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Space Groups and Ionic Crystals

Lecture 4

Periodic Translation

Unit Cells

Bravais Lattices

Crystal Symmetry Elements

Lecture 5

Space Groups

Ionic Crystals

Lecture 6

Diffraction

Miller Indices

Bragg's Law

What tools do we need to describe, understand and determine the structure of materials?

1) The size and shape of the 3D repeating unit – the 'unit cell'.

2) What symmetry elements exist within the unit cell.

3) Where the atoms sit within the unit cell.

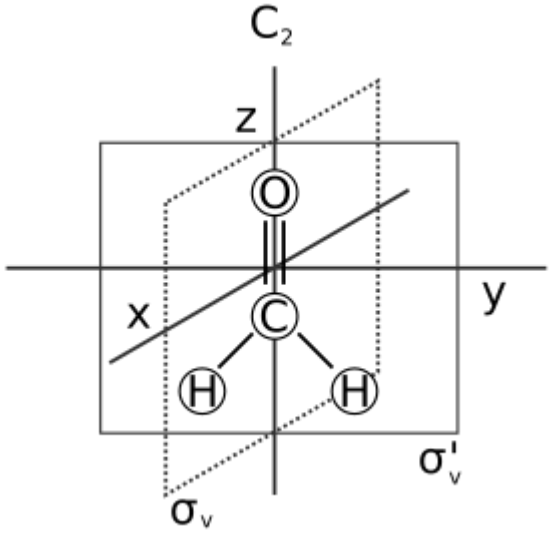
Q: How is all of this determined experimentally?

A: By diffraction (most commonly with X-rays, but also with neutrons and electrons – see Lecture 6).

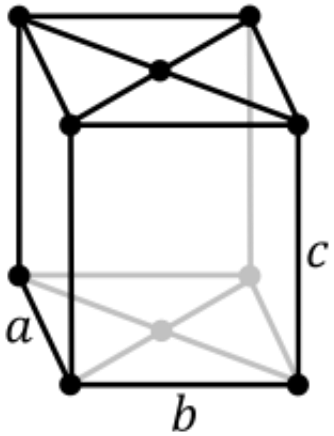
The Grand Idea:

Point Groups + Translational Symmetry ⇒ Space Groups

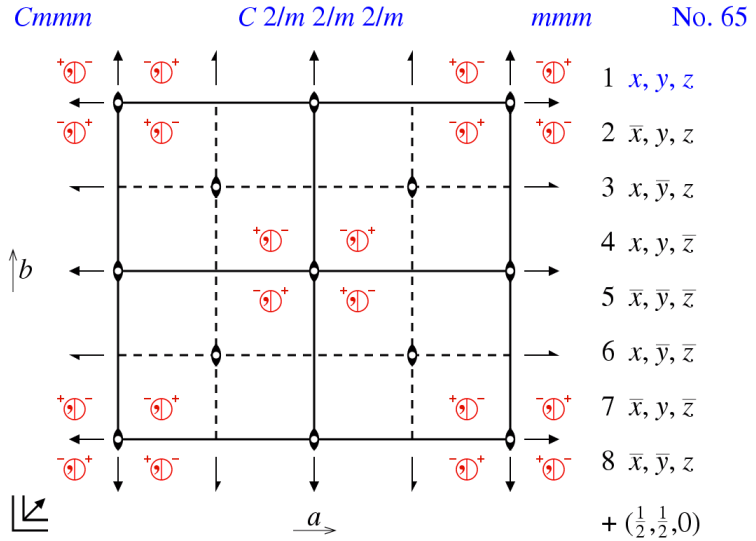
To understand the symmetry of crystals, the grand idea is that we will combine point group symmetry elements with translational symmetry to generate a range of periodic symmetries called **Space Groups** ('space' because we're now occupying space with a symmetric object rather than just growing an object around a 'point').



+



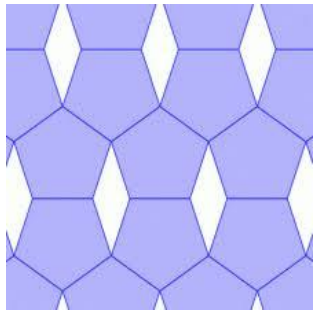
⇒

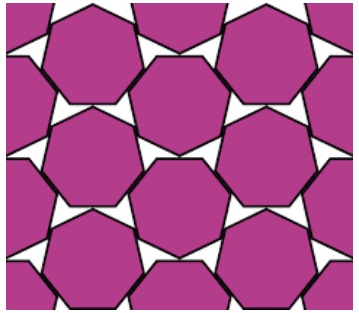


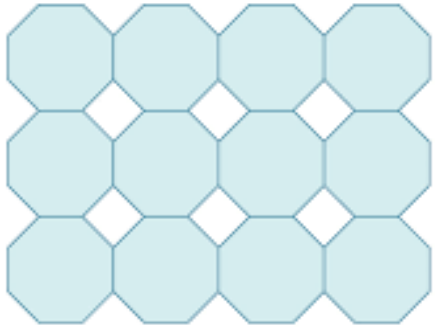
The Grand Idea:

Point Groups + Translational Symmetry ⇒ Space Groups

For reasons we won't dwell on, it turns out that not all point group symmetries are compatible with each Bravais lattice: e.g., triclinic cells can't have rotational axes or mirror planes (and can only have inversion centres); it's not possible to have 5-fold, 7-fold, 8-fold, etc., rotational symmetry in a periodic crystal.







32 Point Groups + 14 Bravais Lattices ⇒ 230 Space Groups

Crystal system	Hermann-Mauguin (full)	Hermann-Mauguin (short)	Shubnikov[1]	Schoenflies	Orbifold	Coxeter	Order
Triclinic	1	1	1	C_1	11	$[\,]^+$	1
	$\bar{1}$	$\bar{1}$	$\bar{2}$	$C_i = S_2$	×	$[2^+,2^+]$	2
Monoclinic	2	2	2	C_2	22	$[2]^+$	2
	m	m	m	$C_s = C_{1h}$	*	$[\,]$	2
	$\frac{2}{m}$	2/m	$2:m$	C_{2h}	2*	$[2,2^+]$	4
Orthorhombic	222	222	$2:2$	$D_2 = V$	222	$[2,2]^+$	4
	mm2	mm2	$2\cdot m$	C_{2v}	*22	[2]	4
	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	mmm	$m\cdot 2:m$	$D_{2h} = V_h$	*222	[2,2]	8
Tetragonal	4	4	4	C_4	44	$[4]^+$	4
	$\bar{4}$	$\bar{4}$	$\bar{4}$	S_4	2×	$[2^+,4^+]$	4
	$\frac{4}{m}$	4/m	$4:m$	C_{4h}	4*	$[2,4^+]$	8
	422	422	$4:2$	D_4	422	$[4,2]^+$	8
	4mm	4mm	$4\cdot m$	C_{4v}	*44	[4]	8
	$\bar{4}$2m	$\bar{4}$2m	$\bar{4}\cdot m$	$D_{2d} = V_d$	2*2	$[2^+,4]$	8
	$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	4/mmm	$m\cdot 4:m$	D_{4h}	*422	[4,2]	16
Trigonal	3	3	3	C_3	33	$[3]^+$	3
	$\bar{3}$	$\bar{3}$	$\bar{6}$	$C_{3i} = S_6$	3×	$[2^+,6^+]$	6
	32	32	$3:2$	D_3	322	$[3,2]^+$	6
	3m	3m	$3\cdot m$	C_{3v}	*33	[3]	6
	$\bar{3}\frac{2}{m}$	$\bar{3}$m	$\bar{6}\cdot m$	D_{3d}	2*3	$[2^+,6]$	12
Hexagonal	6	6	6	C_6	66	$[6]^+$	6
	$\bar{6}$	$\bar{6}$	$3:m$	C_{3h}	3*	$[2,3^+]$	6
	$\frac{6}{m}$	6/m	$6:m$	C_{6h}	6*	$[2,6^+]$	12
	622	622	$6:2$	D_6	622	$[6,2]^+$	12
	6mm	6mm	$6\cdot m$	C_{6v}	*66	[6]	12
	$\bar{6}$m2	$\bar{6}$m2	$m\cdot 3:m$	D_{3h}	*322	[3,2]	12
	$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	6/mmm	$m\cdot 6:m$	D_{6h}	*622	[6,2]	24
Cubic	23	23	$3/2$	T	332	$[3,3]^+$	12
	$\frac{2}{m}\bar{3}$	m$\bar{3}$	$\bar{6}/2$	T_h	3*2	$[3^+,4]$	24
	432	432	$3/4$	O	432	$[4,3]^+$	24
	$\bar{4}$3m	$\bar{4}$3m	$3/\bar{4}$	T_d	*332	[3,3]	24
	$\frac{4}{m}\bar{3}\frac{2}{m}$	m$\bar{3}$m	$\bar{6}/4$	O_h	*432	[4,3]	48

Crystal Molecular

https://en.wikipedia.org/wiki/Crystallographic_point_group

Crystal Systems, Bravais Lattices, and Space Groups

7 Crystal Systems

- Triclinic, Monoclinic, Orthorhombic, Tetragonal, Trigonal, Hexagonal, Cubic

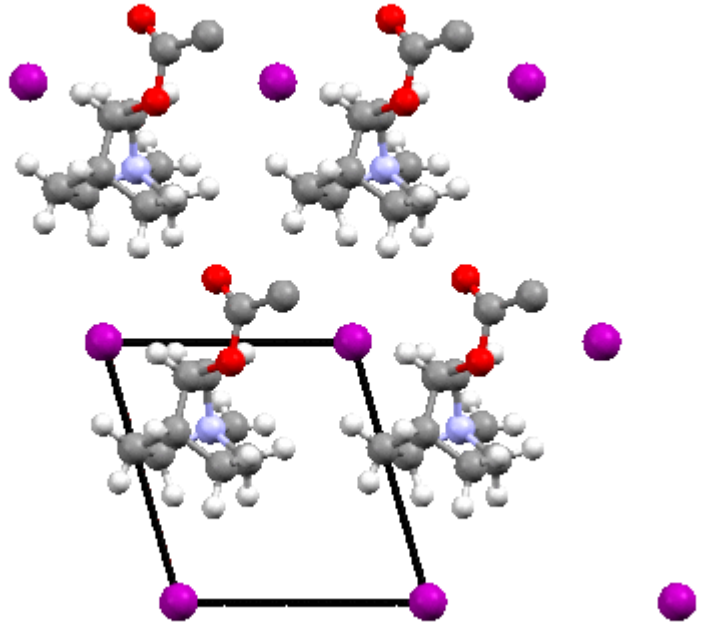
14 Bravais Lattices

- Location of atoms: Primitive (P), Base-Centred (C), Body-Centred (I) or Face-Centred (F)

230 Space Groups

A crystal structure with space group *P*1

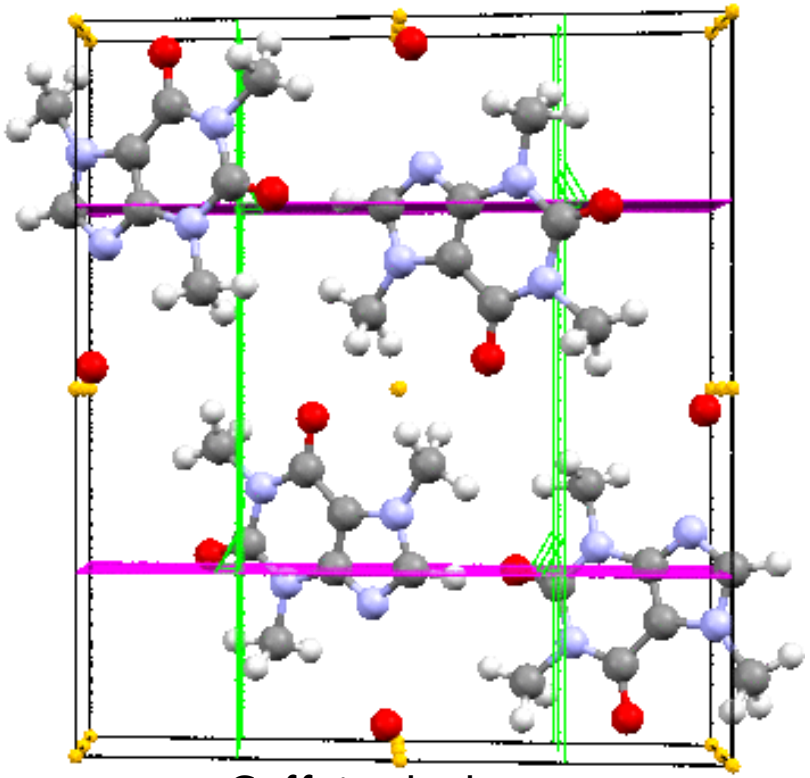
- Primitive triclinic cell
- Only symmetry present is translation along each of the axes



