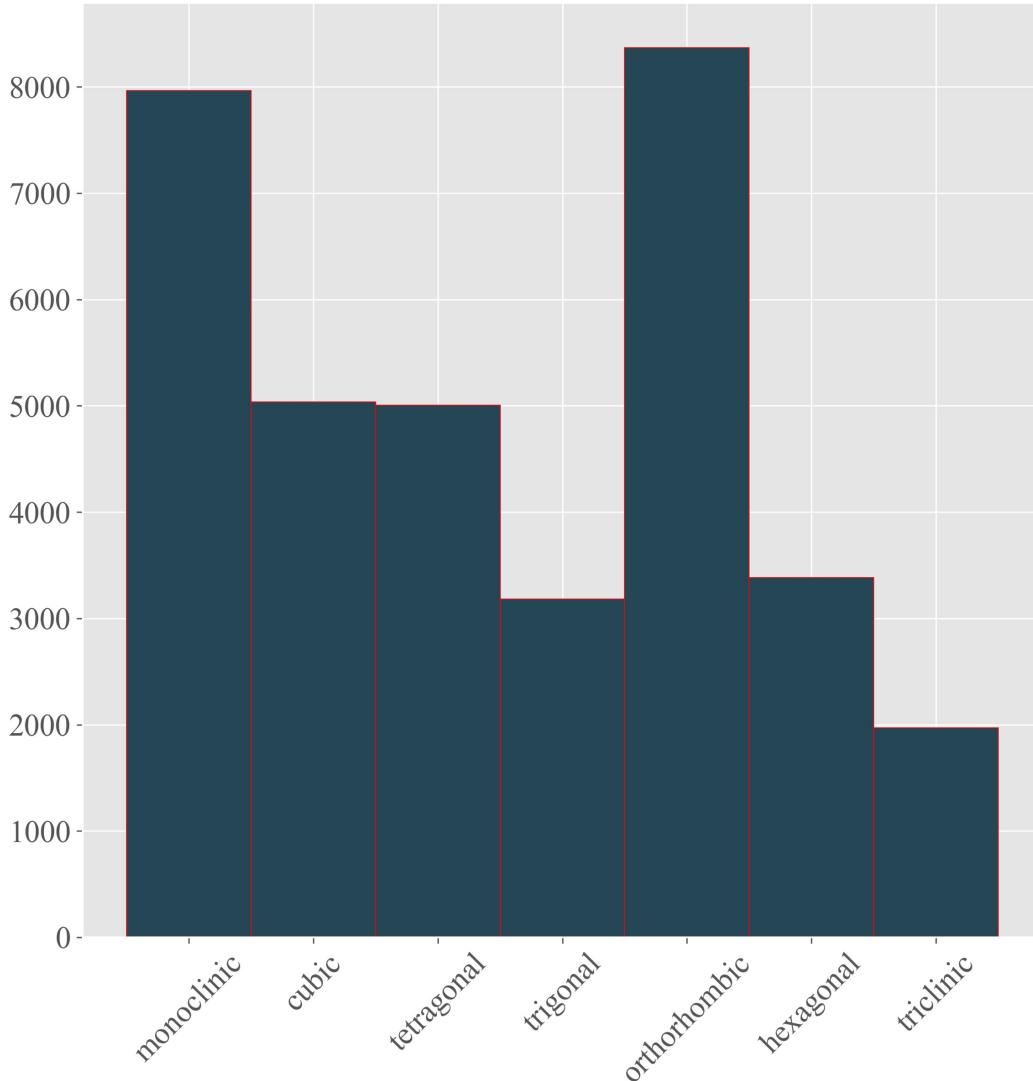
Rhombohedral
(or Trigonal)



Hexagonal

You need to remember these (essential for materials science)!

Distribution of Crystal Systems



Number of entries in
the Inorganic Crystal
Structure Database

Collected by
Dr Dan Davies

Lattice Centering

Symbol	Name	Description
P	Primitive (Simple)	Lattice points on cell corners
I	Body Centered <u>(Innenzentrierte)</u>	Additional point in centre of cell
F	Face Centered	Additional point in centre of each face
A,B,C	Base Centered	Additional point on pair of faces (letter determines pair).
R	Rhombohedral	Distinct to hexagonal system

14 Bravais Lattices in 3D

Axial System		Lattice Centering	
Name	Axial Lengths and Angles	Name	Symbol
Cubic	$a=b=c$ $\alpha=\beta=\gamma=90^\circ$	Simple Body-Centered Face-Centered	P I F
Tetragonal	$a=b \neq c$ $\alpha=\beta=\gamma=90^\circ$	Simple Body-Centered	P I
Orthorhombic	$a \neq b \neq c$ $\alpha=\beta=\gamma=90^\circ$	Simple Body-Centered Base-Centered Face-Centered	P I C F
Rhombohedral (trigonal)	$a=b=c$ $\alpha=\beta=\gamma \neq 90^\circ$	Rhombohedral	R
Hexagonal	$a=b \neq c$ $\alpha=\beta=90^\circ, \gamma=120^\circ$	Simple	P
Monoclinic	$a \neq b \neq c$ $\alpha=\gamma=90^\circ \neq \beta$	Simple Base-Centered	P C
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple	P

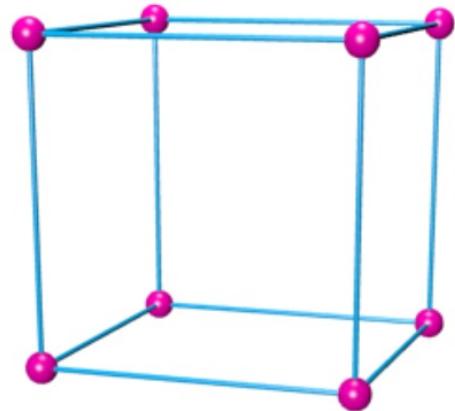
Note:

The terms
“simple” and
“primitive” used
interchangeably.

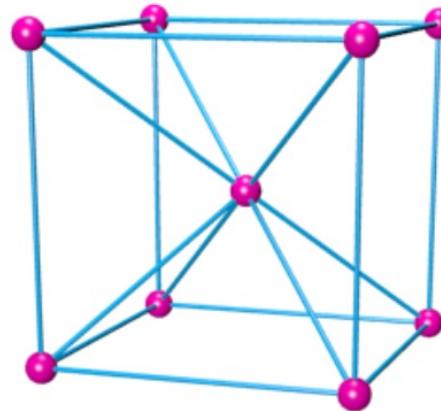
Remember, they
have one lattice
point per unit cell!

Bravais Lattice: Cubic

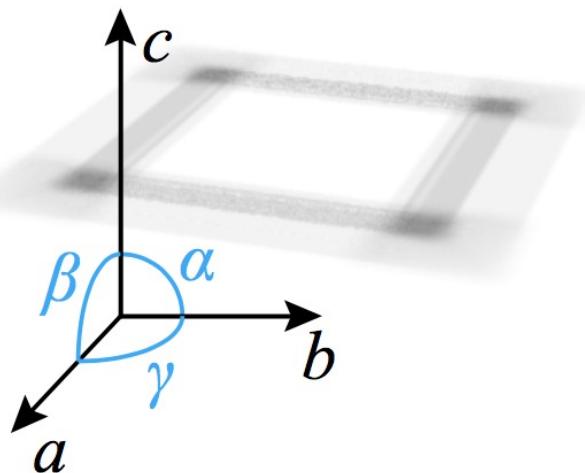
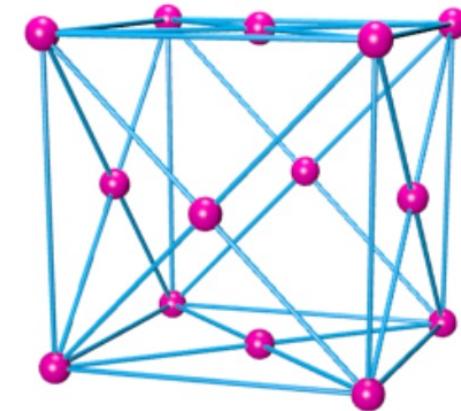
P



I



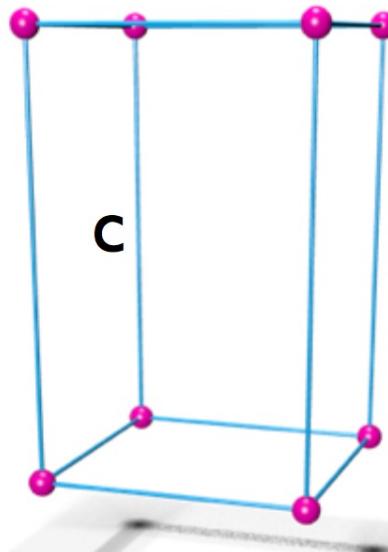
F



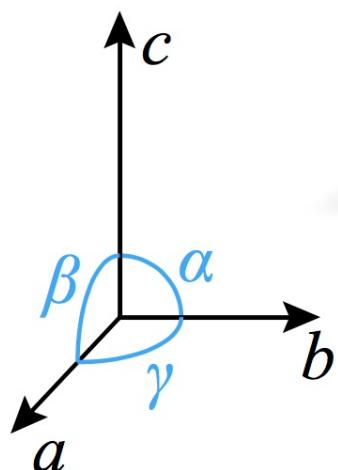
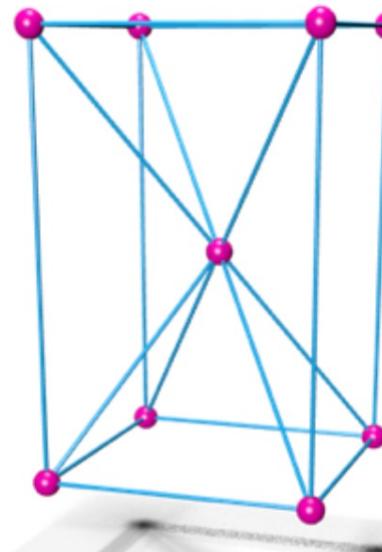
$$\begin{aligned}a &= b = c \\ \alpha &= \beta = \gamma = 90^\circ\end{aligned}$$

Bravais Lattice: Tetragonal

P



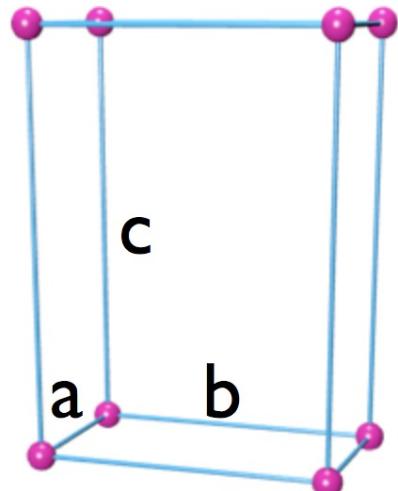
I



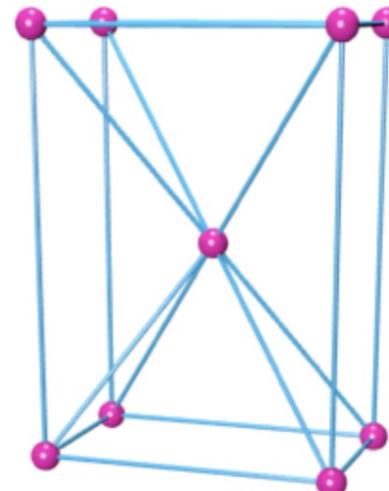
$$\begin{aligned}a &= b \neq c \\ \alpha &= \beta = \gamma = 90^\circ\end{aligned}$$

Bravais Lattice: Orthorhombic

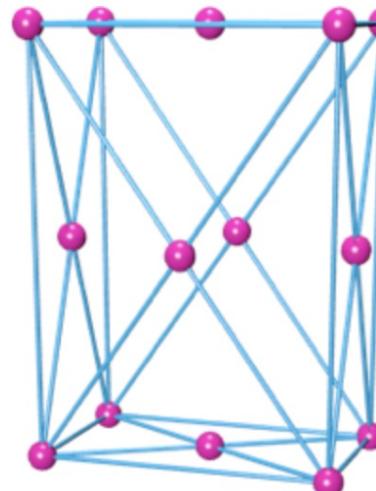
P



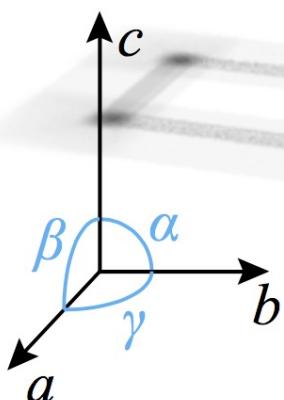
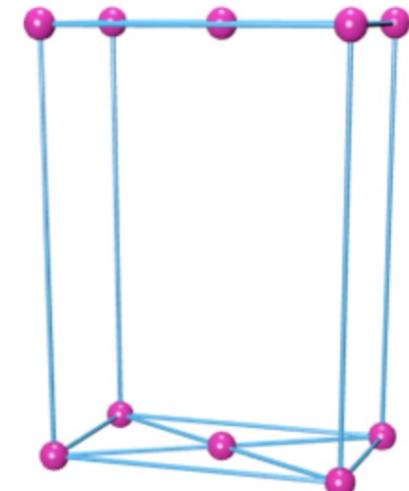
I



F

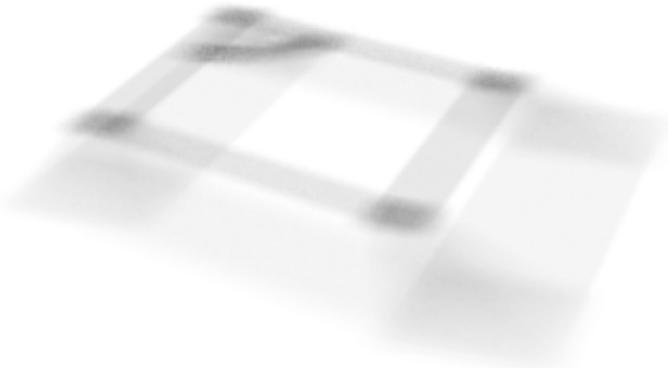
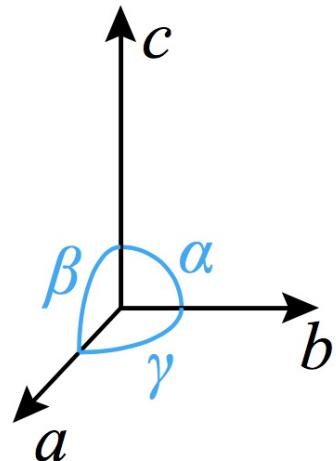
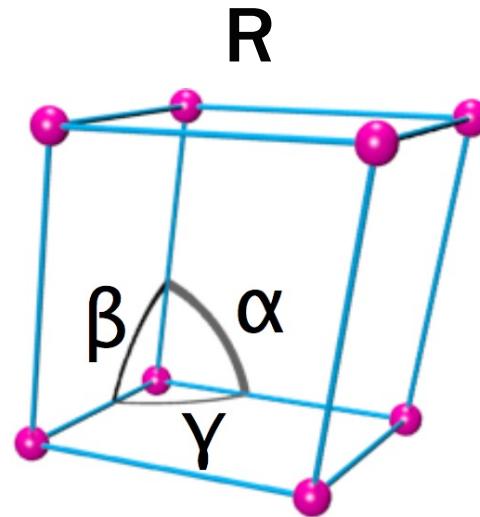


C



$$\begin{aligned}a &\neq b \neq c \\ \alpha &= \beta = \gamma = 90^\circ\end{aligned}$$

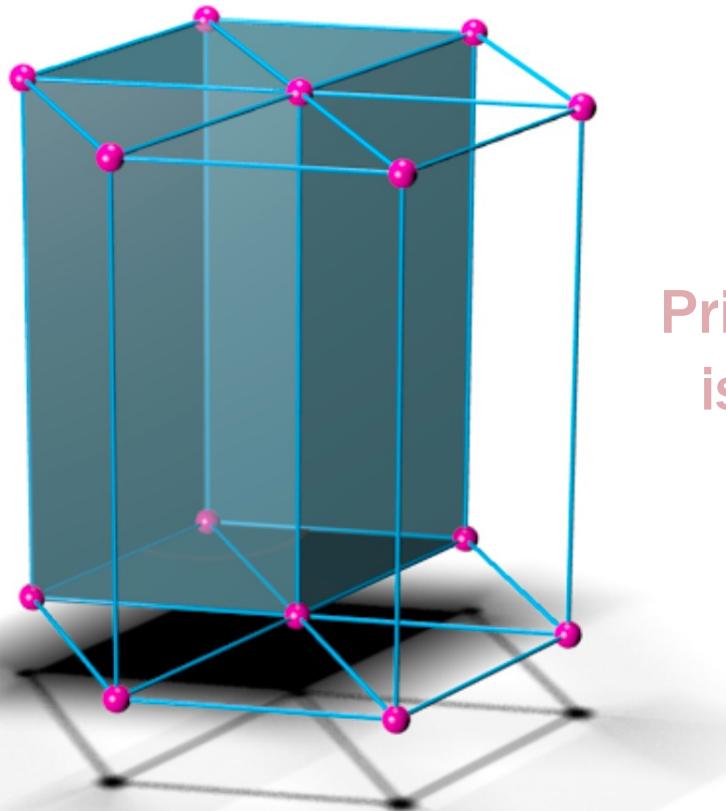
Bravais Lattice: Rhombohedral



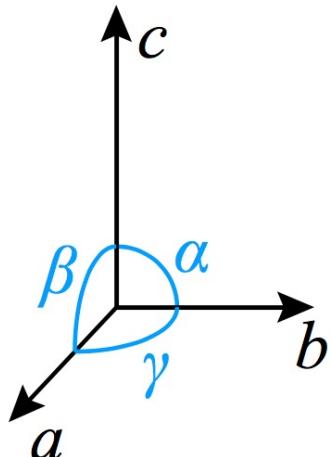
$a=b=c$
 $\alpha=\beta=\gamma \neq 90^\circ$

Bravais Lattice: Hexagonal

P



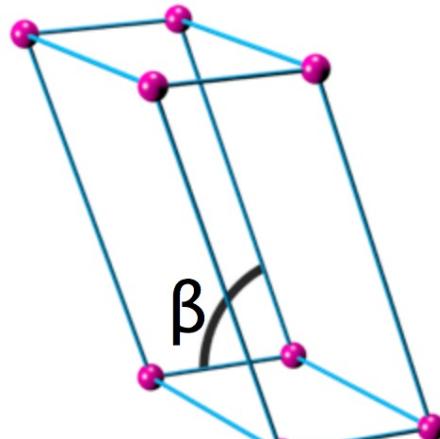
Primitive unit cell
is shaded blue



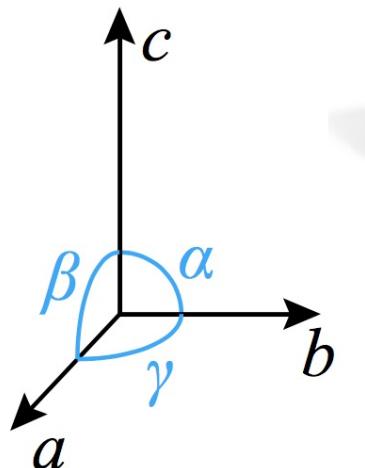
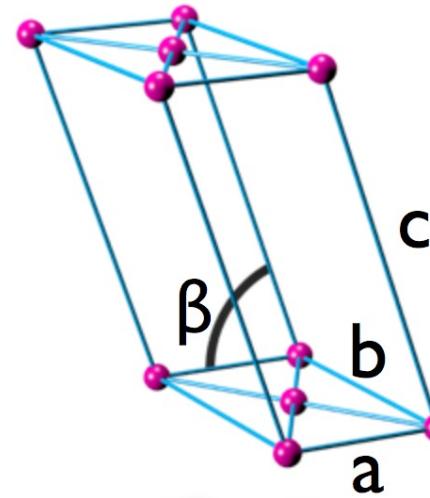
$$a=b \neq c$$
$$\alpha=\beta=90^\circ, \gamma=120^\circ$$

Bravais Lattice: Monoclinic

P

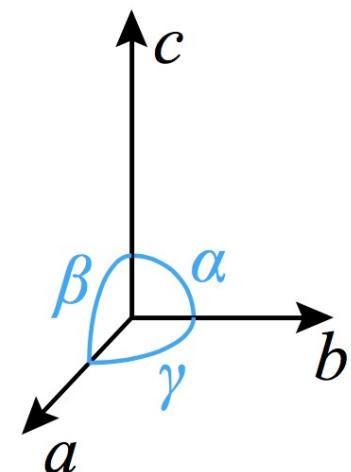
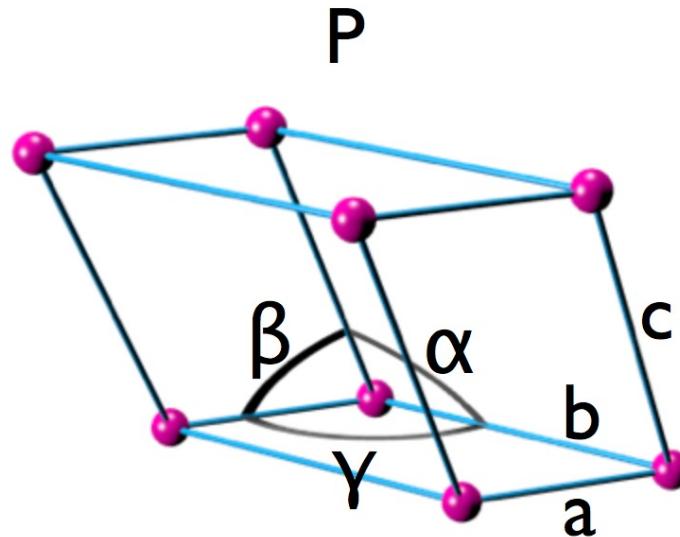


C



$$\begin{aligned}a &\neq b \neq c \\ \alpha &= \gamma = 90^\circ \neq \beta\end{aligned}$$

Bravais Lattice: Triclinic



$a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$

Units of Length (for Materials)

Unit	SI (m)
Ångstrom	$1 \text{ \AA} = 10^{-10} \text{ m}$
Picometer	$1 \text{ pm} = 10^{-12} \text{ m}$
Nanometer	$1 \text{ nm} = 10^{-9} \text{ m}$
Micron	$1 \text{ \mu m} = 10^{-6} \text{ m}$
Bohr (H atom)	$a_0 = 5.29 \times 10^{-11} \text{ m}$

Lattice constant of Si: $a = 5.43 \text{ \AA}$

Bond length of H₂: $r = 0.74 \text{ \AA}$

Thickness of a thin-film solar cell: $d = 500 \text{ nm}$

Volume of a Unit Cell

Vector products: $V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$

Cell lengths and angles: $V = abc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma) + 2(\cos\alpha \cos\beta \cos\gamma)^{\frac{1}{2}}$

Lattice System	Constraint	Volume
Cubic	$a = b = c$	a^3
Tetragonal	$a = b \neq c$	a^2c
Orthorhombic	$a \neq b \neq c$	abc

Unit cell volume of Si: $V = 160.10 \text{ \AA}^3$

Summary: Lattices

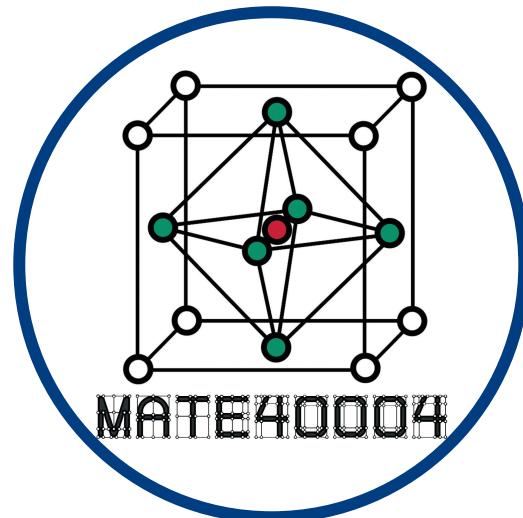
Class outcomes:

- Define crystal structure, lattice, basis
- Define unit cell and identify it in a lattice
- List 7 crystal systems in 3D
- Understand centring and 14 Bravais lattices
- Calculate the volume of a simple unit cell

MATE40004 – Structure 1

Crystallography
B. Symmetry

Professor Aron Walsh
Department of Materials
Imperial College London



<http://www.imperial.ac.uk/people/a.walsh>

Recap: Periodic Crystals

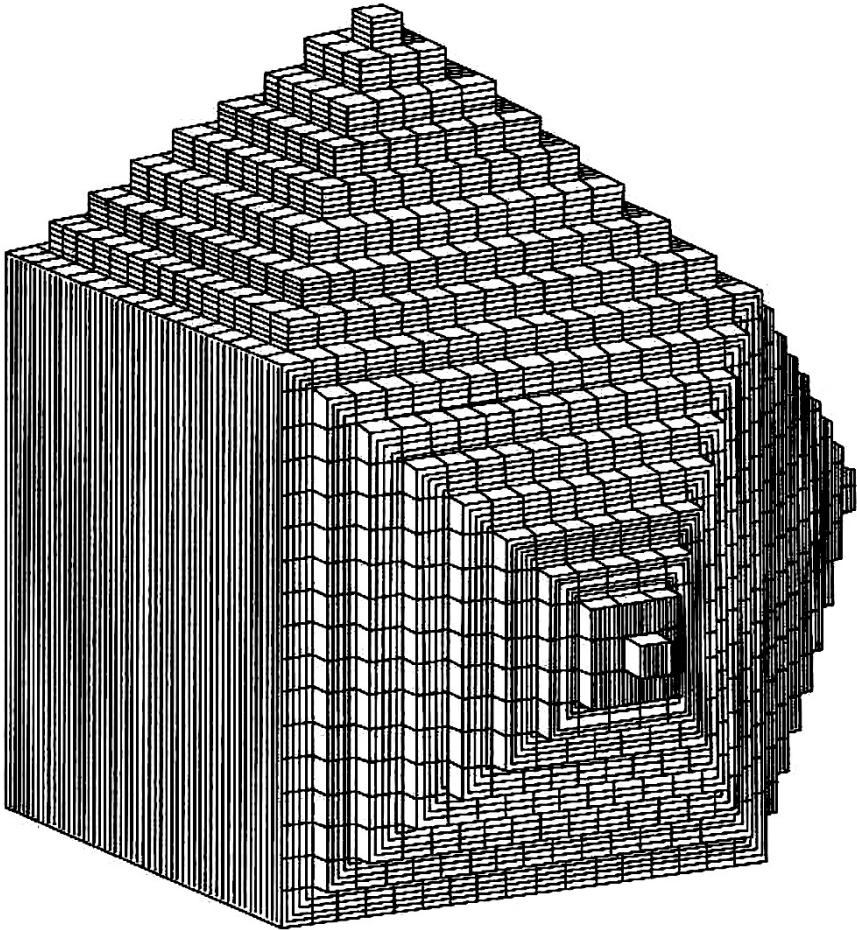
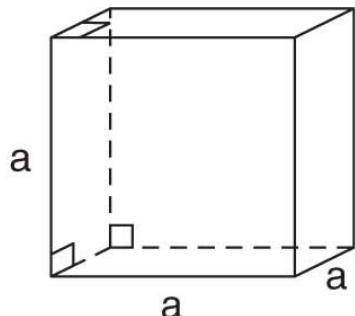


Image: Kittel, Solid-State Physics (1953)

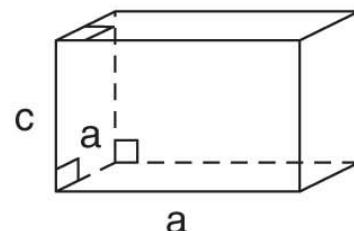
The structure of a crystalline material can be described by a unit cell repeated by translational symmetry

