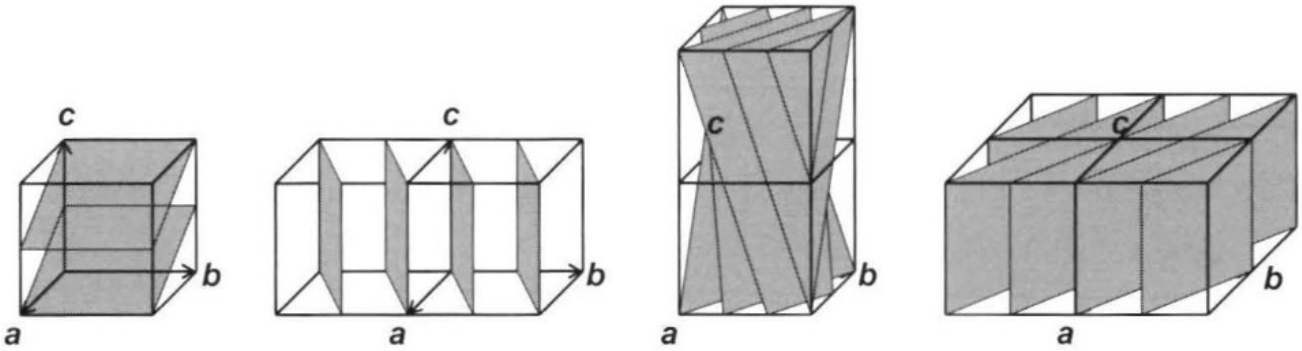
Work through these problems for next time:

1.3 Write down indices for the following sets of equidistant planes:



1.4 Sketch a set of equidistant 113 planes in a cubic unit cell.

1.5 Sketch a set of equidistant $1\bar{1}3$ planes in a cubic unit cell.

1.6 State the Bravais lattice and write down the crystallographic point-group symbol for a structure of space-group symbol: (a) $C2/m$, (b) $Fmm2$, (c) $I4/mmm$, (d) $P312$, (e) $R\bar{3}m$, (f) $P\bar{6}m2$, (g) $F23$, (h) $P2_13$, (i) $Ia\bar{3}d$.

1.7 Is it possible for a c glide plane to have the direction of: (a) a axis, (b) b axis, (c) c axis? If not, why is this not allowed?

For problem 1.6:

- **Parse the symbol.**
  Split it into **lattice centering** (first capital letter: P, A, B, C, I, F, R) and the **symmetry part** (numbers, bars, m's, glides/screws). E.g., C2/m → lattice C; symmetry 2/m.
- **Identify the crystal family/system from the symmetry part.**
  Highest fold tells you the family: triclinic (1, -1), monoclinic (2 or m or 2/m), orthorhombic (222, mm2, mmm), tetragonal (4, -4, 4/m, 422, 4mm, -42m, 4/mmm), trigonal (3, -3, 32, 3m, -3m), hexagonal (6, -6, 6/m, 622, 6mm, -6m2, 6/mmm), cubic (23, m-3, 432, -43m, m-3m).
- **Read off the Bravais lattice.**
  Combine the family with the centering letter to name the Bravais lattice (one of the 14).
  Examples: F+orthorhombic → **face-centered orthorhombic**; I+tetragonal → **body-centered tetragonal**; R → **rhombohedral** (trigonal); trigonal symbols starting with P use the **hexagonal primitive** Bravais lattice. (The hexagonal family contains both trigonal and hexagonal crystal systems.)
- **Derive the point group from the space group by removing translations.**
  - **Replace screw axes by pure rotations** (e.g., $2_1 \rightarrow 2$, $3_1/3_2 \rightarrow 3$, $4_1/4_2/4_3 \rightarrow 4$, $6_1 \ldots 6_5 \rightarrow 6$).
  - **Replace glide planes by mirrors** (a, b, c, n, d, e → m).
    The result is the **point-group HM symbol** (possibly with orientation details like 312 vs 321, both belonging to point group **32**). CCP4Wikipedia

Quick cheat-sheet (family ↔ typical point-group symbols)

- **Triclinic:** 1, –1
- **Monoclinic:** 2, m, 2/m
- **Orthorhombic:** 222, mm2, mmm
- **Tetragonal:** 4, –4, 4/m, 422, 4mm, –42m, 4/mmm
- **Trigonal:** 3, –3, 32, 3m, –3m
- **Hexagonal:** 6, –6, 6/m, 622, 6mm, –6m2, 6/mmm
- **Cubic:** 23, m–3, 432, –43m, m–3m.

32 Crystallographic Point Groups

Crystal System	Unit Cell	Required symmetry	Point groups
Cubic	Cubic	3-fold axes along body diagonal	$23, m\bar{3}, \bar{4}3m, 432, m\bar{3}m$
Tetragonal	Tetragonal	4-fold axis	$4, \bar{4}, 4/m, 422, 4mm, \bar{4}m2, 4/mmm$
Hexagonal	Hexagonal	6-fold axis	$6, \bar{6}, 6/m, 622, 6mm, \bar{6}m2, 6/mmm$
Trigonal	Hexagonal or Rhombohedral	3-fold axis	$3, \bar{3}, 32, 3m, \bar{3}m$
Orthorhombic	Orthorhombic	Three mutually perpendicular 2-fold axes or mirror planes	$222, 2mm, mmm$
Monoclinic	Monoclinic	2-fold axis or mirror plane	$2, m, 2/m$
Triclinic	Triclinic	none	$1, \bar{1}$

International Tables for Crystallography
Index of the 230 space groups

https://onlinelibrary.wiley.com/iucr/itc/doi/10.1107/97809553602060000928

Hexagonal

P6	168	$P6_1$	169	$P6_5$	170	$P6_2$	171
$P6_4$	172	$P6_3$	173	*P-6*	174	*P6/m*	175
$P6_3/m$	176	*P622*	177	$P6_122$	178	$P6_522$	179
$P6_222$	180	$P6_422$	181	$P6_322$	182	*P6mm*	183
P6cc	184	$P6_3cm$	185	$P6_3mc$	186	*P-6m2*	187
P -6 c2	188	*P-62m*	189	*P-62c*	190	*P6/mmm*	191
P6/mcc	192	$P6_3/mcm$	193	$P6_3/mmc$	194		

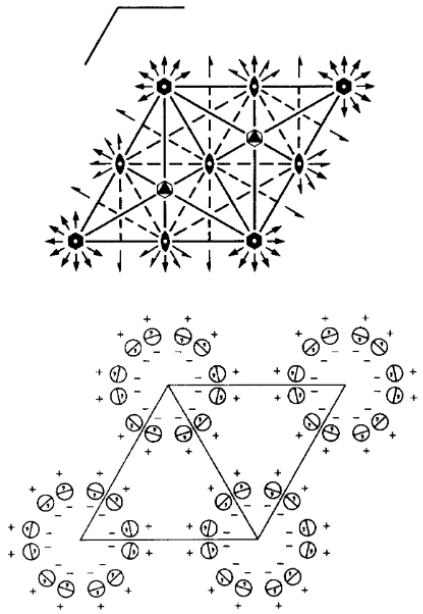
P6/mmm D_{6h}^{1} **6/*mmm*** **Hexagonal**

No. 191 ***P6/m2/m2/m*** **Patterson symmetry *P6/mmm***

•**"6"** = sixfold rotation axis along the *c*-axis (the hexagonal axis).

•**"/m"** = a mirror plane perpendicular to the sixfold axis (i.e., a *horizontal* mirror plane at c = 0).

•**"mm"** = mirror planes parallel to the *c*-axis:



Origin at centre (6/*m m m*)

•One **6-fold rotation axis** along *c*

•**Six 2-fold axes** perpendicular to *c* (in the basal plane)

•**Horizontal mirror** plane perpendicular to *c*

•**Six vertical mirror planes** containing *c*

•**Inversion center** at the origin

Name the crystal system, Bravais lattice and point group from the following short Hermann-Mauguin space group symbols.

$I4_1/a$

$Fd\bar{3}m$

Name the crystal system, Bravais lattice and point group from the following short Hermann-Mauguin space group symbols.

$I4_1/a$

Crystal system: *tetragonal*
Bravais lattice: *body centered tetragonal*
Point group: $4/m$ (C_{4h})
nonsymmorphic space group

$Fd\bar{3}m$

Crystal system: *cubic*
Bravais lattice: *face centered cubic*
Point group: $m\bar{3}m$ (O_h)
nonsymmorphic space group

How do we represent Crystal Structures?

- Sometimes there are hundreds of atoms per unit cell
- We don’t want to draw them all out
- How do we represent the crystal structures more compactly?
- How can we use software to better visualize crystal structures?

Learning objectives:

Represent Crystal Structures: Understand the compact formalism used to describe complex crystal structures, including the space group, unit cell dimensions, and Wyckoff sites.

Interpret Wyckoff Sites: Learn how to use Wyckoff site information from the International Tables for Crystallography to determine atom positions, multiplicity, and site symmetry within a unit cell.

Handle Centered Lattices: Understand how centering operations (like face-centering) generate additional atomic positions from a single set of fractional coordinates.

Calculate Crystal Density: Be able to calculate the theoretical density of a crystal using its unit cell dimensions, atomic contents (derived from Wyckoff multiplicities), and atomic masses.

CaF_2 (fluorite)

Space Group	$Fm\bar{3}m$ (#225)			
Lattice parameters	$a = 5.46$ Å			
Atom	Wyckoff Site	x	y	z
Ca	4a	0	0	0
F	8c	1/4	1/4	1/4

How to read the notation (Hermann–Mauguin) $Fm\bar{3}m$

For cubic point groups the three symbol positions map to fixed direction families. The **full symbol** for m-3m is **4/m −3 2/m**, interpreted as:

•**First position (〈100〉): 4/m** → three 4-fold axes along x, y, z, each with a mirror plane ⊥ to the axis (i.e., {100} mirrors).

•**Second position (〈111〉): −3** → four body-diagonal **3-fold rotoinversion** axes (each axis runs through opposite cube corners).

•**Third position (〈110〉): 2/m** → six 2-fold axes along face diagonals, each with a mirror plane ⊥ to the axis (i.e., {110} mirrors).

•The condensed **m-3m** omits the explicit "4/" and "2/" because those rotations are implied by the mirrors and −3.