(R)-(-)-3-Acetoxy-quinuclidine methiodide

A crystal structure with space group $P2_1/a$

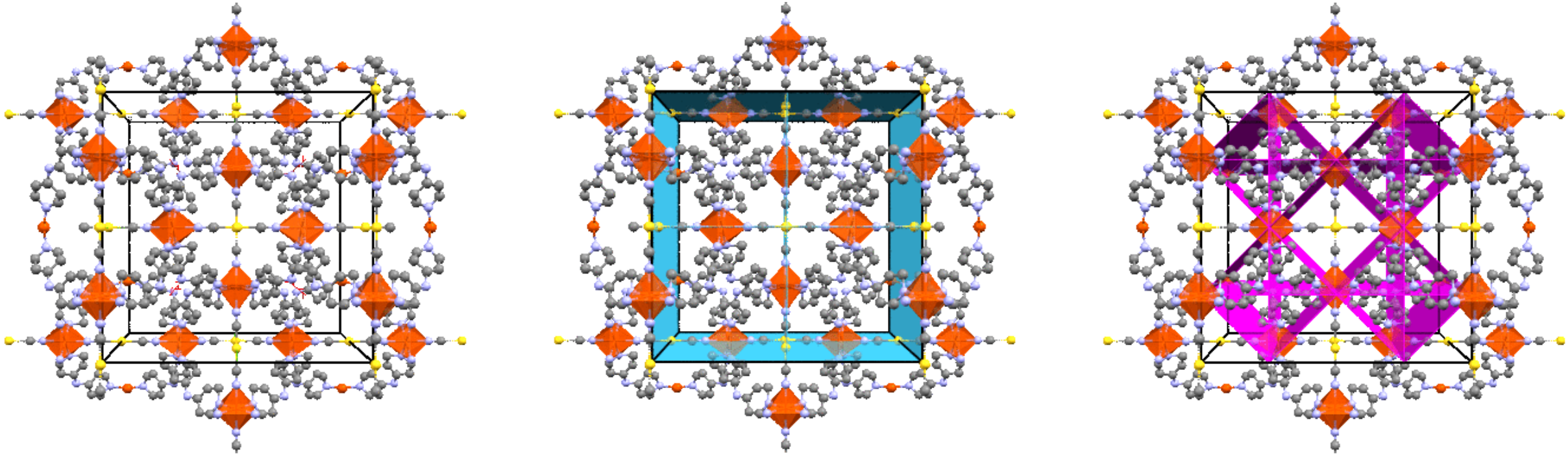
- Primitive monoclinic cell
- Four different symmetry elements: E, inversion centres (orange), 2_1 screw axes (green) and glide planes (pink)



Caffeine hydrate

A crystal structure with space group $I4_1/amd$

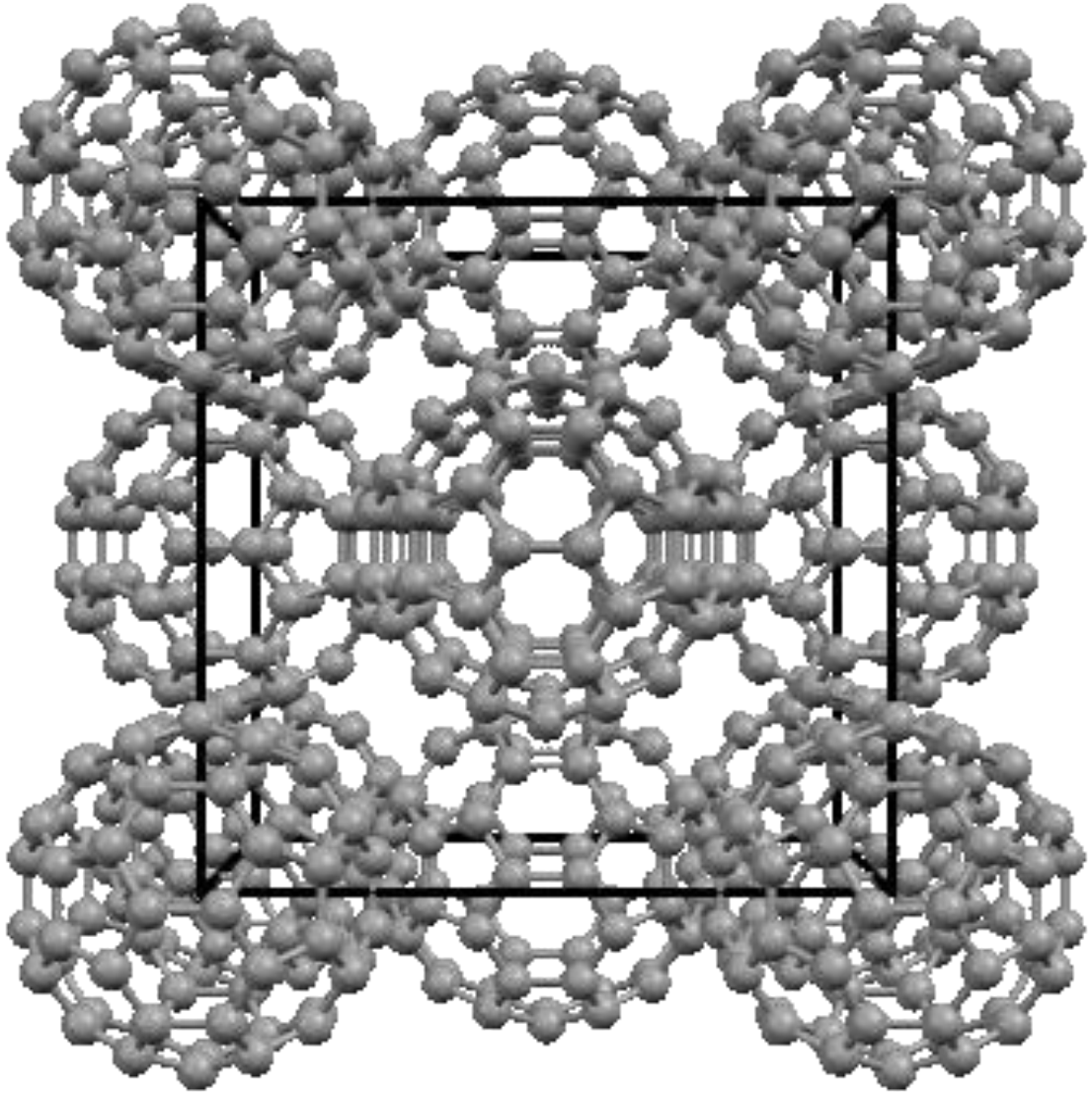
- Body-centred tetragonal cell
- A lot of symmetry! (32 symmetry elements)



4_1 screw axes (red), 2-fold rotation axes (green), mirror planes (blue), two different types of glide planes

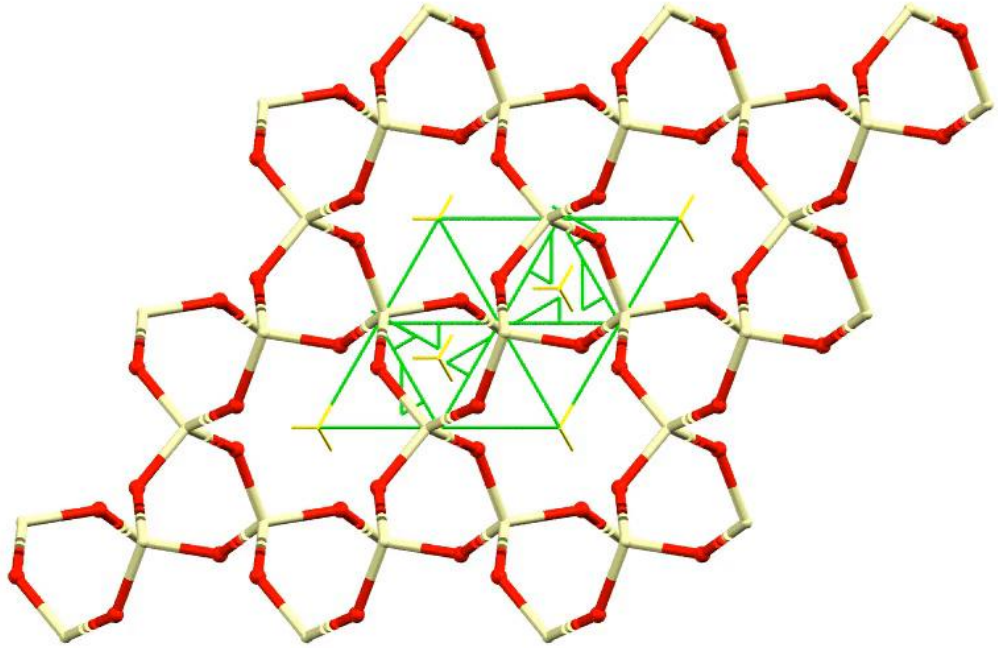
A crystal structure with space group $Fm\bar{3}$

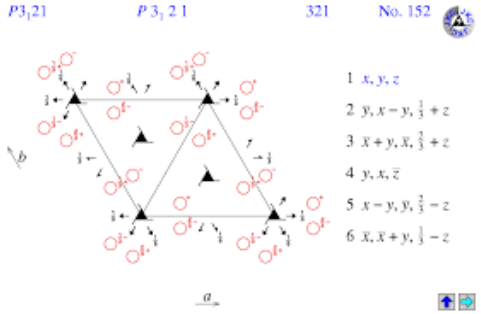
- Face-centred cubic cell
- A lot of symmetry! (96 symmetry elements)
- Only require 2 ½ carbon atoms to define the entire structure

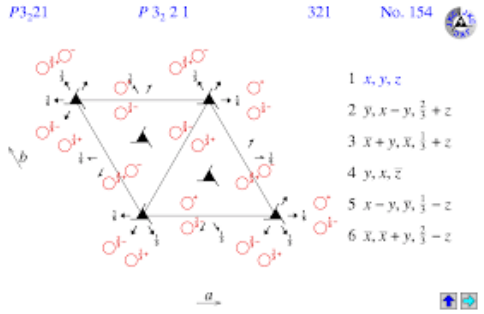


A crystal structure with space group $P3_121$ / $P3_221$

- Primitive trigonal cell
- No improper symmetry elements (only screw axes and rotation axes)
- Chiral
  - 'right-handed' crystals are $P3_121$
  - 'left-handed' crystals are $P3_221$
- Crystal exhibits piezoelectric properties (quartz oscillator crystal in your watch/phone/laptop/…)



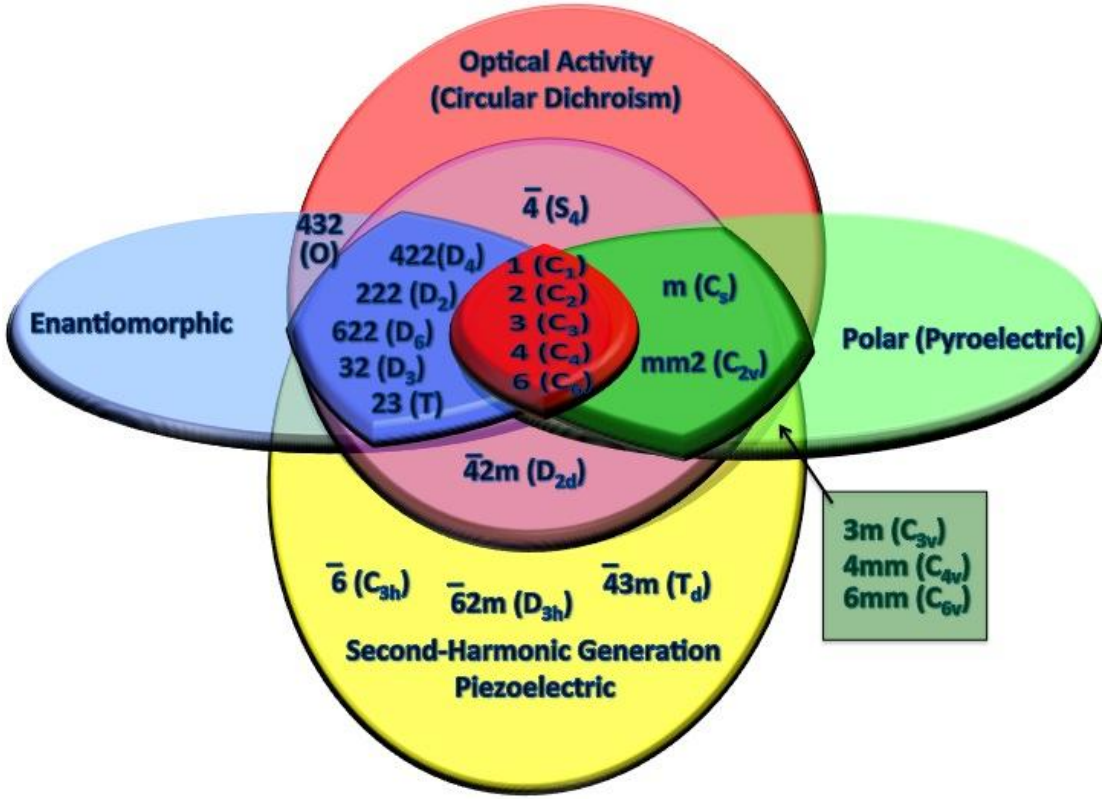




Q: Why do we need to understand crystal symmetry?