A macroscopic crystal will contain more than 10^{20} unit cells

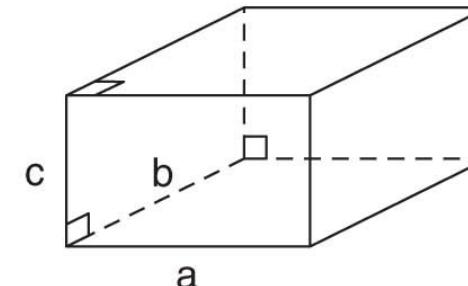
Recap: 7 Crystal Systems in 3D



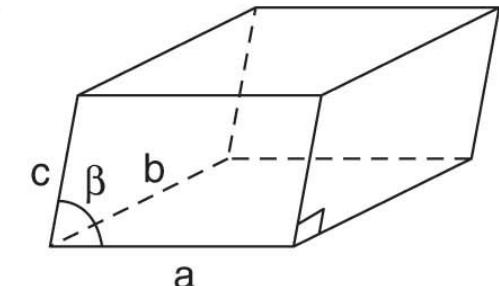
Cubic



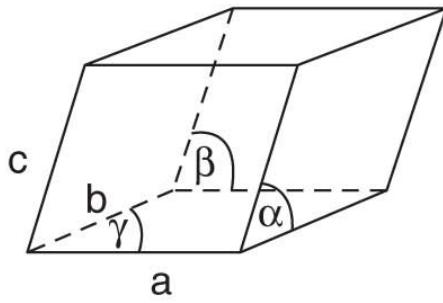
Tetragonal



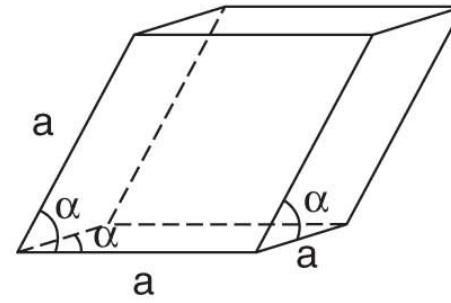
Orthorhombic



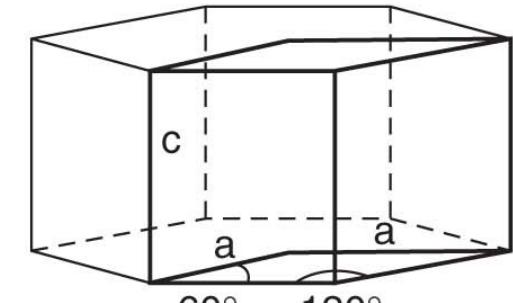
Monoclinic



Triclinic



Rhombohedral
(or Trigonal)



Hexagonal

Remember the constraints on lengths (a, b, c) and angles (α, β, γ)

Outline of Crystallography

Part 1

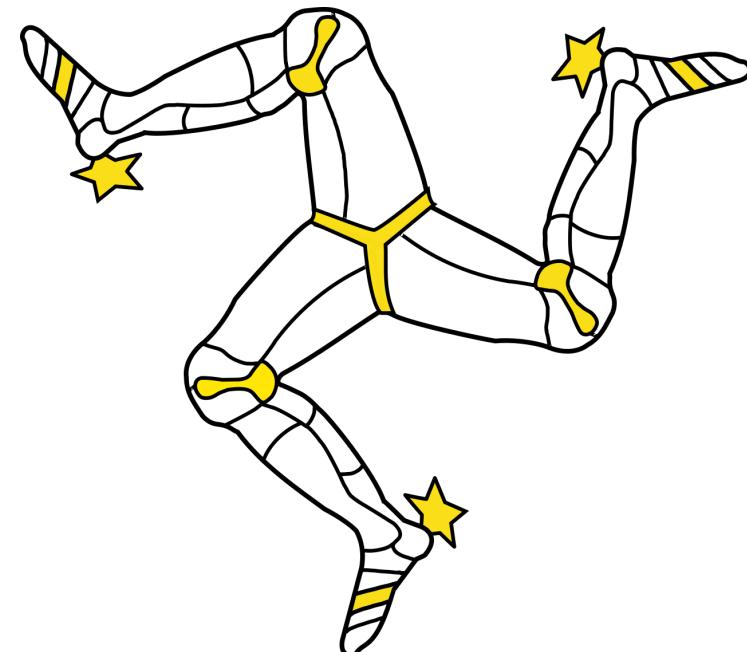
- A. Lattices
- B. Symmetry
- C. Geometry
- D. Packing

Symmetry

The property of an object whereby it appears unchanged following a transformation



Mirror symmetry
Butterfly wings



Rotational symmetry
Triskele on Isle of Man flag

Symmetry in Materials Science

Symmetry of a molecule or crystal can be used to predict and explain properties including:

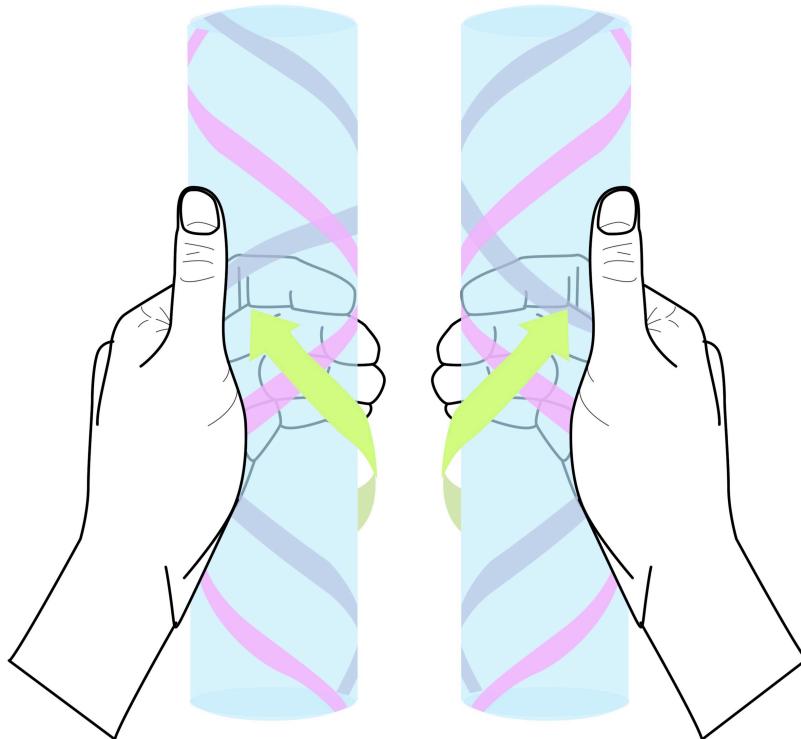
- **Bonding** – allowed combinations of atomic orbitals to form chemical (e.g. σ , π , δ) bonds
- **Vibrations** – normal modes of chemical systems including Infrared spectra

Symmetry simplifies characterisation

e.g. for a cubic crystal with $a=b=c$, you only need to measure a property along one axis

Symmetry in Materials Science

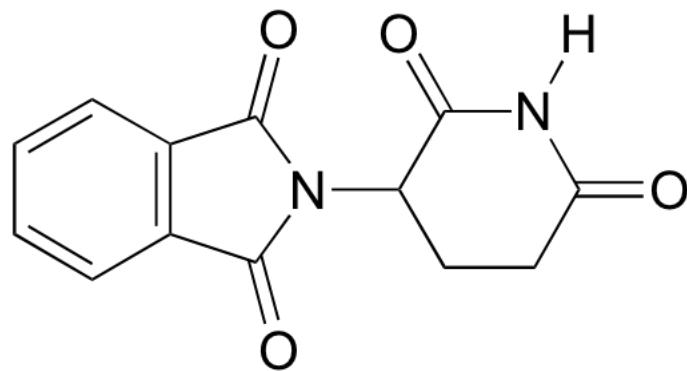
Chiral molecules/crystals cannot be superimposed on their mirror images, with profound effects



DNA is chiral. The helix can be right or left handed, but nature exclusively prefers right (B-DNA)

Symmetry in Materials Science

Chiral molecules/crystals cannot be superimposed on their mirror images, with profound effects



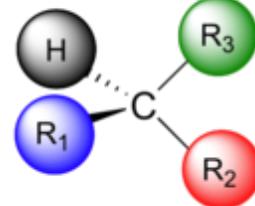
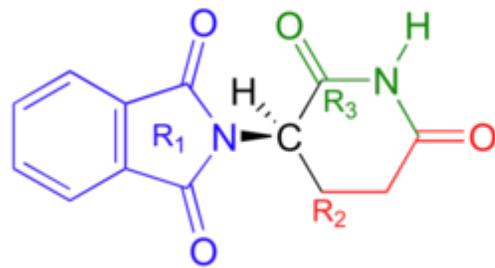
thalidomide

Drug prescribed in 1960s Europe to treat morning sickness in pregnant women

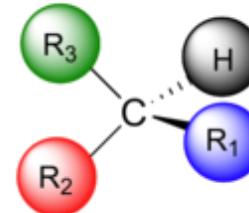
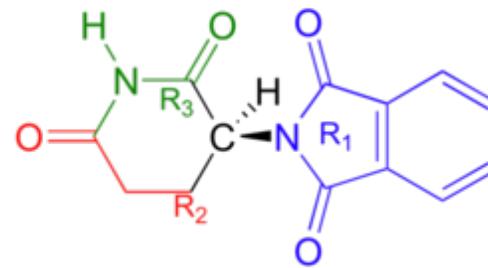
Symmetry in Materials Science

Chiral molecules/crystals cannot be superimposed on their mirror images, with profound effects

Causes birth defects



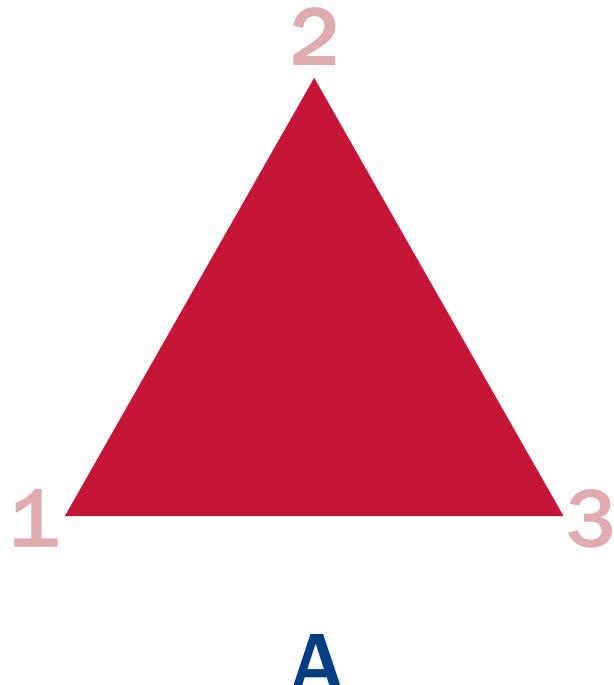
Treats morning sickness



Mixture of right and left-handed forms led to over 10,000 cases of phocomelia (limb malformations) in babies

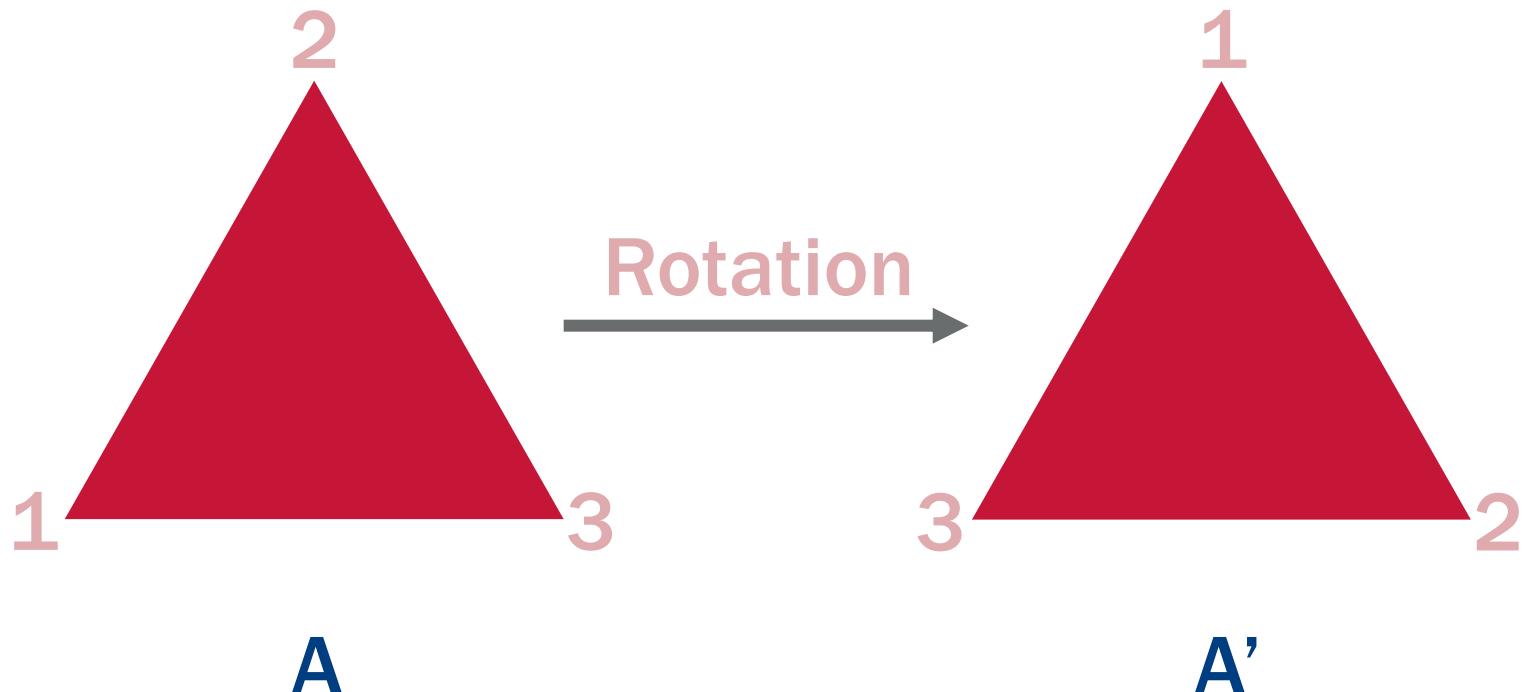
Introduction to Symmetry

What operations can we perform on A that leave it *indistinguishable*?



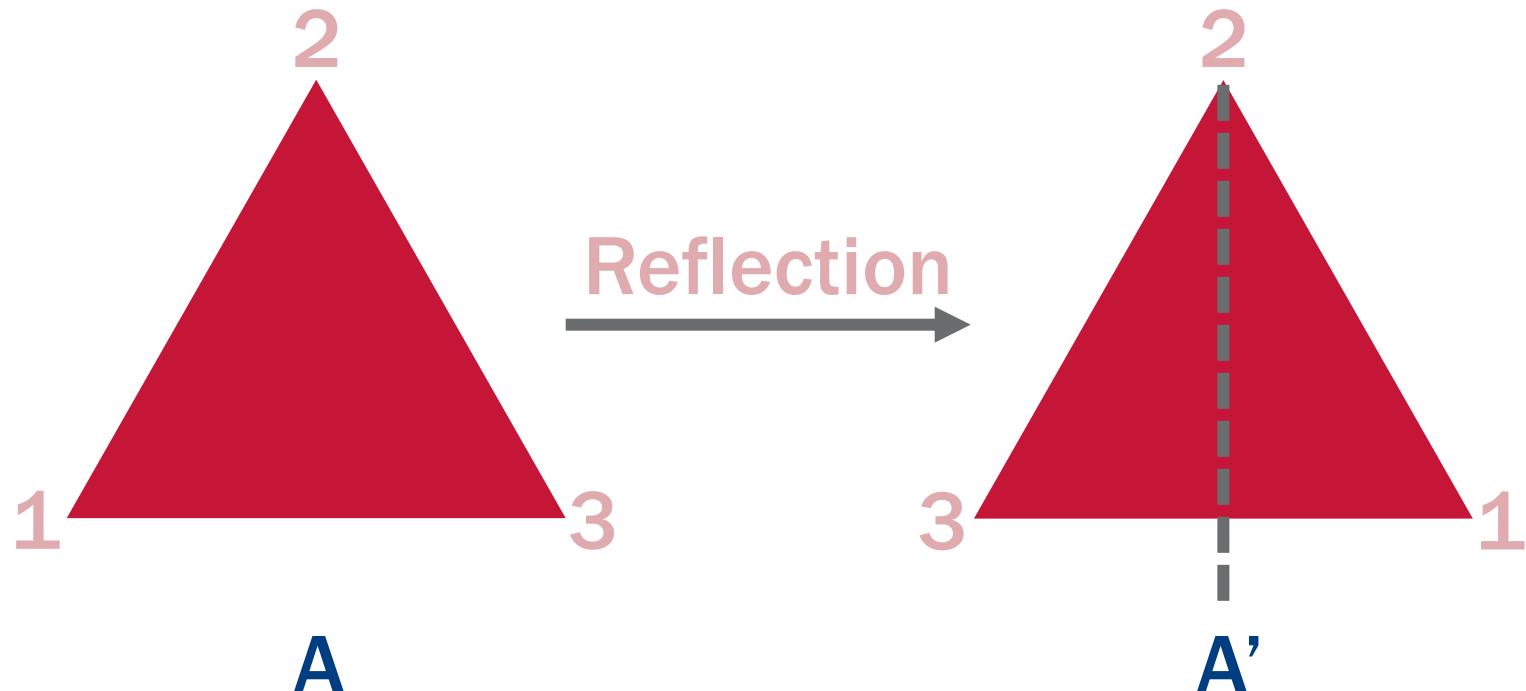
Introduction to Symmetry

What operations can we perform on A
that leave it *indistinguishable*?



Introduction to Symmetry

What operations can we perform to A that leave it *indistinguishable*?



Symmetry Terminology

The formal maths (branch of abstract algebra) is beyond our scope, but some definitions:

Symmetry operation – transformation of an object that leaves it indistinguishable

Symmetry element – point of reference for a symmetry operation, e.g. rotation axis

Point group – set of symmetry operations used to classify molecules

Space group – 32 crystal point groups \times 14 Bravais lattices yields 230 unique space groups

230 The Space Group List Project



by Frank Hoffmann



More information at
crystalsymmetry.wordpress.com

Crystal structures drawn with VESTA
 K. Momma and F. Izumi, J. Appl. Crystallogr. 2011, 44, 1272-1276

Example – PCN-20

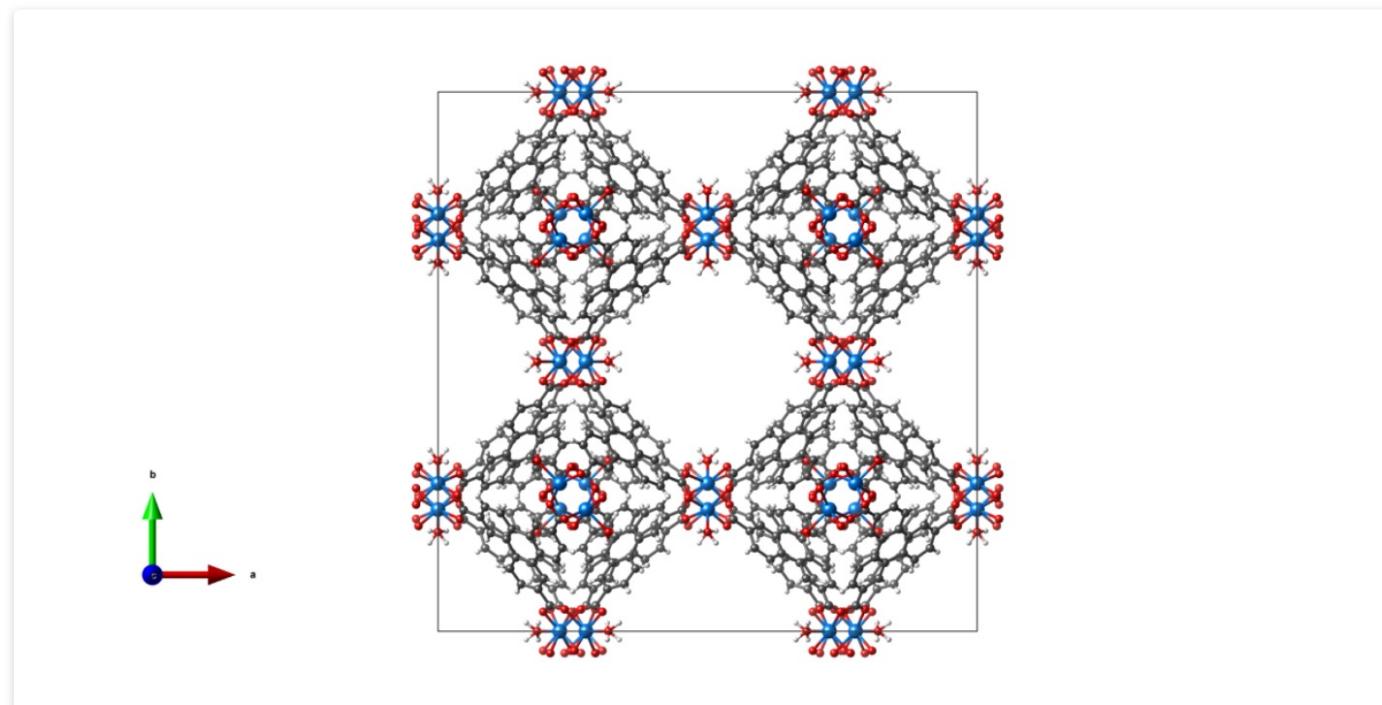
A Large-Surface-Area Boracite-Network-Topology Porous MOF Constructed from a Conjugated Ligand Exhibiting a High Hydrogen Uptake Capacity

X.-S. Wang, S. Ma, D. Yuan, J.W. Yoon, Y.K. Hwang, J.-S. Chang, X. Wang, M.R.Jorgensen, Y.-S. Chen, H.-C. Zhou

[Inorg.Chem. \(2009\), 48, 7519](http://dx.doi.org/10.1002/in.20905)

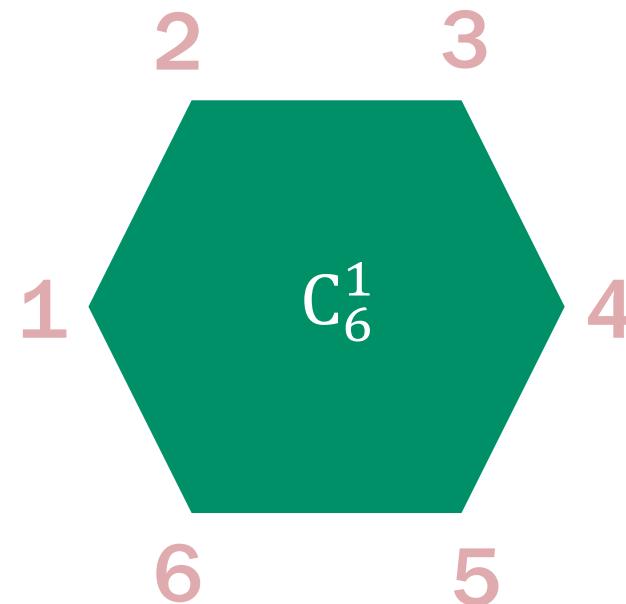
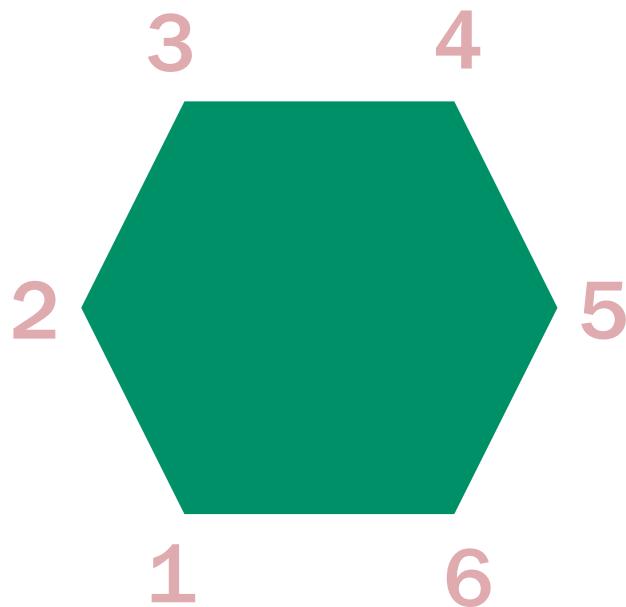
CIF

<http://1drv.ms/1mBQIYt>



Rotational Symmetry

The operation of a proper rotation is given the symbol C_n . The subscript is the order of the rotation

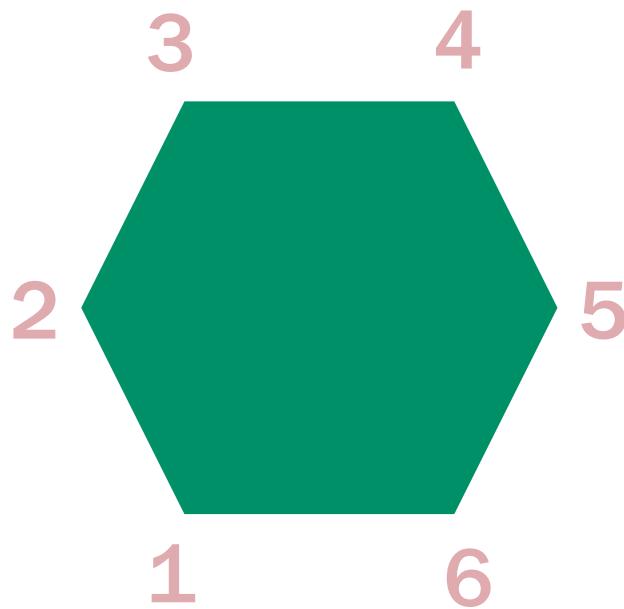


C_6 rotational axis

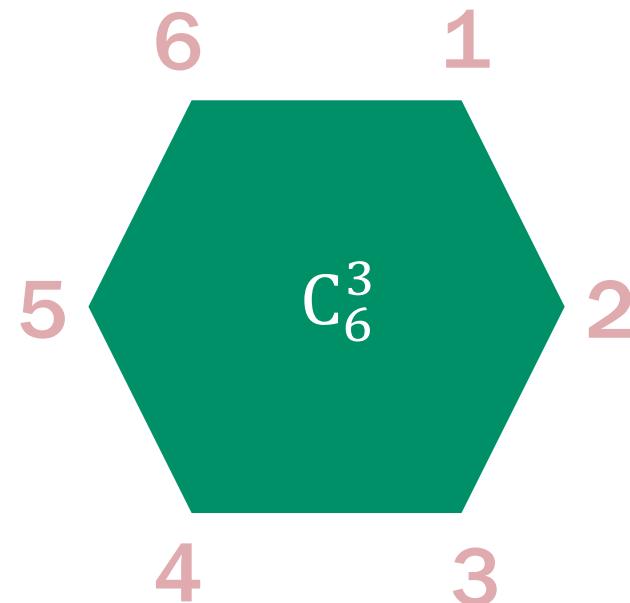
Rotations by $(360/n)^\circ$

Rotational Symmetry

The operation of a proper rotation is given the symbol C_n . The subscript is the order of the rotation



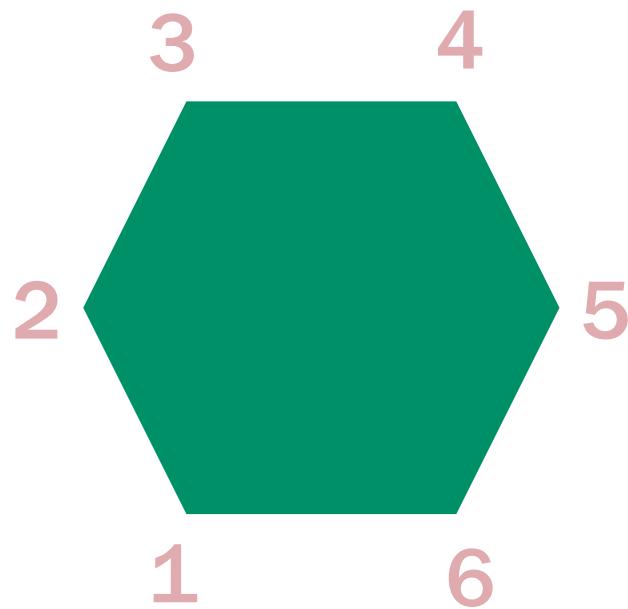
C_6 rotational axis



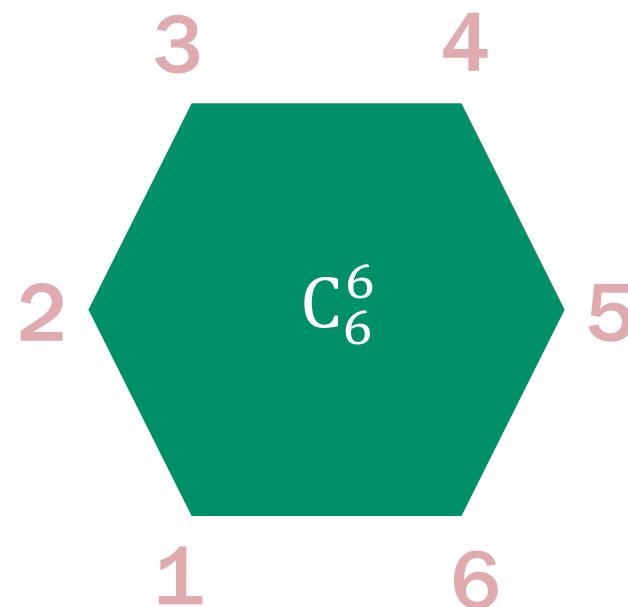
Rotations by $(360/n)^\circ$

Rotational Symmetry

The operation of a proper rotation is given the symbol C_n . The subscript is the order of the rotation