Fm-3m O_h^5 *m-3m* Cubic

No. 225 *F4/m-32/m* **Patterson symmetry *Fm-3m***

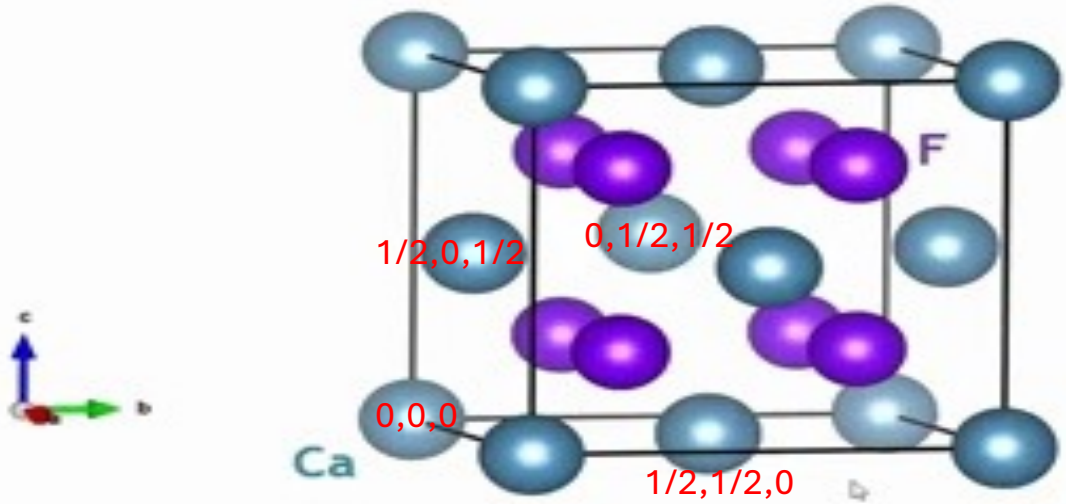
Multiplicity, Wyckoff letter, Site symmetry			Coordinates						Reflection conditions
			(0, 0, 0)+ (0, 1/2, 1/2)+ (1/2, 0, 1/2)+ (1/2, 1/2, 0)+						*h*, *k*, *l* permutable General:
192	*l*	1	(1) *x*, *y*, *z* (5) *z*, *x*, *y* (9) *y*, *z*, *x* (13) *y*, *x*, -*z* (17) *x*, *z*, -*y* (21) *z*, *y*, -*x* (25) -*x*, -*y*, -*z* (29) -*z*, -*x*, -*y* (33) -*y*, -*z*, -*x* (37) -*y*, -*x*, *z* (41) -*x*, -*z*, *y* (45) -*z*, -*y*, *x*	(2) -*x*, -*y*, *z* (6) *z*, -*x*, -*y* (10) -*y*, *z*, -*x* (14) -*y*, -*x*, -*z* (18) -*x*, *z*, *y* (22) *z*, -*y*, *x* (26) *x*, *y*, -*z* (30) -*z*, *x*, *y* (34) *y*, -*z*, *x* (38) *y*, *x*, *z* (42) *x*, -*z*, -*y* (46) -*z*, *y*, -*x*	(3) -*x*, *y*, -*z* (7) -*z*, -*x*, *y* (11) *y*, -*z*, -*x* (15) *y*, -*x*, *z* (19) -*x*, -*z*, -*y* (23) -*z*, *y*, *x* (27) *x*, -*y*, *z* (31) *z*, *x*, -*y* (35) -*y*, *z*, *x* (39) -*y*, *x*, -*z* (43) *x*, *z*, *y* (47) *z*, -*y*, -*x*	(4) *x*, -*y*, -*z* (8) -*z*, *x*, -*y* (12) -*y*, -*z*, *x* (16) -*y*, *x*, *z* (20) *x*, -*z*, *y* (24) -*z*, -*y*, -*x* (28) -*x*, *y*, *z* (32) *z*, -*x*, *y* (36) *y*, *z*, -*x* (40) *y*, -*x*, -*z* (44) -*x*, *z*, -*y* (48) *z*, *y*, *x*		*hkl*: *h* + *k*, *h* + *l*, *k* + *l* = 2*n* 0*kl*: *k*, *l* = 2*n* *hhl*: *h* + *l* = 2*n* *h*00: *h* = 2*n*
									Special: as above, plus
96	*k*	. . *m*	*x*, *x*, *z* -*z*, -*x*, *x* *x*, *x*, -*z* -*x*, -*z*, -*x*	-*x*, -*x*, *z* -*z*, *x*, -*x* -*x*, -*x*, -*z* *x*, -*z*, *x*	-*x*, *x*, -*z* *x*, *z*, *x* *x*, -*x*, *z* *z*, *x*, -*x*	*x*, -*x*, -*z* -*x*, *z*, -*x* -*x*, *x*, *z* *z*, -*x*, *x*	*z*, *x*, *x* *x*, -*z*, -*x* *x*, *z*, -*x* -*z*, *x*, *x*	*z*, -*x*, -*x* -*x*, -*z*, *x* -*x*, *z*, *x* -*z*, -*x*, -*x*	no extra conditions
96	*j*	*m* . .	0, *y*, *z* -*z*, 0, *y* *y*, 0, -*z* 0, -*z*, -*y*	0, -*y*, *z* -*z*, 0, -*y* -*y*, 0, -*z* 0, -*z*, *y*	0, *y*, -*z* *y*, *z*, 0 *y*, 0, *z* *z*, *y*, 0	0, -*y*, -*z* -*y*, *z*, 0 -*y*, 0, *z* *z*, -*y*, 0	*z*, 0, *y* *y*, -*z*, 0 0, *z*, -*y* -*z*, *y*, 0	*z*, 0, -*y* -*y*, -*z*, 0 0, *z*, *y* -*z*, -*y*, 0	no extra conditions
48	*i*	*m* . *m* 2	1/2, *y*, *y* -*y*, 1/2, *y*	1/2, -*y*, *y* -*y*, 1/2, -*y*	1/2, *y*, -*y* *y*, *y*, 1/2	1/2, -*y*, -*y* -*y*, *y*, 1/2	*y*, 1/2, *y* *y*, -*y*, 1/2	*y*, 1/2, -*y* -*y*, -*y*, 1/2	no extra conditions
48	*h*	*m* . *m* 2	0, *y*, *y* -*y*, 0, *y*	0, -*y*, *y* -*y*, 0, -*y*	0, *y*, -*y* *y*, *y*, 0	0, -*y*, -*y* -*y*, *y*, 0	*y*, 0, *y* *y*, -*y*, 0	*y*, 0, -*y* -*y*, -*y*, 0	no extra conditions
48	*g*	2 . *m* *m*	*x*, 1/4, 1/4 1/4, *x*, 3/4	-*x*, 3/4, 1/4 3/4, -*x*, 3/4	1/4, *x*, 1/4 *x*, 1/4, 3/4	1/4, -*x*, 3/4 -*x*, 1/4, 1/4	1/4, 1/4, *x* 1/4, 1/4, -*x*	3/4, 1/4, -*x* 1/4, 3/4, *x*	*hkl*: *h* = 2*n*
32	*f*	. 3 *m*	*x*, *x*, *x* *x*, *x*, -*x*	-*x*, -*x*, *x* -*x*, -*x*, -*x*	-*x*, *x*, -*x* *x*, -*x*, *x*	*x*, -*x*, -*x* -*x*, *x*, *x*			no extra conditions
24	*e*	4 *m* . *m*	*x*, 0, 0	-*x*, 0, 0	0, *x*, 0	0, -*x*, 0	0, 0, *x*	0, 0, -*x*	no extra conditions
24	*d*	*m* . *m* *m*	0, 1/4, 1/4	0, 3/4, 1/4	1/4, 0, 1/4	1/4, 0, 3/4	1/4, 1/4, 0	3/4, 1/4, 0	*hkl*: *h* = 2*n*
8	*c*	-4 3 *m*	1/4, 1/4, 1/4			1/4, 1/4, 3/4			*hkl*: *h* = 2*n*
4	*b*	*m* -3 *m*	1/2, 1/2, 1/2						no extra conditions
4	*a*	*m* -3 *m*	0, 0, 0						no extra conditions

Fm-3m	O_h^5	*m-3m*	**Cubic**
No. 225	***F4/m-32/m***		**Patterson symmetry *Fm-3m***

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			
			(0, 0, 0)+	(0, 1/2, 1/2)+	(1/2, 0, 1/2)+	(1/2, 1/2, 0)+
192	*l*	1	(1) *x*, *y*, *z*	(2) -*x*, -*y*, *z*	(3) -*x*, *y*, -*z*	(4) *x*, -*y*, -*z*
			(5) *z*, *x*, *y*	(6) *z*, -*x*, -*y*	(7) -*z*, -*x*, *y*	(8) -*z*, *x*, -*y*
			(9) *y*, *z*, *x*	(10) -*y*, *z*, -*x*	(11) *y*, -*z*, -*x*	(12) -*y*, -*z*, *x*
			(13) *y*, *x*, -*z*	(14) -*y*, -*x*, -*z*	(15) *y*, -*x*, *z*	(16) -*y*, *x*, *z*
			(17) *x*, *z*, -*y*	(18) -*x*, *z*, *y*	(19) -*x*, -*z*, -*y*	(20) *x*, -*z*, *y*
			(21) *z*, *y*, -*x*	(22) *z*, -*y*, *x*	(23) -*z*, *y*, *x*	(24) -*z*, -*y*, -*x*
			(25) -*x*, -*y*, -*z*	(26) *x*, *y*, -*z*	(27) *x*, -*y*, *z*	(28) -*x*, *y*, *z*
			(29) -*z*, -*x*, -*y*	(30) -*z*, *x*, *y*	(31) *z*, *x*, -*y*	(32) *z*, -*x*, *y*
			(33) -*y*, -*z*, -*x*	(34) *y*, -*z*, *x*	(35) -*y*, *z*, *x*	(36) *y*, *z*, -*x*
			(37) -*y*, -*x*, *z*	(38) *y*, *x*, *z*	(39) -*y*, *x*, -*z*	(40) *y*, -*x*, -*z*
			(41) -*x*, -*z*, *y*	(42) *x*, -*z*, -*y*	(43) *x*, *z*, *y*	(44) -*x*, *z*, -*y*
			(45) -*z*, -*y*, *x*	(46) -*z*, *y*, -*x*	(47) *z*, -*y*, -*x*	(48) *z*, *y*, *x*

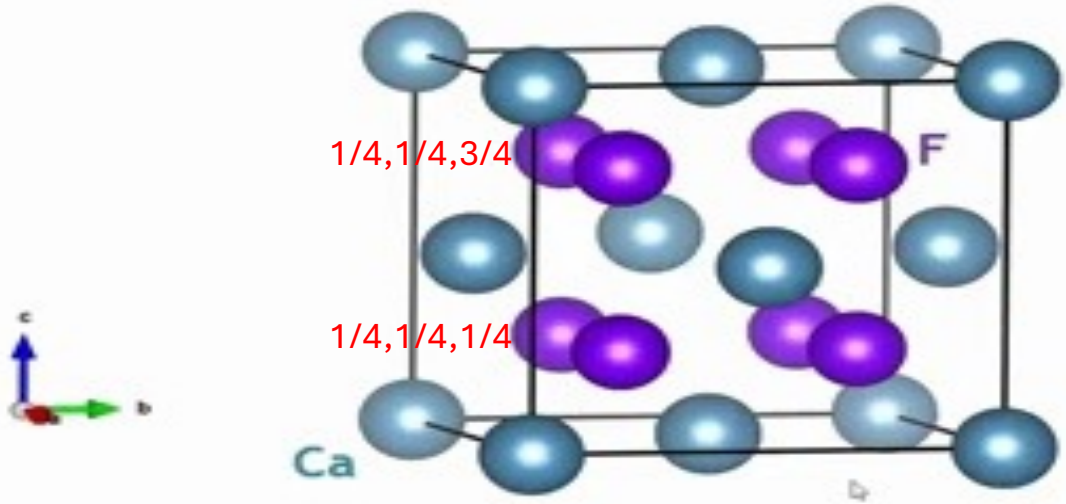
8	*c*	-4 3 *m*	1/4, 1/4, 1/4	1/4, 1/4, 3/4
4	*b*	*m* -3 *m*	1/2, 1/2, 1/2	
4	*a*	*m* -3 *m*	0, 0, 0	