A: So we can work out and describe the structures of materials.

A: Materials properties depend on symmetry.



Non-centrosymmetric symmetries (those that don't contain inversion centres)

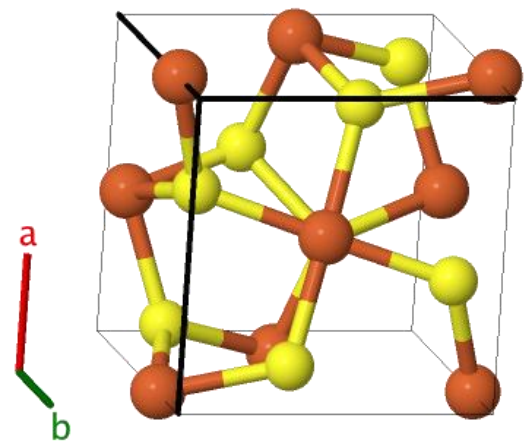
doi: 10.1021/cm980140w

Space Groups

A **Space Group** is defined as a set of symmetry elements (and respective symmetry operations) which *completely* describes the spatial arrangement of a 3D periodic pattern.

Fe
S

FeS_2 Low Temp Pyrite



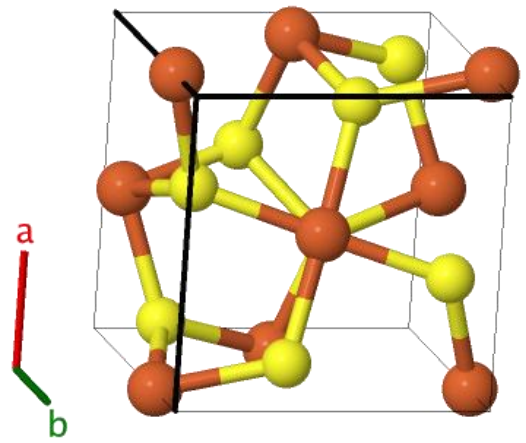
P c a 2_1

Space Group Notation

The space group usually consists of 4 symbols:

Fe
S

FeS_2 Low Temp Pyrite



Symmetry elements of the unit cell with respect to 3 viewing directions (primary, secondary, tertiary) describe the Point Group of the unit cell.

P c a 2_1

These are ***generators*** and generate all of the symmetry elements of the space group

2_1 Screw Axis // **c**

Glide Plane *a* ⊥ **b**

Glide Plane *c* ⊥ **a**

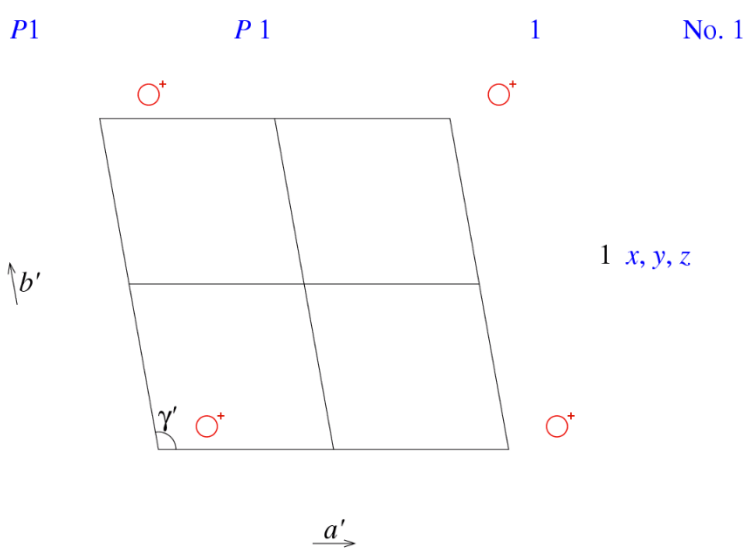
FeS_2 belongs to orthorhombic crystal system where **viewing directions** are along the **a** axis then **b** axis then **c** axis

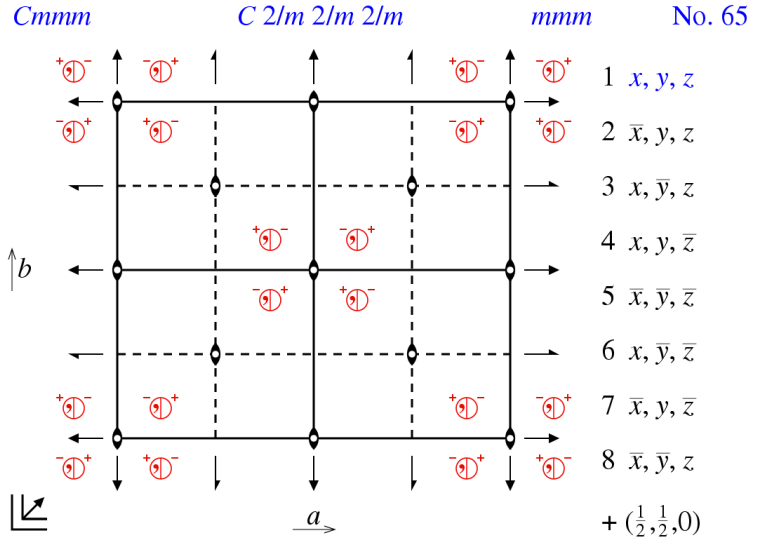
Rotation and screw axes are parallel to the specified viewing direction. Mirror and glide planes are perpendicular to the given direction.

Bravais Lattice Type

P primitive, F face-centred, I body-centred, C base-centred

Space Group Diagrams





A 2D projection of the unit cell.

Symbols are used to show the location of symmetry elements within a unit cell and list the symmetry-equivalent positions.

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

Convention for Viewing Directions

- Monoclinic: determined by convention
- Tetragonal, trigonal, hexagonal: rotation axis of highest order is, by definition, parallel to the **c**-axis and the first viewing direction

	Crystal System	primary	secondary	tertiary
	Triclinic	N/A		
	Monoclinic	*b* (*c*)		
	Orthorhombic	*a*	*b*	c
$a = b$	Tetragonal	c	*a*	[110]
$a = b$	Trigonal	c	*a*	[210]
$a = b$	Hexagonal	c	*a*	[210]
$a = b = c$	Cubic	c	[111]	[110]

Viewing axes are chosen to show *new* symmetry elements

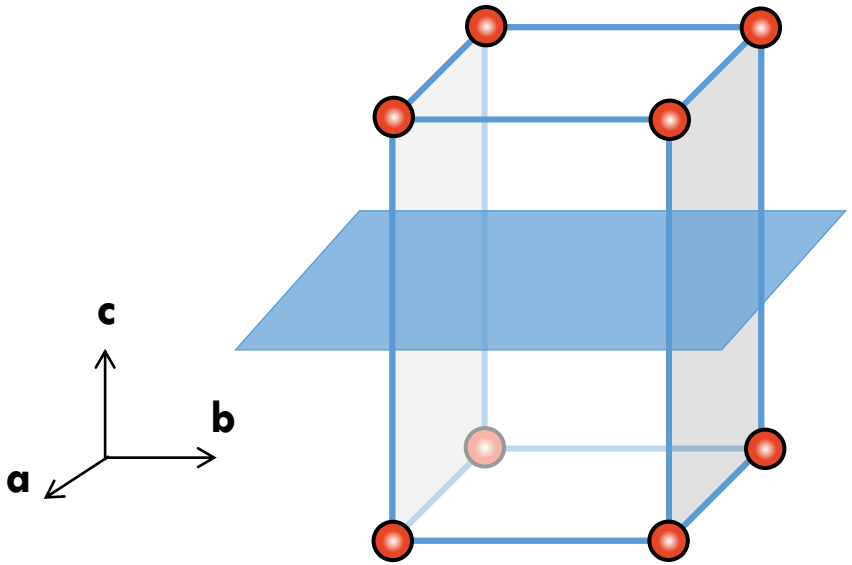
[110] is perpendicular to the face-diagonal; [111] is perpendicular to the space-diagonal…

Example

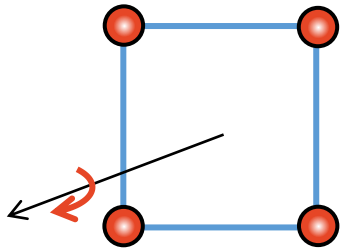
- Tetragonal crystal system: $a = b \neq c$; $\alpha=\beta=\gamma= 90°$
- **Primary** viewing direction along c-axis

$P\,4/m$

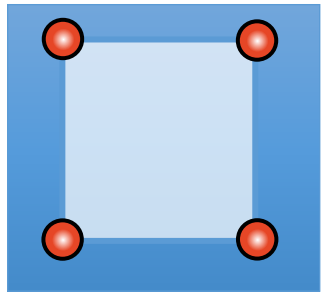
c-axis



Primitive unit cell → "*P*"



4-fold
rotation axis



Mirror plane

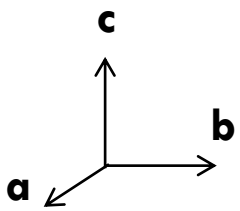
Example

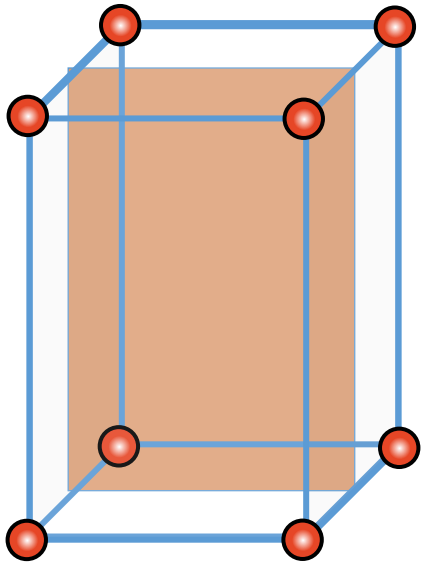
- Tetragonal crystal system: $a = b \neq c$; $\alpha=\beta=\gamma= 90°$
- **Secondary** viewing direction along a-axis

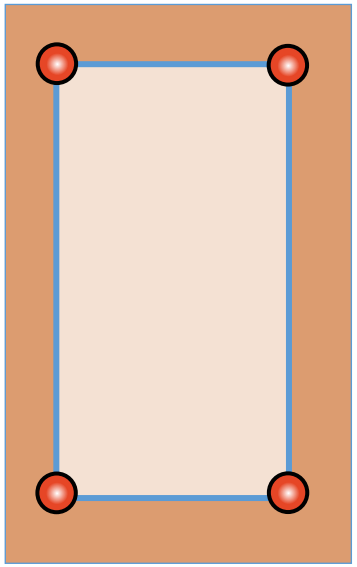
$P4/m\,m$

c-axis

a-axis







Mirror plane

Example

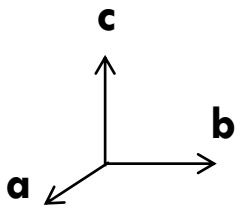
- Tetragonal crystal system: $a = b \neq c$; $\alpha = \beta = \gamma = 90°$
- **Tertiary** viewing direction along [110] direction

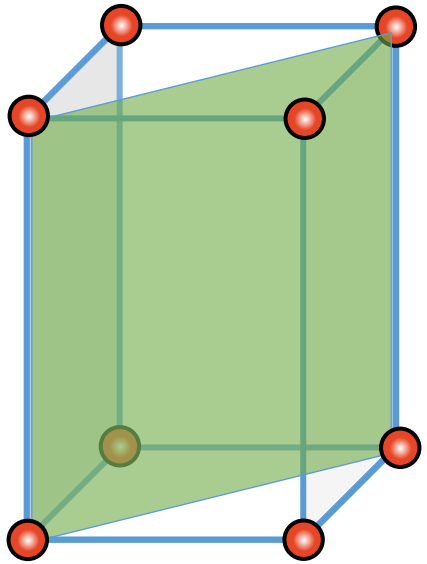
$P4/m\,m\,m$

c-axis

a-axis

[110]