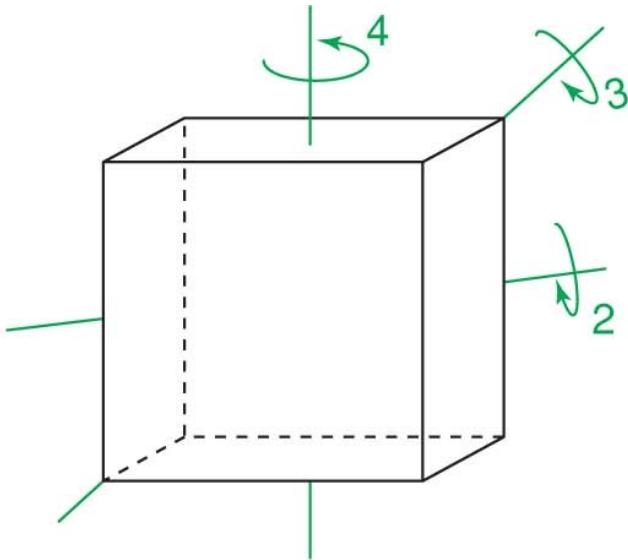
C_6 rotational axis
Rotations by $(360/n)^\circ$



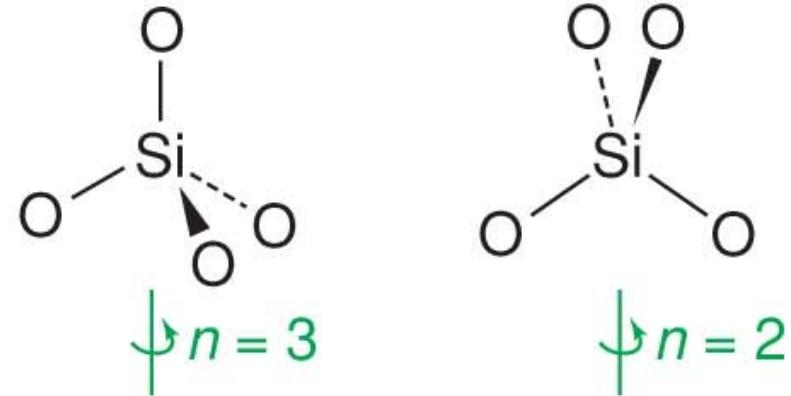
$C_6^6 = E = \text{Identity operation}$

Rotational Symmetry

The operation of a proper rotation is given the symbol C_n . The subscript is the order of the rotation



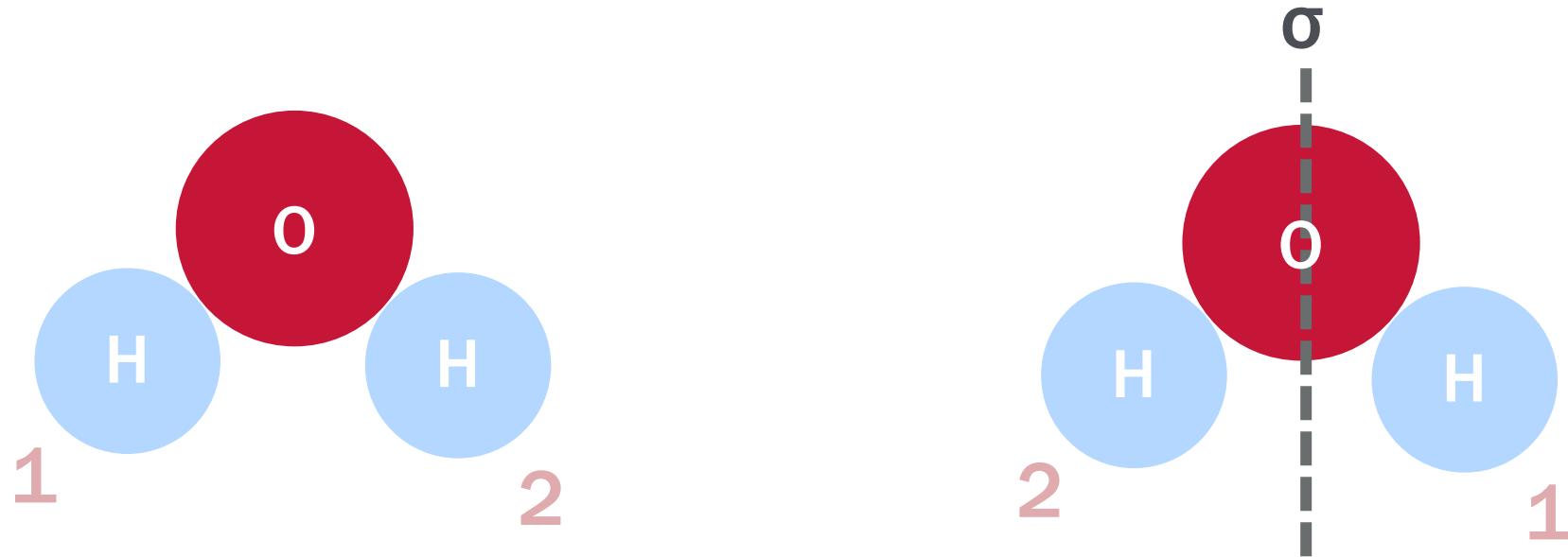
Three rotational axes
of a cube, $(360/n)^\circ$



Silicon oxide
tetrahedron

Reflection (Mirror) Symmetry

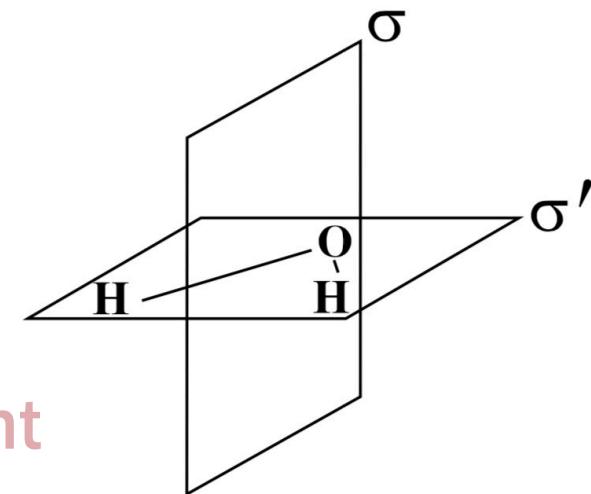
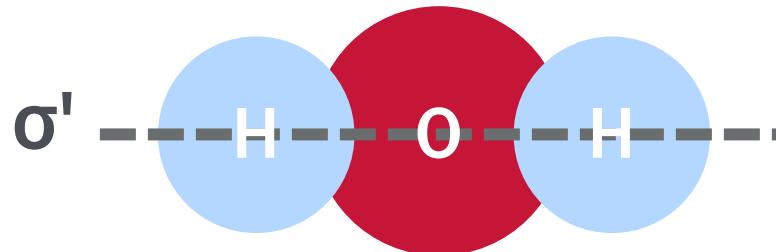
The operation of a reflection through a plane is given the symbol σ . Note that $\sigma^2 = E$ (identity)



For an atom reflected through the x axis: $(x,y,z) \rightarrow (-x,y,z)$

Reflection (Mirror) Symmetry

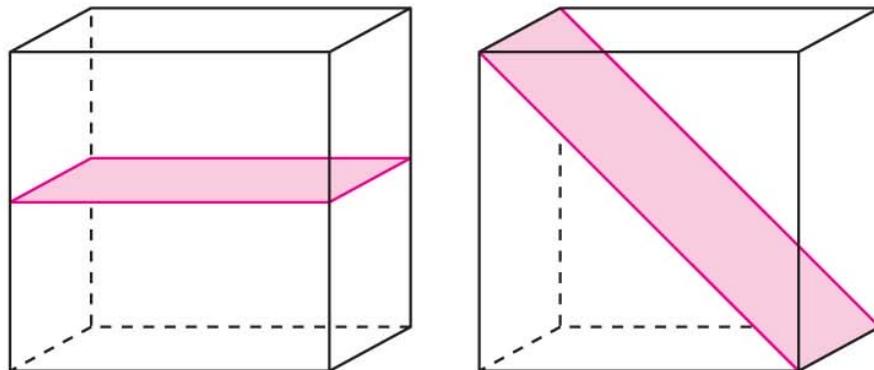
The operation of a reflection through a plane is given the symbol σ . Note that $\sigma^2 = E$ (identity)



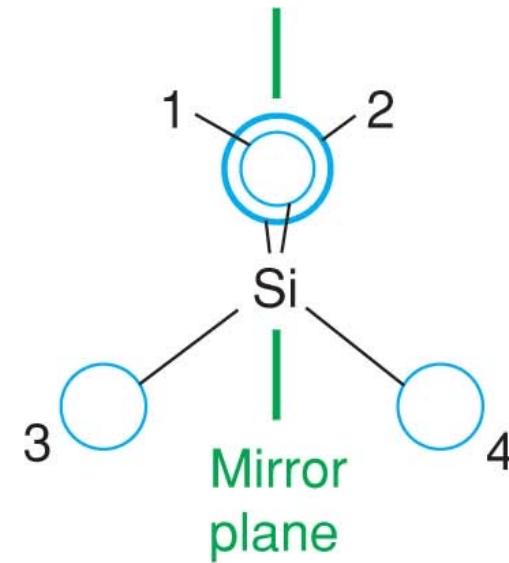
Water has a second mirror plane at right angles to the first

Reflection (Mirror) Symmetry

The operation of a reflection through a plane is given the symbol σ . Note that $\sigma^2 = E$ (identity)



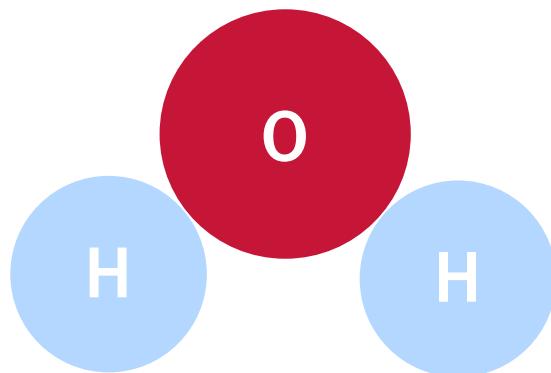
2 (of 9) reflection
planes in a cube



Silicon oxide
tetrahedron

Symmetry Elements of Water

H_2O features the identity (E), two reflection planes (σ and σ'), and a C_2 rotational axis



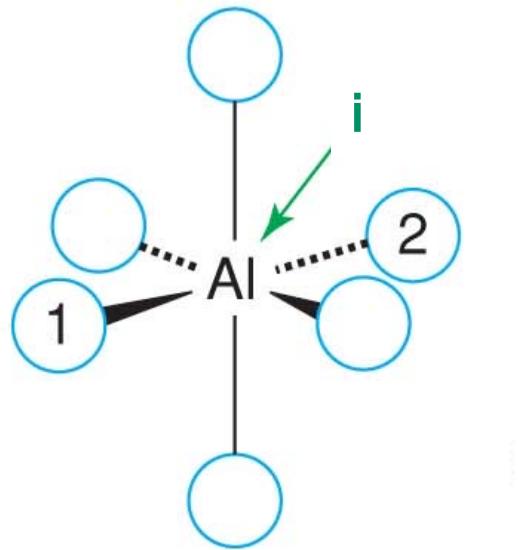
All symmetry operations can be defined in matrix form and described by group theory

Advanced: The associated point group of water is C_{2v}

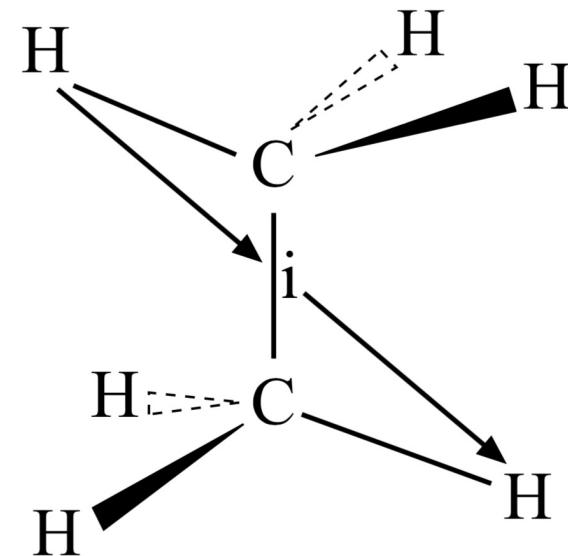
Note: The v label arises as the mirror planes are vertical with respect to the C_2 axis

Inversion Symmetry

A centre of inversion (also called “centre of symmetry”) is given the symbol i . Note $i^2 = E$



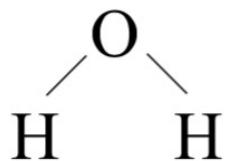
Centre of inversion (i)
 $(x,y,z) \rightarrow (-x,-y,-z)$



The projection is not
always through a bond

Quiz

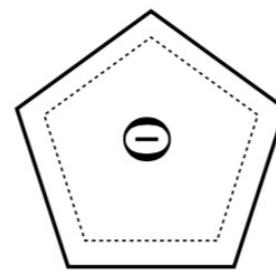
Which molecules have inversion centres?



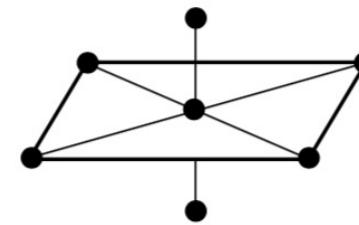
A



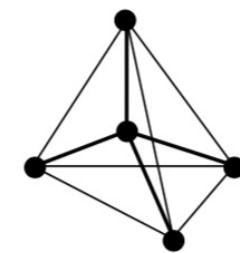
B



C



D

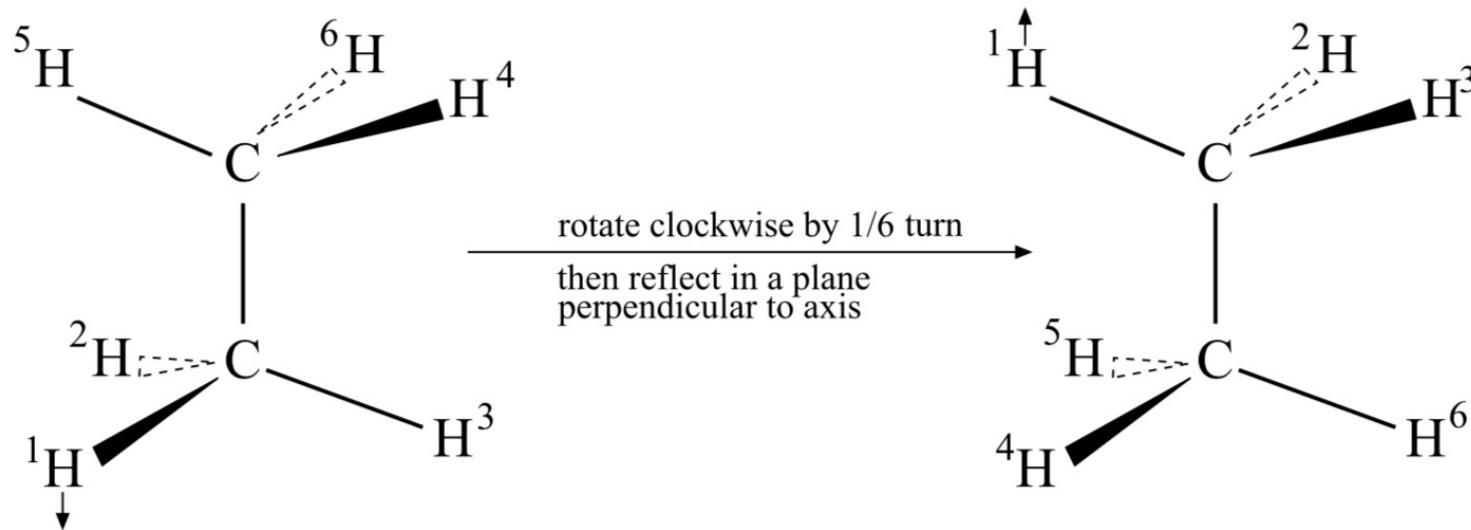


E

Improper Rotations

An improper rotation is given the symbol S_n .

It is also called “rotation-reflection” and the subscript is the order of the rotation

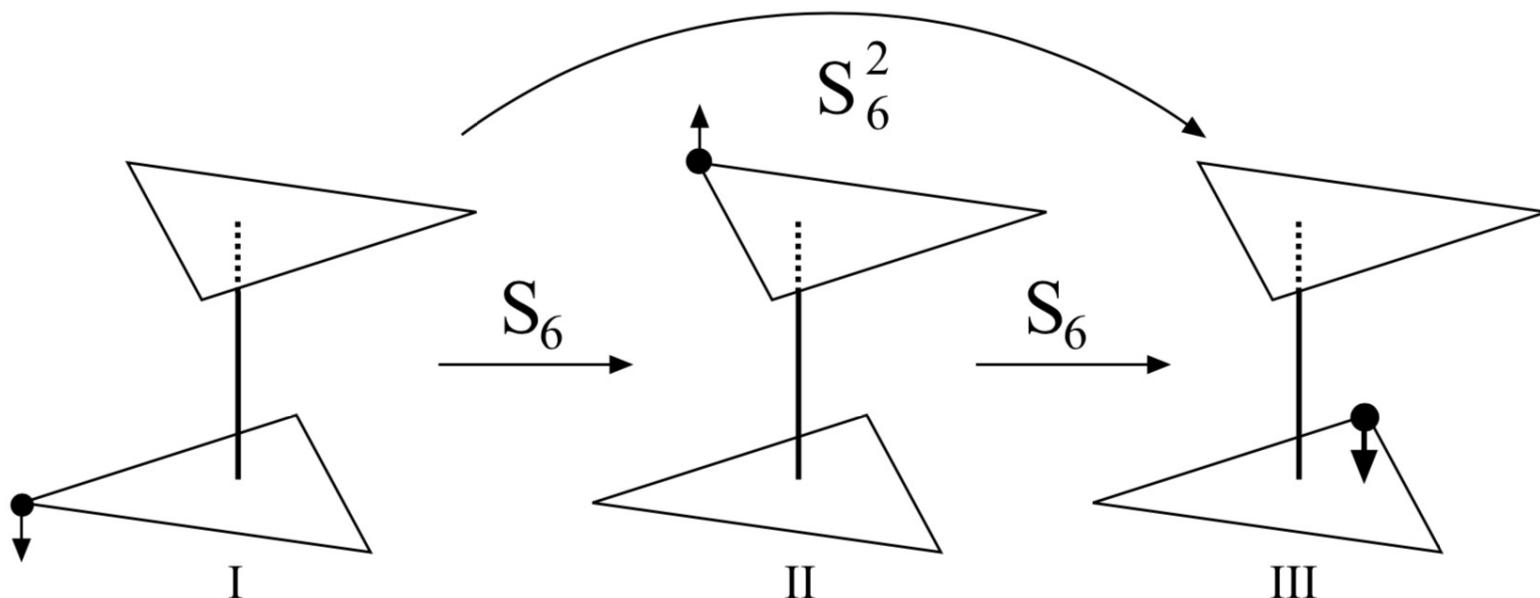


Improper rotation (S_6)

C_6 rotation + σ reflection (in a perpendicular plane)

Improper Rotations

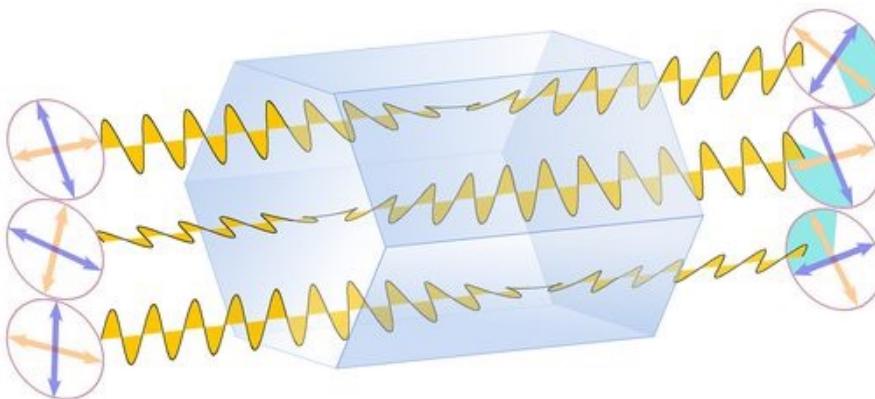
An improper rotation is given the symbol S_n .
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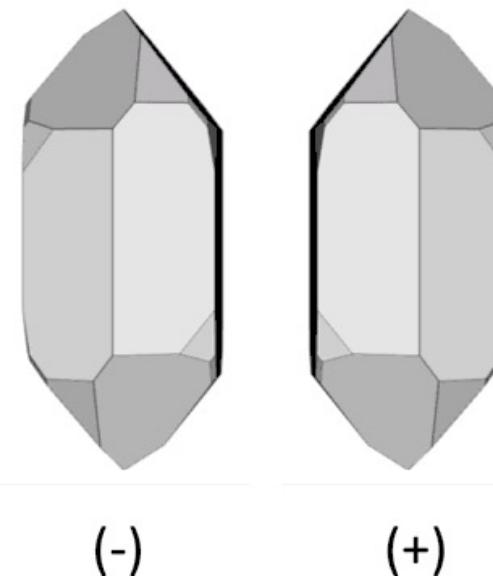
Back to Chirality

A chiral object *cannot* be superposed on its mirror image. Mirror related versions are enantiomorphs (crystals) or enantiomers (molecules)

Chiral objects lack both i and σ elements

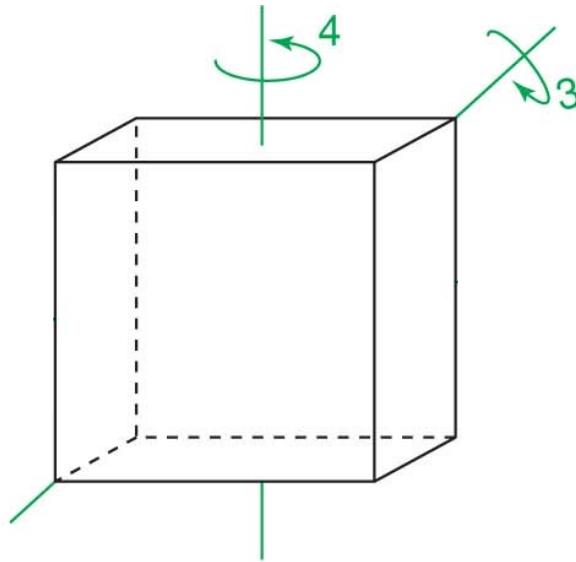


Optical activity of an enantiomorphic crystal

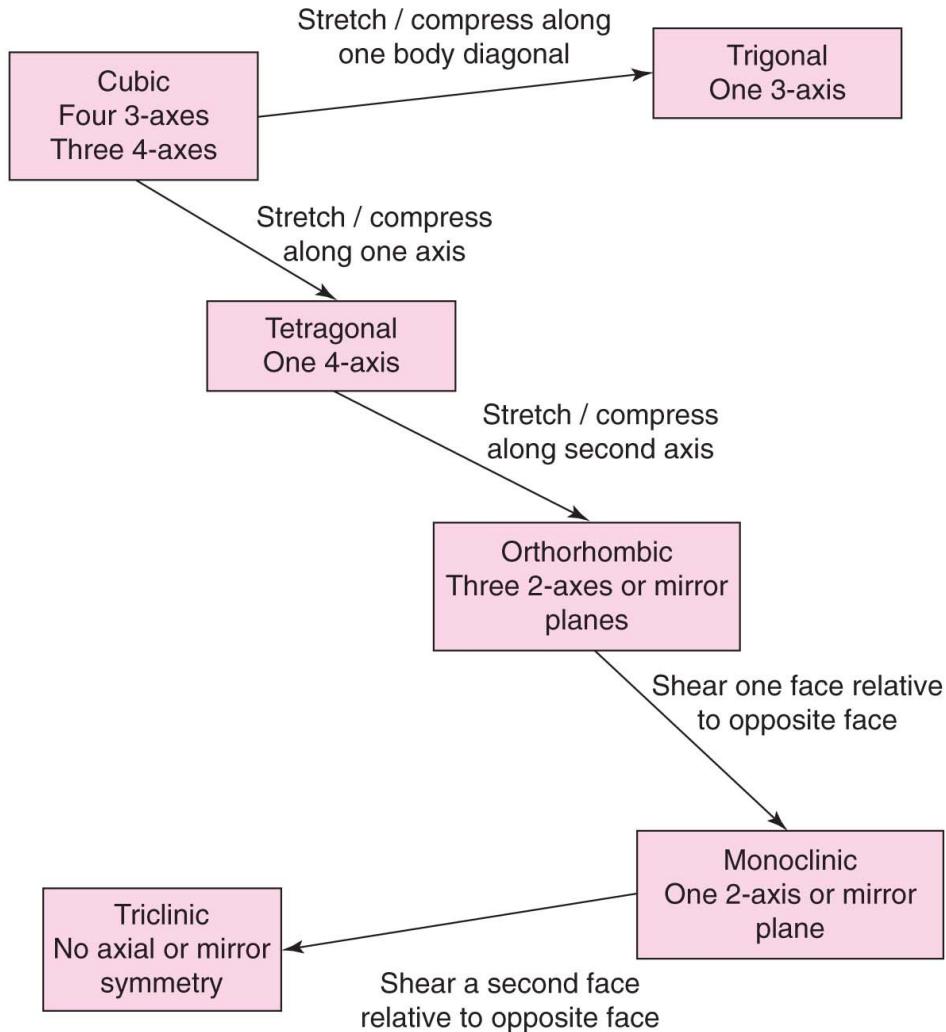


Animation of Quartz from
IUCr newsletter: <https://bit.ly/2IBCvuz>

Relationship Between Crystal Systems



Cubic cells have the highest symmetry and all other crystal systems lose symmetry elements



Advanced: Information Only

Important concepts to introduce,
but won't be explored until second year

Molecular point groups

- Algorithm for assigning labels

Notation for crystal symmetry

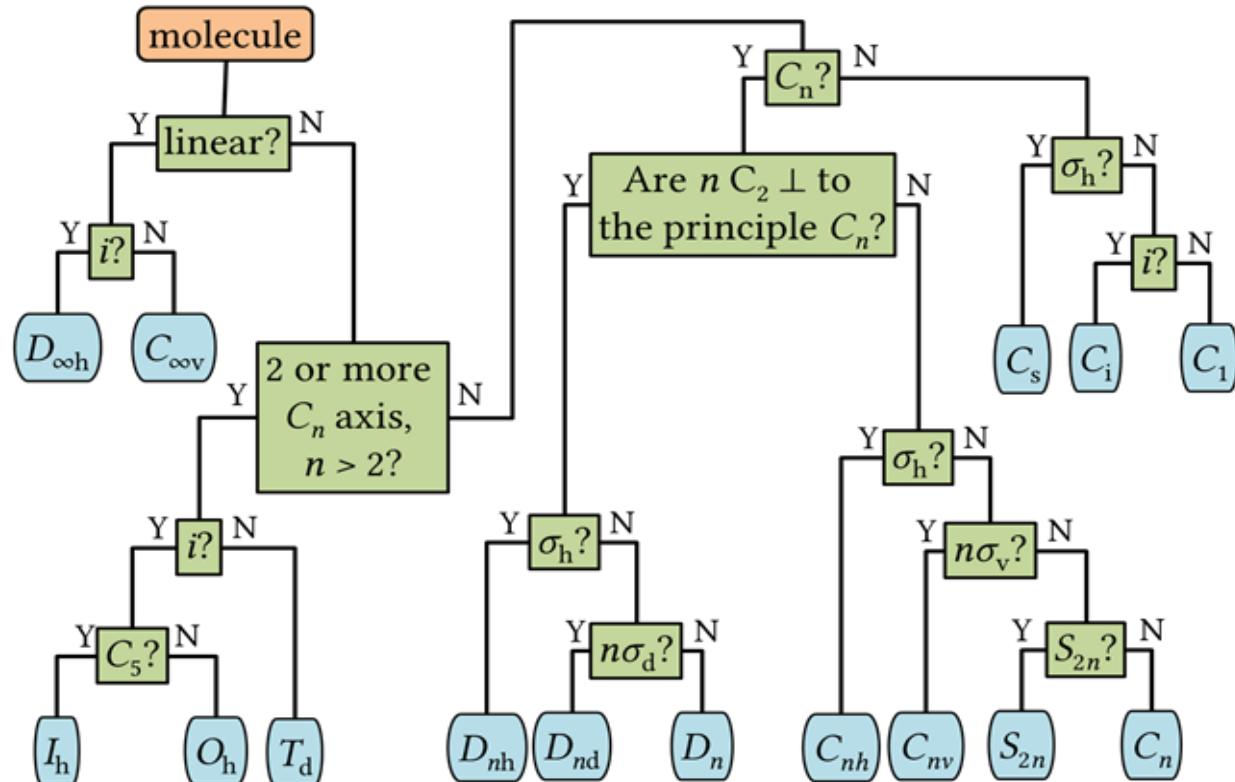
- Hermann-Mauguin symbols

Assigning Molecular Point Groups

A common way to label molecules. Chemists use a flowchart based on symmetry elements