Space Group	$Fm\bar{3}m$ (#225)			
Lattice parameters	$a = 5.46$ Å			
Atom	Wyckoff Site	x	y	z
Ca	4a	0	0	0
F	8c	1/4	1/4	1/4



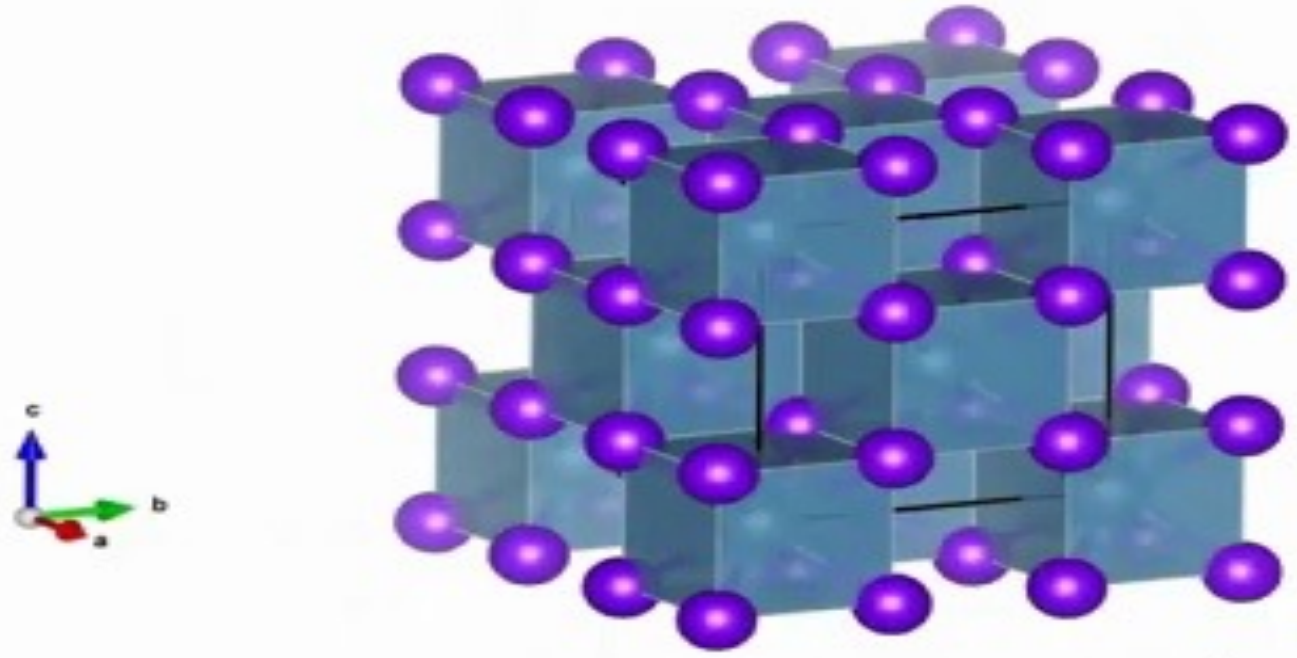
Ca (4a)	0,0,0	½,½,0	½,0,½	0,½,½
F (8c)	¼,¼,¼	¾,¾,¼	¾,¼,¾	¼,¾,¾
	¼,¼,¾	¾,¾,¾	¾,¼,¼	¼,¾,¼

Space Group	$Fm\bar{3}m$ (#225)			
Lattice parameters	$a = 5.46$ Å			
Atom	Wyckoff Site	x	y	z
Ca	4a	0	0	0
F	8c	1/4	1/4	1/4



Ca (4a)	0,0,0	½,½,0	½,0,½	0,½,½
F (8c)	¼,¼,¼	¾,¾,¼	¾,¼,¾	¼,¾,¾
	¼,¼,¾	¾,¾,¾	¾,¼,¼	¼,¾,¼

Space Group	$Fm\bar{3}m$ (#225)			
Lattice parameters	$a = 5.46$ Å			
Atom	Wyckoff Site	x	y	z
Ca	4a	0	0	0
F	8c	1/4	1/4	1/4



Calculations of Theoretical Density

Calculations of Theoretical Density

density = (mass of atoms within unit cell)/(unit cell volume)

From the Wyckoff site multiplicities we see that there are four CaF_2 formula units within the unit cell (Z=4) $\rightarrow$ 4 Ca + 8 F.

Calculations of Theoretical Density

density = (mass of atoms within unit cell)/(unit cell volume)

From the Wyckoff site multiplicities we see that there are four CaF_2 formula units within the unit cell (Z=4) → 4 Ca + 8 F.

$$mass = 4(40.08\ \text{amu}) + 8(19.00\ \text{amu}) = 312.32\ \text{amu}$$

$$mass = 312.32\ \text{amu} \times \frac{1\ \text{g}}{6.022 \times 10^{23}\ \text{amu}} = 5.186 \times 10^{-22}\ \text{g}$$

Calculations of Theoretical Density

density = (mass of atoms within unit cell)/(unit cell volume)

From the Wyckoff site multiplicities we see that there are four CaF_2 formula units within the unit cell (Z=4) → 4 Ca + 8 F.

$$mass = 4(40.08\ \text{amu}) + 8(19.00\ \text{amu}) = 312.32\ \text{amu}$$

$$mass = 312.32\ \text{amu} \times \frac{1\ \text{g}}{6.022 \times 10^{23}\ \text{amu}} = 5.186 \times 10^{-22}\ \text{g}$$

$$volume = (5.46 \times 10^{-8}\ \text{cm})^3 = 1.628 \times 10^{-22}\ \text{cm}^3$$

$$density = \frac{mass}{volume} = \frac{5.186 \times 10^{-22}\ \text{g}}{1.628 \times 10^{-22}\ \text{cm}^3} = 3.19\ \text{g/cm}^3$$

Unit Cell Volumes: http://webmineral.com/help/CellDimensions.shtml#.YADu-ehKhPY

Crystal Structure Drawing Programs

- Vesta (Freeware)
  - https://jp-minerals.org/vesta/en/
- Diamond
  - https://www.crystalimpact.com/diamond/
- CrystalMaker
  - http://www.crystalmaker.com/

Summary - Representing Crystal Structures (Example: CaF_2)

Why compact representations?
Unit cells can contain many atoms → instead of listing all positions, we use:
Space group symmetry
Unit cell dimensions
Wyckoff positions + fractional coordinates of unique atoms

Case study: Calcium Fluoride (CaF_2)
Space group: **Fm-3m (#225)**, cubic, a = 5.46 Å
Atoms: Ca at Wyckoff 4a (0,0,0), F at 8c (¼,¼,¼)
Multiplicities & centering operations generate all atoms in unit cell
Coordination: Ca in cubic (octahedral) environment; F in tetrahedral environment

Density calculation
4 CaF_2 units per cell → 4 Ca + 8 F = 312.32 amu
Converted mass: 5.19×10^{-22} g
Cell volume: $(5.46 \times 10^{-8}\ \text{cm})^3 = 1.63 \times 10^{-22}\ \text{cm}^3$
Density = **3.19 g/cm^3** (reasonable for a mineral solid)

Tools
Visualization/drawing: **VESTA (free)**, CrystalMaker, Diamond
Useful for measuring distances/angles & building polyhedral views

Learning Objectives

By the end of this lecture, you should be able to:

Classify extended solids into metallic, ionic, and covalent types, based on bonding and structural features.

Explain packing in metallic solids, including two-dimensional hexagonal packing and its extension into three dimensions.

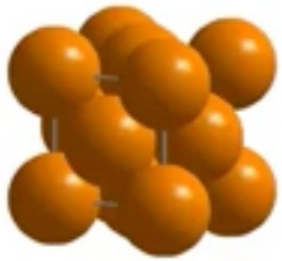
Differentiate close-packed structures: hexagonal close-packed (HCP) vs cubic close-packed (FCC), including stacking sequences (ABAB vs ABCABC).

Describe metallic unit cells (FCC, BCC, primitive cubic) and compare their coordination numbers and packing efficiencies.

Recognize periodic trends in metallic crystal structures and their relation to bonding and band filling.

Identify variations and intermetallic structures, such as alternative stacking sequences (e.g., ABAC), ordered compounds (CsCl, Cu_3Au), and high-coordination examples (e.g., $SmCo_5$).

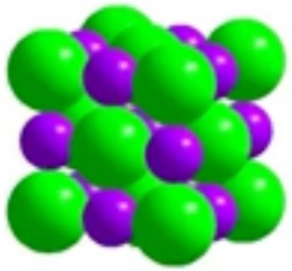
Extended Solids



Metallic Solids (Al, Fe, …)

Bonding: Atoms held together by delocalized metallic bonding

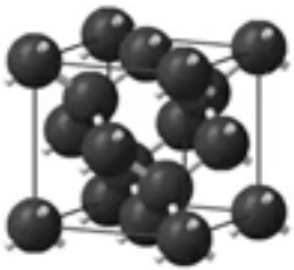
Structural Attributes: Closely packed atoms (large coordination numbers, symmetric structures)



"Ionic" Solids (Al_2O_3, CaF_2, …)

Bonding: Atoms held together by electrostatic attractions between ions of opposite charge

Structural Attributes: Symmetric structures that maximize cation-anion interactions, but minimize cation-cation and anion-anion interactions

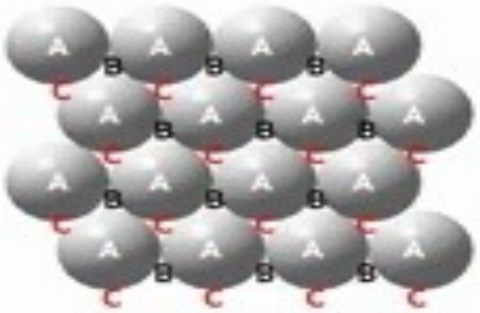


Covalent-Network Solids (WO_3, C, SiO_2, …)

Bonding: Extended networks of atoms held together by covalent bonds

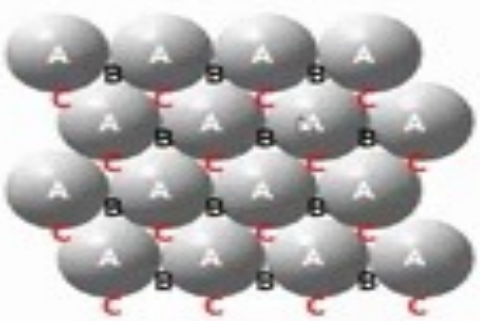
Structural Attributes: Lower coordination numbers and densities than metallic and ionic solids