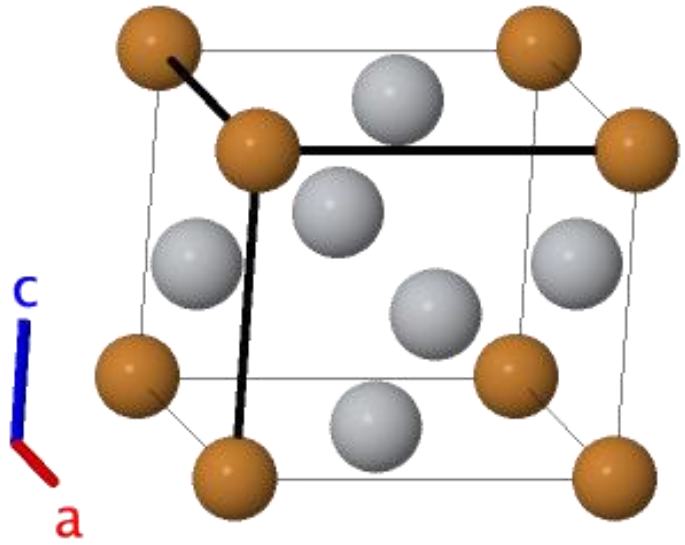


Mirror plane

Examples of *P4/mmm* Structures

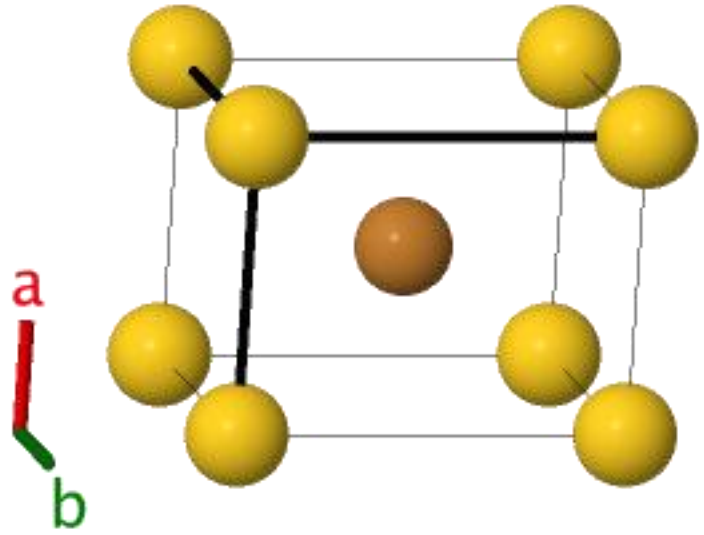
Cu
Ti

$CuTi_3$



Au
Cu

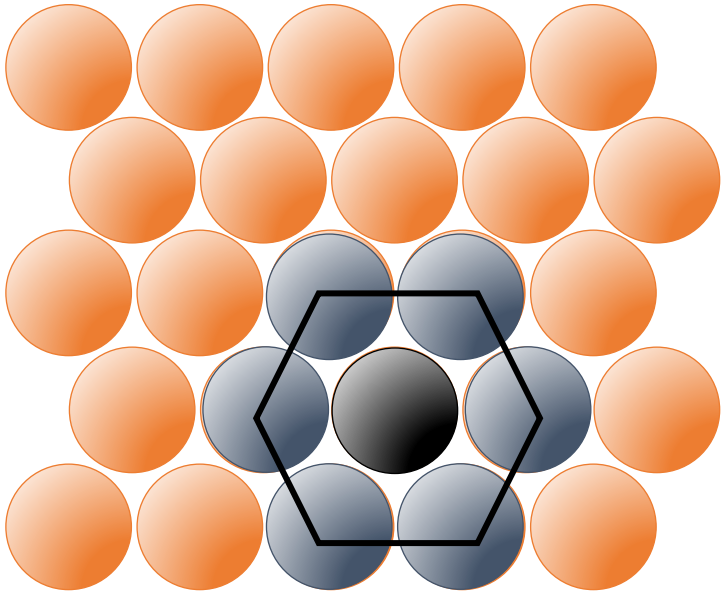
CuAu



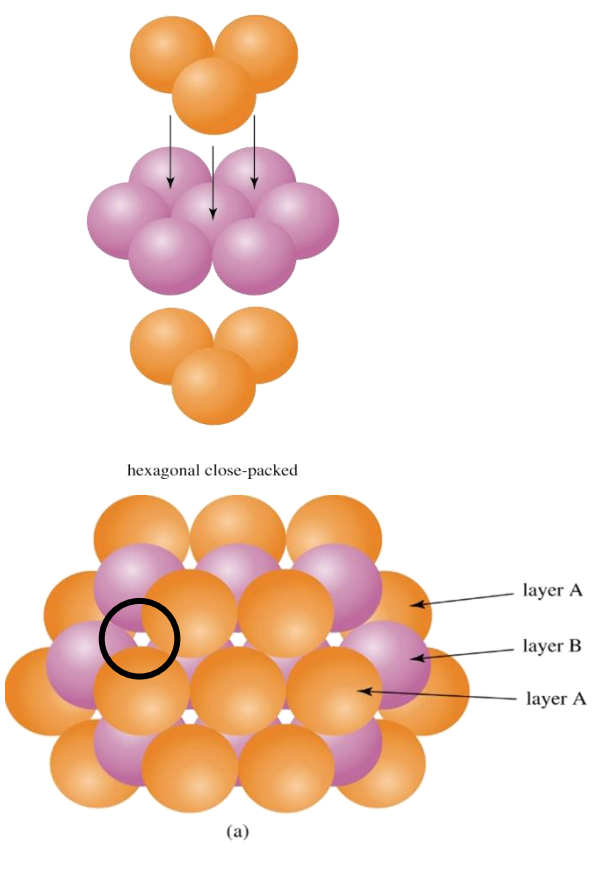
https://materialsproject.org/materials/mp-522/#

http://aflowlib.org/CrystalDatabase/tetragonal_spacegroup.html

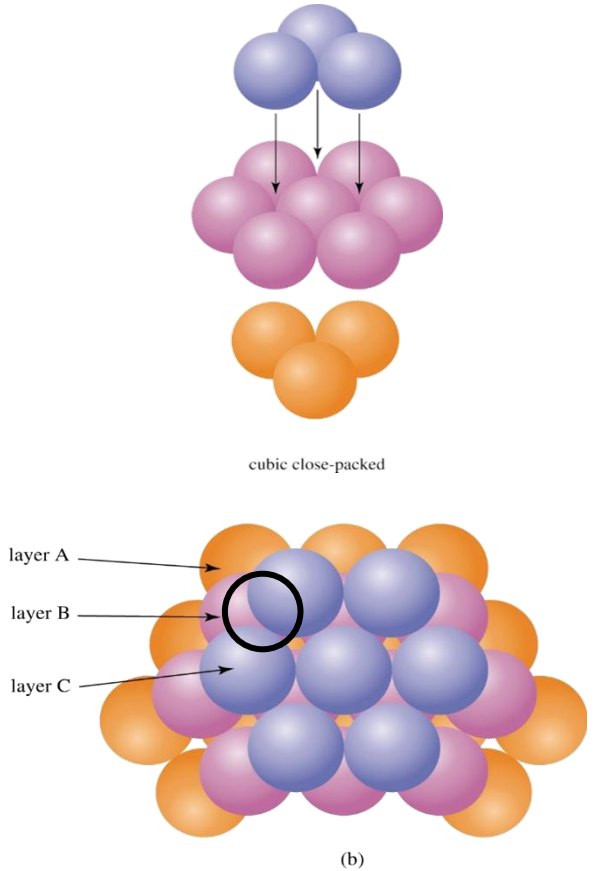
Cubic and Hexagonal Close-Packing



- 2 choices for the third layer
- 12 nearest neighbours



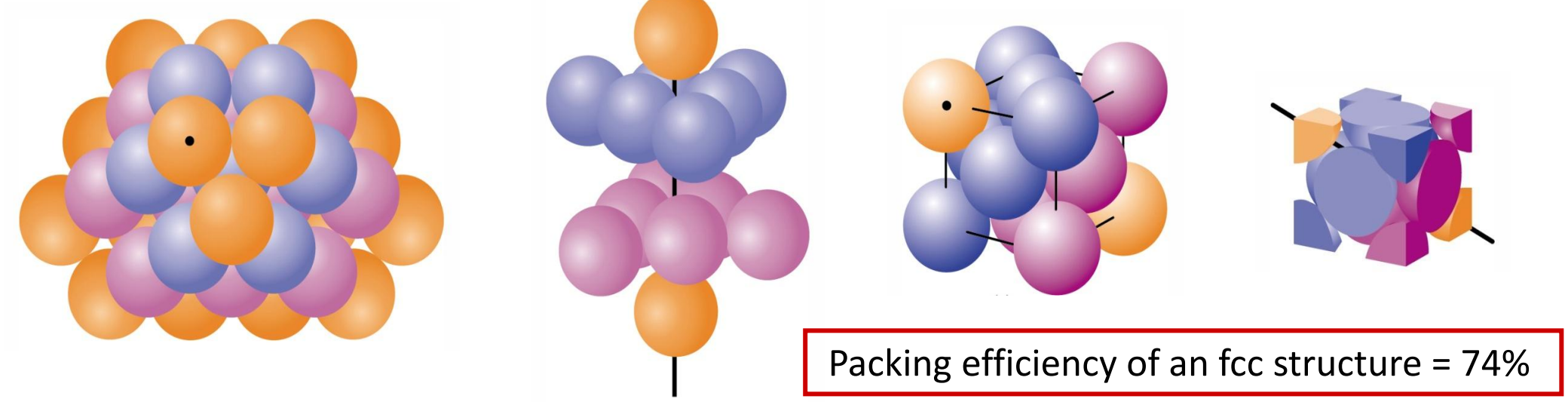
ABAB pattern
Hexagonal close-packed (hcp)



ABCABC pattern
Cubic close-packed (ccp) or
Face-centred cubic (fcc)

Cubic Close-Packed Unit Cell

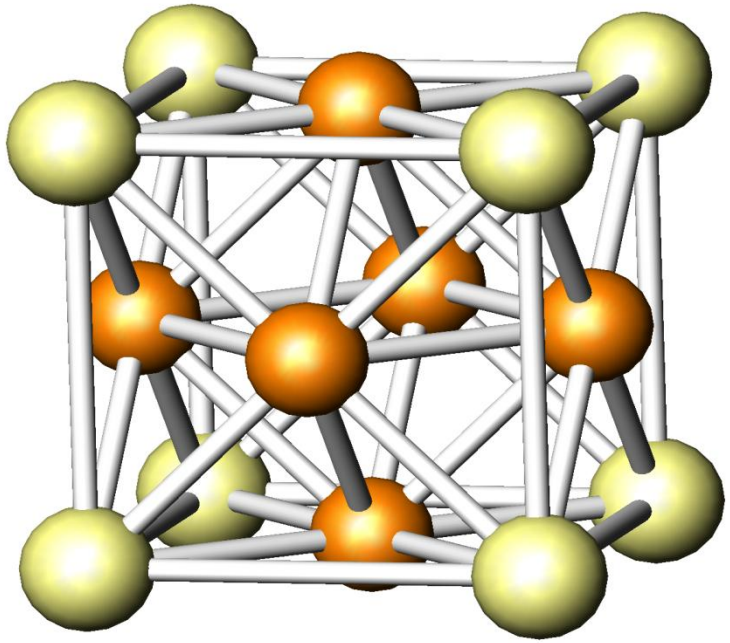
- Adopted by many elemental metals



Packing efficiency of an fcc structure = 74%

Recommended revision: See 'Close packing', 'Packing and unit cells' and 'Common crystal structure' links at https://scilearn.sydney.edu.au/fychemistry/iChem/