	Operation
E	Identity
C_n	Rotation
σ	Reflection
i	Inversion
S_n	Improper Rotation

σ_d - diagonal
 σ_v - vertical
 σ_h - horizontal



We will test this in the classroom activities session

Hermann-Mauguin Symbols

International notation for space groups
describing the symmetry elements of a crystal

- First letter: P, I, F, A, B, C, R

Lattice centering (from first lecture)

- Set of characters: e.g. 2 m m

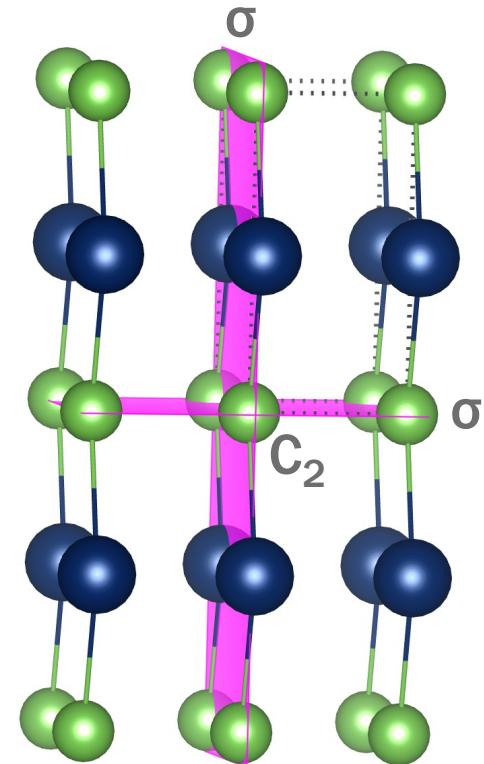
Symmetry elements parallel or perpendicular to
the lattice vectors

Hermann-Mauguin Symbols

International notation for space groups
describing the symmetry elements of a crystal

Mirror in ac plane
C₂ along c axis
Primitive lattice
Mirror in bc plane

Pmm2



Summary: Symmetry

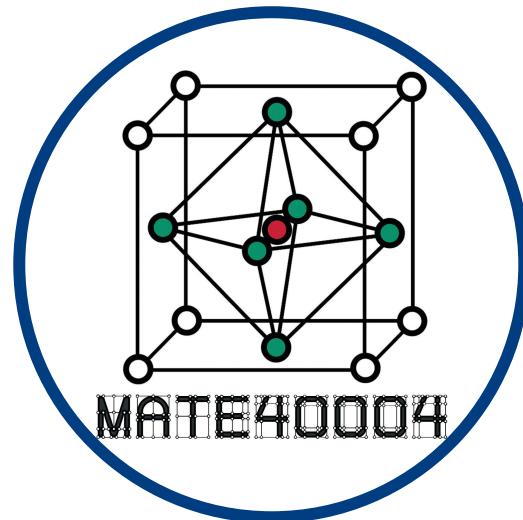
Class outcomes:

- Define symmetry element and operation
- Identify symmetry elements in an object
identity, rotational axis, reflection plane,
centre of inversion, improper rotation axis
- Apply symmetry operations to an object
- Understand chirality and identify a chiral centre

MATE40004 – Structure 1

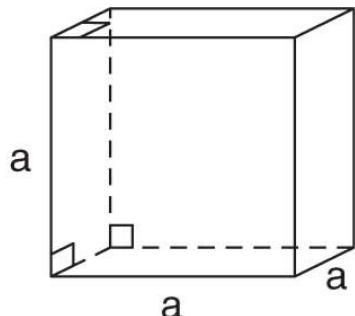
Crystallography
C. Geometry

Professor Aron Walsh
Department of Materials
Imperial College London

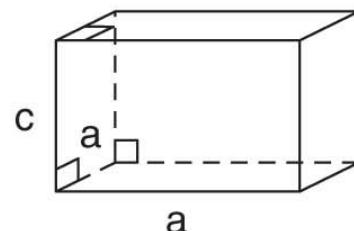


<http://www.imperial.ac.uk/people/a.walsh>

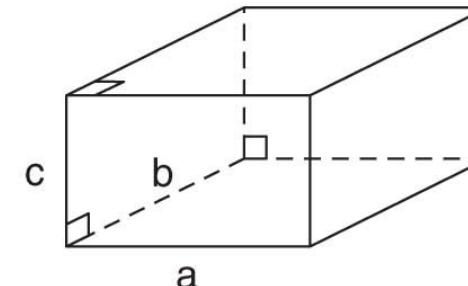
Recap: 7 Crystal Systems in 3D



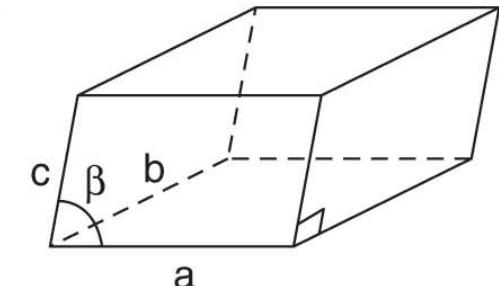
Cubic



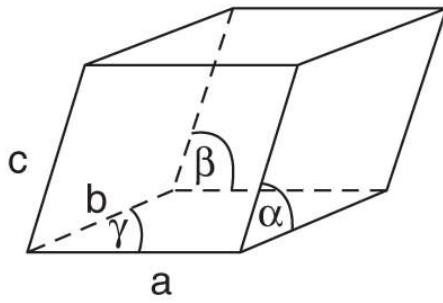
Tetragonal



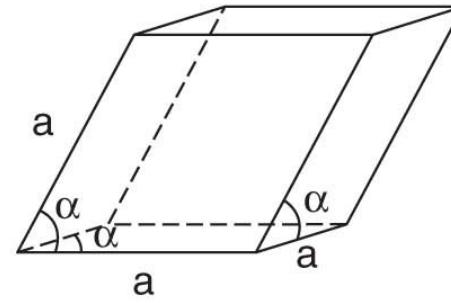
Orthorhombic



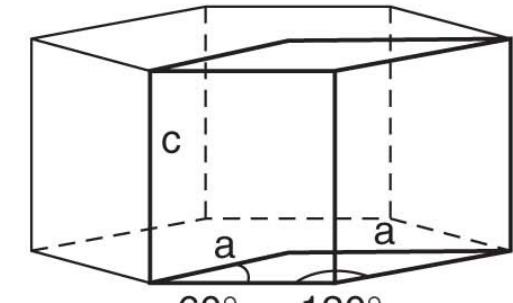
Monoclinic



Triclinic



Rhombohedral
(or Trigonal)



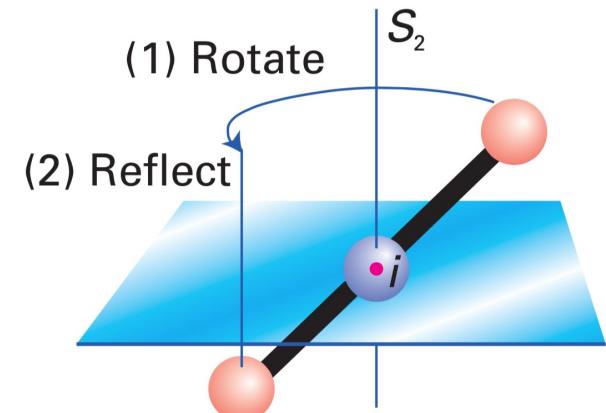
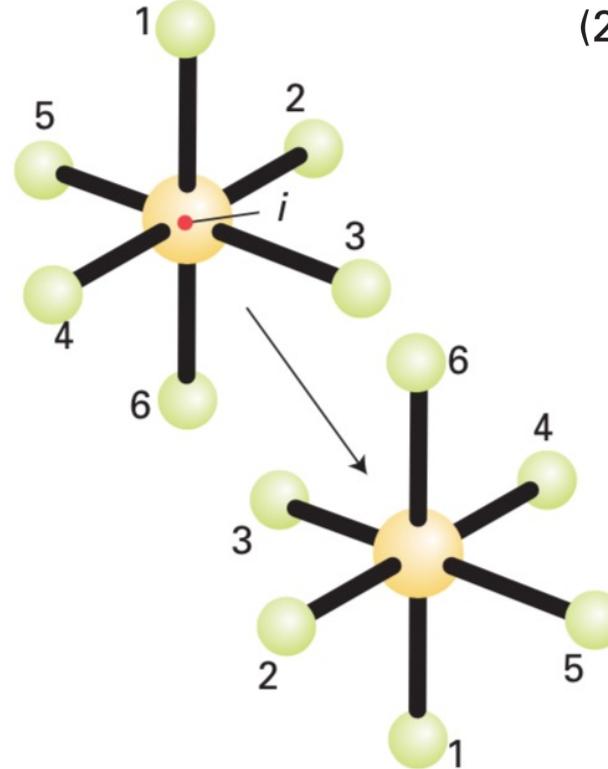
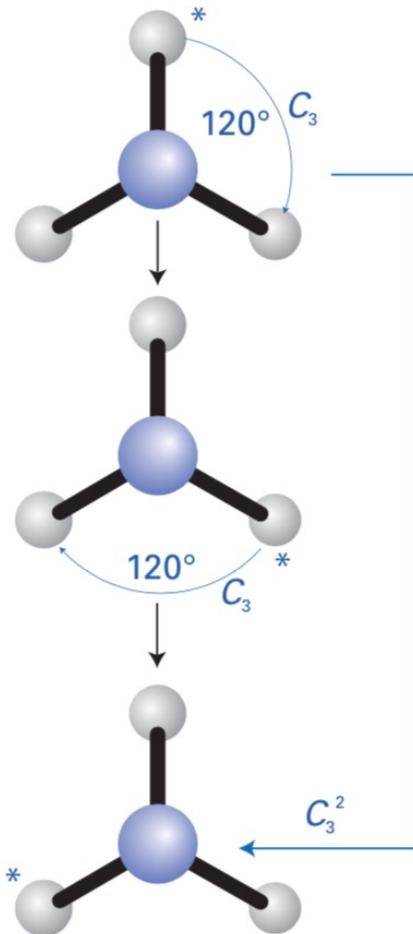
Hexagonal

Remember the constraints on lengths (a, b, c) and angles (α, β, γ)

Recap: Molecular Symmetry

Operation	Element	Symbol
Identity	'whole of space'	E
Rotation by $360^\circ/n$	n-fold rotation axis	C_n
Reflection	mirror plane	σ
Inversion	centre of inversion	i
Rotation by $360^\circ/n$ followed by reflection in a perpendicular plane	n-fold improper rotation axis	S_n

Recap: Molecular Symmetry



Note: $S_2 = i$

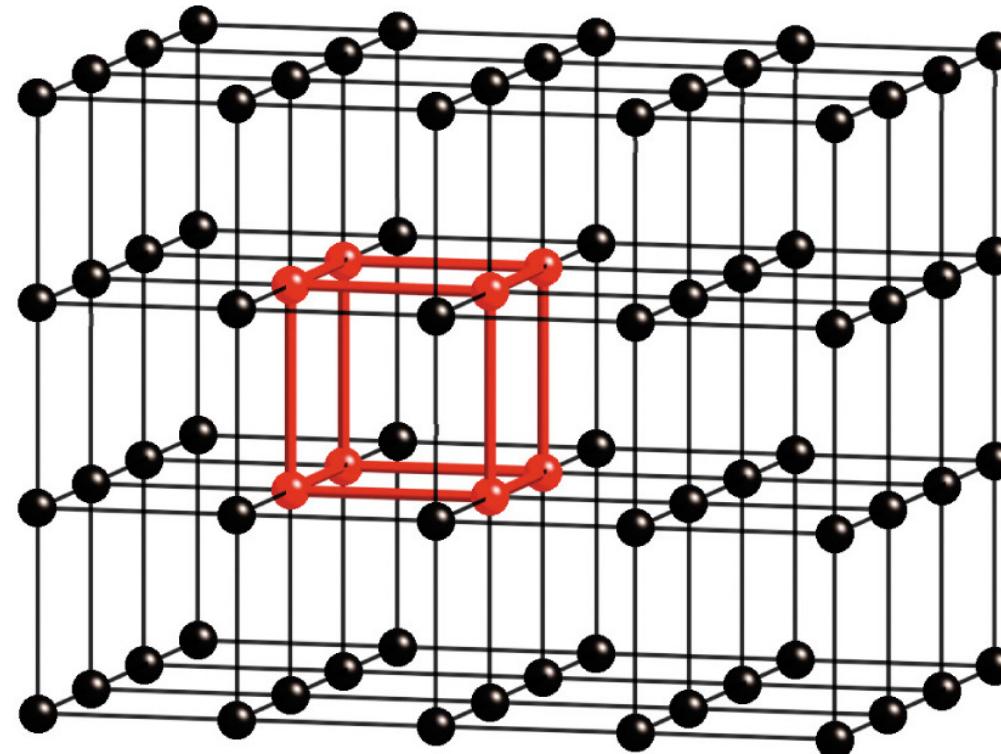
Outline of Crystallography

Part 1

- A. Lattices
- B. Symmetry
- C. Geometry
- D. Packing

Definition of the Unit Cell

Unit cell: the simplest portion of a structure that fills all space when repeated by translation



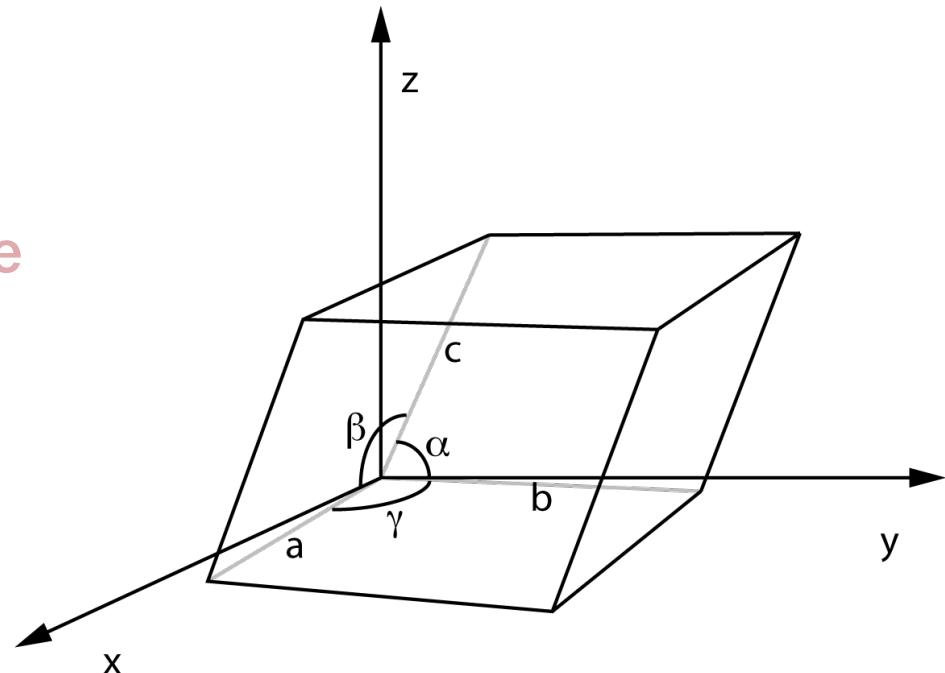
Which Bravais lattice is shown above?

Atoms: Cartesian Coordinates

Problem: lattice vectors \mathbf{a} , \mathbf{b} , \mathbf{c} do not have to lie along the x , y , z Cartesian axes

Cartesian coordinates (x,y,z) are ambiguous for crystals, especially in hexagonal and rhombohedral lattices

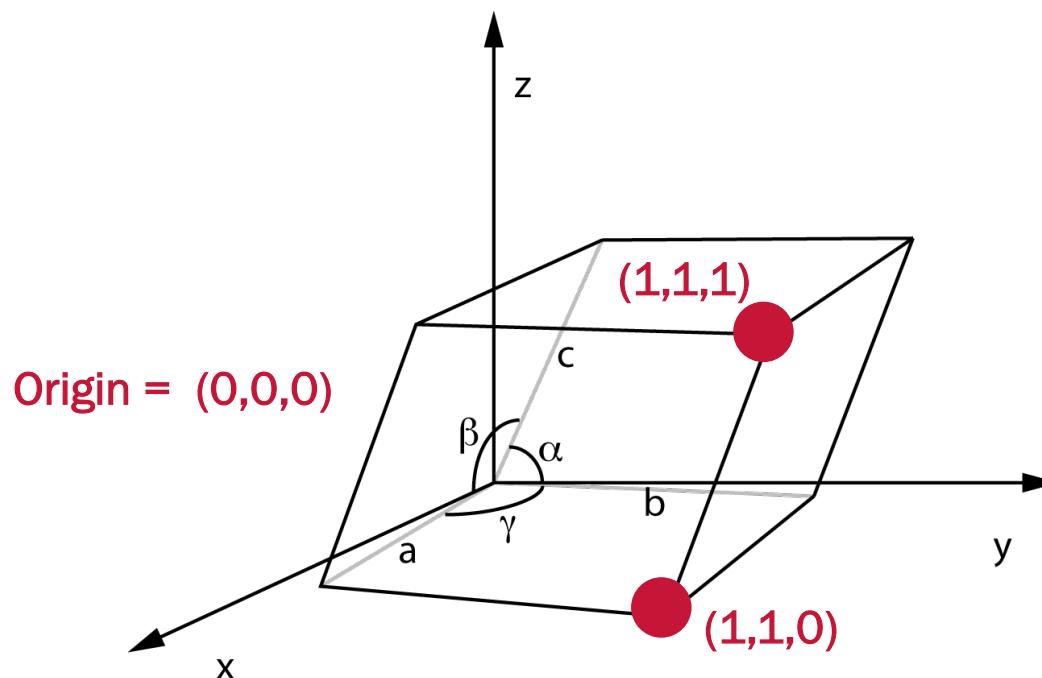
Recall, the Cartesian coordinate system has three axes that are pairwise perpendicular



Atoms: Fractional Coordinates

Solution: define atomic coordinates within a unit cell as fractions of the lattice vectors \mathbf{a} , \mathbf{b} , \mathbf{c}

The unit cell spans 0 to 1, e.g. (0.5, 0.5, 0.5) specifies an atom at the center of the unit cell

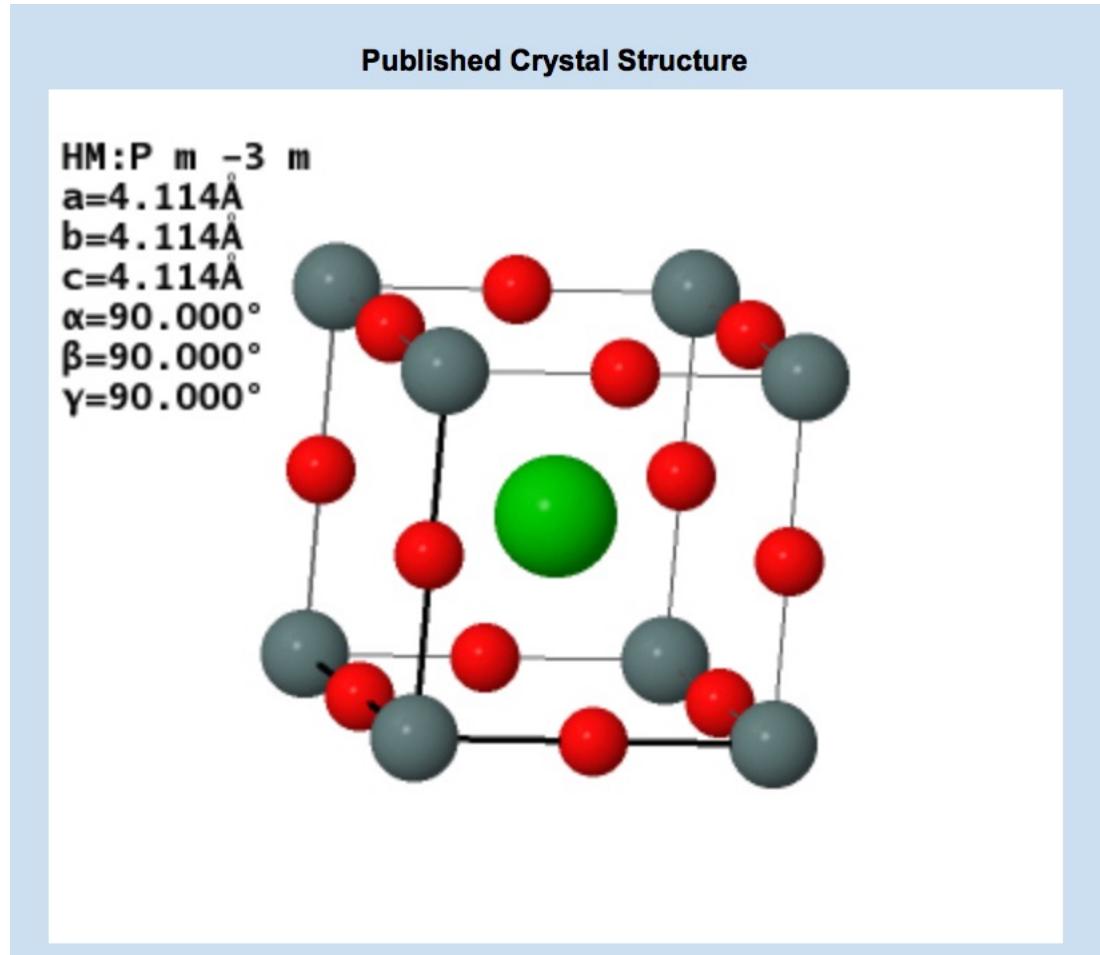


Example BaSnO₃ (Perovskite Structure)

Published Crystal Structure Data								
Cell Parameters	4.11443(3) 4.11443(3) 4.11443(3) 90. 90. 90.							
Volume	69.65	Formula Units per Cell			1	Calc. Dens. 7.25		
Space Group	P m -3 m(221)	Pearson Symbol			cP5	Meas. Dens.		
Crystal System	cubic	Crystal Class			m-3m	Laue Class m-3m		
Wyckoff Sequence	d b a	Structure Type			Perovskite-CaTiO ₃			
Axis Ratios	a/b 1.0000	b/c 1.0000	c/a 1.0000					
Remark								
EL	Lbl	OxState	WyckSymb	X	Y	Z	U	SOF H
Ba	1	+2.00	1b	0.5	0.5	0.5	0.0037(6)	1.
Sn	1	+4.00	1a	0	0	0	0.014(5)	1.
O	1	-2.00	3d	0.5	0	0	0.008(2)	1.

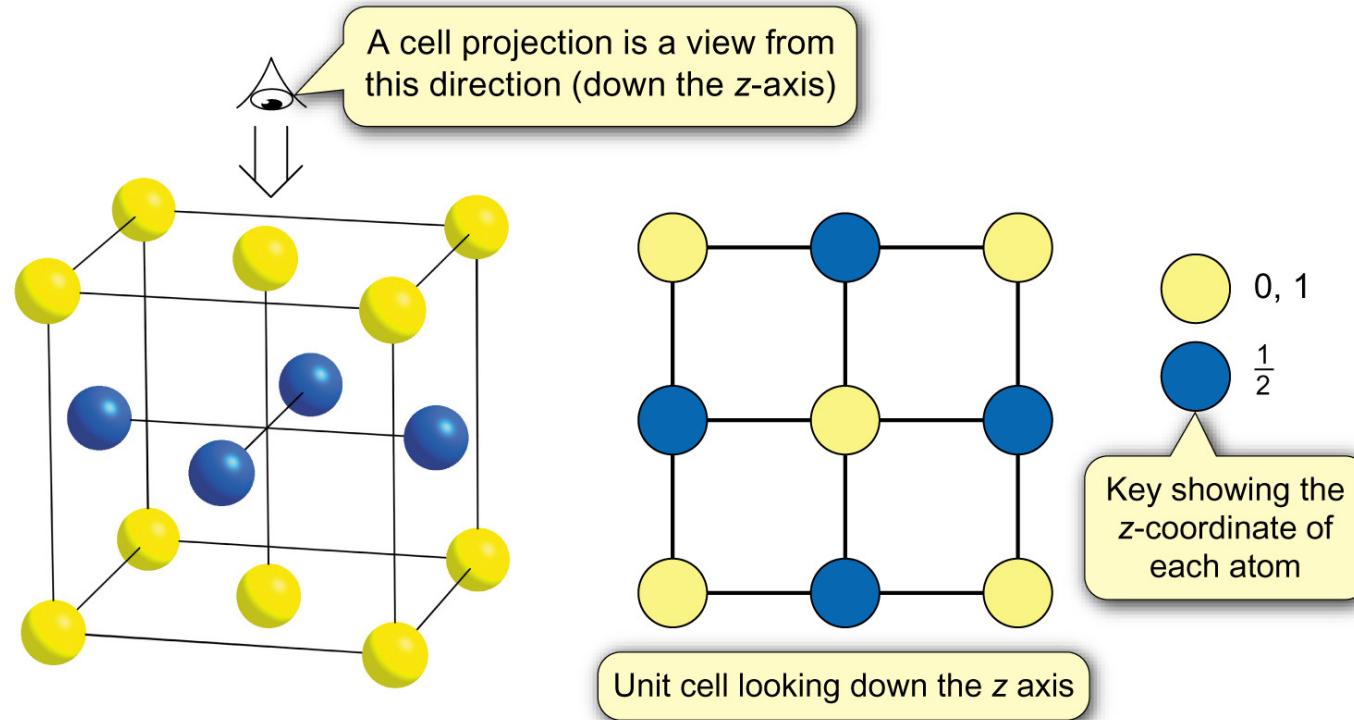
What does the unit cell look like?