Close packed structures

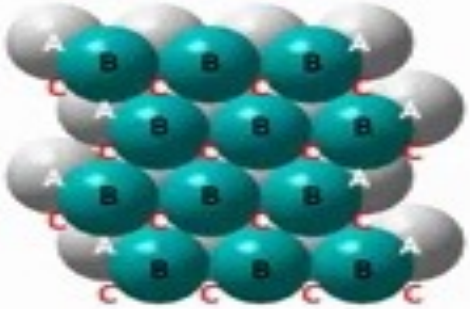


Spheres form a close packed hexagonal layer

Close packed structures

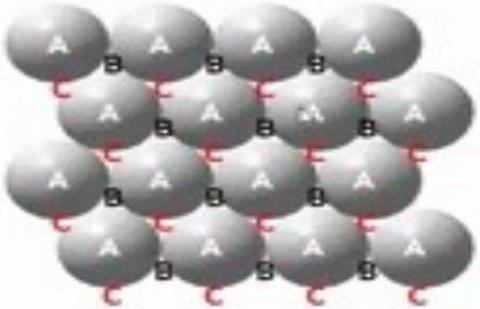


Spheres form a close packed hexagonal layer

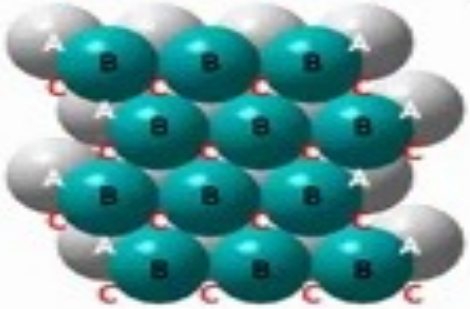


Second layer of spheres sit in the depressions marked with a B

Close packed structures



Spheres form a close packed hexagonal layer

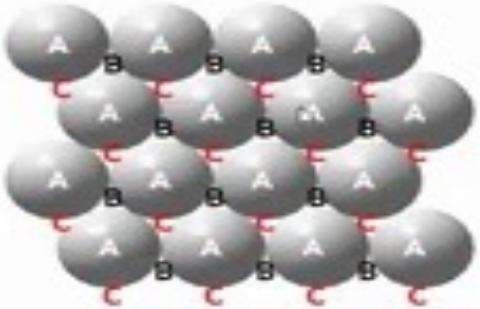


Second layer of spheres sit in the depressions marked with a B

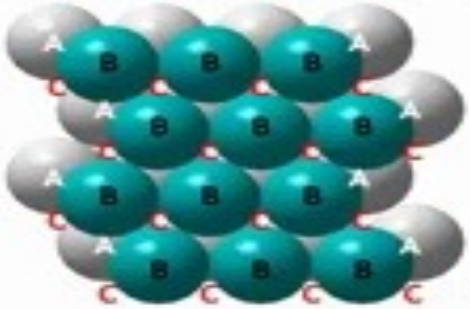
Third layer of spheres sit in depressions directly over the spheres in the first layer.

Hexagonal close packing (ABAB...)

Close packed structures



Spheres form a close packed hexagonal layer

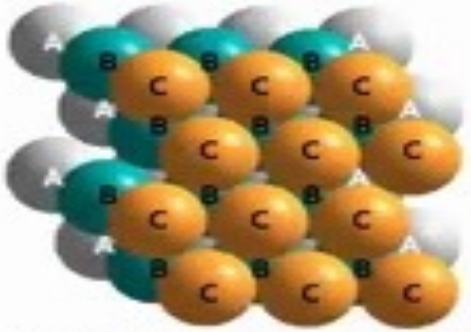


Second layer of spheres sit in the depressions marked with a B

Third layer of spheres sit in depressions directly over the spheres in the first layer.

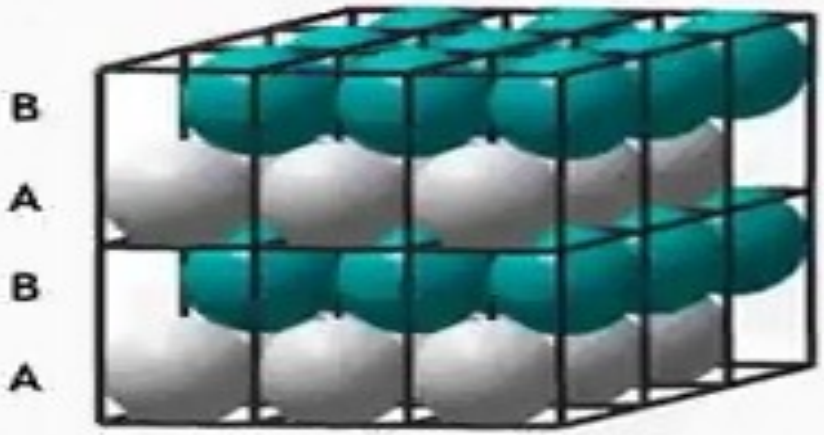
Hexagonal close packing (ABAB...)

Third layer of spheres sit in the depressions marked with a C.

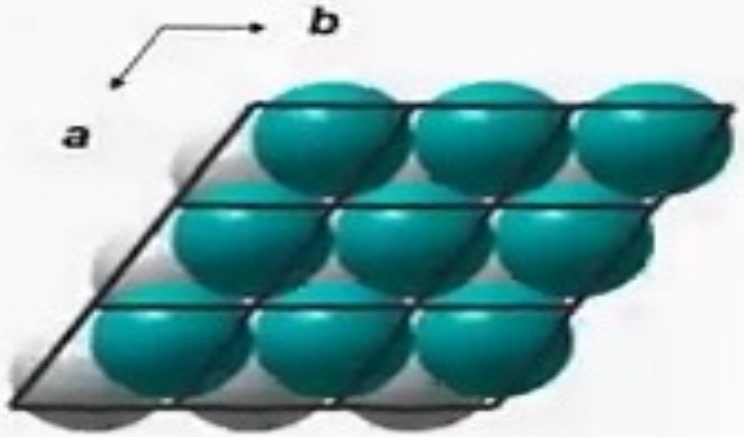


Cubic close packing (ABCABC...)

Hexagonal Close Packed Metal



Layer packing view



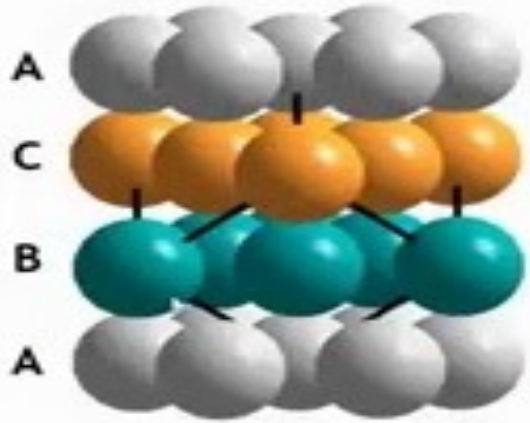
top view

Example: Mg
Space Group: $P6_3/mmc$ (#194)
Unit Cell: a = 3.21 Å, c = 5.21 Å

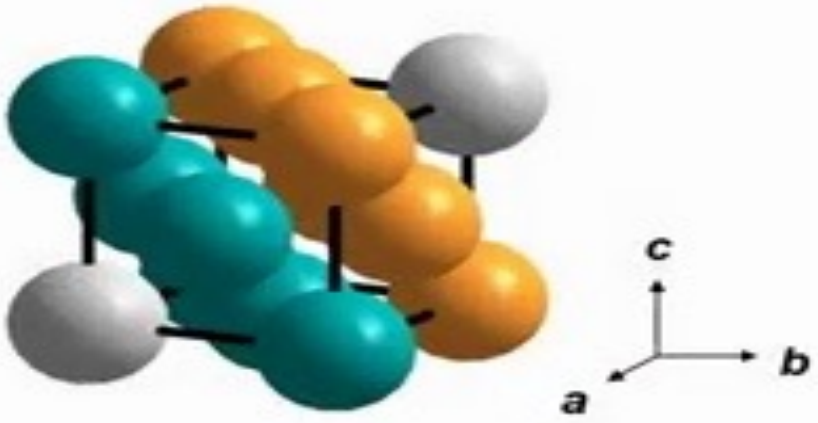
	Wyckoff Site	x	y	z
Mg	2a ($\bar{6}m2$)	1/3	2/3	1/4

Note: Different colors are used to show layers, all atoms are equivalent

Cubic Close Packed Metal



Layer packing view

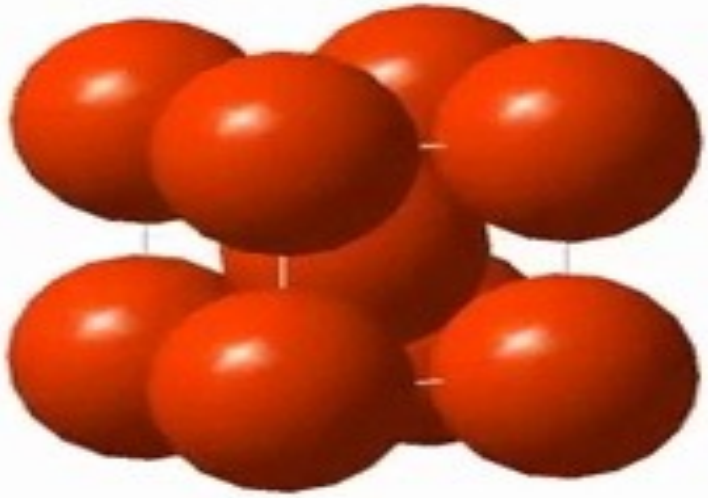


Example: Cu
Space Group: $Fm\bar{3}m$ (#225)
Unit Cell: a = 3.62 Å

	Wyckoff Site	x	y	z
Cu	4a ($m\bar{3}m$)	0	0	0

Note: Different colors are used to show layers, all atoms are equivalent

Body-centered cubic metal



Example: α-Fe
Space Group: $Im\bar{3}m$ (#229)
Unit Cell: a = 2.87 Å

	Wyckoff Site	x	y	z
Fe	2a ($m\bar{3}m$)	0	0	0

Primitive cubic metal

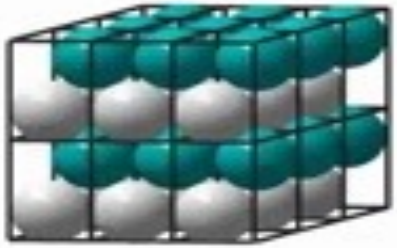
Example: α-Po
Space Group: $Pm\bar{3}m$ (#221)
Unit Cell: a = 3.36 Å

	Wyckoff Site	x	y	z
Po	1a ($m\bar{3}m$)	0	0	0

Structures of Elemental Metals

Li	Be											
Na	Mg											Al
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl

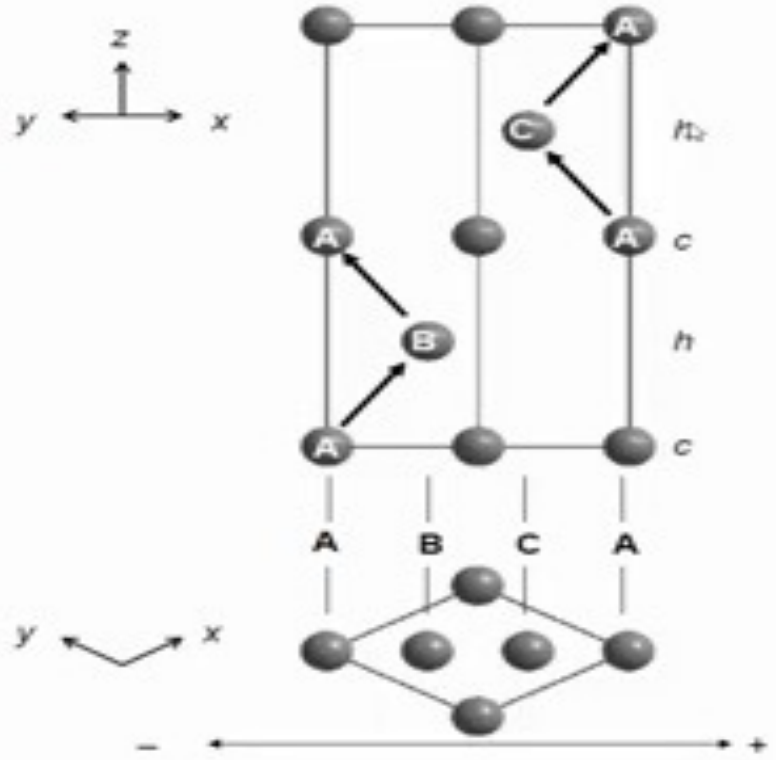
Body Centered Cubic



Hexagonal close packing

Face Centered Cubic

Mixed Hexagonal-Cubic Stacking



Ramsdell symbol: 4H
Jagodzinski–Wyckoff notation: $(hc)_2$

ICSD #102655
$P6_3/mmc$ (194) hexagonal
a = 3.770, c = 12.159 Å

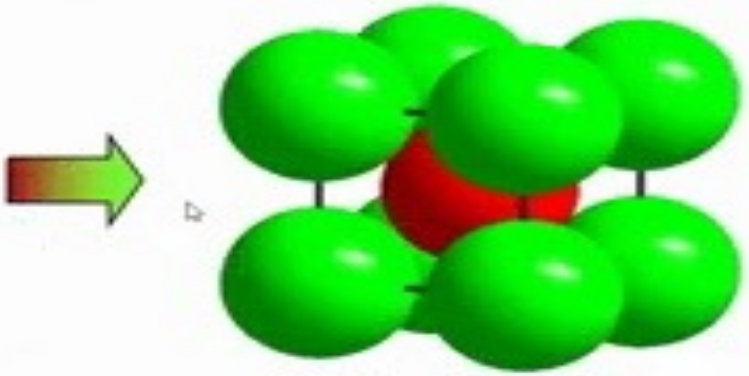
Atom	Wyck.	x	y	z
La	2a	0	0	0
La	2c	⅓	⅔	¼

Intermetallic Compounds

ordered variants

Body-centered cubic metal

Space Group: $Im\bar{3}m$

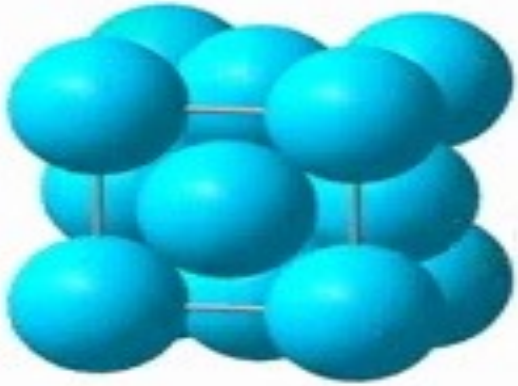


CsCl Structure

Space Group: $Pm\bar{3}m$

Examples

CuZn
LaAg
MgAu
CoAl
PdIn
CdPr



Face-centered cubic metal

Space Group: $Fm\bar{3}m$

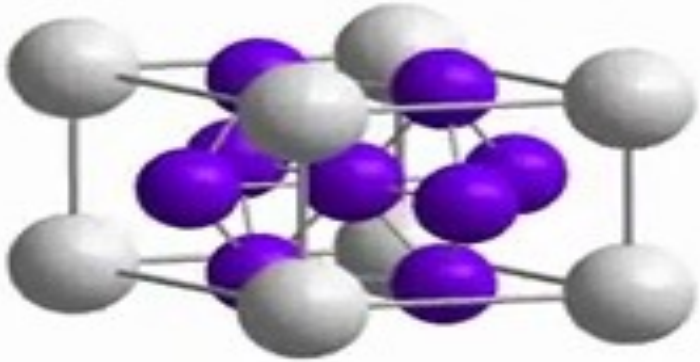
Cu_3Au Structure

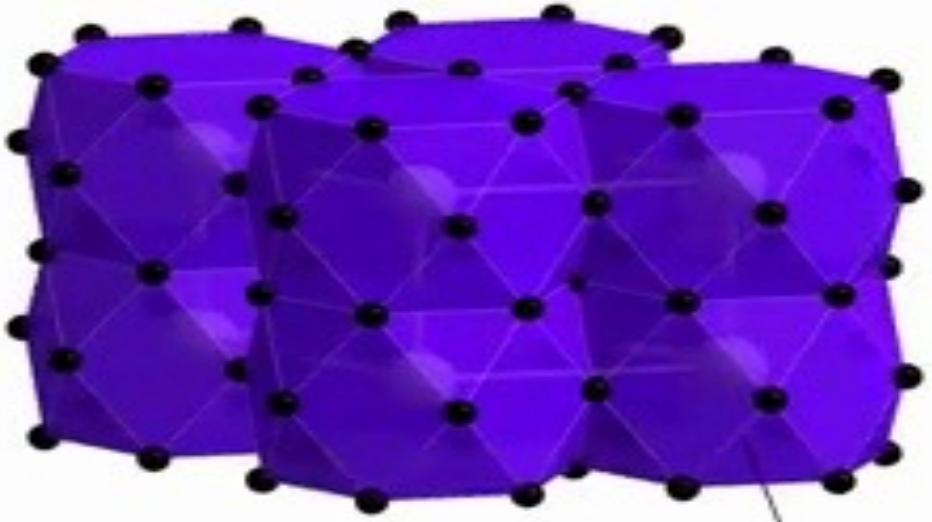
Space Group: $Pm\bar{3}m$

Examples

Cu_3Au
Cr_3Pt
Ni_3Al
Pt_3Al
Sn_3Ca

$SmCo_5$ Structure





Example: $SmCo_5$
Space Group: *P6/mmm* (#191)
Unit Cell: a = 5.00 Å, c = 3.96 Å

	Wyckoff Site	x	y	z
Sm	1a (6/mmm)	0	0	0
Co(1)	2c (-6m2)	1/3	2/3	0
Co(2)	3g (mmm)	1/2	0	1/2

Sm is coordinated by 18 Co ions (6-capped hexagonal prism)

Summary:

Extended (non-molecular) solids can be classified as **metallic, ionic, or covalent** based on bonding and structural features.

Metallic solids favor close packing due to delocalized electrons, leading to dense structures like **HCP (ABAB)** and **FCC/CCP (ABCABC)**.

Unit cells:
HCP: 2 atoms, 12 neighbors, 74% packing.
FCC: atoms on corners + faces, 12 neighbors, 74% packing.
BCC: body atom + corners, 8 neighbors, lower packing.
Primitive cubic: corners only, 6 neighbors, lowest packing.

Stacking variations (e.g., ABAC) exist in rare-earth and other metals; described with Ramstell or Jagodinsky–Y-Coff notation.

Ordered intermetallics (e.g., CsCl, Cu_3Au) arise when different atoms occupy lattice sites, reducing symmetry.

Some complex structures, such as **$SmCo_5$**, exhibit unusually high coordination (CN = 18).

Choice of metallic structure is influenced by **band structure and bonding**, not just packing efficiency.

Ionic Structures

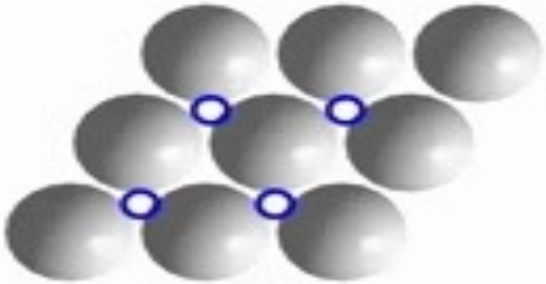
Many ionic structure types can be described as a close packing of anions with cations filling voids or holes in the structure. Generally we will consider two types of holes (for the cations)

- Octahedral holes - Voids are surrounded by 6 anions and lead to octahedral coordination of the cation
- Tetrahedral holes - Voids are surrounded by 4 anions and lead to tetrahedral coordination of the cation

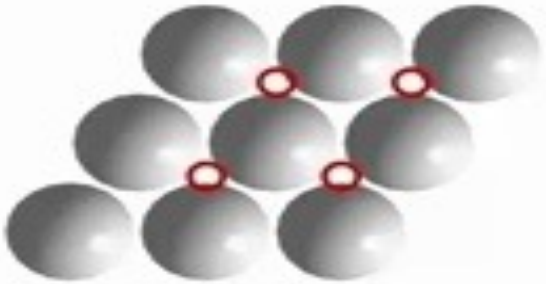
Why would anions want to close pack?

For a detailed answer to this question see: M. O'Keeffe, *Acta Cryst. A* **33**, 924-927 (1977)]