Cubic Close-Packed Unit Cell



Face-centred cubic cell with atoms in faces highlighted

8 atoms at vertices (yellow), each shared between 8 unit cells

$8 \times 1/8 = 1$ atom per unit cell

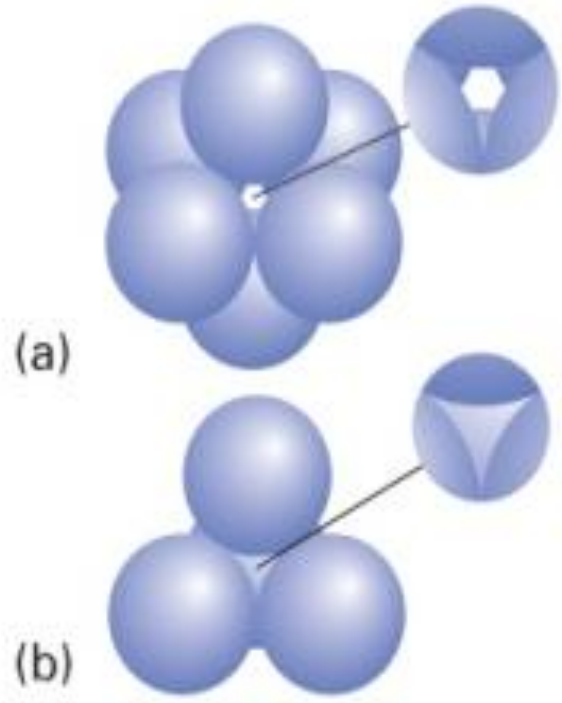
6 atoms on faces (orange), each shared between 2 unit cells

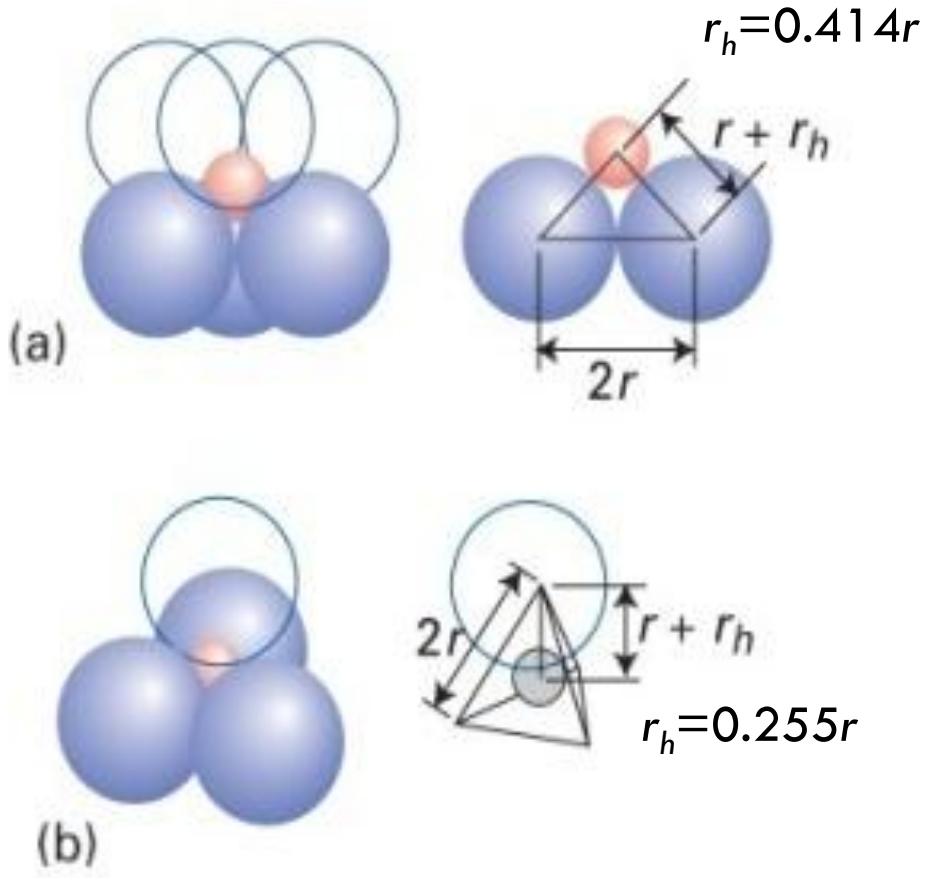
$6 \times 1/2 = 3$ atoms per unit cell

$1 + 3 =$ **4 atoms per ccp unit cell**

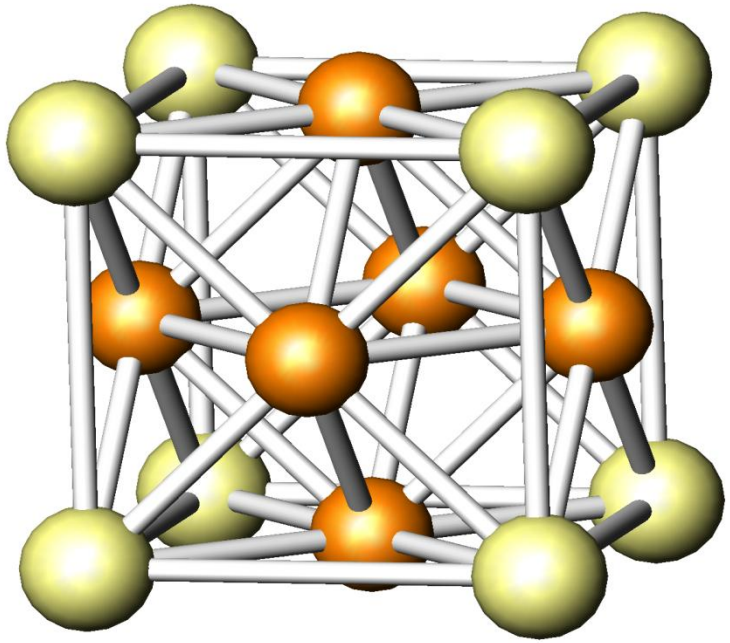
Interstitial Sites in ccp and hcp

Type (left) and relative size (right) of interstitial sites in close-packed metal structures (a: octahedral; b: tetrahedral).

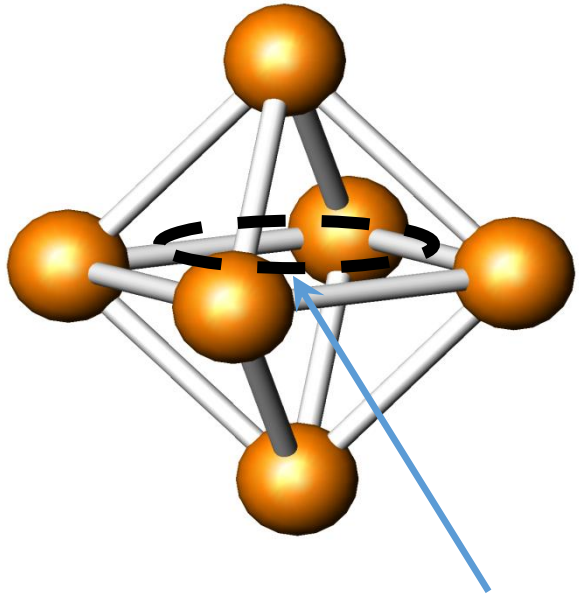




Octahedral Interstitial Holes



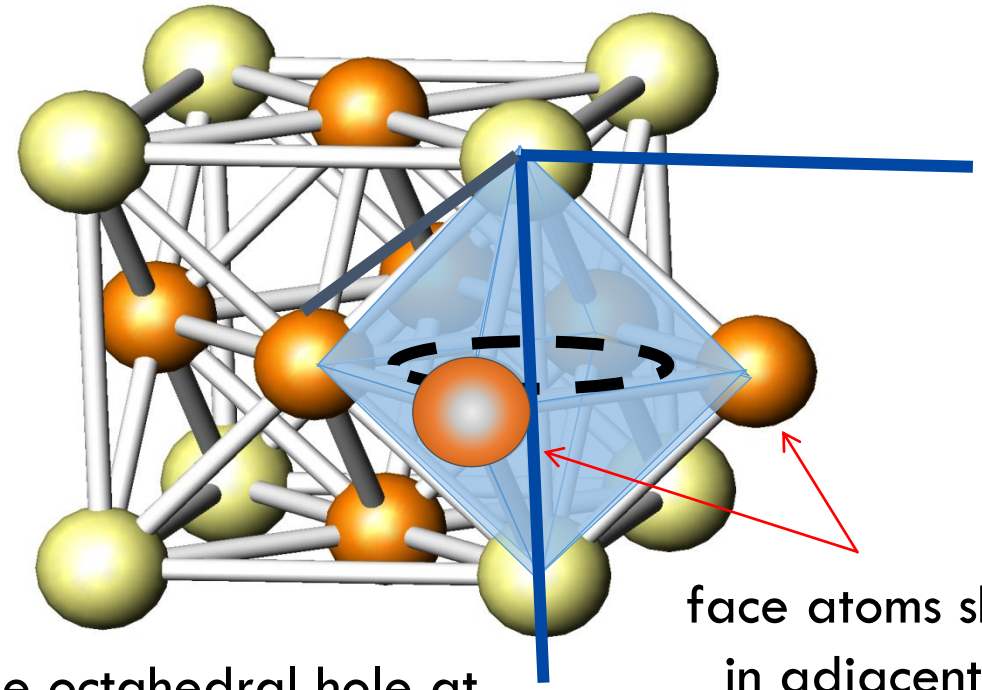
Face-centred cubic cell with atoms in faces highlighted



Octahedral hole in the centre of the unit cell – i.e., an octahedral interstice

→ One octahedral hole completely within the unit cell

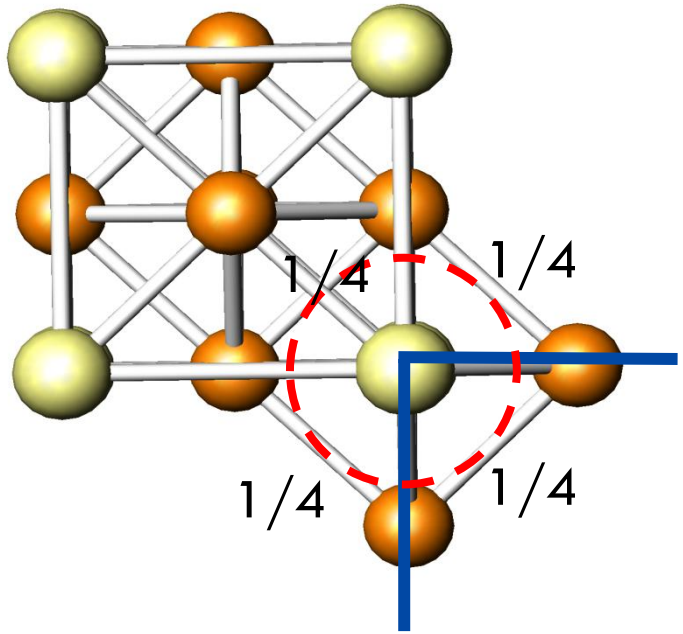
Octahedral Interstitial Holes



One octahedral hole at each cube edge

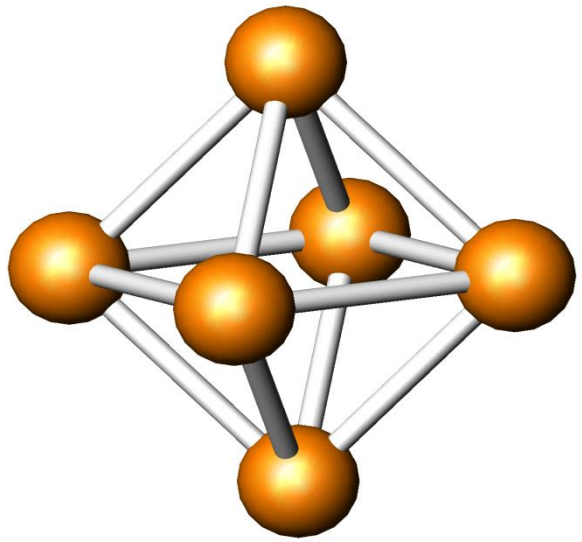
face atoms shared in adjacent unit cells

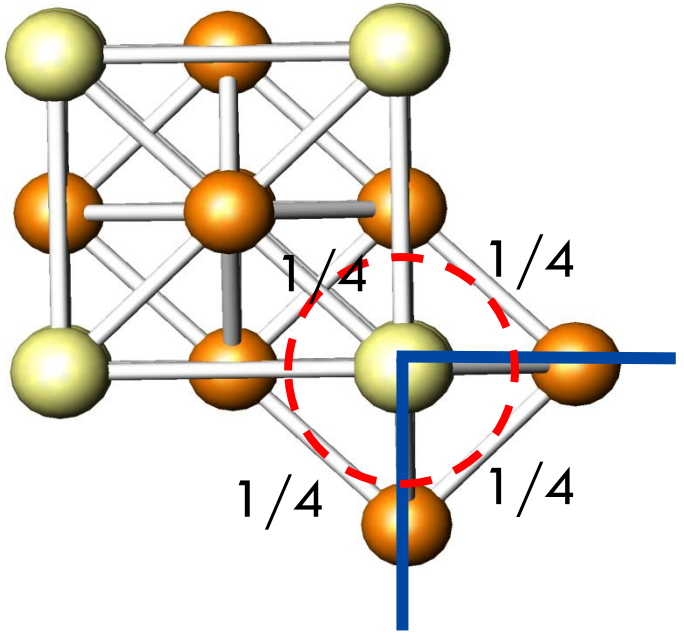
Each edge hole shared between 4 unit cells
→ ¼ hole per unit cell