Example BaSnO₃ (Perovskite Structure)

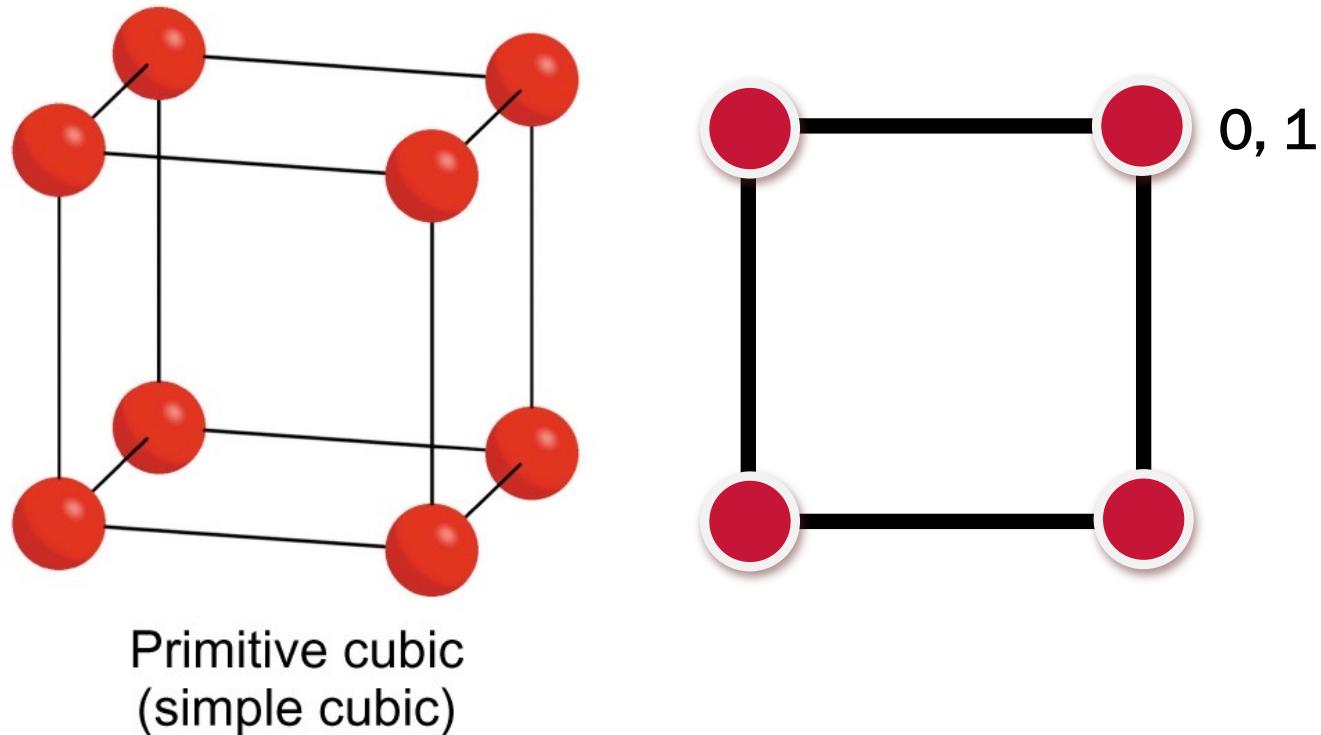


Cell Projection Diagrams

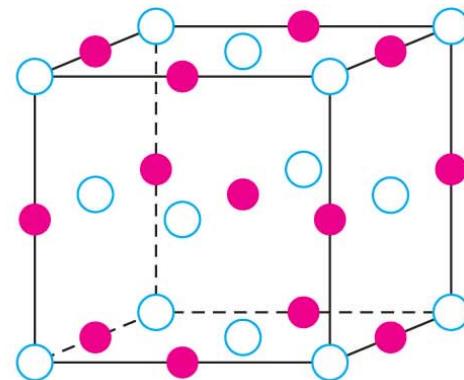
2D representation of 3D unit cell, looking from above. x, y are normal, z is a fractional coordinate



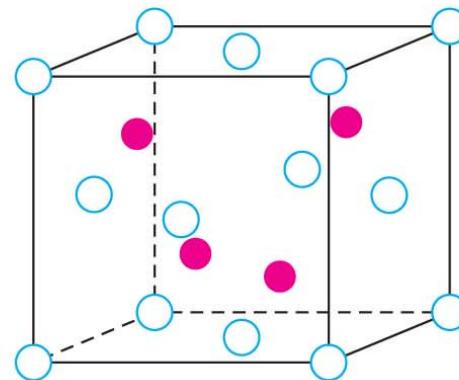
Cell Projection Diagrams (Simple)



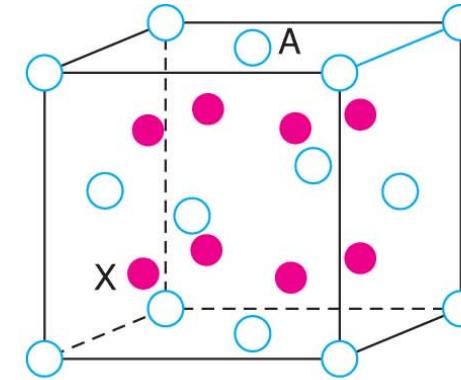
Cell Projection Diagrams (Advanced)



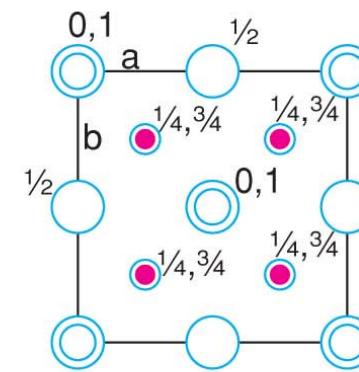
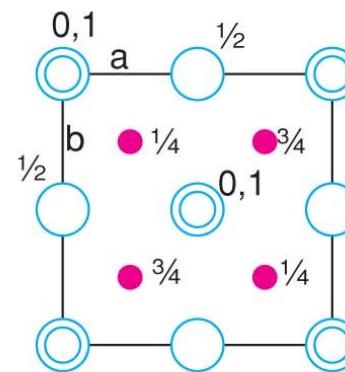
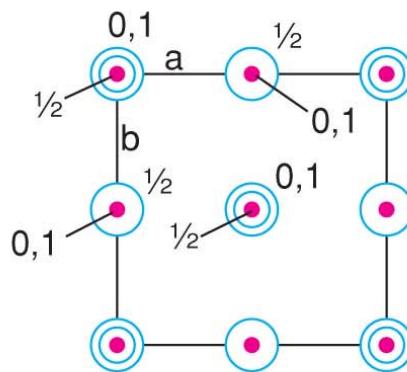
NaCl



ZnS

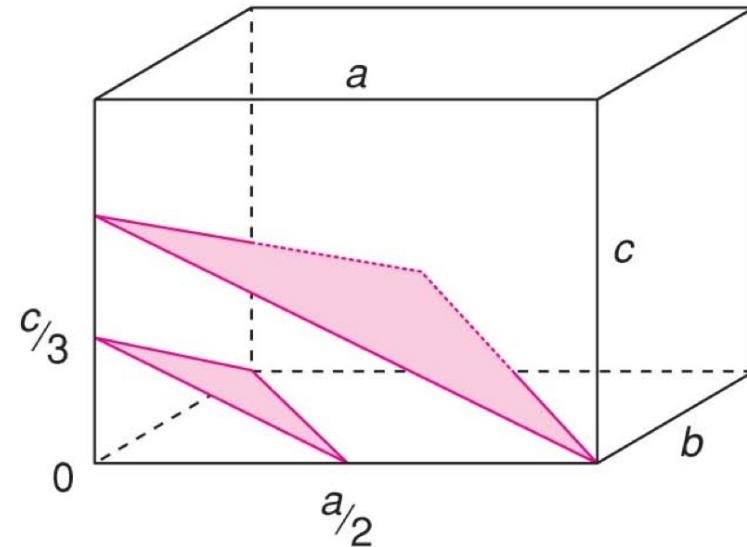
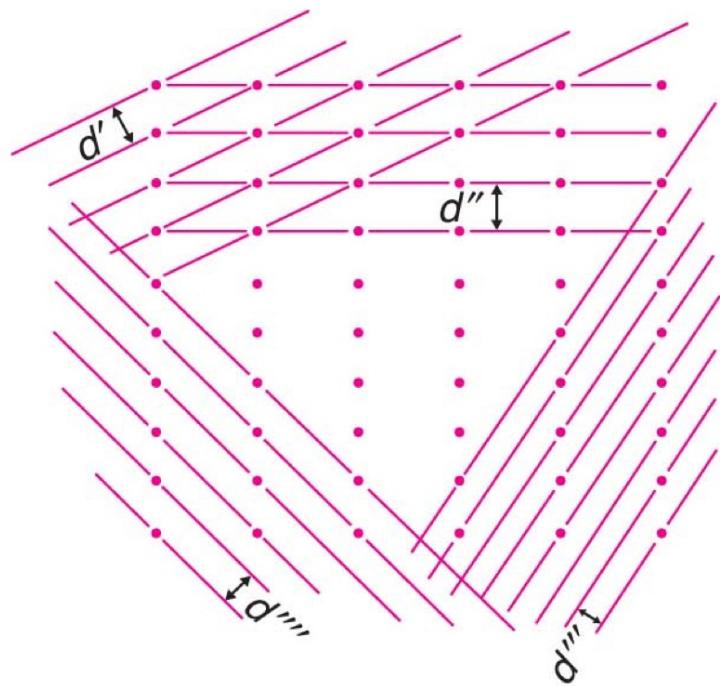


Na₂O



Lattice Directions and Planes

Lattice points can be connected to define directions and planes – useful across materials science



Lattice planes in two and three dimensions

Lattice Directions and Planes

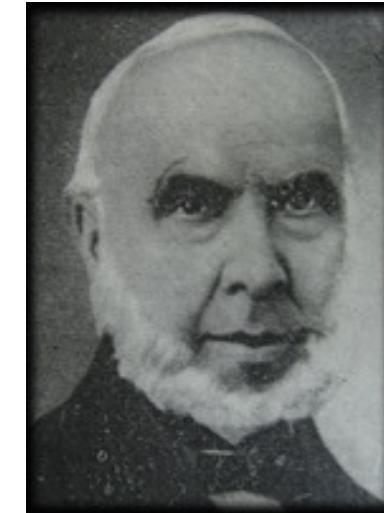
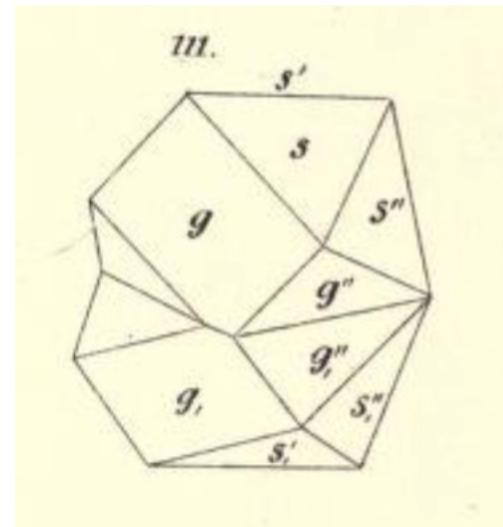
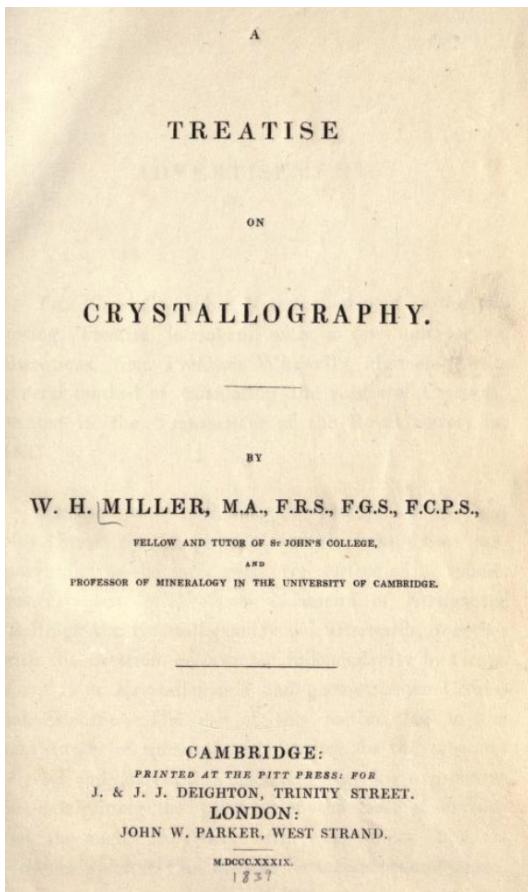
Miller Indices: Notation for crystal geometry that is independent of Bravais lattice type

Notation	Meaning
(h,k,l)	Point (note the commas)
$[hkl]$	Direction
$\langle hkl \rangle$	Family of equivalent directions
(hkl)	Plane
$\{hkl\}$	Family of equivalent planes

Warning: Different books/papers may use different notation 😔

William Miller FRS (1801–1880)

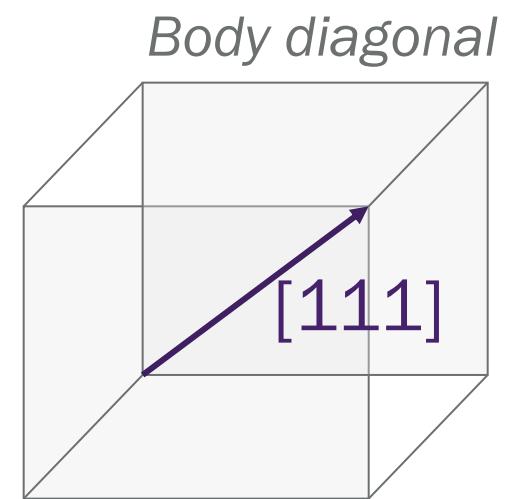
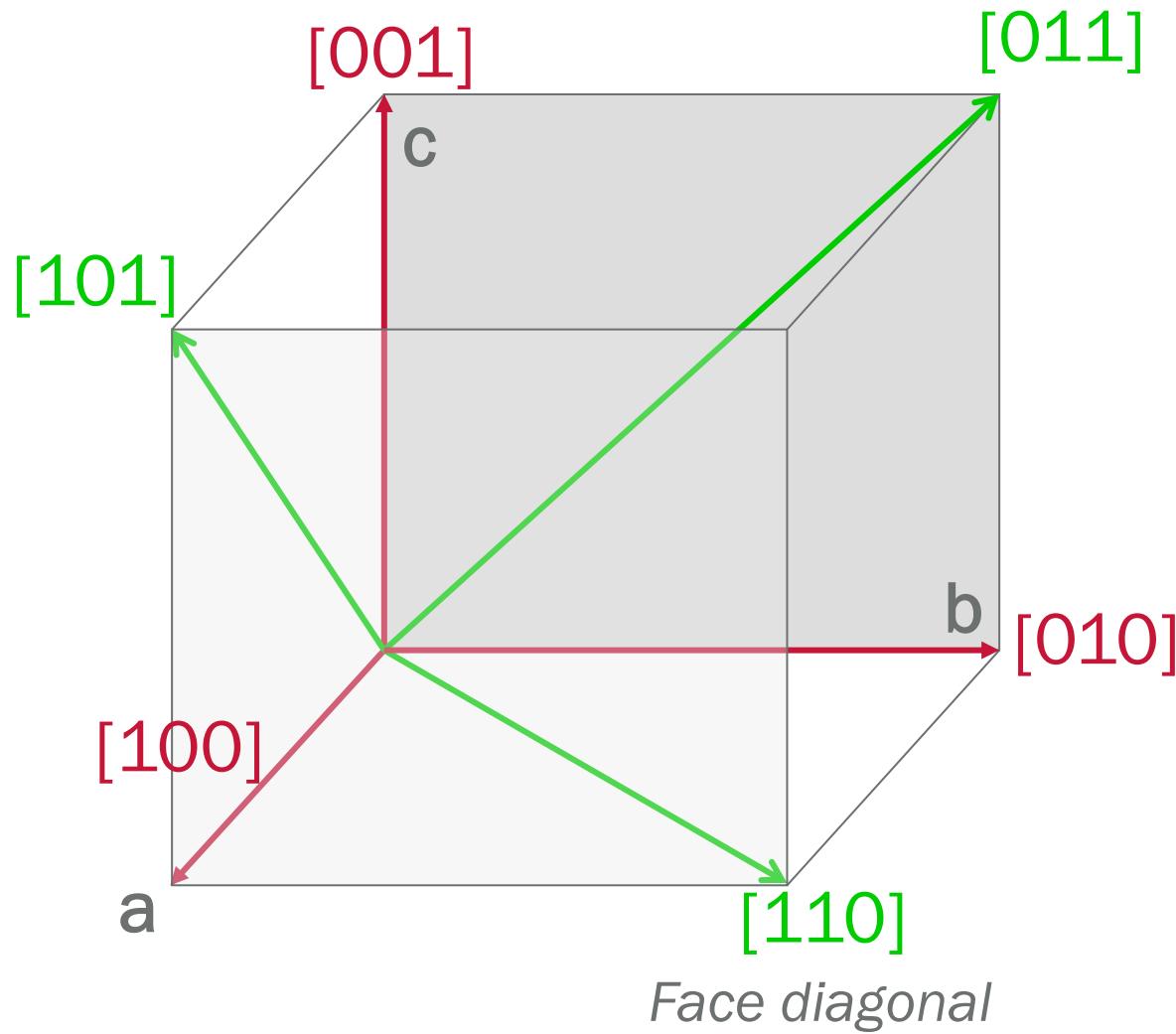
Born in Wales. Professor of Mineralogy at University of Cambridge (at age 31)



Detailed mathematical theory connecting
lattice points and crystal facets

1839 Book: <https://archive.org/details/treatiseoncrysta00millrich>

Simple Lattice Directions



Lattice Directions: Recipe

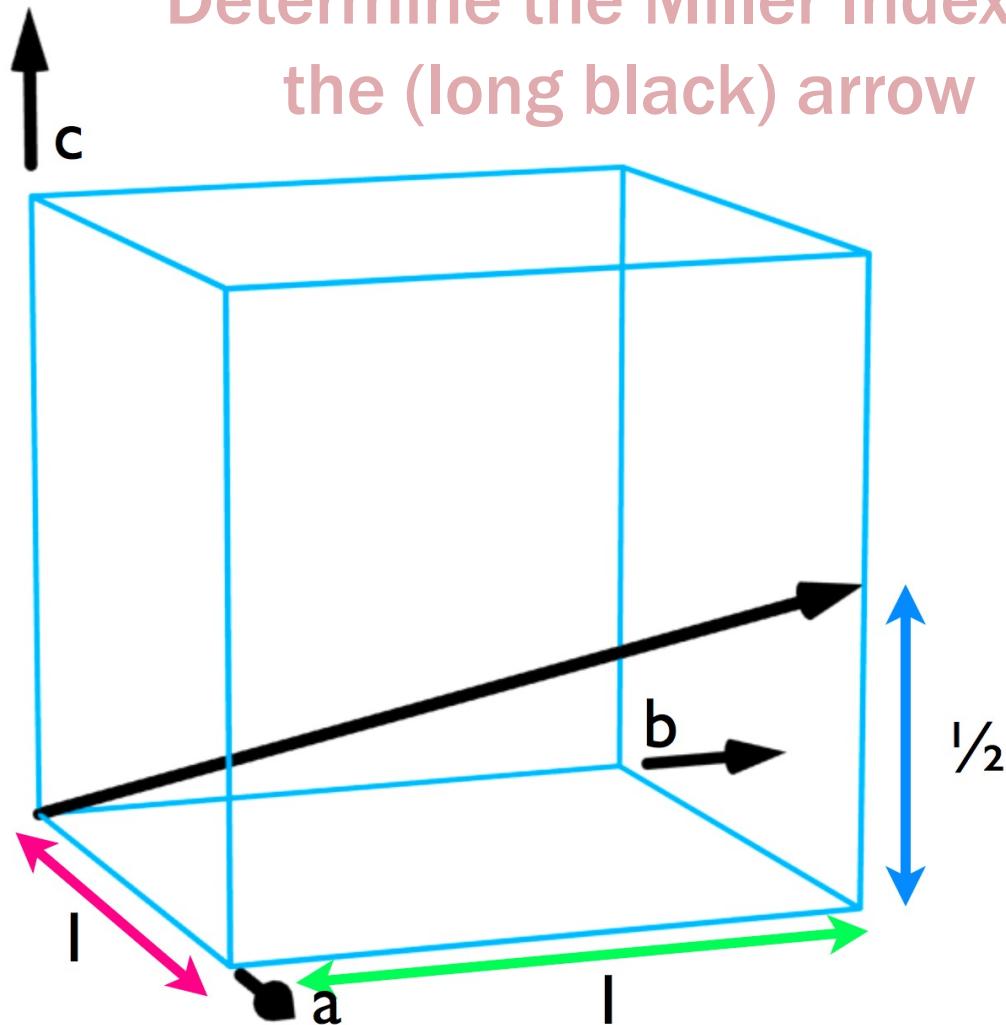
Determine the Miller Index of a lattice direction

1. Determine the fractional length of the projections on the three axes of the unit cell
2. Reduce to smallest set of integers using a common factor
3. Negative numbers are sometimes indicated by a bar ($\bar{1} = -1$) for convenience
4. A Miller index for a single direction is given in square brackets [hkl]

Lattice Directions: Example 1

Determine the Miller Index of
the (long black) arrow

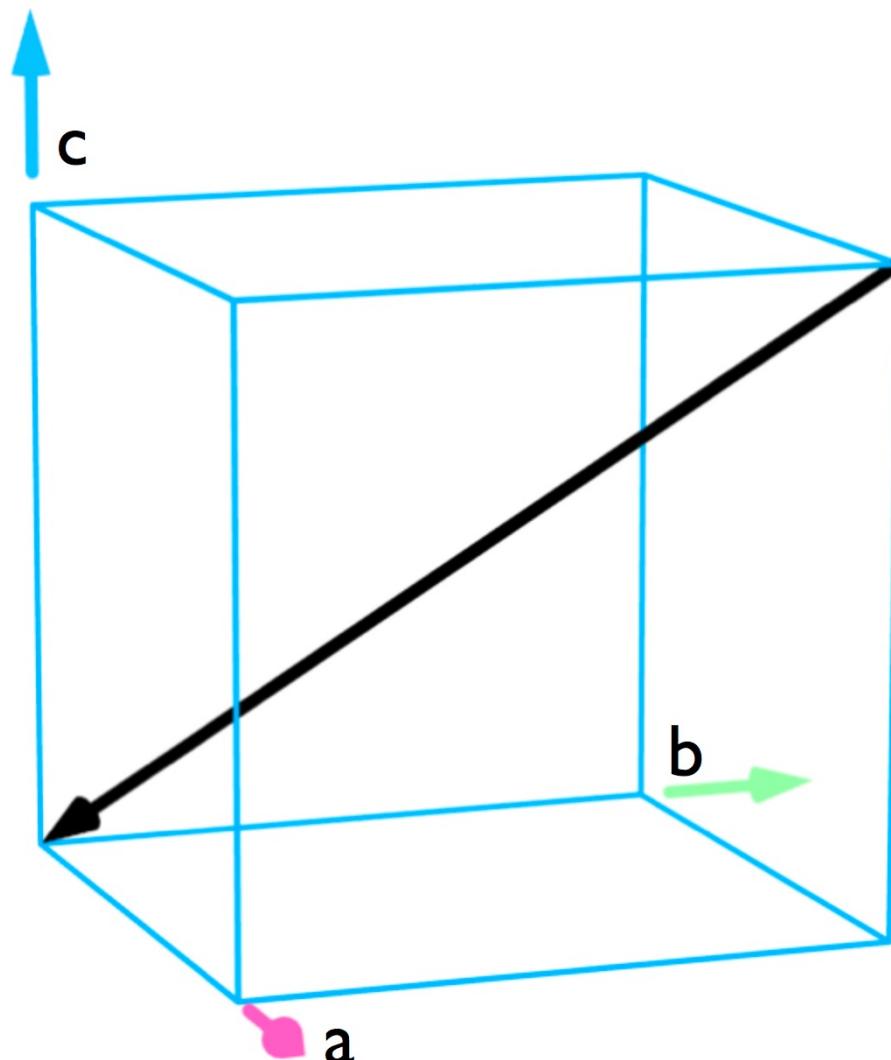
$$\begin{matrix} a & b & c \\ | & | & \frac{1}{2} \\ [221] \end{matrix}$$



Lattice Directions: Example 2

[$\bar{1} \bar{1} \bar{1}$]

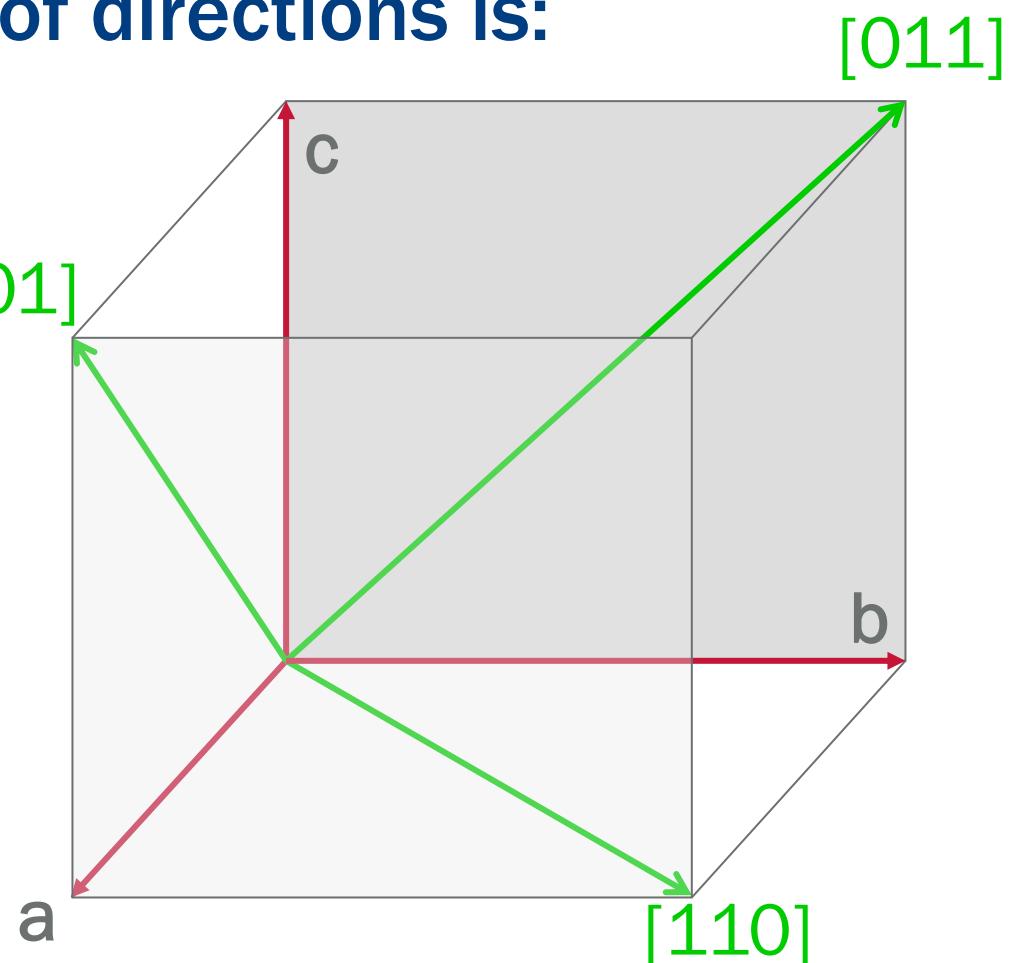
Overbar
indicates
negative
numbers



Family of Lattice Directions

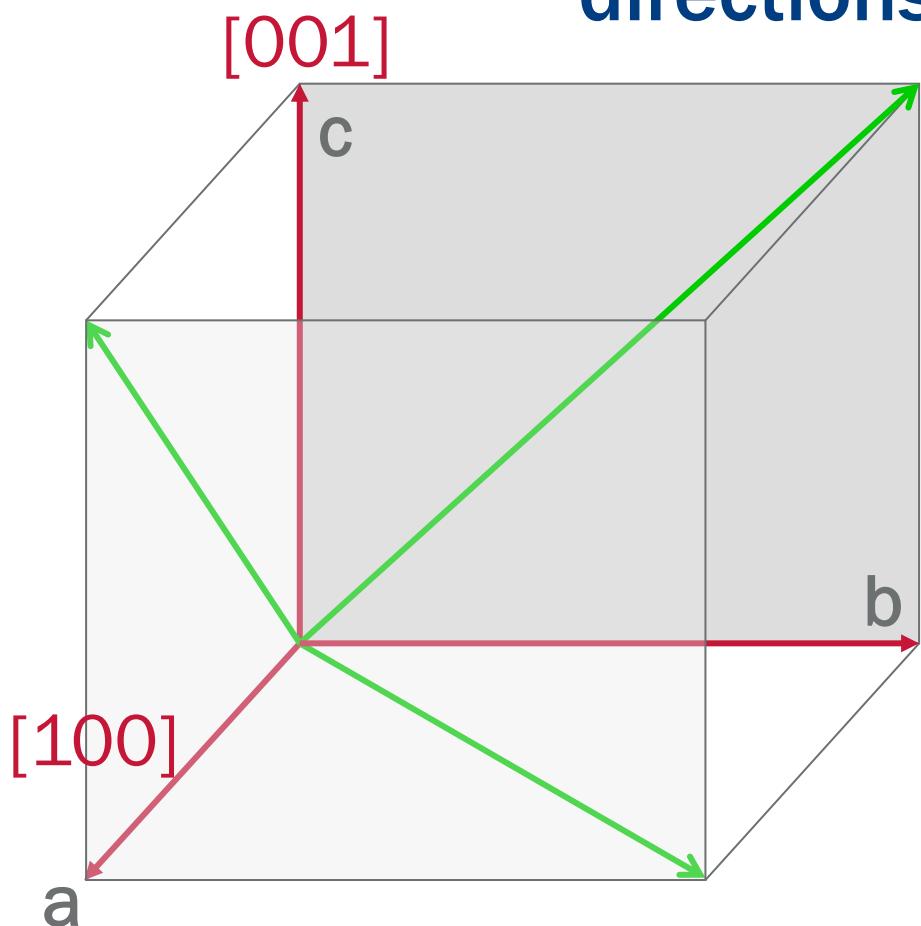
Example of $\langle 110 \rangle$ for a cubic crystal. The full family of directions is:

- $[1\bar{1}0]$
- $[\bar{1}10]$
- $[1\bar{1}\bar{0}]$
- $[\bar{1}\bar{1}0]$
- $[10\bar{1}]$
- $[\bar{1}0\bar{1}]$
- $[01\bar{1}]$
- $[0\bar{1}\bar{1}]$
- $[101]$
- $[011]$



Family of Lattice Directions

In non-cubic systems the number of equivalent directions is reduced



For $\langle 100 \rangle$

Cubic: $[100], [010], [001], [\bar{1}00], [0\bar{1}0], [00\bar{1}]$

Tetragonal: $[100], [010], [\bar{1}00], [0\bar{1}0]$

Orthorhombic: $[100], [\bar{1}00]$

$[010]$

3D Printing Crystals



Ian Saginor
@volcanoclast

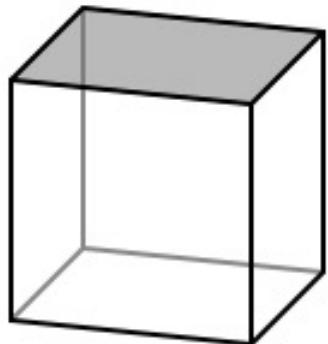
Follow



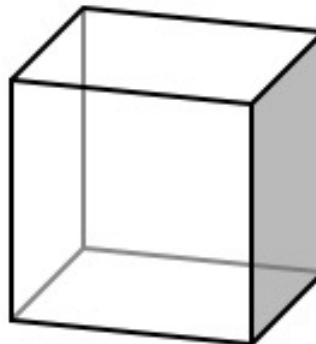
3D printed Miller Index model for Mineralogy class. Designed by my student.