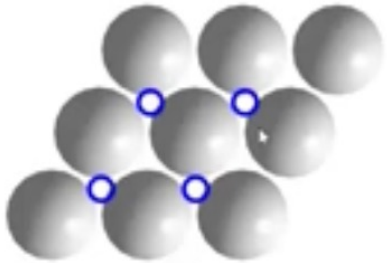
Octahedral Holes

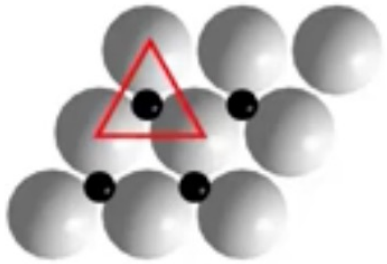


Tetrahedral (+) Holes

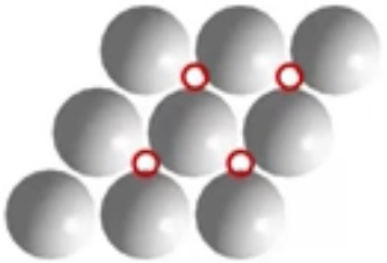


Octahedral Holes

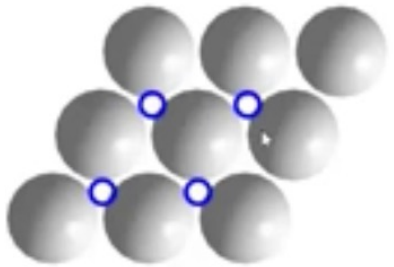


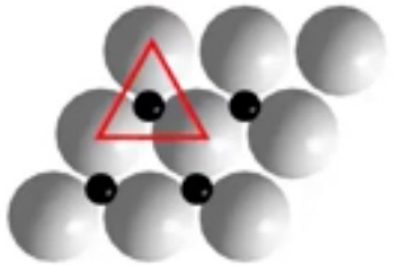


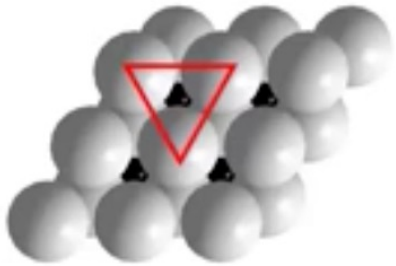
Tetrahedral (+) Holes



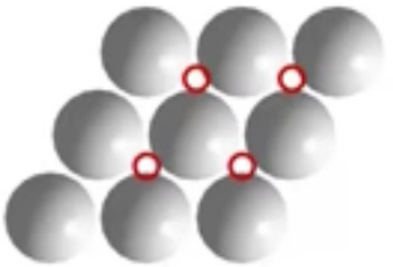
Octahedral Holes



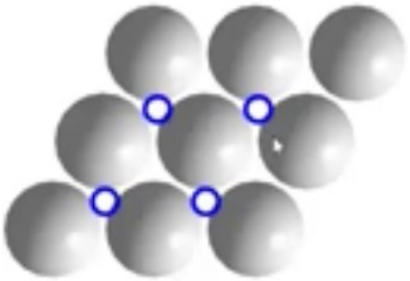


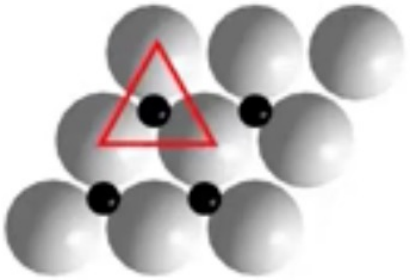


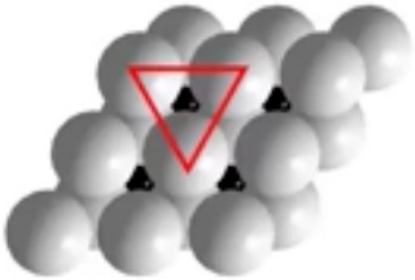
Tetrahedral (+) Holes



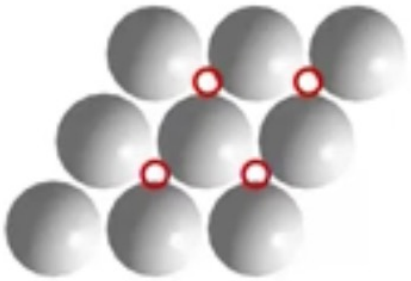
Octahedral Holes

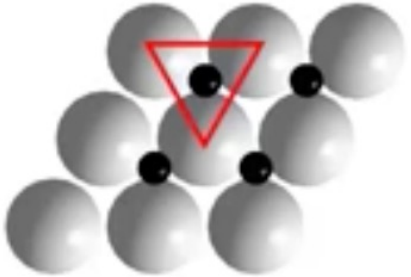


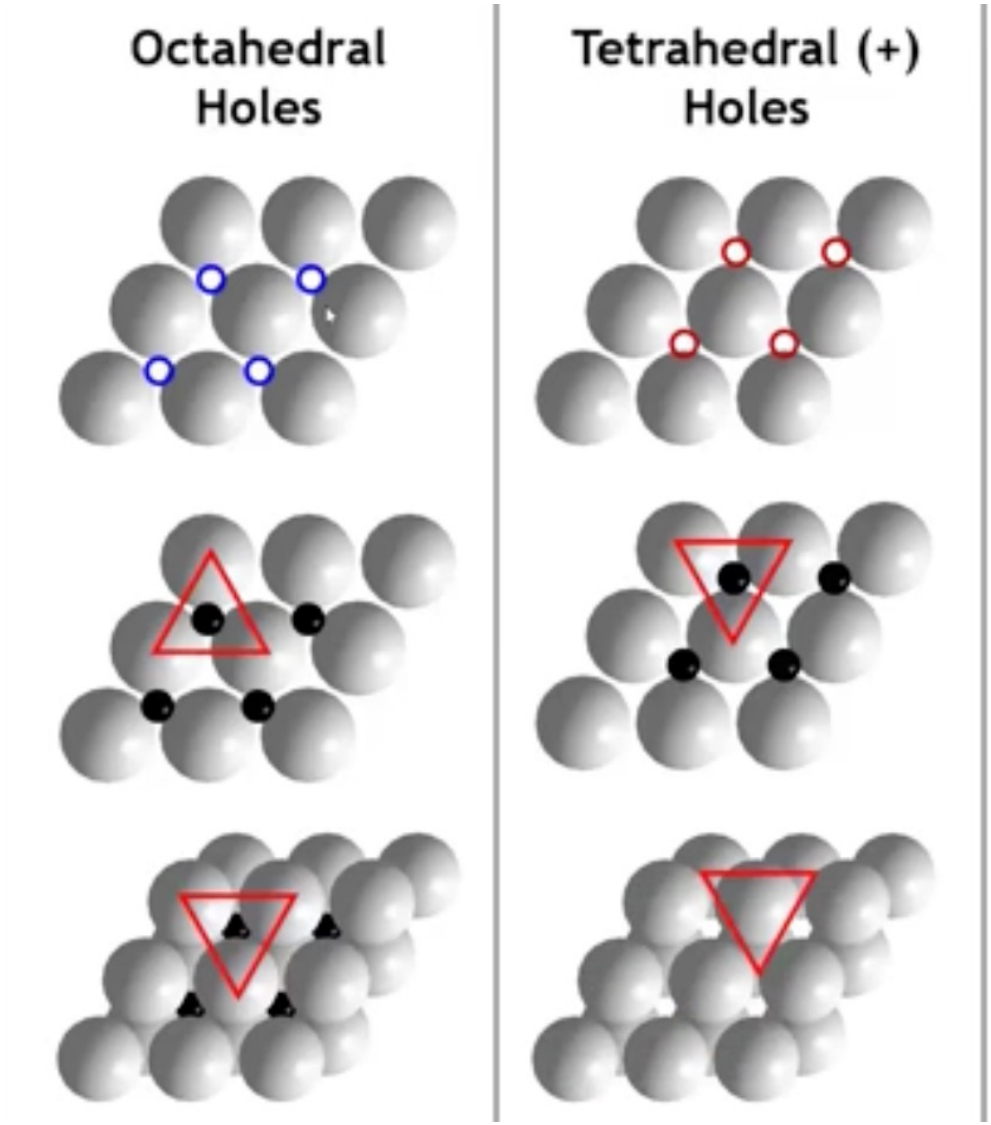


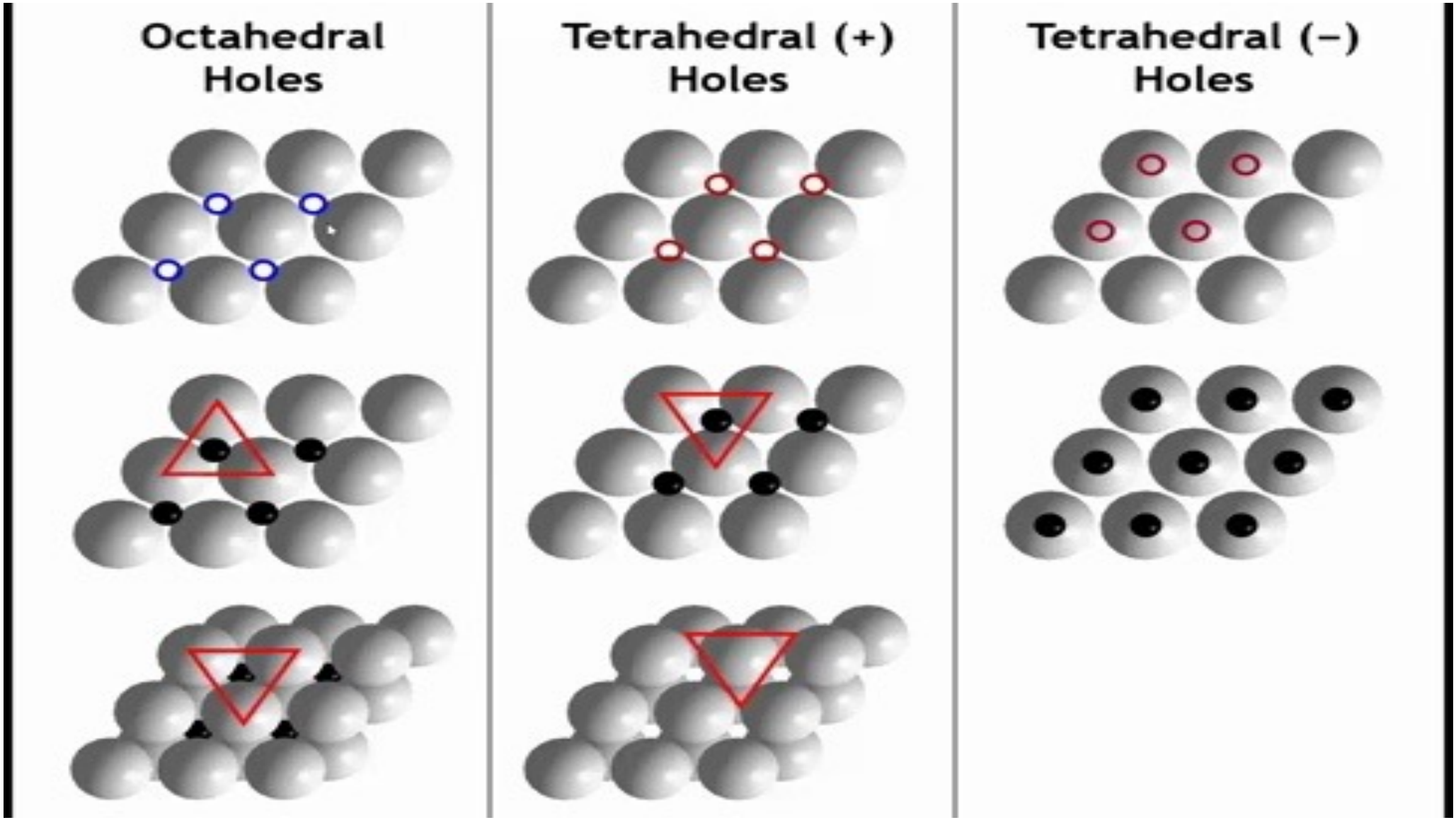


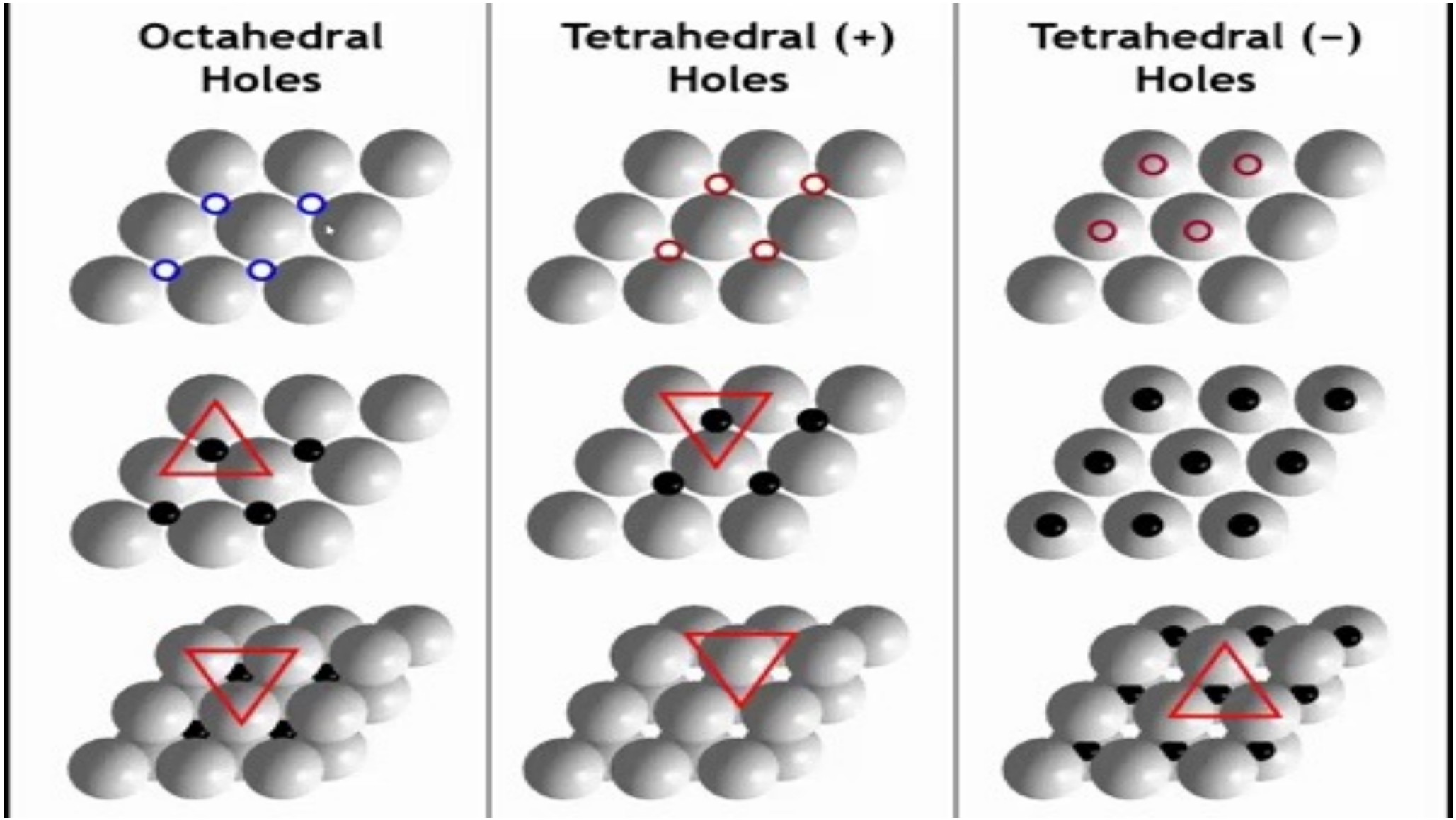
Tetrahedral (+) Holes






Octahedral Holes
Tetrahedral (+) Holes

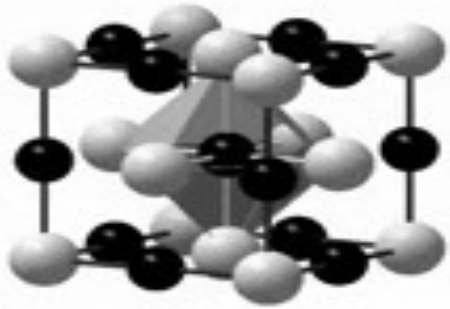
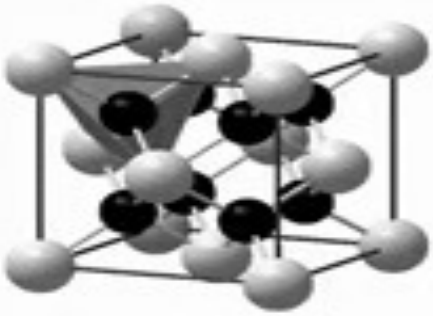
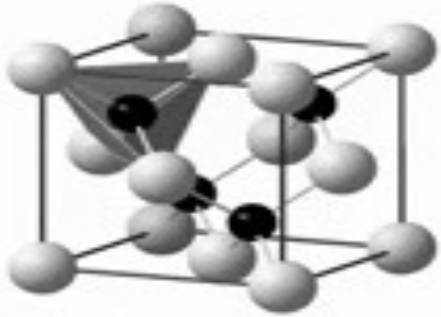
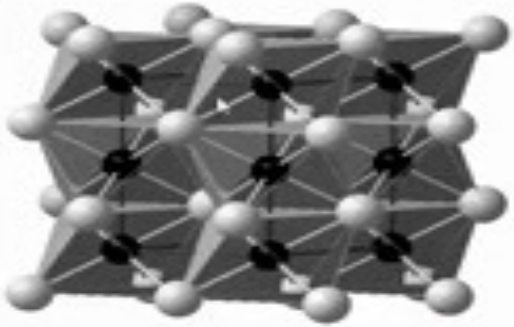
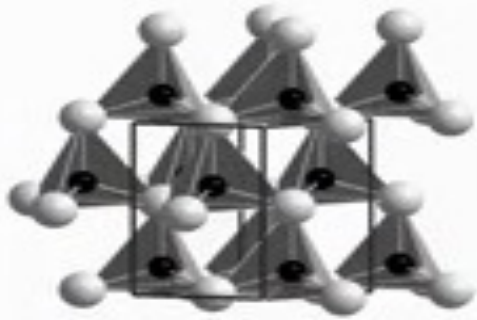

Octahedral Holes
Tetrahedral (+) Holes
Tetrahedral (–) Holes


Octahedral Holes
Tetrahedral (+) Holes
Tetrahedral (–) Holes

Eutactic Structures

Hole filling in total	*General formula*	*Structure type hcp of anions*	*Structure type ccp of anions*	*The plane-filling sequence*
all octahedral	CA	NiAs	NaCl	all full
½	CA_2	CdI_2	$CdCl_2$	empty and full
½	CA_2	$CaCl_2$		all ½ full
⅓	CA_3	BiI_3	YCl_3	empty and ⅔ full
⅓	CA_3	$RuBr_3$		all ⅓ full