12 edges × ¼ hole/edge = 3 shared "edge" octahedral holes per unit cell

Octahedral Interstitial Holes

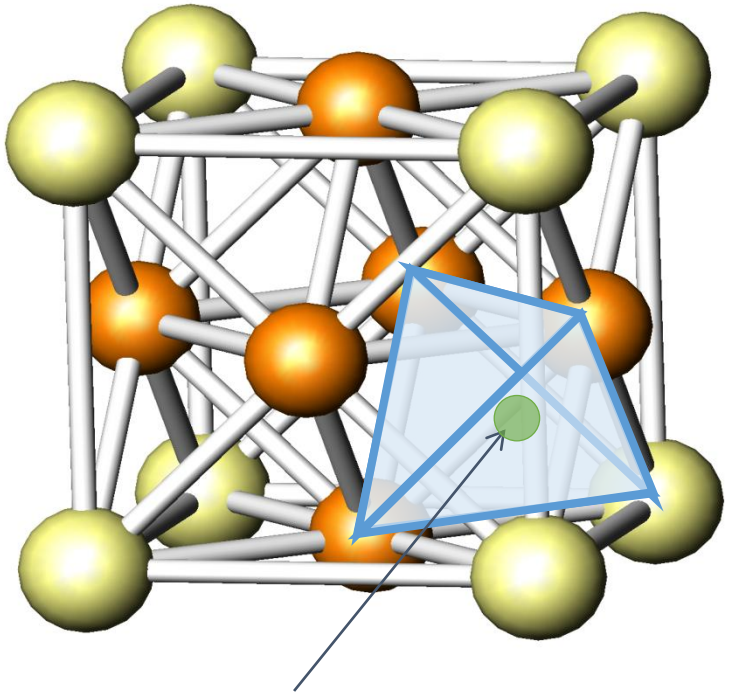




1 octahedral hole completely within the unit cell + 3 shared "edge" octahedral holes per unit cell = **4 octahedral holes per unit cell**

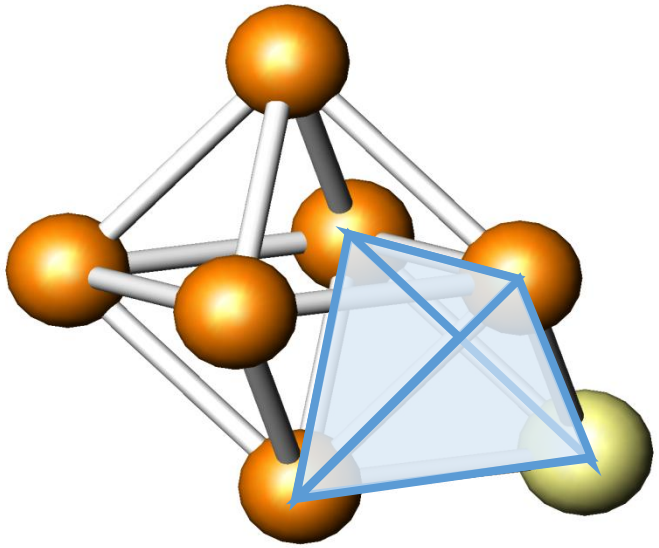
i.e., 1 octahedral hole per ccp atom

Tetrahedral Interstitial Holes



One tetrahedral hole per octahedron face (or per cube vertex)

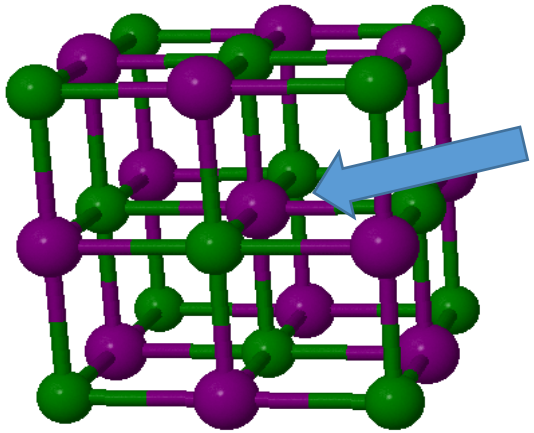
8 tetrahedral holes per unit cell



Tetrahedral hole – i.e., a tetrahedral interstice

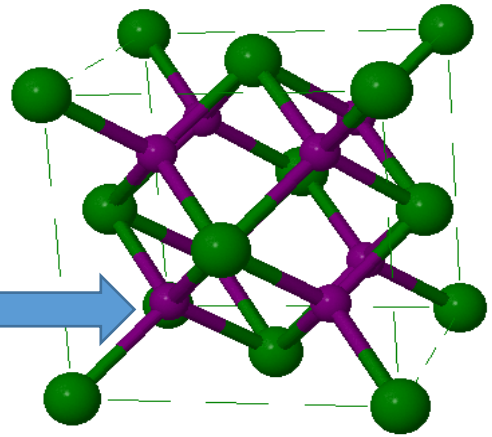
i.e., 2 tetrahedral holes per ccp atom

Octahedral and tetrahedral holes



1 octahedral hole per ccp atom

2 tetrahedral holes per ccp atom



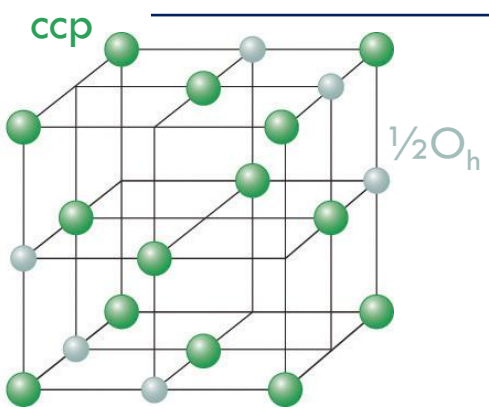
Octahedral and tetrahedral holes

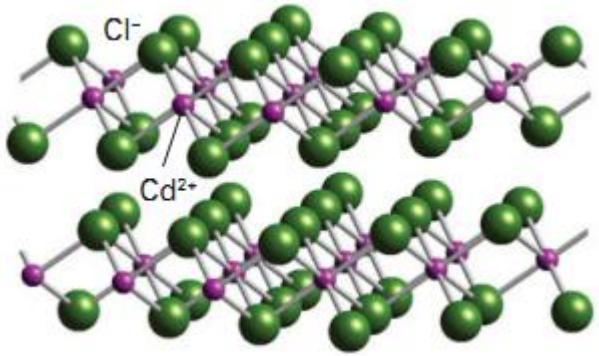
The filling of interstitial sites within a ccp unit cell gives rise to different crystal structures.

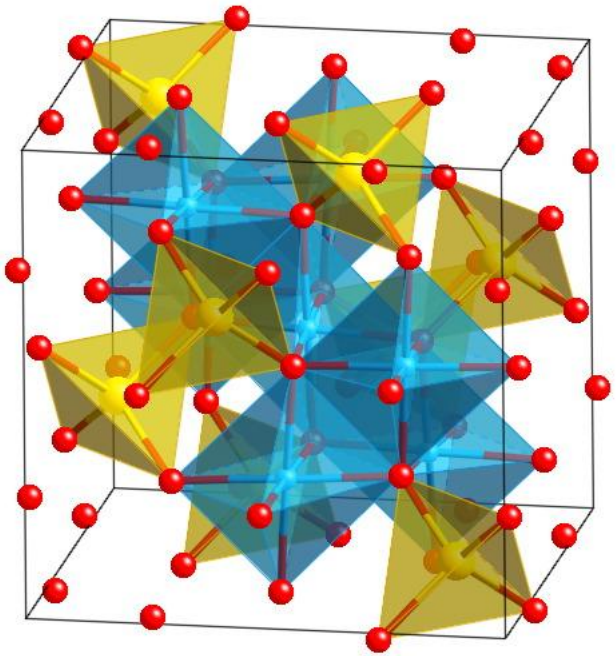
Anion	Filling of Interstitial Sites		Structure	Examples
Packing	T_d	O_h		
ccp (fcc)	-	all	rock-salt	NaCl, MgO, LaN
	-	1/2	cadmium chloride	$CdCl_2$, $NiCl_2$
	half	-	zinc blende (sphalerite)	ZnS, CuCl, BN
	all	-	anti-fluorite	Na_2O, Li_2S
	1/8	1/2	spinel	$MgAl_2O_4$



Octahedral and tetrahedral holes







Anion	Filling of Interstitial Sites		Structure	Examples
Packing	T_d	O_h		
	-	all	rock-salt	NaCl, MgO, LaN
		1/2	cadmium chloride	$CdCl_2$, $NiCl_2$
ccp (fcc)	half	-	zinc blende (sphalerite)	ZnS, CuCl, BN
	all	-	anti-fluorite	Na_2O, Li_2S
	1/8	1/2	spinel	$MgAl_2O_4$

Common ccp and hcp structures

Anion	Filling of Interstitial Sites		Structure	Examples
Packing	T_d	O_h		
ccp	-	all	rock-salt	NaCl, MgO, LaN
	-	1/2	cadmium chloride	$CdCl_2$, $NiCl_2$
	1/2	-	zinc blende (sphalerite)	ZnS, CuCl, BN
	all	-	anti-fluorite	Na_2O, Li_2S
	1/8	1/2	spinel	$MgAl_2O_4$
hcp	-	all	nickel arsenide	NiAs, FeS
	-	1/2	cadmium iodide	CdI_2, $Mg(OH)_2$
	1/2	-	wurtzite	ZnS, BeO
	-	1/2	rutile	TiO_2, CrO_2

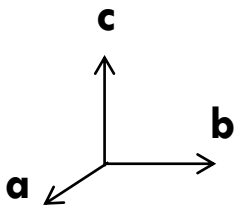
Ionic Structures: Rock Salt

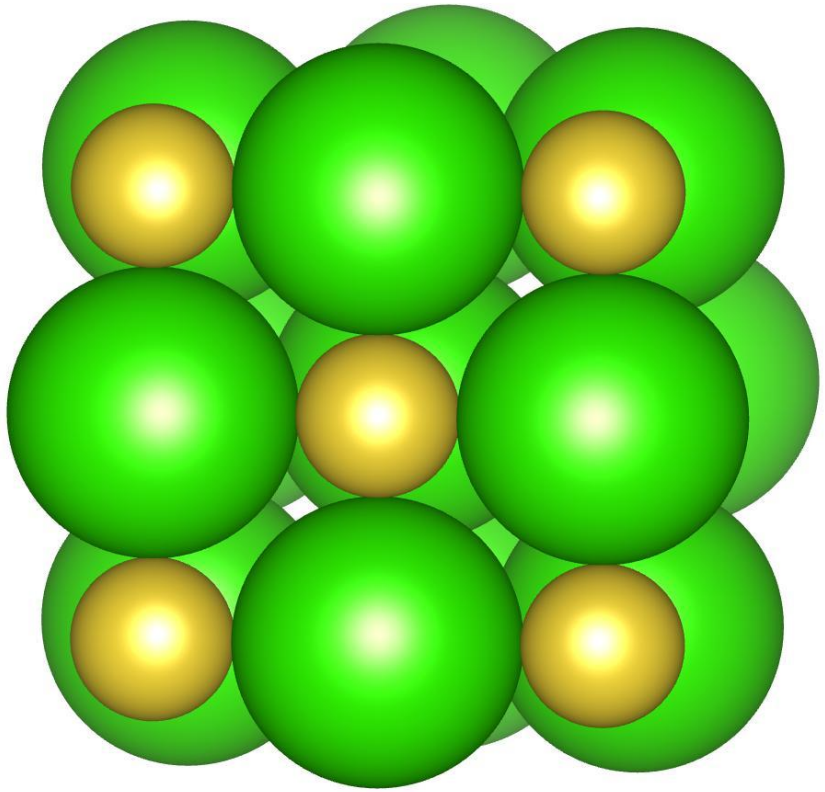


Rock salt (NaCl) has cubic close-packed structure of Cl^- anions with Na^+ cations occupying all the octahedral interstitial sites.

en.wikipedia.org/wiki/Sodium_chloride

- Face-centred cubic unit cell → "F"
- Along c-axis have mirror plane (m)
- [111] ⊥ to space-diagonal has 3-fold inversion axis ($\bar{3}$)
- [110] ⊥ to face-diagonal has mirror plane (m)

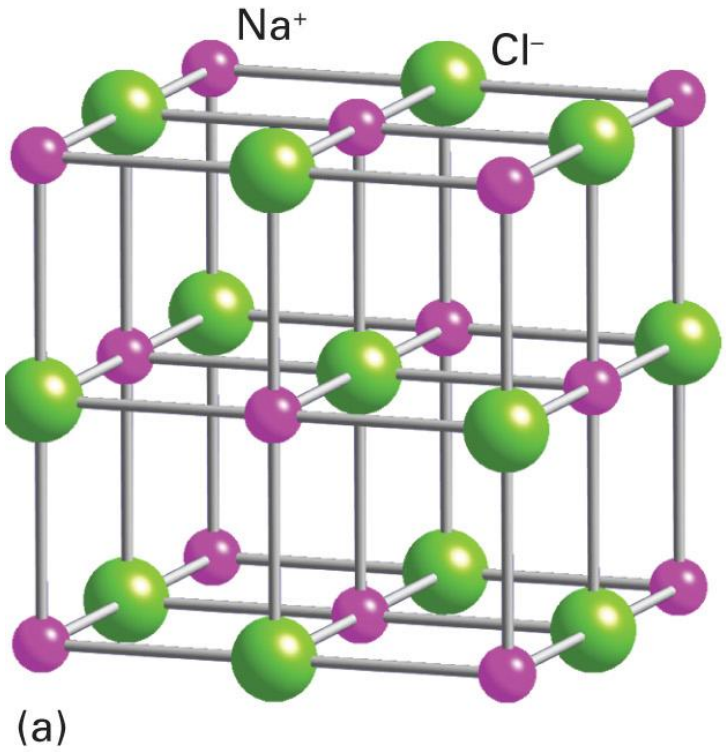




$Fm\bar{3}m$

https://materialsproject.org/materials/mp-22862/

Ionic Structures: Rock Salt



The empirical formula is determined by counting the atoms and partial atoms within the boundary of the unit cell.