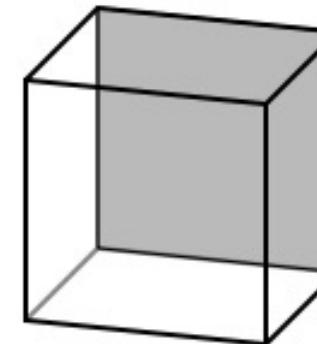
Low Index Lattice Planes



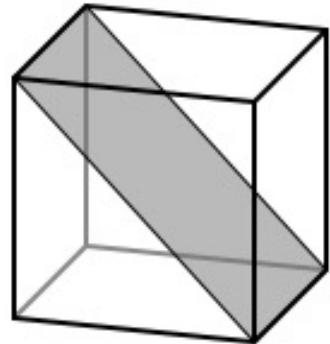
(001)



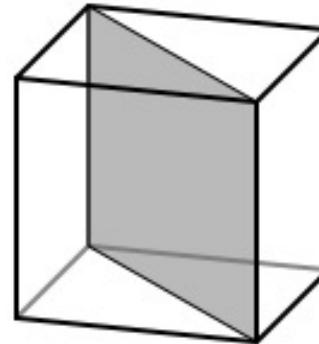
(100)



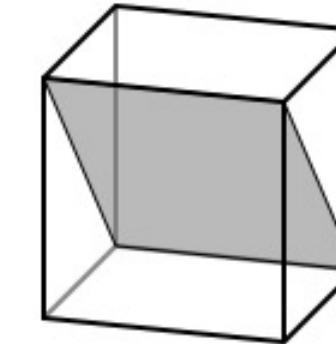
(010)



(101)

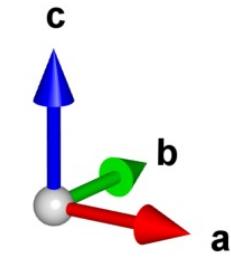


(110)



(011)

“Low index” refers
to (hkl) formed of
0s and 1s only



Note the (hkl) plane is the surface normal to the $[hkl]$ direction

Lattice Planes: Recipe

A lattice can be decomposed into an infinite series of parallel, equally spaced planes

– key for diffraction experiments (final lecture)

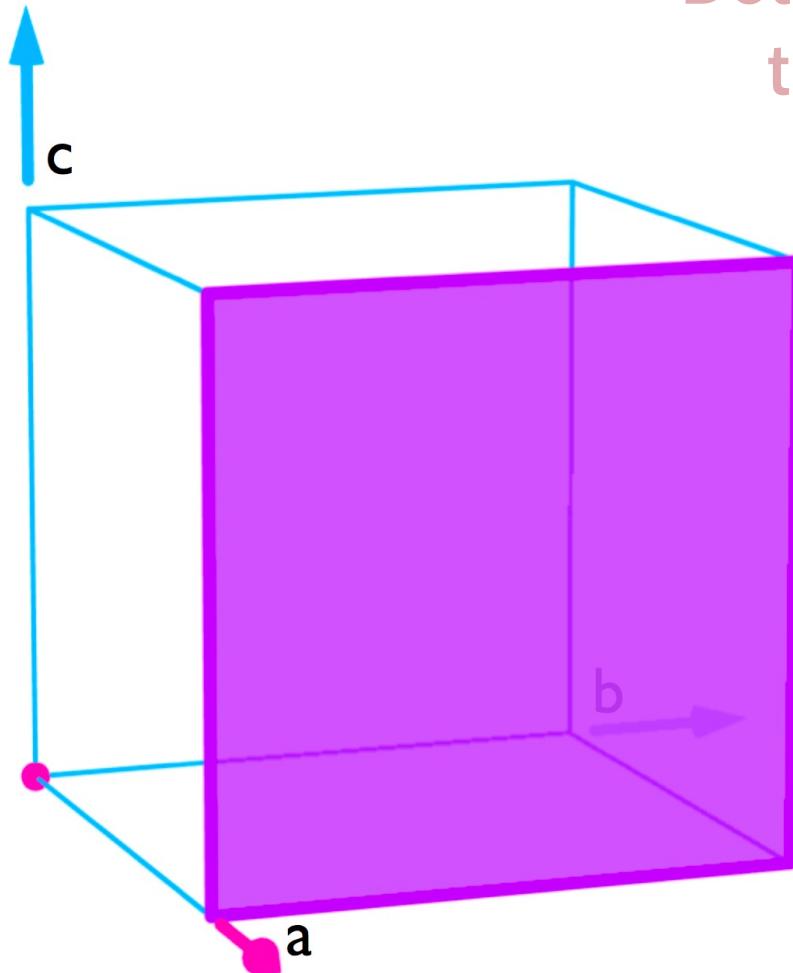
1. Determine intercepts of the plane with unit cell axes
2. If a plane is parallel to an axis, take the intercept as infinity
3. Take reciprocals ($1/x$) of the fractional coordinates

e.g.

Intercepts: $\frac{1}{2}a$, $1b$, $\frac{1}{4}c$

Miller index: (214)

Lattice Planes: Example 1

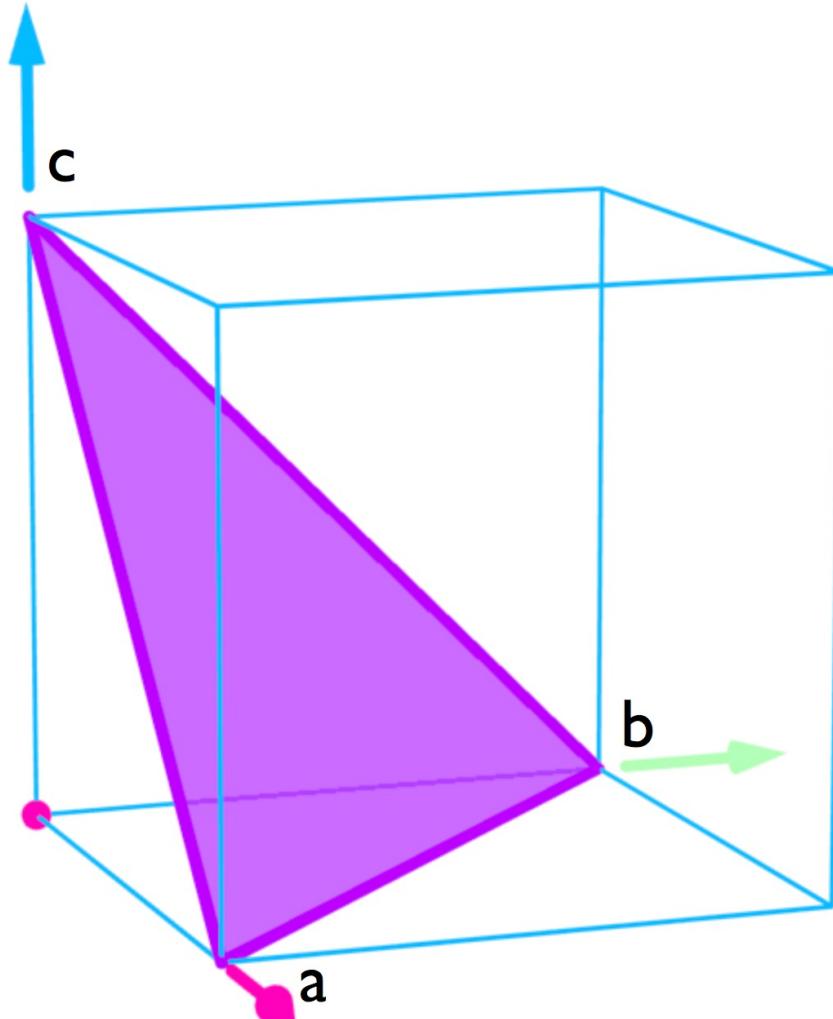


Determine the Miller Index of
the (shaded pink) plane

	a	b	c
Intercepts	1	∞	∞
Reciprocal	1	0	0
Miller Indices	(100)		

● = Origin

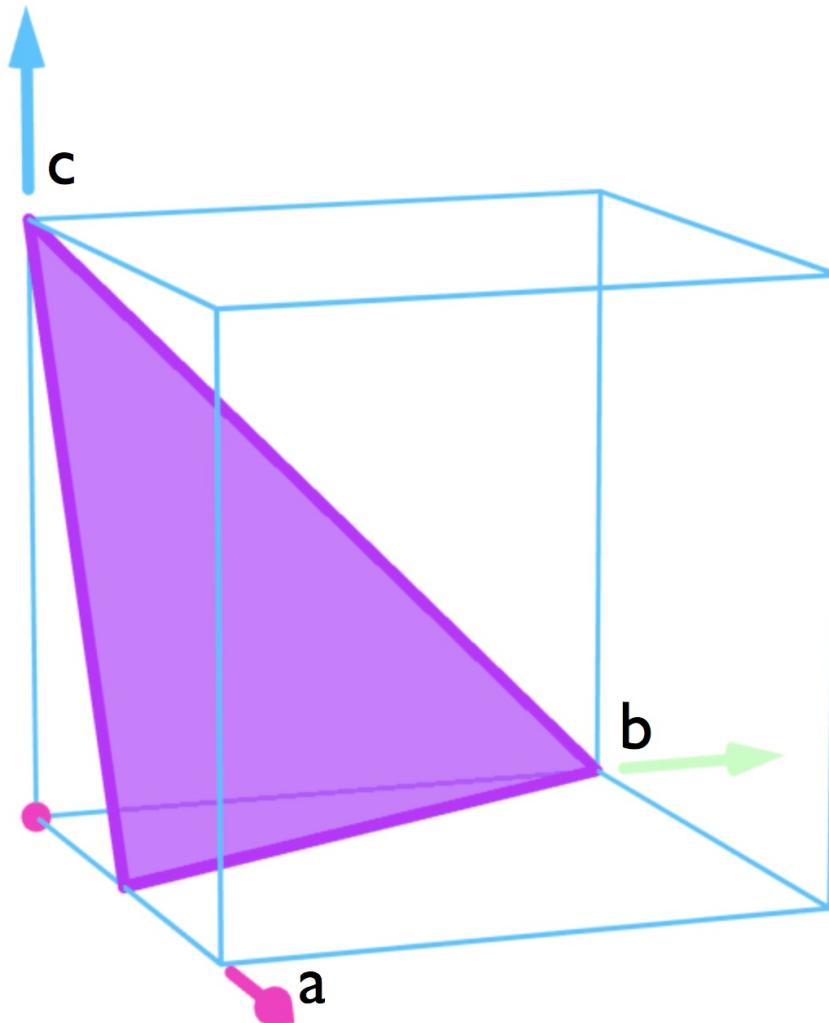
Lattice Planes: Example 2



	a	b	c
Intercepts	l	l	l
Reciprocal	l	l	l
Miller Indices	$(\bar{l} \bar{m} \bar{n})$		

● = Origin

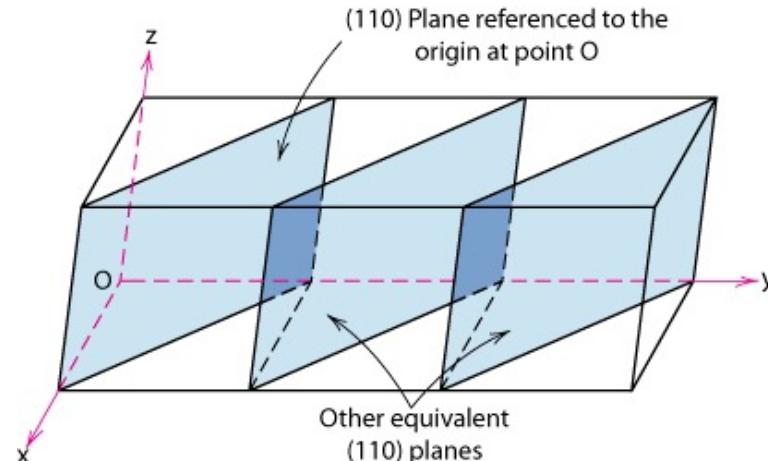
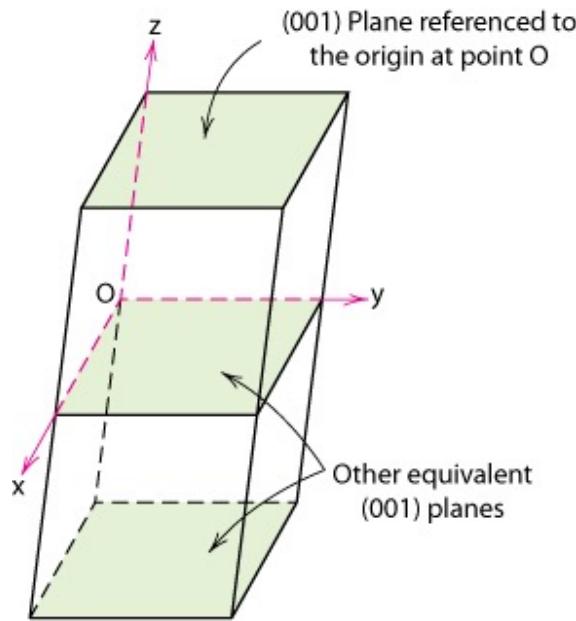
Lattice Planes: Example 3



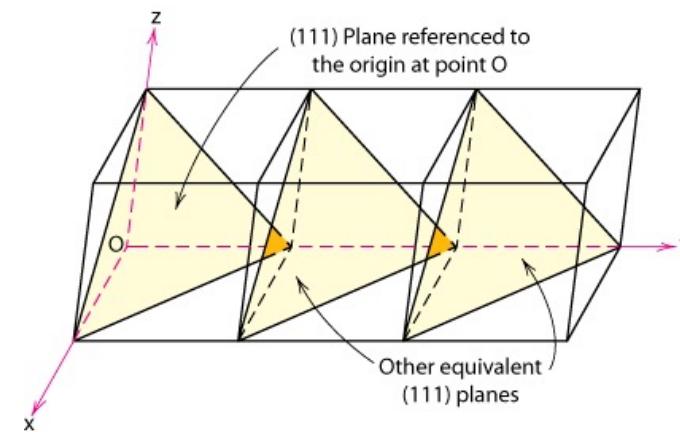
	<i>a</i>	<i>b</i>	<i>c</i>
Intercepts	$\frac{1}{2}$	1	1
Reciprocal	2	1	1
Miller Indices	(211)		

● = Origin

Equivalent Lattice Planes

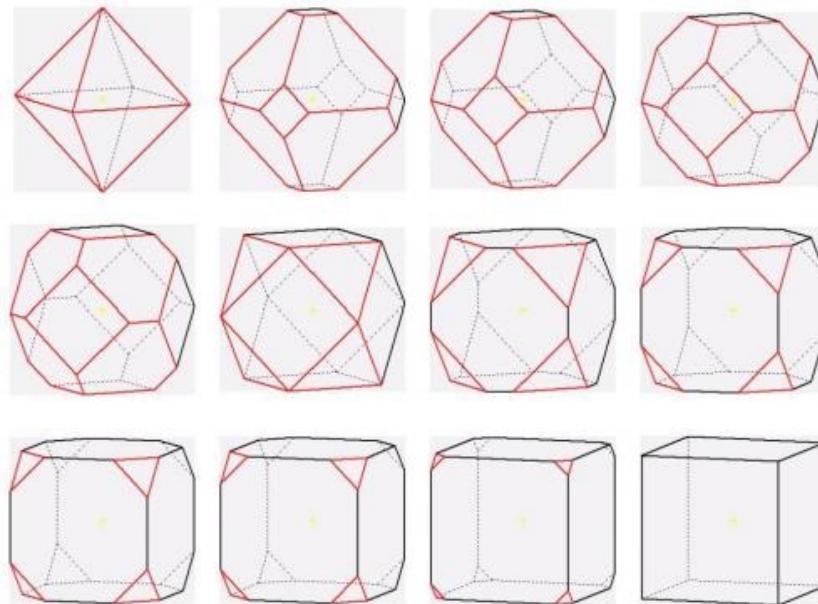


Family of equally
spaced lattice planes



Shape of Crystals

The relative energy (thermodynamics) and growth rate (kinetics) of each Miller plane determines the shape of real crystals



Different forms of
a cubic crystal -
can you name all
the surfaces?

Weiss Zone Law

Determine if a particular direction lies in a particular plane e.g. does [111] lie in (100)?

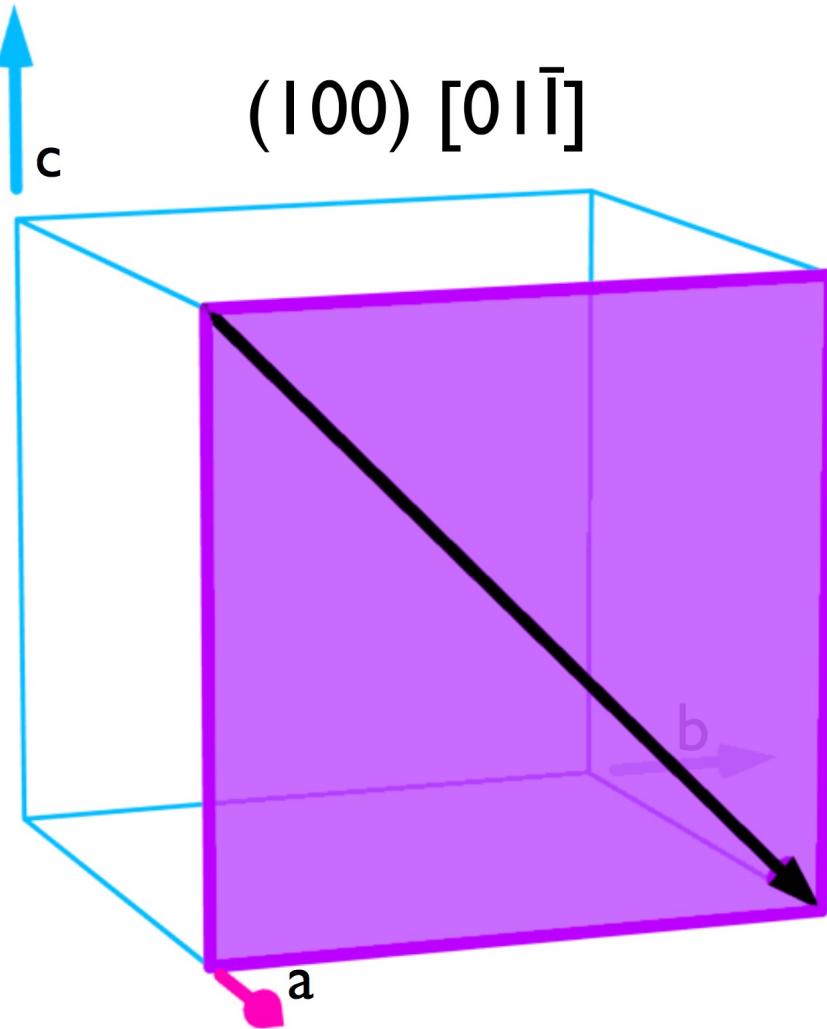
The Zone Law:

If $[uvw]$ lies in (hkl) then:

$$hu + kv + lw = 0$$

Note: the form arises from a scalar (dot) product

The Zone Law: Example



If $[uvw]$ lies in (hkl)
then:

$$hu + kv + lw = 0$$

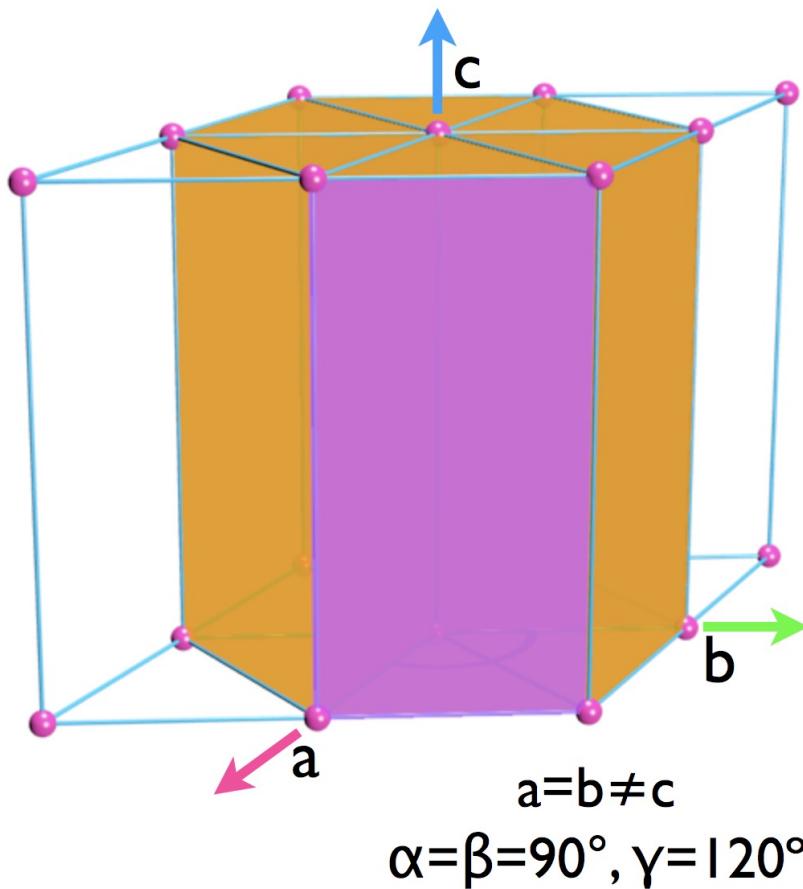
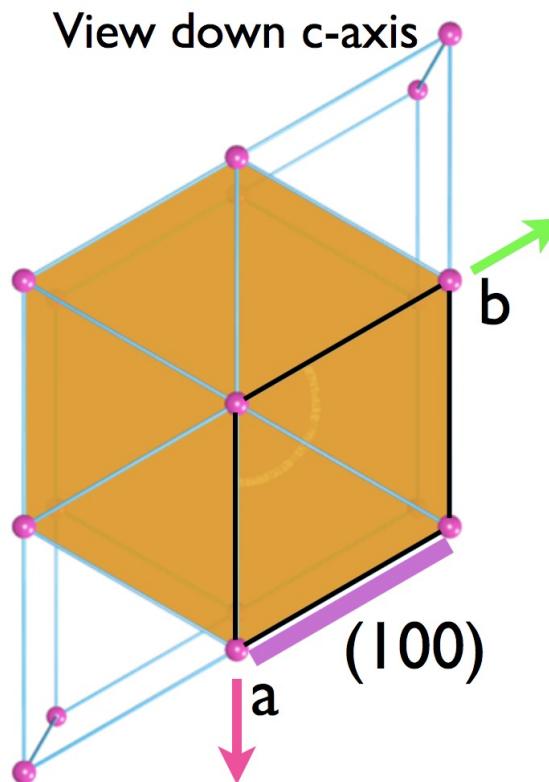


$$1 \times 0 + 0 \times 0 + 0 \times 1 = 0$$

Direction lies in plane!