⅔	C_2A_3		La_2O_3	empty, full, full *
⅔	C_2A_3	Al_2O_3		all ⅔ full
all tetrahedral	C_2A	not possible	Li_2O	all full
½	CA	ZnS wurtzite	ZnS sphalerite	all ½ full

Eutactic Structures

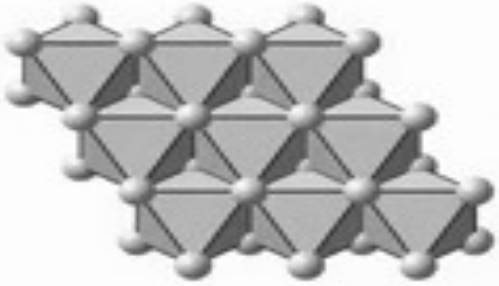
	octahedral holes filled	tetrahedral holes filled	50% of tetrahedral holes filled
ccp anion array	 NaCl ($Fm\bar{3}m$)	 Li_2O ($Fm\bar{3}m$)	 Sphalerite ($F\bar{4}3m$)
hcp anion array	 NiAs ($P6_3/mmc$)	This combination leads to face sharing tetrahedra, which are highly unfavorable.	 Wurtzite ($P6_3mc$)

Eutactic Structures

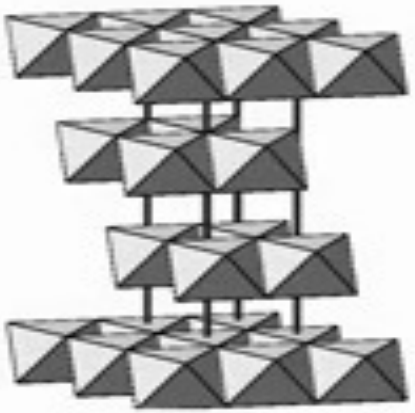
Hole filling in total	*General formula*	*Structure type hcp of anions*	*Structure type ccp of anions*	*The plane-filling sequence*
all octahedral	CA	NiAs	NaCl	all full
½	CA_2	CdI_2	$CdCl_2$	empty and full
½	CA_2	$CaCl_2$		all ½ full
⅓	CA_3	BiI_3	YCl_3	empty and ⅔ full
⅓	CA_3	$RuBr_3$		all ⅓ full
⅔	C_2A_3		La_2O_3	empty, full, full *
⅔	C_2A_3	Al_2O_3		all ⅔ full
all tetrahedral	C_2A	not possible	Li_2O	all full
½	CA	ZnS wurtzite	ZnS sphalerite	all ½ full

Layered Structures

alternating filled and empty layers

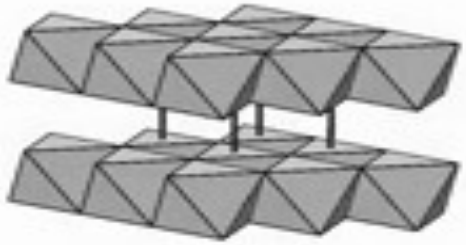


A layer with all of the octahedral holes filled



ccp anion array

hcp anion array



$CdCl_2$ $(R\bar{3}m)$

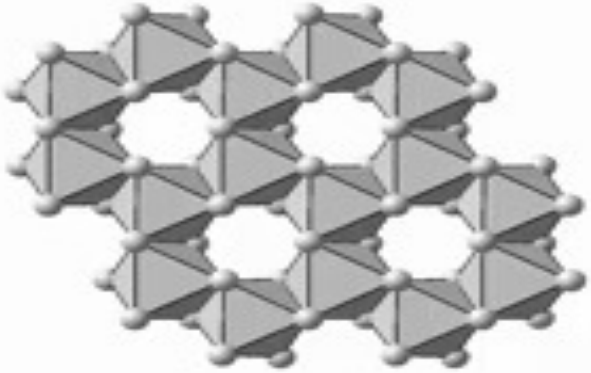
alternating layers of filled and empty octahedral holes

CdI_2 $(P\bar{3}m1)$

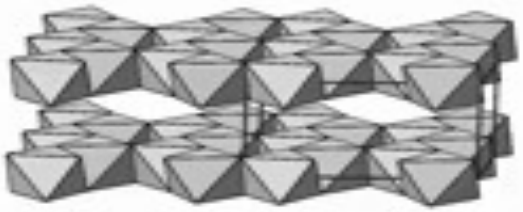
alternating layers of filled and empty octahedral holes