Reminder of some material from 1st year

Na: 8 x 1/8 + 6 x ½ = 4

Cl: 12 x 1/4 + 1 x 1 = 4

Na_4Cl_4 = NaCl

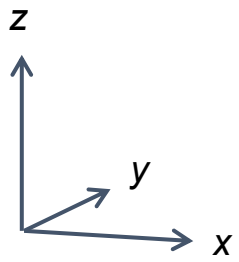
Coordination = 6:6

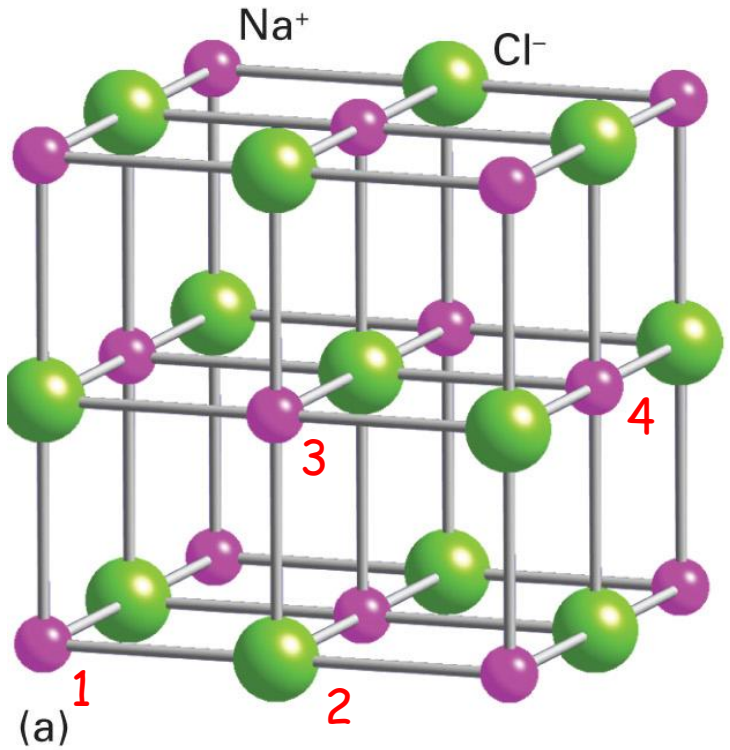
Note: the first number refers to the cation, the second to the anion.

Ionic Structures: Rock Salt

The rock salt structure of NaCl

$Fm\bar{3}m$





Fractional coordinates

1: (0, 0, 0)

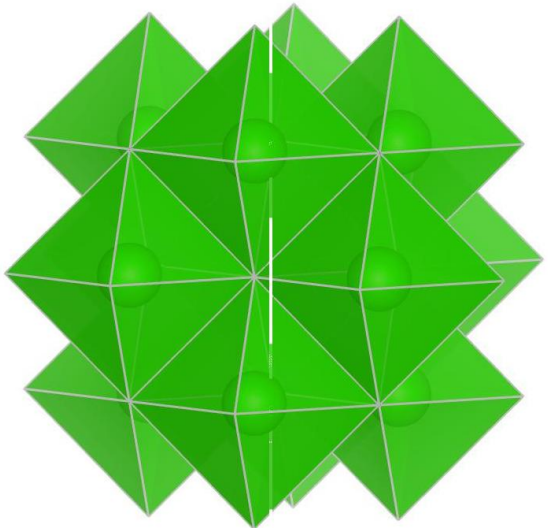
2: (½, 0, 0)

3:

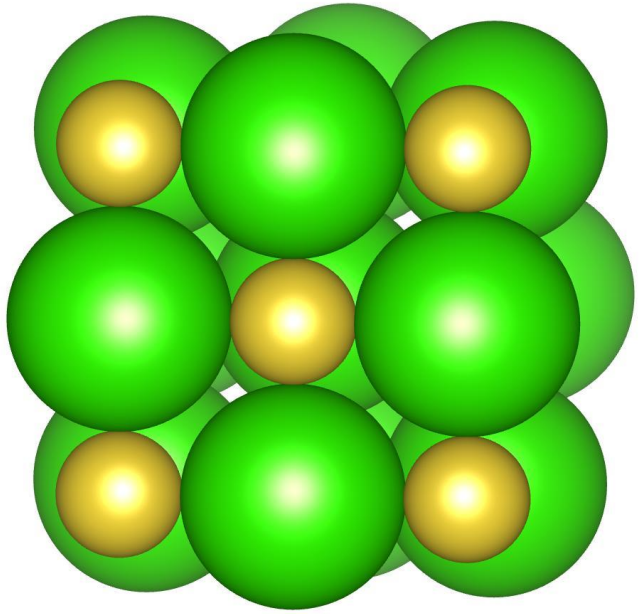
4:

Ionic Structures: Rock Salt

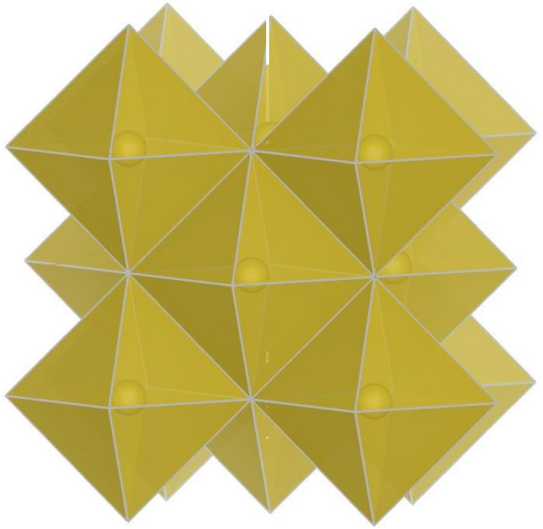
Various structural representations highlight different structure features.



Polyhedral representation
($ClNa_6$ octahedra)



Close-packed
representation



Polyhedral representation
($NaCl_6$ octahedra)

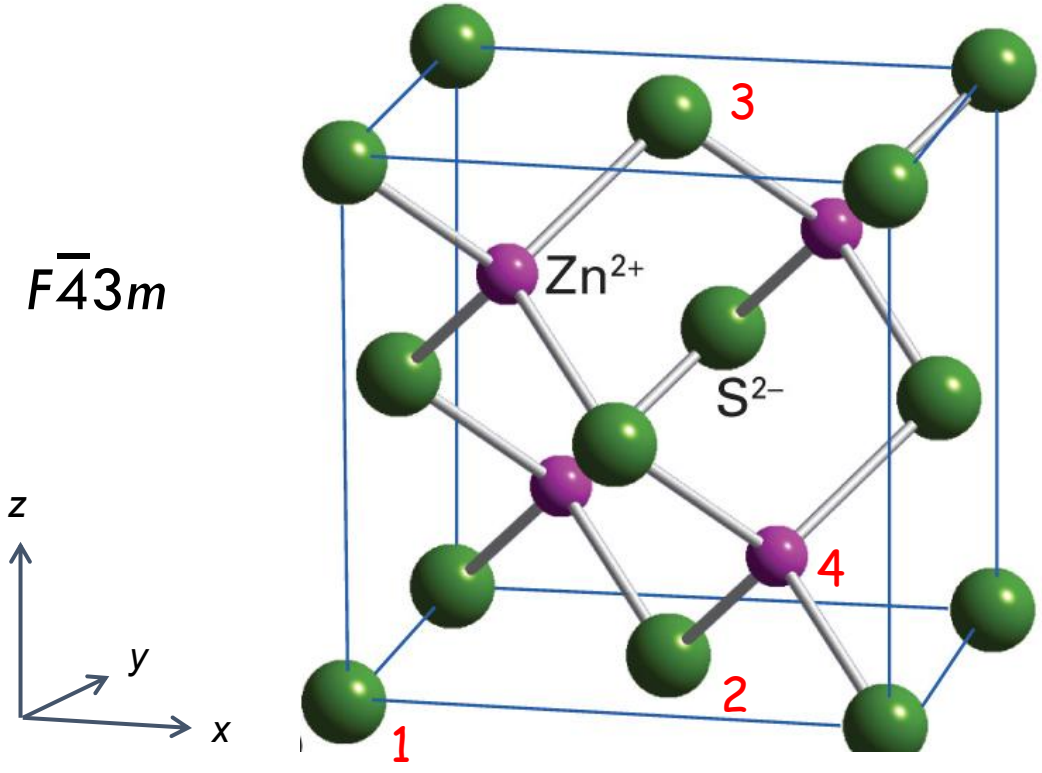
Ionic Structures: Zinc Blende



en.wikipedia.org/wiki/Sphalerite

ccp **S^{2-} anions** with **Zn^{2+} cations** in <u>half</u> of the tetrahedral interstitial sites

$F\bar{4}3m$



<u>Fractional coordinates</u>

1:

2:

3:

4:

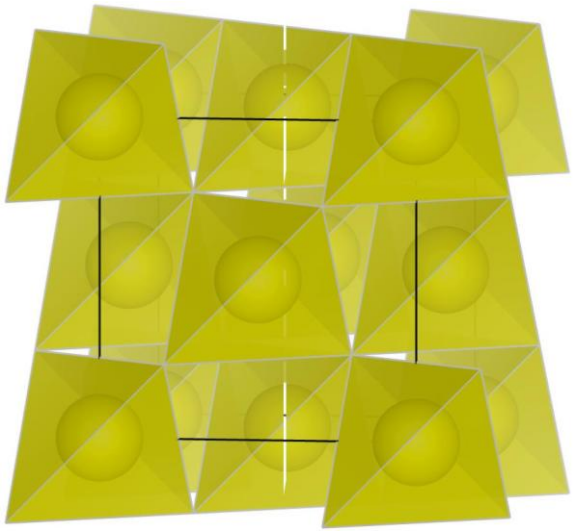
Composition =

Coordination =

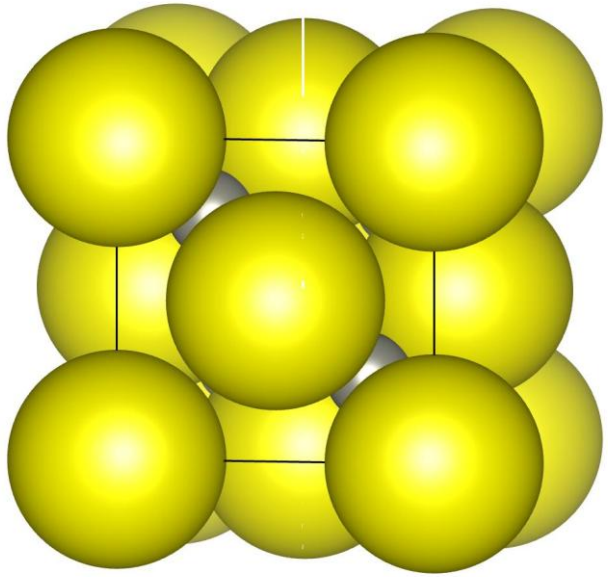
https://materialsproject.org/materials/mp-10695/

Ionic Structures: Zinc Blende

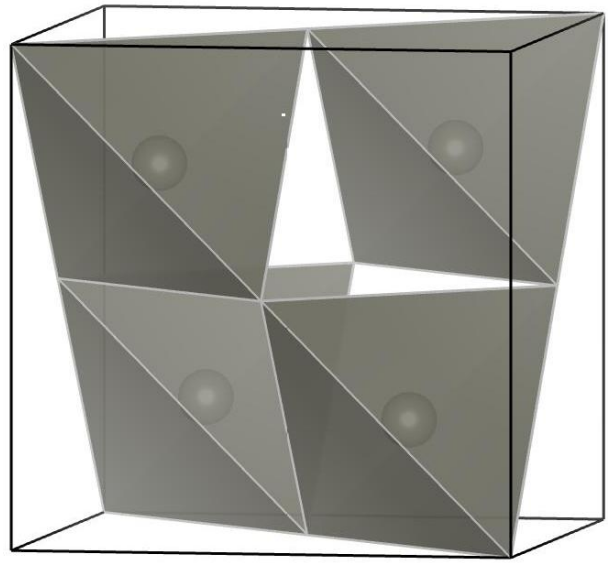
Various structural representations highlight different structure features.