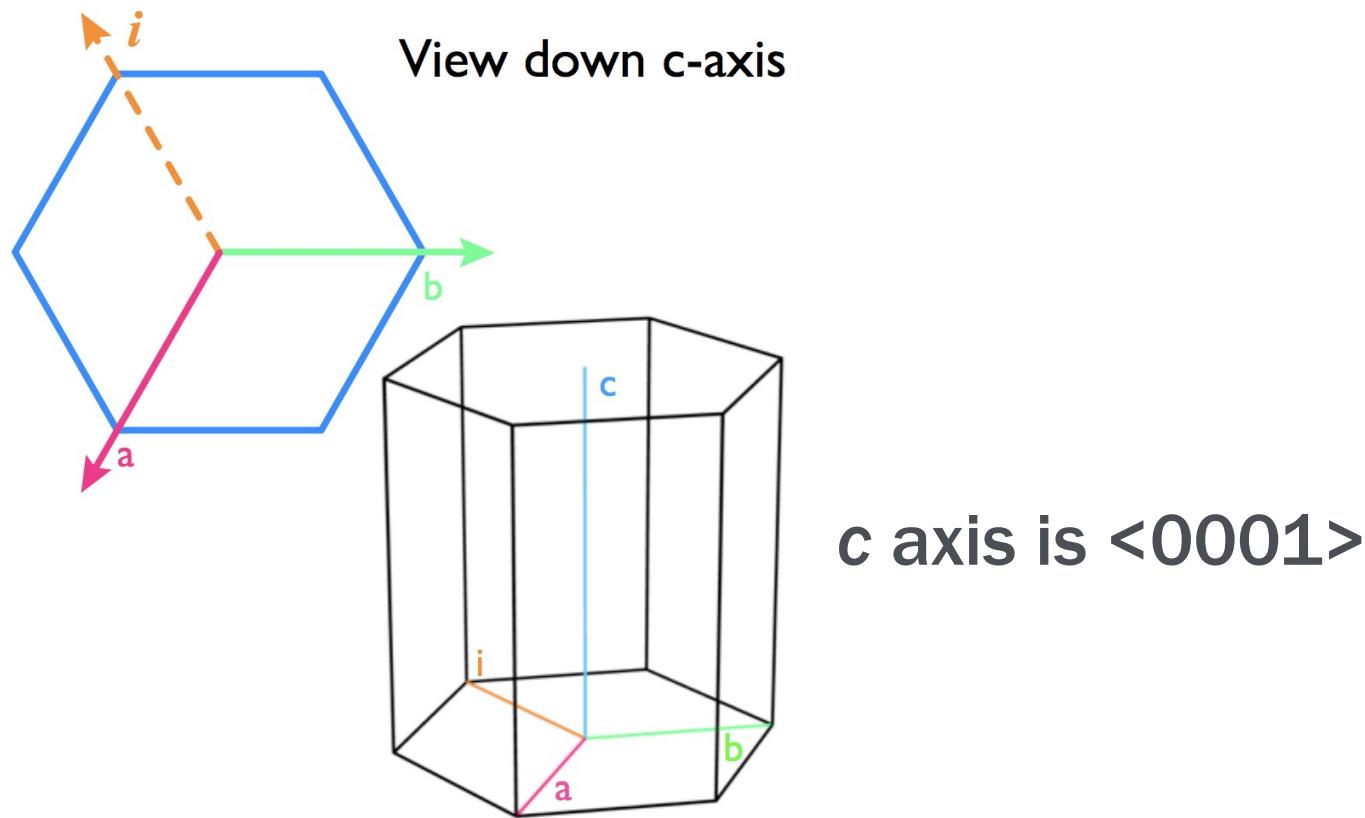
Exception: Hexagonal (hkl)

Standard (hkl) indexing scheme does not describe six-fold rotational symmetry of hexagonal lattices



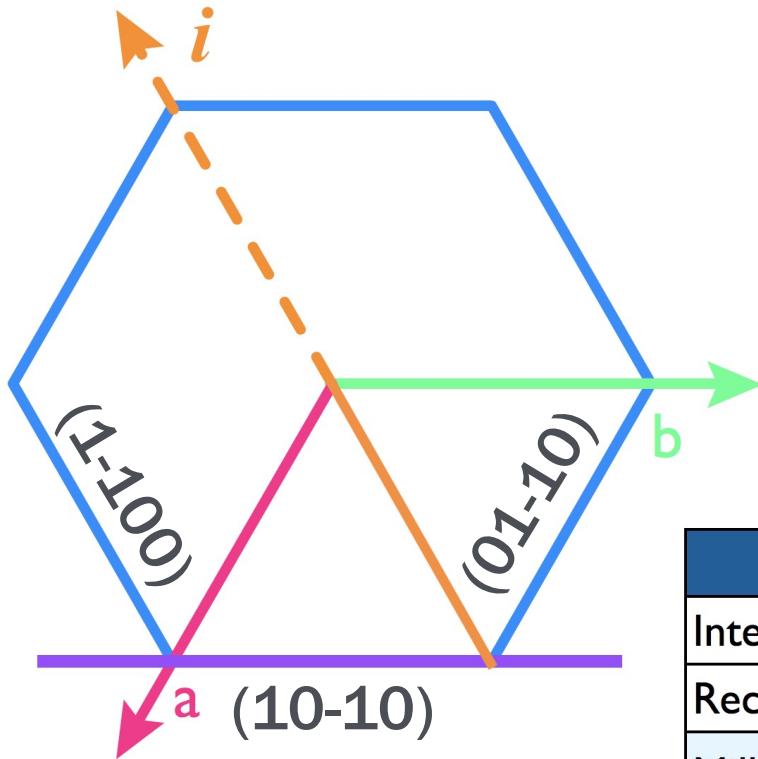
Exception: Hexagonal ($hki\bar{l}$)

Solution: Use Miller-Bravais coordinates. Define an additional axis: $(hkl) \rightarrow (hki\bar{l})$, where $i = -(a+b)$



Exception: Hexagonal ($hkil$)

Solution: Use Miller-Bravais coordinates. Define an additional axis: $(hkl) \rightarrow (hkil)$, where $i = -(a+b)$



All 6 sides belong to the same family, but only apparent with $(hkil)$

	a	b	i	c
Intercepts	l	∞	\bar{l}	∞
Reciprocal	l	0	\bar{l}	0
Miller Indices	$(l\ 0\ \bar{l}\ 0)$			

Summary: Geometry

Class outcomes:

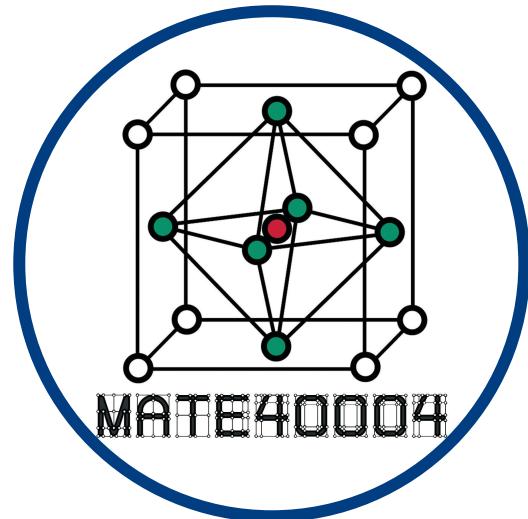
- Describe unit cells using fractional coordinates
- Draw a unit cell projection diagram
- Explain notation for Miller indices
- Determine crystal directions and planes
- Apply the zone law for directions and planes

MATE40004 – Structure 1

Crystallography

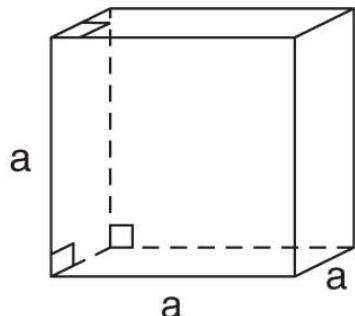
D. Packing

Professor Aron Walsh
Department of Materials
Imperial College London

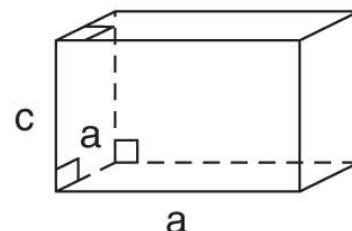


<http://www.imperial.ac.uk/people/a.walsh>

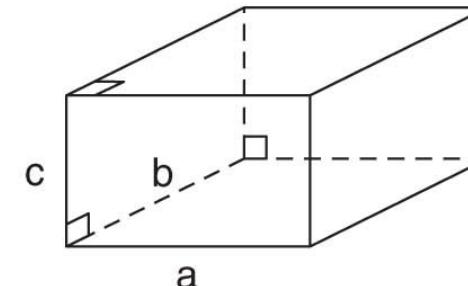
Recap: 7 Crystal Systems in 3D



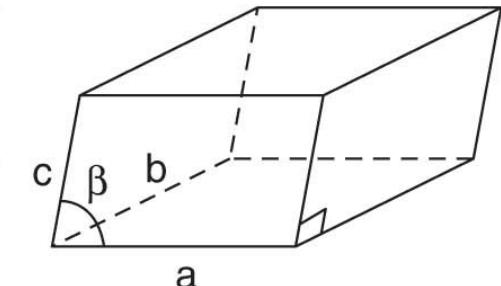
Cubic



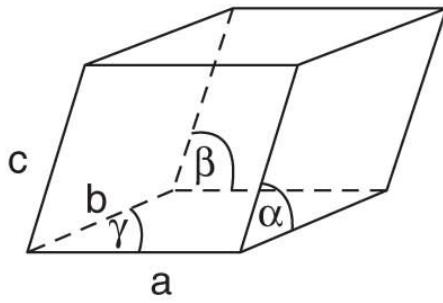
Tetragonal



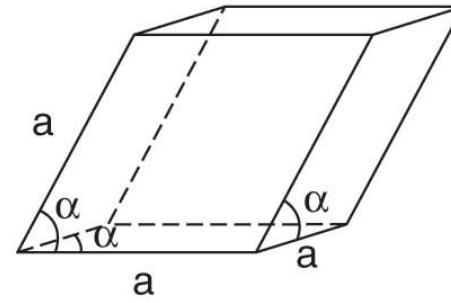
Orthorhombic



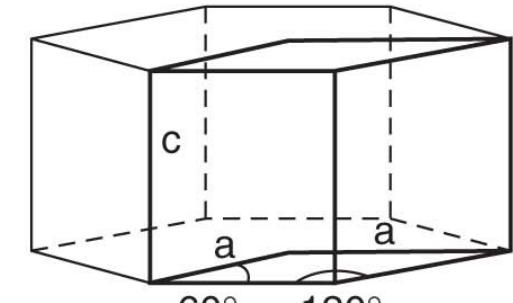
Monoclinic



Triclinic



Rhombohedral
(or Trigonal)



Hexagonal

Remember the constraints on lengths (a, b, c) and angles (α, β, γ)

Recap: 5 Symmetry Operations

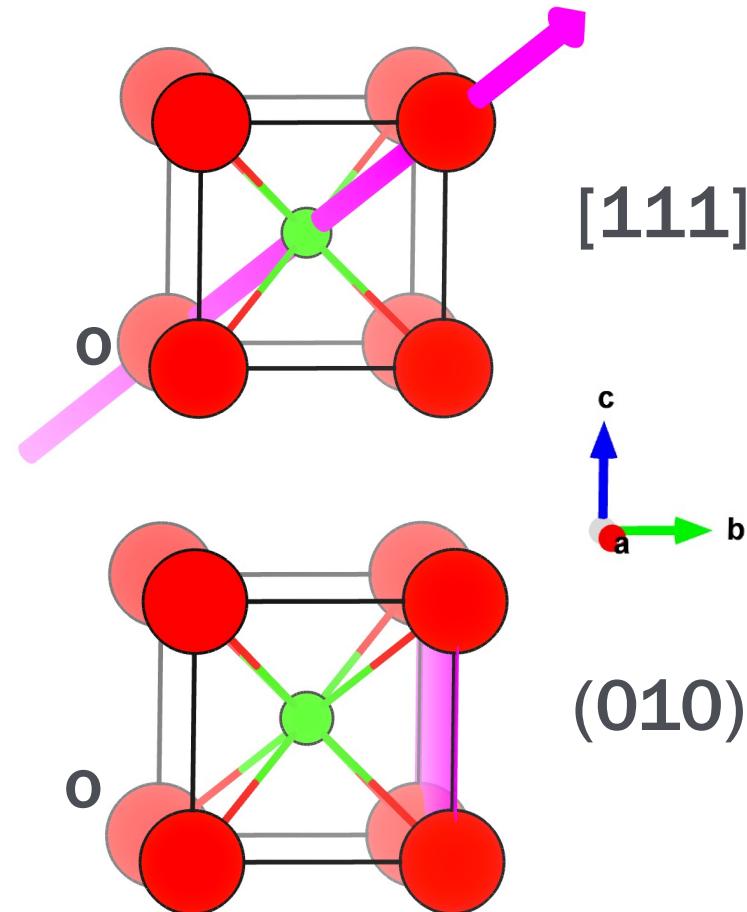
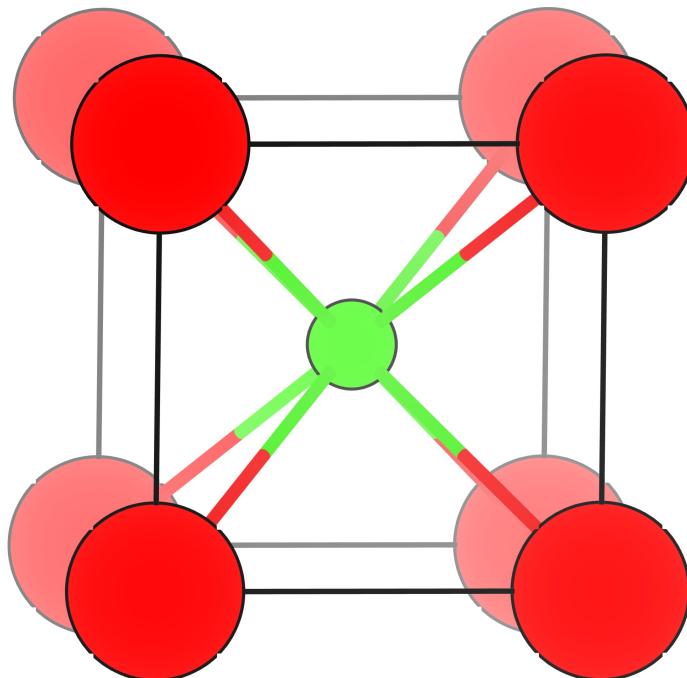
Operation	Element	Symbol
Identity	'whole of space'	E
Rotation by $360^\circ/n$	n-fold rotation axis	C_n
Reflection	mirror plane	σ
Inversion	centre of inversion	i
Rotation by $360^\circ/n$ followed by reflection in a perpendicular plane	n-fold improper rotation axis	S_n

Recap: Crystal Coordinates

Cubic crystal system

Cs $(0,0,0)$

Cl $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$



Lattice points (h,k,l) , directions $[hkl]$, and planes (hkl)

Outline of Crystallography

Part 1

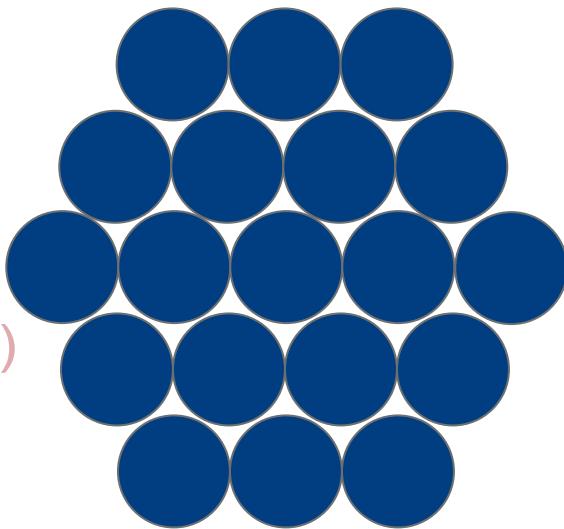
- A. Lattices
- B. Symmetry
- C. Geometry
- D. Packing

Packing Spheres

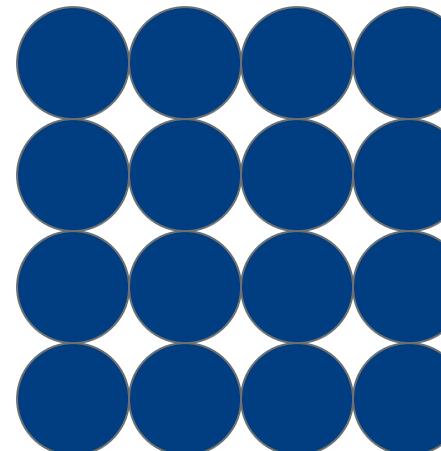
Which has the most efficient packing?

A

Close
packing
(74% in 3D)



vs.



B

Simple
cubic
(52% in 3D)

Packing of objects has fascinated mathematicians and physicists for centuries! Many mathematical physicists spend their entire career on this topic

Crystals as Packing of Spheres

Atoms (and ions) are hard spheres with a characteristic radius

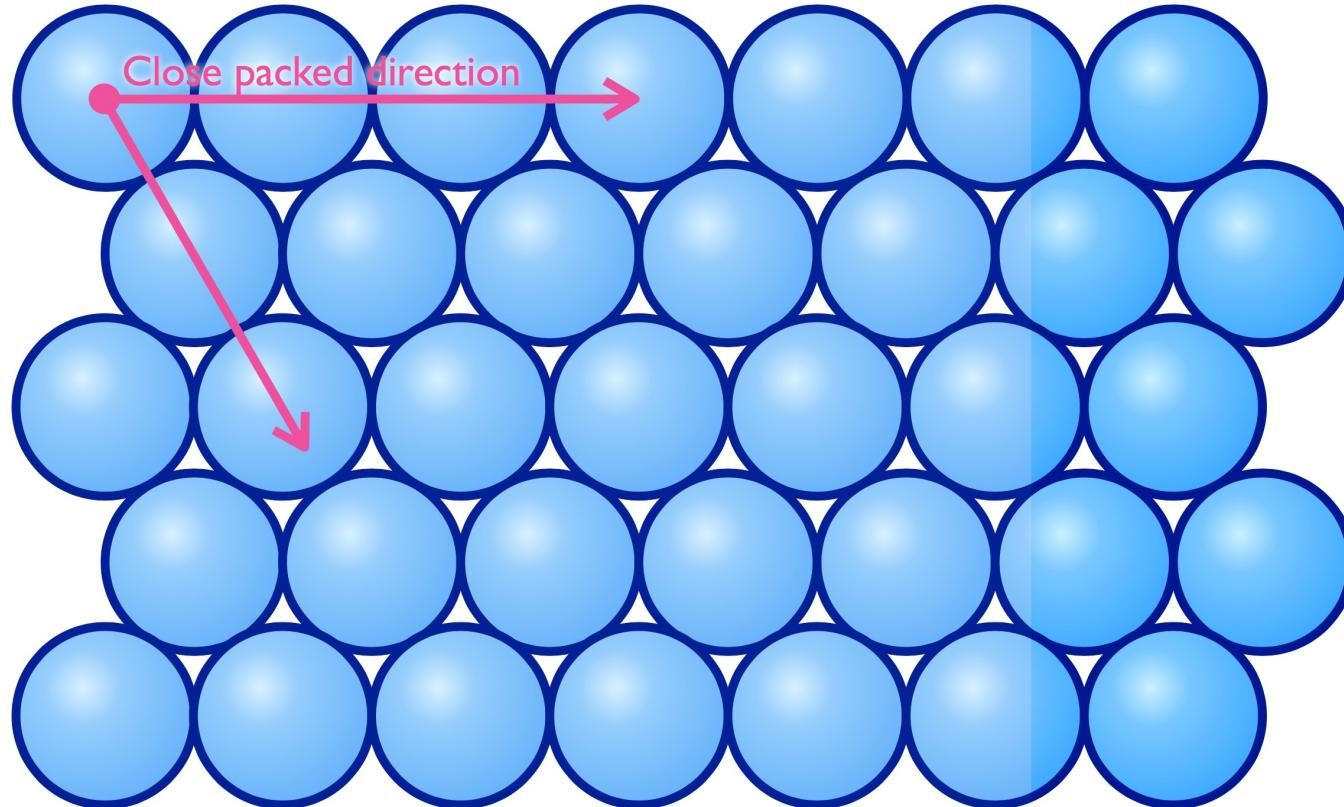
This approximation fails for certain electronic configurations and coordination environments

The most efficient way for spheres to pack is to minimise empty space

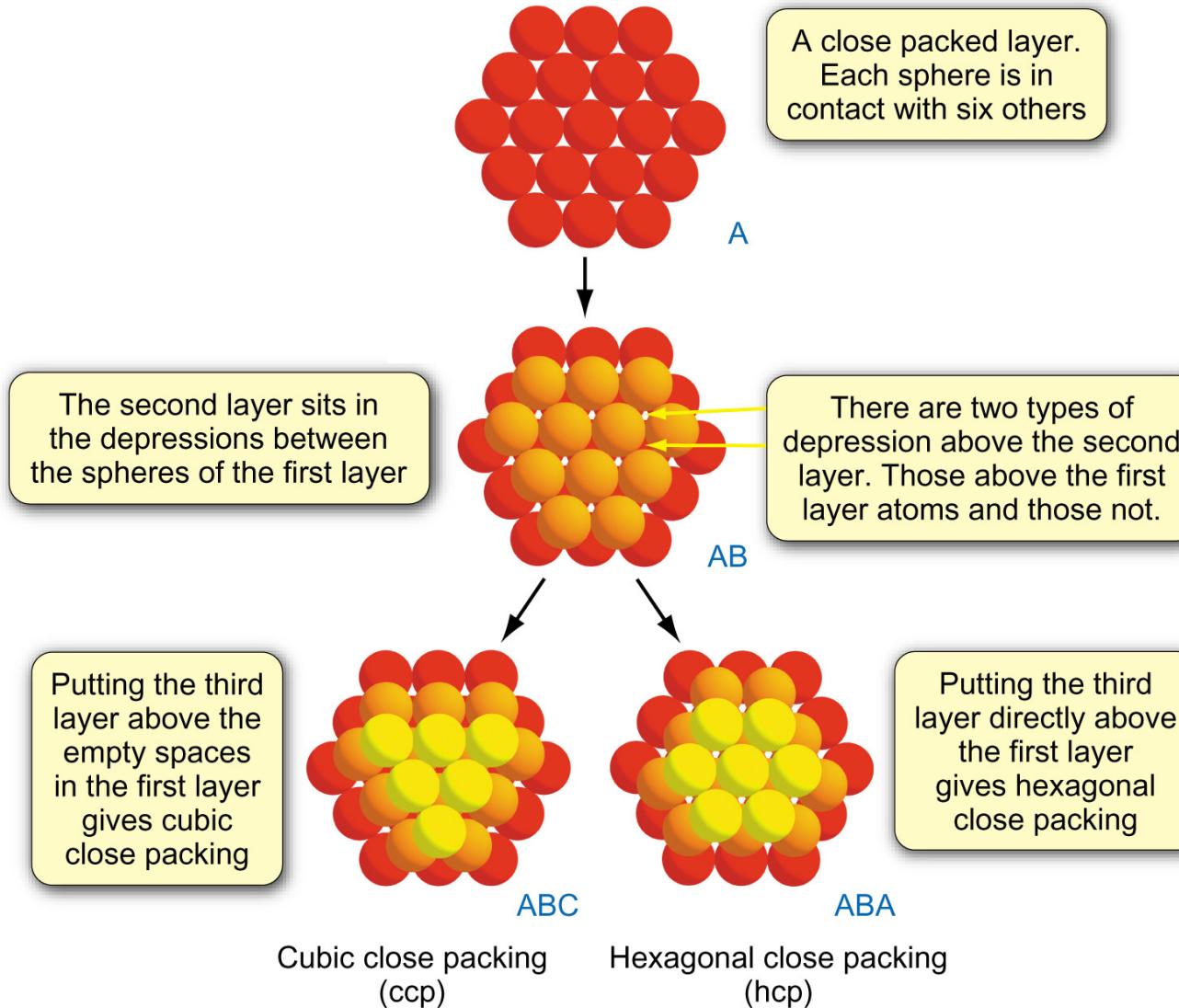
This is termed “close packing” – valid at macroscopic (e.g. canon balls) and microscopic (e.g. atoms) length scales

Close Packed Plane in 2D

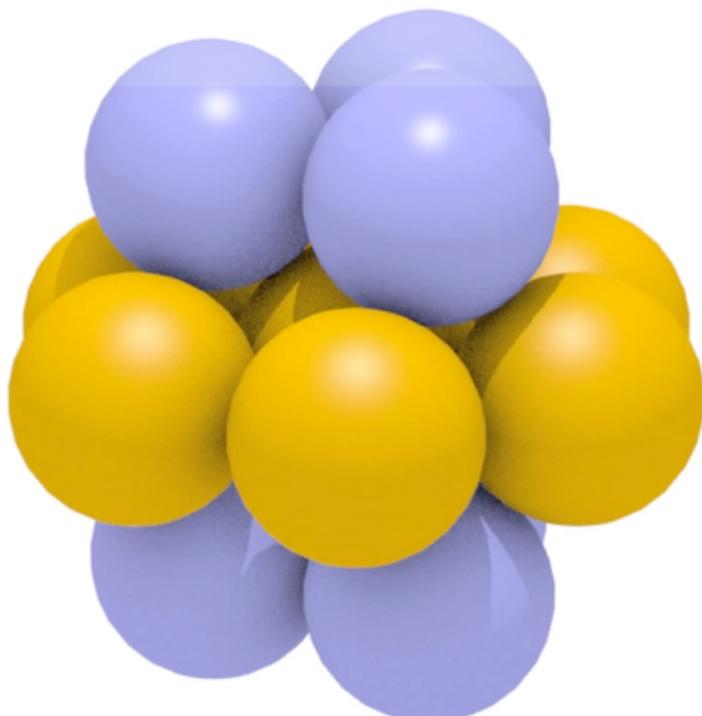
Each atom is in contact with 6 other atoms in the same plane



Close Packing in 3D



Close Packing in 3D



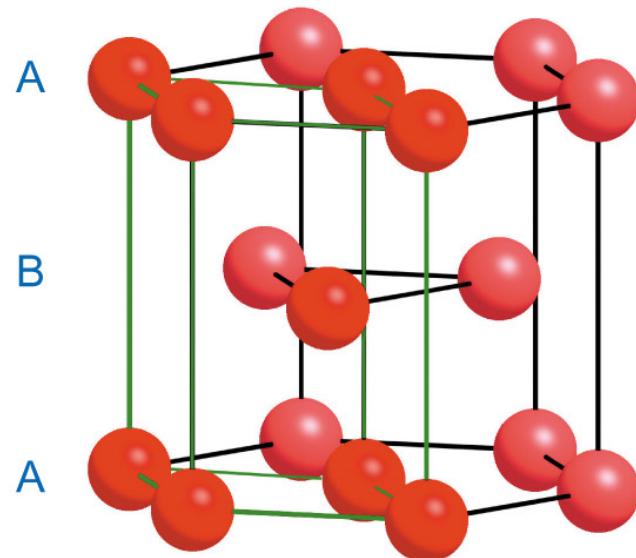
A B A B



A B C A B C

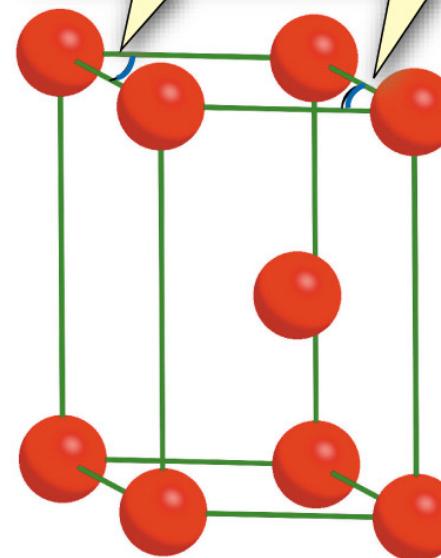
Unit Cell for Hexagonal Close Packing

Unit cell in green



Hexagonal repeating unit
for hexagonal close packing

These angles are 60°



Unit cell for
hexagonal close packing

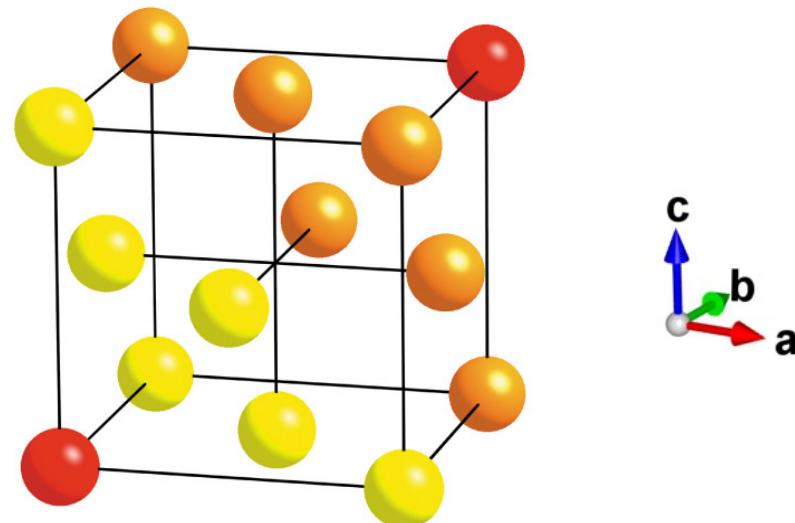
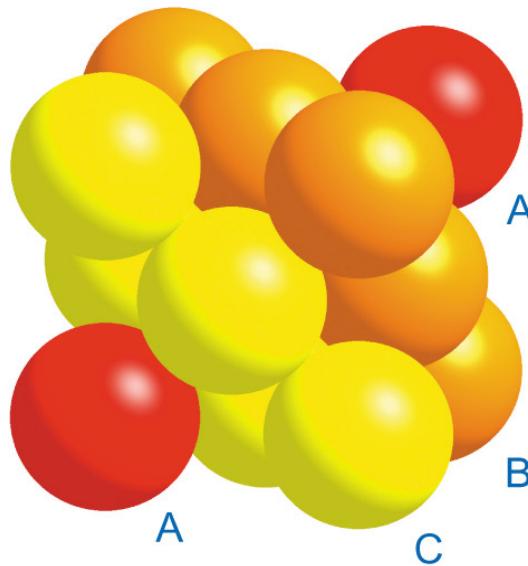
Atomic
coordinates

A1 (0,0,0)

A2 ($\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$)

Unit Cell for Cubic Close Packing

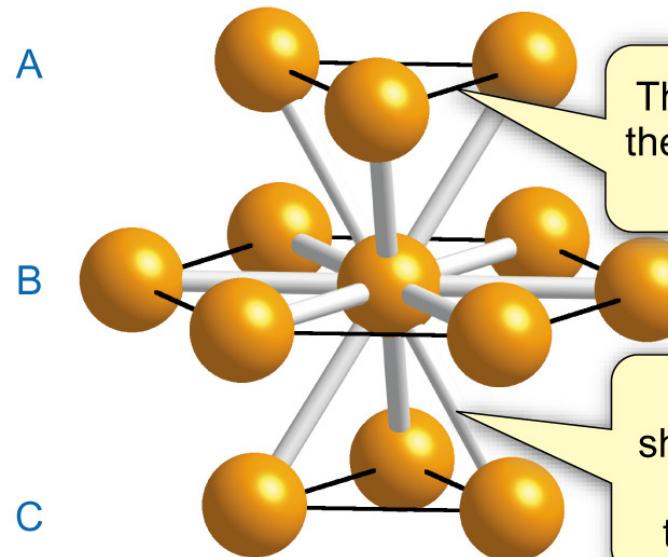
Cubic-closed packed (ccp) is also known as face-centred cubic (fcc) as there are atoms on the 6 faces as well the 8 vertices



Along which direction are the fcc layers stacked?