Layered Structures

alternating 2/3-filled and empty layers

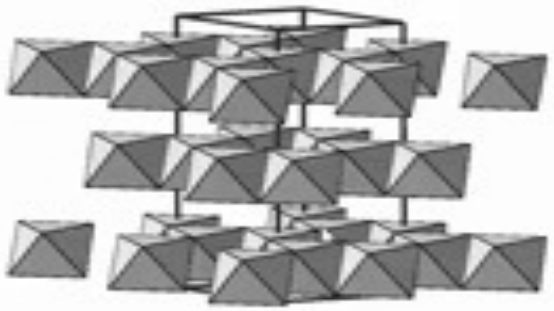


A layer with 2/3 of the octahedral holes filled



ccp anion array

hcp anion array



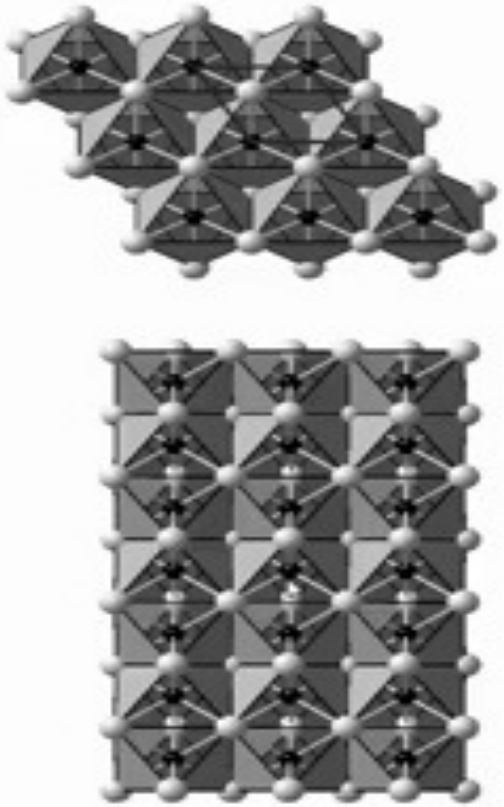
YCl_3 $(C2/m)$
alternating layers of 2/3-filled and empty octahedral holes

BiI_3 $(R\bar{3})$
alternating layers of 2/3-filled and empty octahedral holes

NiAs Structure

Space Group: $P6_3/mmc$

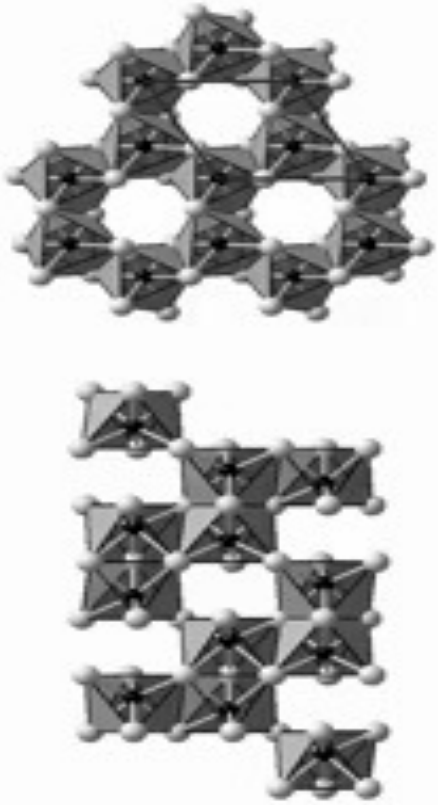
hcp anion array with 100% of the octahedral holes filled



Corundum Structure

Space Group: $R\text{-}3c$

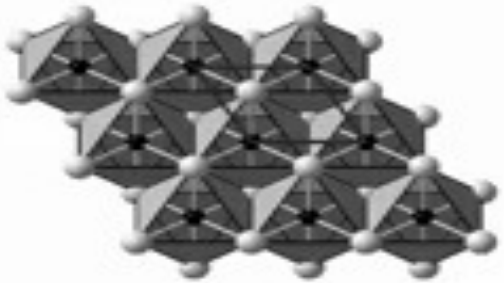
hcp anion array with 2/3 of the octahedral holes filled

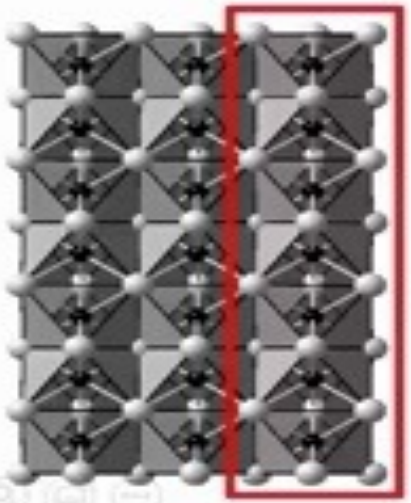


NiAs Structure

Space Group: $P6_3/mmc$

hcp anion array with 100% of the octahedral holes filled



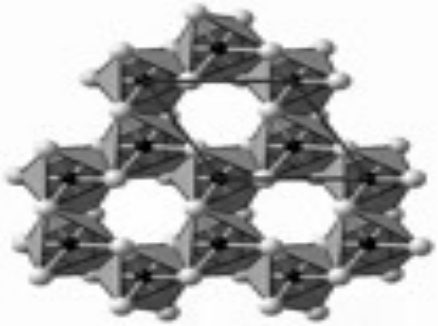


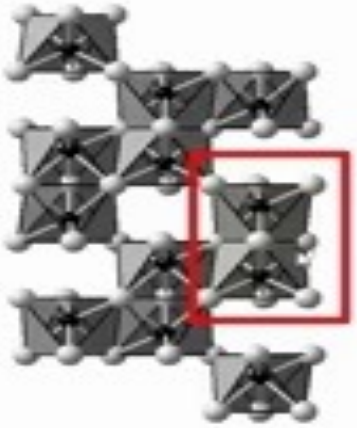
Infinite chains of face-sharing octahedra

Corundum Structure

Space Group: $R\text{-}3c$

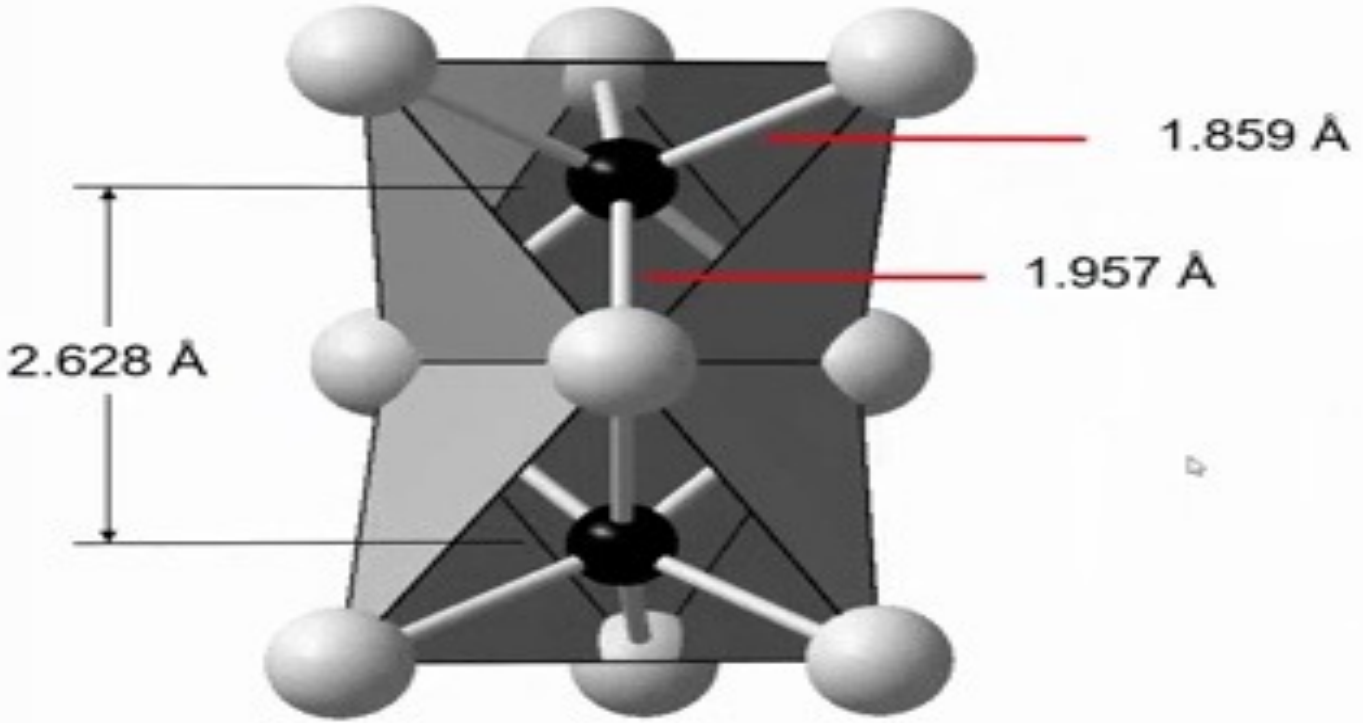
hcp anion array with 2/3 of the octahedral holes filled





Pairs of face-sharing octahedra, cations can shift away from each other

A closer look at bonding in Al_2O_3



Summary

- Ionic solids can be described as **close-packed arrays of anions** with **cations filling interstitial holes** (octahedral or tetrahedral).
- **Octahedral holes**: 6 anion neighbors (1:1 ratio with anions). Filling these gives structures like **NaCl** (cubic) or **NiAs** (hexagonal).
- **Tetrahedral holes**: 4 anion neighbors (2:1 ratio with anions). Filling these gives structures like **Li_2O (anti-fluorite)** or **CaF_2 (fluorite)**.
- **Partial filling** of holes leads to important structures:
  - Half tetrahedral holes → **zinc blende (ZnS)** or **wurtzite**.
  - Half octahedral holes → **$CaCl_2$**, **$CdCl_2$**, **CdI_2** (layered structures).
  - One-third octahedral holes → **corundum (Al_2O_3)**, **hematite (Fe_2O_3)**.
- **Symmetry & stability**: Choice of structure depends on cation size/charge and ionicity; highly ionic systems avoid face-sharing polyhedra, while layered or covalent systems tolerate them.

Homework:

1.15 Calculate the percentage of available space that's taken up by touching spheres in primitive and body-centered cubic arrangements.

1.16 Imagine a coordination polyhedron with a cation at the center. Now treat the ions as hard spheres and reduce the size of the cation until the anions just touch. What is the radius r of the cation for anions of unit radius in the following coordinations: (a) cube, (b) octahedron, and (c) tetrahedron. Hint: Body diagonal is $\sqrt{3}$ and face diagonal $\sqrt{2}$ times the cube edge.

1.17 From unit-cell parameters in figures in this chapter, calculate the following shortest distances: (a) Na–Cl and Na–Na in NaCl, (b) Ni–Ni in NiAs, (c) Ca–F in CaF_2, (d) C–C in diamond, (e) Ti–Ti in TiO_2 (rutile), and (f) Ti–O, Sr–O, and O–O in the cubic perovskite $SrTiO_3$ (a = 3.90 Å).