Polyhedral representation
(SZn_4 tetrahedra)



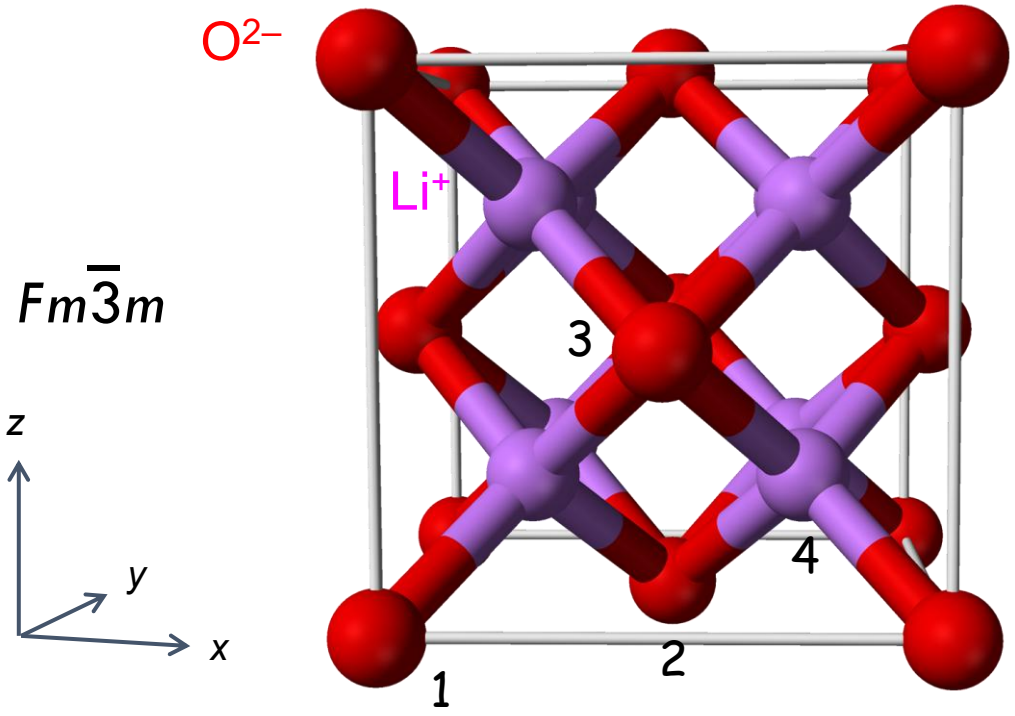
Close-packed
representation



Polyhedral representation
(ZnS_4 tetrahedra)

Ionic Structures: Antifluorite

Lithium oxide: cubic close packing of O^{2-} anions with Li^{+} cations in all the tetrahedral interstitial sites



Fractional coordinates

1:

2:

3:

4:

Composition =

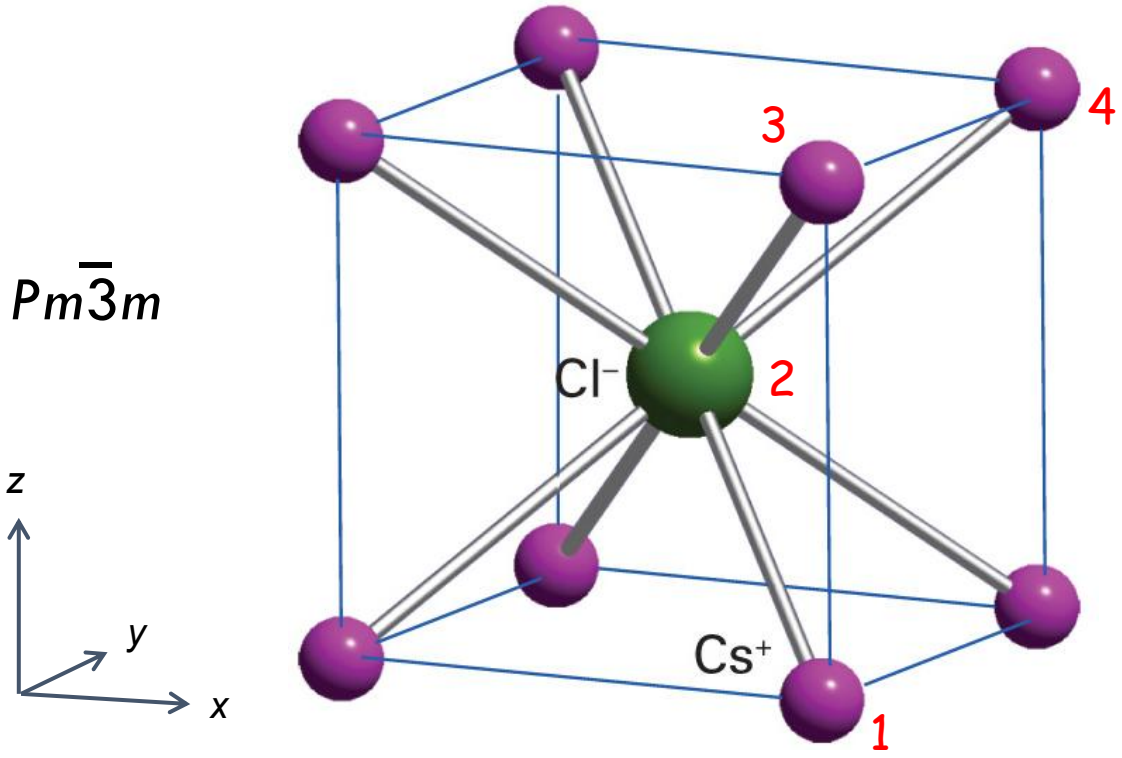
Coordination =

https://materialsproject.org/materials/mp-1960/#

Ionic Structures: Caesium Chloride

Two interpenetrating simple cubic unit cells (not ccp!)

$Pm\bar{3}m$



Fractional coordinates

1:

2:

3:

4:

Composition =

Coordination =

https://www.materialsproject.org/materials/mp-22865/

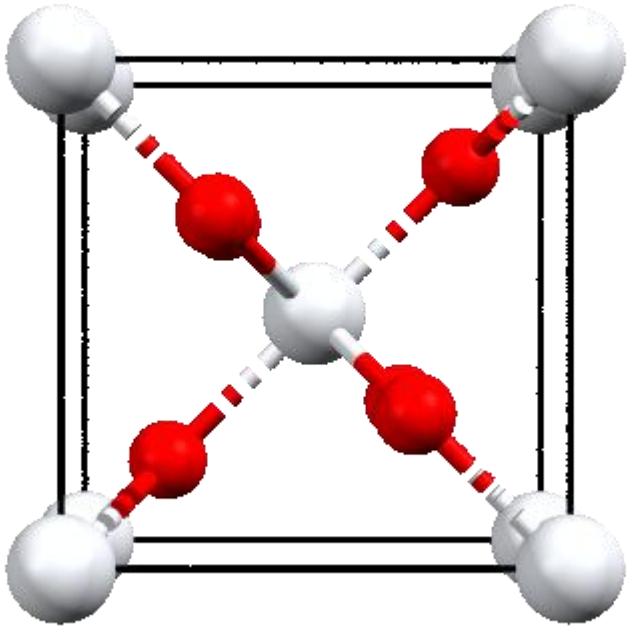
https://en.wikipedia.org/wiki/Rutile

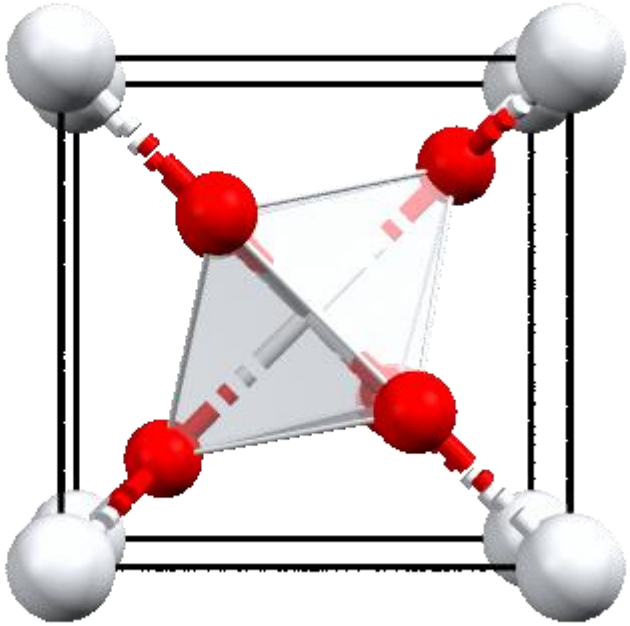
Ionic Structures: Rutile



A distorted hexagonal close-packed (hcp) array of anions with octahedral sites occupied by cations

Ti^{4+} are in body-centred tetragonal unit cell, O^{2-} have local trigonal planar geometries





https://en.wikipedia.org/wiki/Rutile



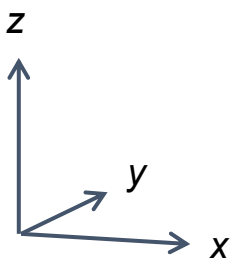
Ionic Structures: Rutile

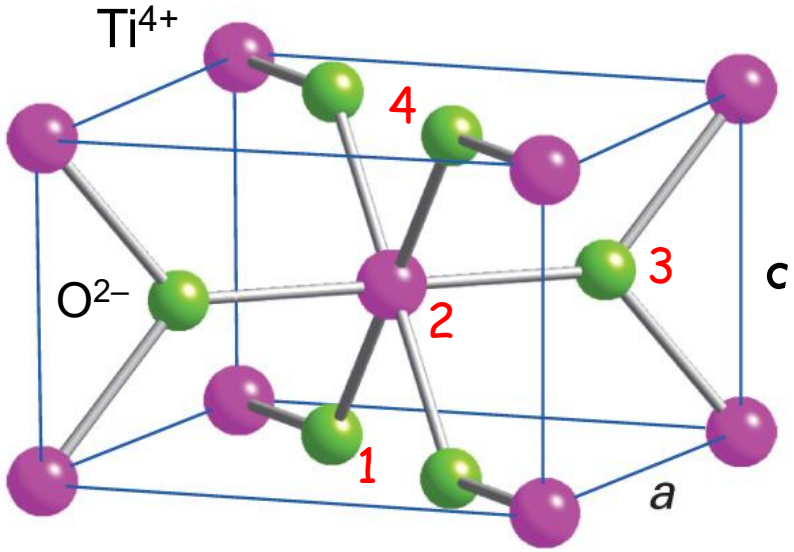
Ti^{4+} are in body-centred tetragonal unit cell, O^{2-} have local trigonal planar geometries

Typically given as a primitive unit cell

$P4_2/mnm$

$a = b$





Fractional coordinates

1:

2:

3:

4:

Composition =

Coordination =

https://materialsproject.org/materials/mp-2657/#

Learning Outcomes

After this lecture you should be able to:

- Understand the terms making up a space group symbol
- Relate ionic structures to filling of interstitial sites
- Determine stoichiometry from a unit cell
- Describe basic ionic structures
- Translate between different structural representations
- Complete the lecture worksheet and Q2&3 of Tutorial Sheet 2 (week 4).

Further reading:

- Weller, Overton, Rourke & Armstrong, Inorganic Chemistry 6th Ed. OUP, 2014, Chapter 3.1–3.5