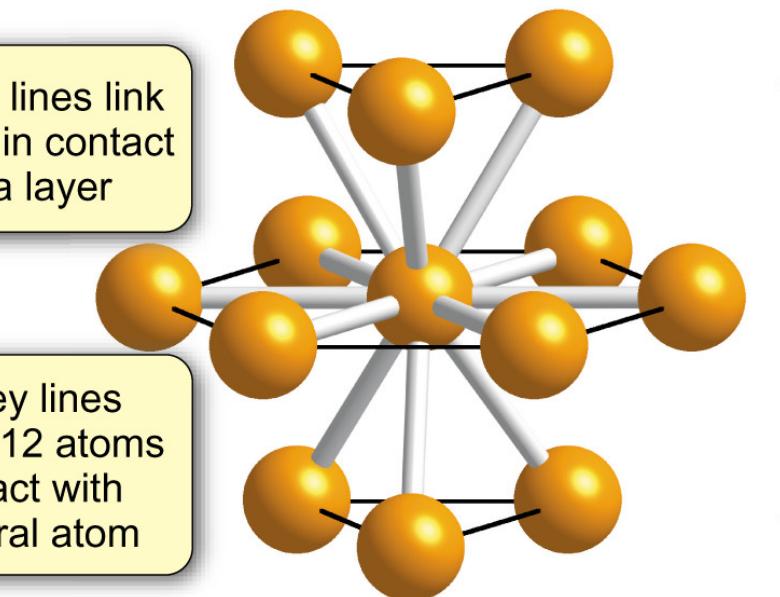
FCC/HCP Coordination Numbers

Coordination number: the number of nearest neighbours an atom has in a crystal



Cubic close packed (ccp)

Coordination number 12

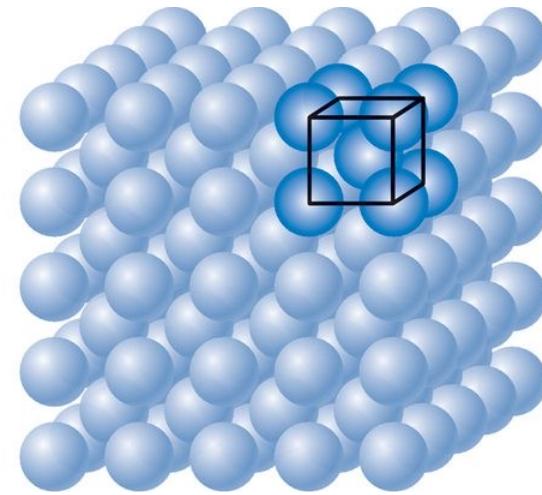
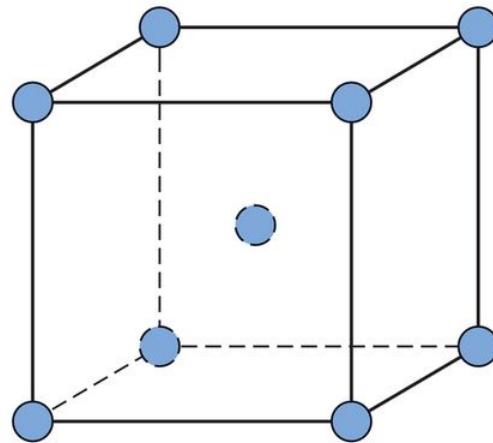
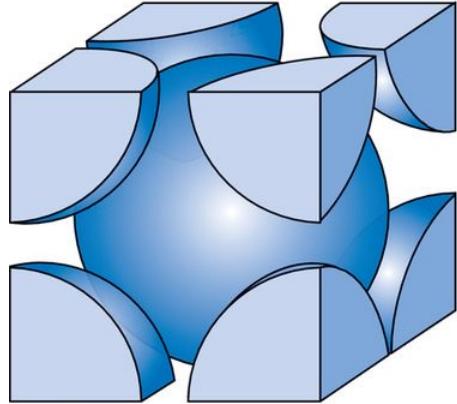


Hexagonal close packed (hcp)

Coordination number 12

Unit Cell for Body-Centered Cubic

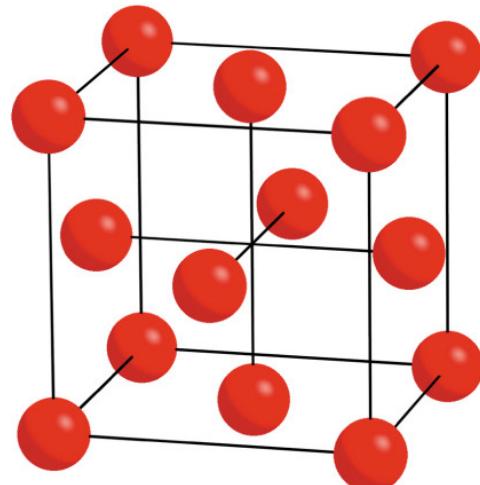
bcc is a common crystal structure for metals



Center and corner atoms “touch” along cube diagonals.
The unit cell length (a) and atom radius (r) are related
by $a = 4r/\sqrt{3}$

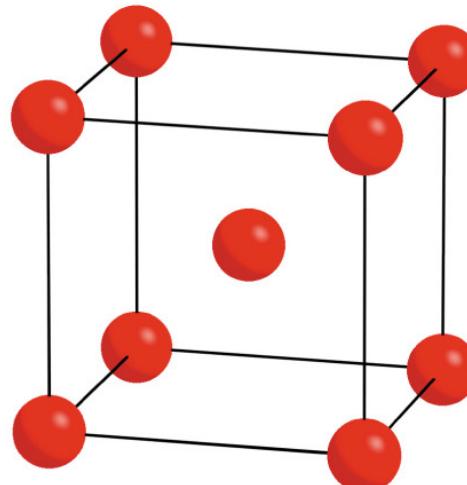
What is the relation between a and r for simple cubic?

Other Coordination Numbers



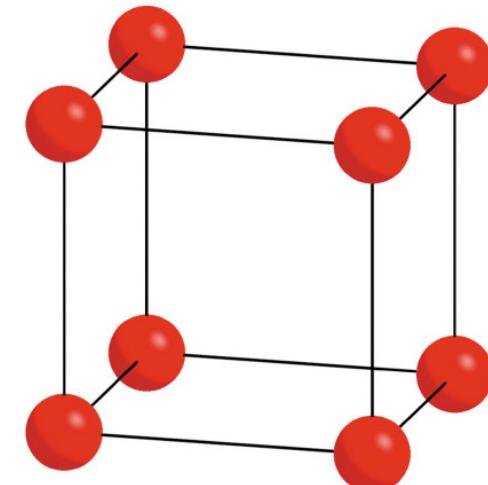
Face-centred cubic (fcc)
(another name for cubic close packed, ccp)

Coordination number 12



Body-centred cubic (bcc)

Coordination number 8



Primitive cubic
(simple cubic)

Coordination number 6

Remember that $N = 12$ for close-packed structures

Crystal Structures of Metals

Metallic bonding is (usually) delocalised and non-directional, thus dense packing is preferred

Metal	Crystal Structure Type
Al, Cu, Au, Pb, Ni, Pt, Ag	fcc
Cd, Co, Ti, Zr, Zn, Tc, Y	hcp
Cr, Fe, Mo, Ta, W, V, Mn	bcc
Po	sc

The energy differences are small. The preference is a subtle balance of chemical interactions

An Aside: Why is Po simple cubic?

Relativistic quantum mechanics (Dirac equation)

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Origin of the stabilized simple-cubic structure in polonium: Spin-orbit interaction versus Peierls instability

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The origin of the stabilized simple-cubic (SC) structure in Po is explored by using the first-principles band calculations. We have found that the prime origin is the inherent strong spin-orbit (SO) interaction in Po, which suppresses the Peierls-type structural instability, as usually occurs in *p*-bonded systems. Based on the systematic analysis of electronic structures, charge densities, Fermi surfaces, and susceptibilities of Se, Te, and Po, we have proven that the stable crystal structure in VIA elements is determined by the competition between the SO splitting and the crystal-field splitting induced by the low-symmetry structural transition. Our study suggests that the large SO interaction would suppress the Peierls instability which is generally expected to occur in one-dimensional conductors.

Packing Fraction (or Efficiency)

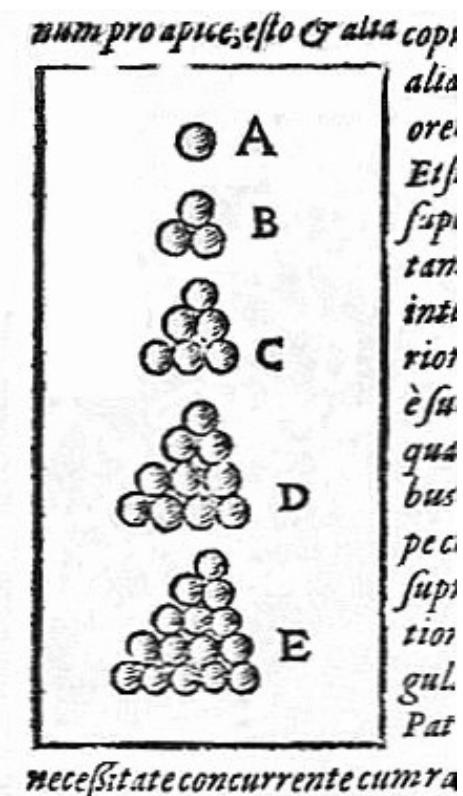
$$\text{Packing fraction} = \frac{\text{Occupied unit cell volume}}{\text{Total unit cell volume}}$$

Recipe for Calculation:

1. Determine number of atoms in unit cell (N_{atom})
2. Calculate the occupied volume (V_{atom})
3. Calculate the total unit cell volume (V_{cell})
4. Packing fraction = $V_{\text{atom}} / V_{\text{cell}}$

Johannes Kepler (1571–1630)

Born in Germany. Mathematician, astronomer, astrologer (laws of planetary motion)



Kepler conjecture:
no arrangement of equally sized spheres filling space
has a greater average density than fcc or hcp (74%)



From Kepler's Conjecture to Theorem



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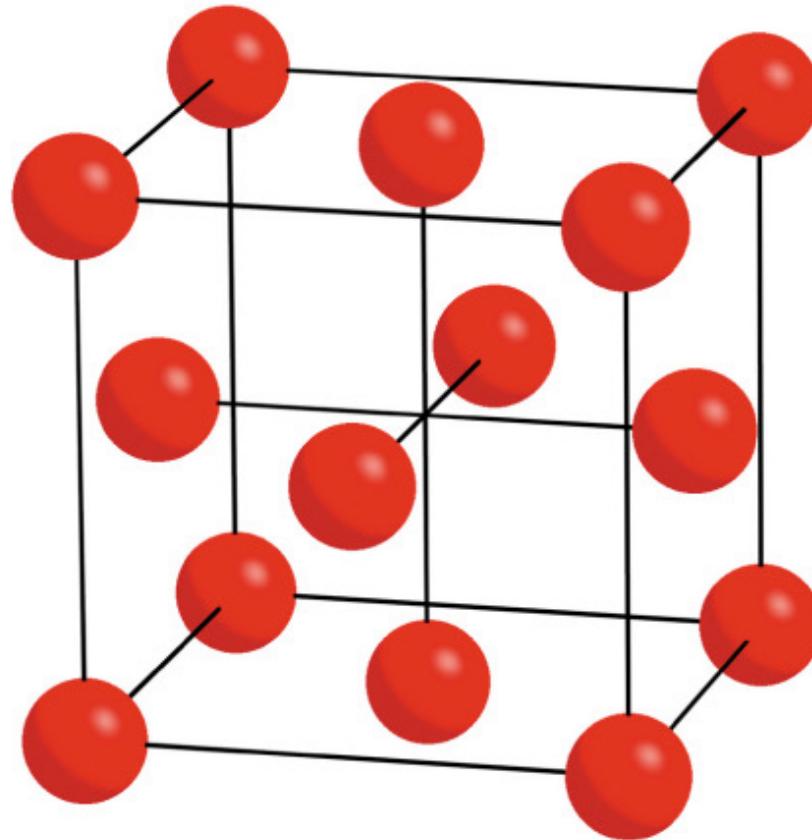
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A FORMAL PROOF OF THE KEPLER CONJECTURE

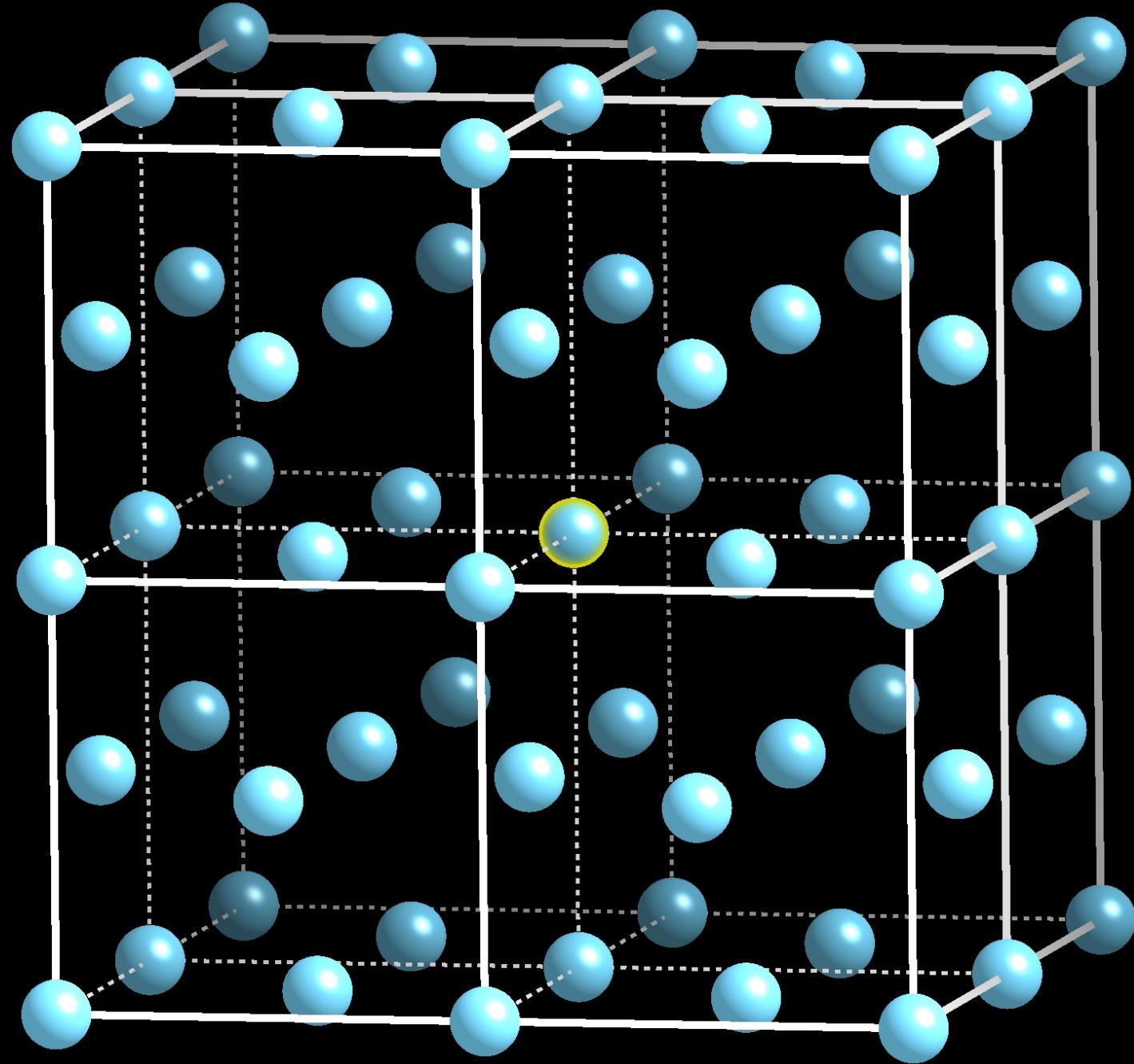
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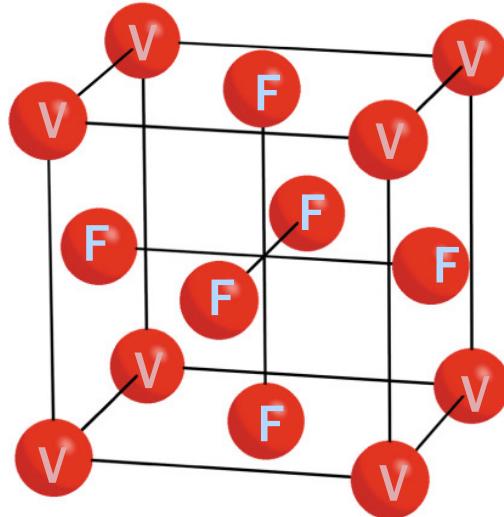
Packing Fraction – fcc



How many atoms are in the unit cell?



Packing Fraction – fcc



Position	No. Atoms	Share	Atoms in Unit Cell
Vertex	8	1/8	$8 \times 1/8$
Face	6	1/2	$6 \times 1/2$

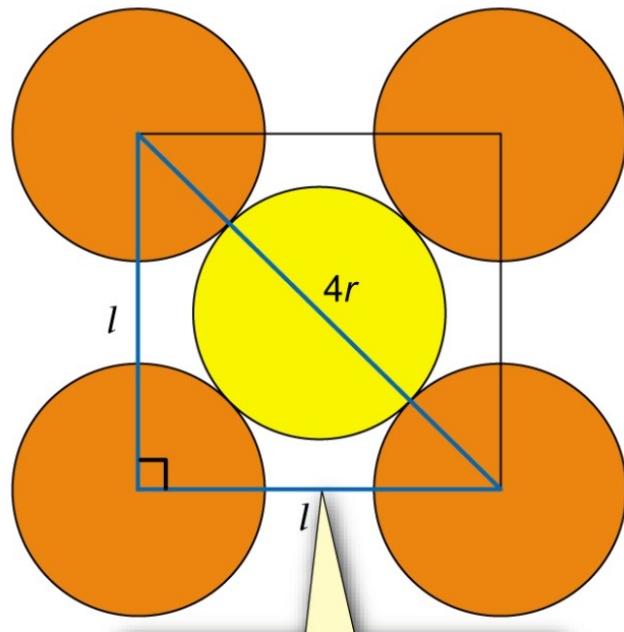
$$N_{\text{atom}} = (8 \times 1/8) + (6 \times 1/2) = 4$$

$$V_{\text{atom}} = 4 \times 4/3\pi r^3 = 16/3\pi r^3$$

This is the volume of atoms inside the unit cell in units of the atomic radius, r^3

Packing Fraction – fcc

Calculate the volume of the unit cell in terms of r^3



The length l can be calculated in terms of the atomic radius r using Pythagoras's theorem

Tip: Identify a unit cell plane where atoms “touch”

$$l^2 + l^2 = (4r)^2$$

$$2l^2 = 16r^2$$

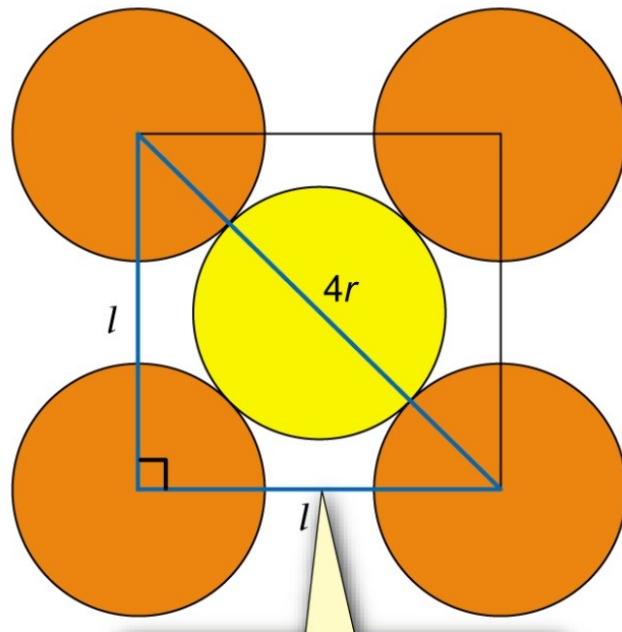
$$l^2 = 8r^2$$

$$l = 8^{1/2}r$$

$$V_{\text{cell}} = l^3 = 8^{3/2}r^3$$

Packing Fraction – fcc

Calculate the final packing fraction



The length l can be calculated in terms of the atomic radius r using Pythagoras's theorem

$$V_{\text{atom}} = \frac{16}{3}\pi r^3$$
$$V_{\text{cell}} = 8^{3/2}r^3$$

Packing Efficiency = 74%

Interstitial Lattice Sites

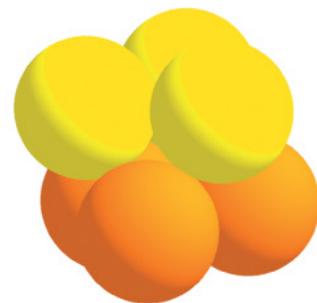
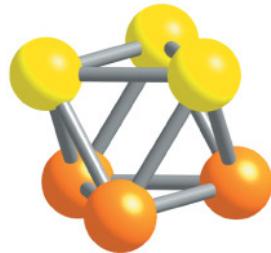
Atoms take up 74% of space in close-packed structures. What about the other 26%

The gaps are termed **interstitial sites**

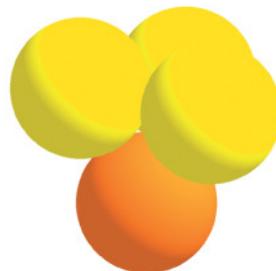
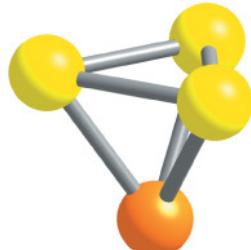
In close-packed structures, there are *octahedral* and *tetrahedral* interstitial sites

Many related crystal structures can be formed by occupying these sites [see course Part 2]

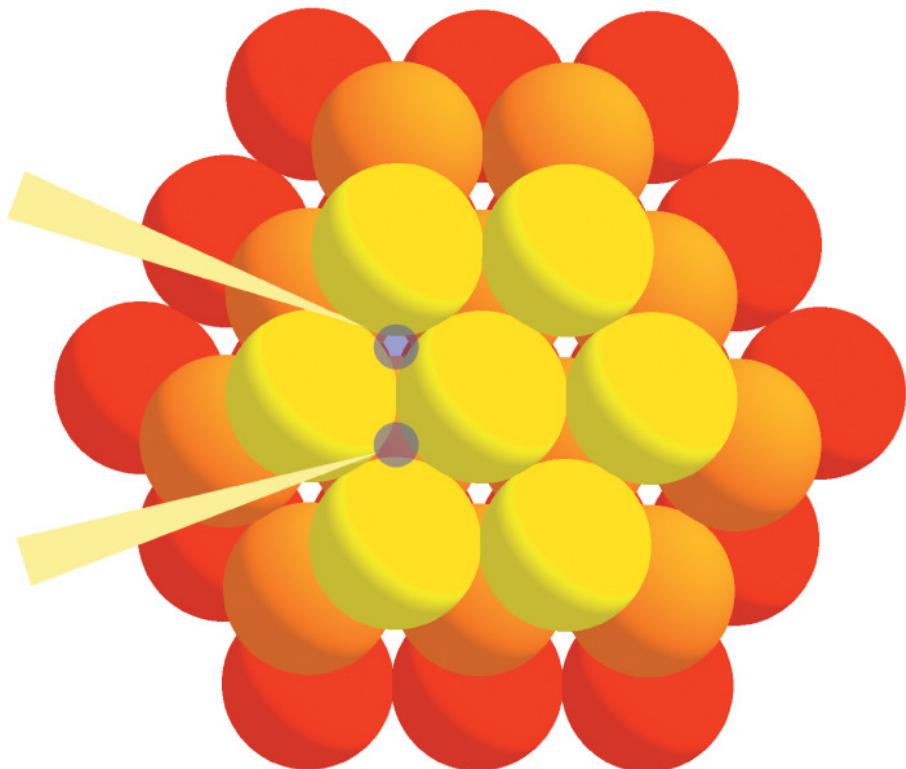
Interstitial Lattice Sites



This is an octahedral site



This is a tetrahedral site

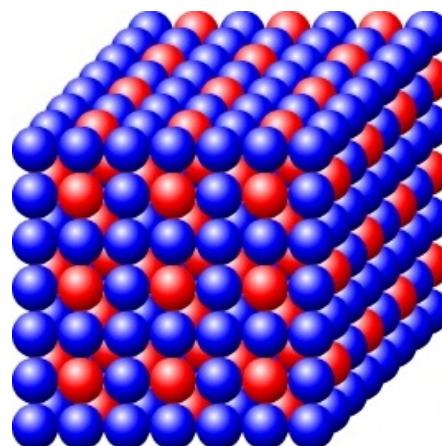


Multiple Elements: Alloys

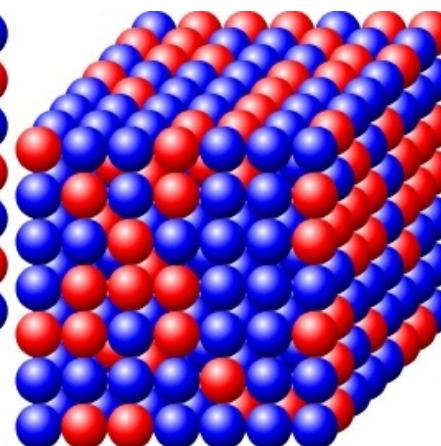
Materials formed by mixing two or more metals.
Modified properties (e.g. enhanced strength)

Solid solutions: relative proportions can be varied,
e.g. A_xB_{1-x} as in bronze (Cu_xSn_{1-x})

Ordered



Disordered



Types of Alloy

Substitutional alloy: direct exchange of A for B (site occupancy changes, but not site position)

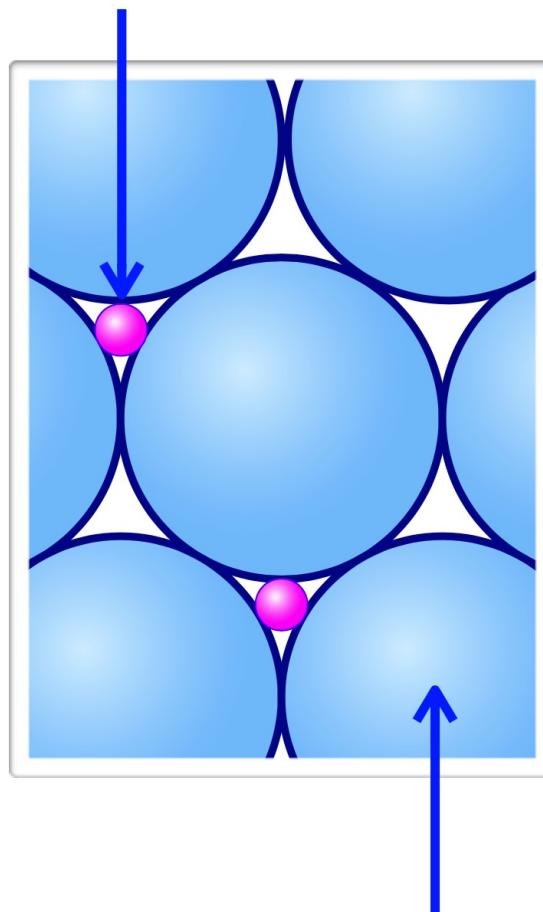
Formed when atom sizes are similar, e.g. Cu (1.28Å) and Zn (1.36Å) in brass

Interstitial alloy: B is incorporated into A on interstitial sites

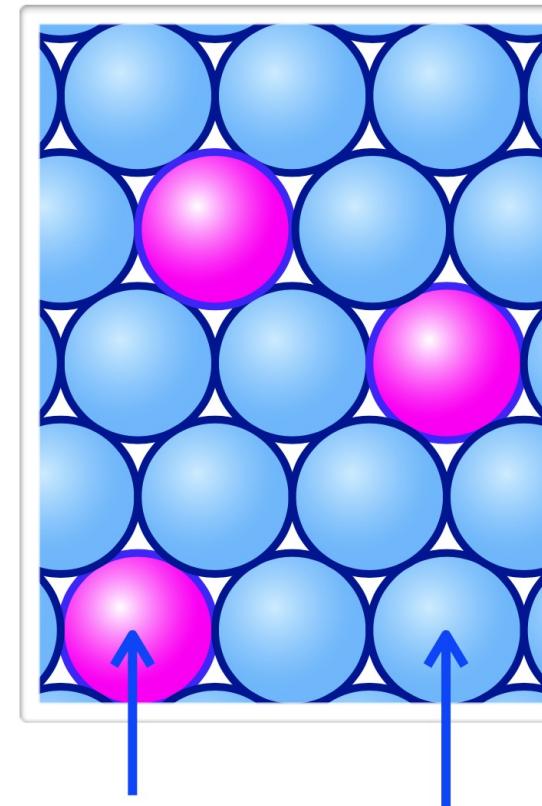
Formed when atom sizes are different, e.g. C (0.86Å) and Fe (1.26Å) in steel

Interstitial vs Substitutional Alloys

Solute Atom



Solvent Atom



Solute Atom

Solvent Atom

Summary: Packing

Class outcomes:

- Explain close packing
- Knowledge of hcp, fcc, sc and bcc structures
- Determine coordination numbers
- Determine packing efficiencies for simple lattices
- Distinguish interstitial and substitutional alloys