CHEM 548: MATERIALS CHEMISTRY

LECTURE 4: SPACE GROUPS AND CRYSTAL STRUCTURES

Wed 09/02/2026

Space-group symbols, Wyckoff sites, crystal-structure representation, close packing, metallic solids, and ionic structures

Reading: Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry*
Ch. 1 §1.1.3, §§1.1.5–1.1.8, §1.4.1, §1.4.2

LEARNING OBJECTIVES

Represent a structure	describe a complex crystal structure by its space group, its unit cell dimensions, and its Wyckoff sites
Read the Tables	use Wyckoff site information from the International Tables for Crystallography to determine atom positions, multiplicity, and site symmetry within a unit cell
Centered lattices	work out how centering operations generate additional atomic positions from a single set of fractional coordinates
Theoretical density	calculate the theoretical density of a crystal from its unit cell dimensions, its atomic contents from Wyckoff multiplicities, and its atomic masses

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?

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



Per *Solid State Materials Chemistry*, §1.1.8.

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:

$$4/m\ \bar{3}\ 2/m$$

$\langle 100 \rangle : 4/m$	three 4-fold axes along x, y, z, each with a mirror plane ⊥ to the axis, the {100} mirrors
$\langle 111 \rangle : \bar{3}$	four body-diagonal 3-fold rotoinversion axes, each running through opposite cube corners
$\langle 110 \rangle : 2/m$	six 2-fold axes along the face diagonals, each with a mirror plane ⊥ to the axis, the {110} mirrors
$m\bar{3}m$	the condensed symbol drops the explicit “4/” and “2/” because those rotations are implied by the mirrors and $\bar{3}$

192	l	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{x},y,\bar{z}$	(4) $x,\bar{y},\bar{z}$
			(5) z,x,y	(6) $z,\bar{x},\bar{y}$	(7) $\bar{z},\bar{x},y$	(8) $\bar{z},x,\bar{y}$
			(9) y,z,x	(10) $\bar{y},z,\bar{x}$	(11) $y,\bar{z},\bar{x}$	(12) $\bar{y},\bar{z},x$
			(13) $y,x,\bar{z}$	(14) $\bar{y},\bar{x},\bar{z}$	(15) $y,\bar{x},z$	(16) $\bar{y},x,z$
			(17) $x,z,\bar{y}$	(18) $\bar{x},z,y$	(19) $\bar{x},\bar{z},\bar{y}$	(20) $x,\bar{z},y$
			(21) $z,y,\bar{x}$	(22) $z,\bar{y},x$	(23) $\bar{z},y,x$	(24) $\bar{z},\bar{y},\bar{x}$
			(25) $\bar{x},\bar{y},\bar{z}$	(26) $x,y,\bar{z}$	(27) $x,\bar{y},z$	(28) $\bar{x},y,z$
			(29) $\bar{z},\bar{x},\bar{y}$	(30) $\bar{z},x,y$	(31) $z,x,\bar{y}$	(32) $z,\bar{x},y$
			(33) $\bar{y},\bar{z},\bar{x}$	(34) $y,\bar{z},x$	(35) $\bar{y},z,x$	(36) $y,z,\bar{x}$
			(37) $\bar{y},\bar{x},z$	(38) y,x,z	(39) $\bar{y},x,\bar{z}$	(40) $y,\bar{x},\bar{z}$
			(41) $\bar{x},\bar{z},y$	(42) $x,\bar{z},\bar{y}$	(43) x,z,y	(44) $\bar{x},z,\bar{y}$
			(45) $\bar{z},\bar{y},x$	(46) $\bar{z},y,\bar{x}$	(47) $z,\bar{y},\bar{x}$	(48) z,y,x

192 points on the general position

12 atoms in the cell from two rows

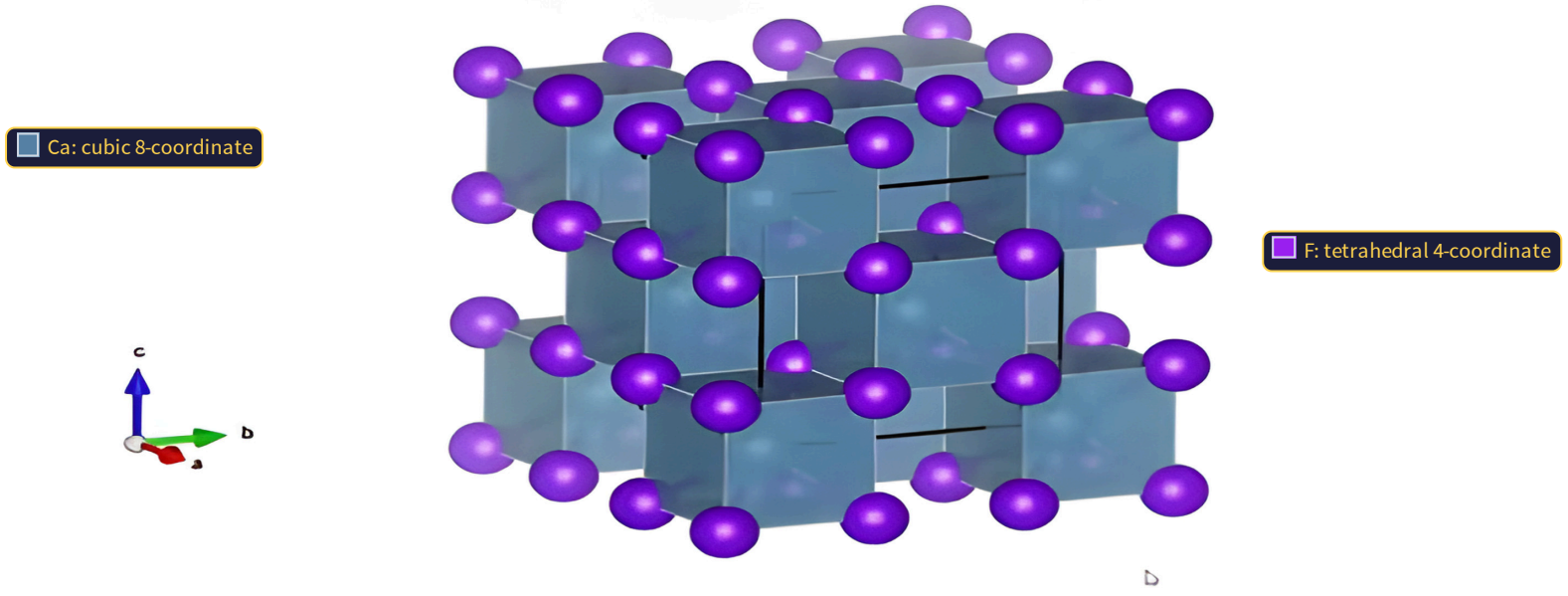
8	c	$\bar{4}\,3\,m$	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{1}{4},\frac{3}{4}$
4	b	$m\,\bar{3}\,m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	
4	a	$m\,\bar{3}\,m$	0,0,0	

8 F on 8c

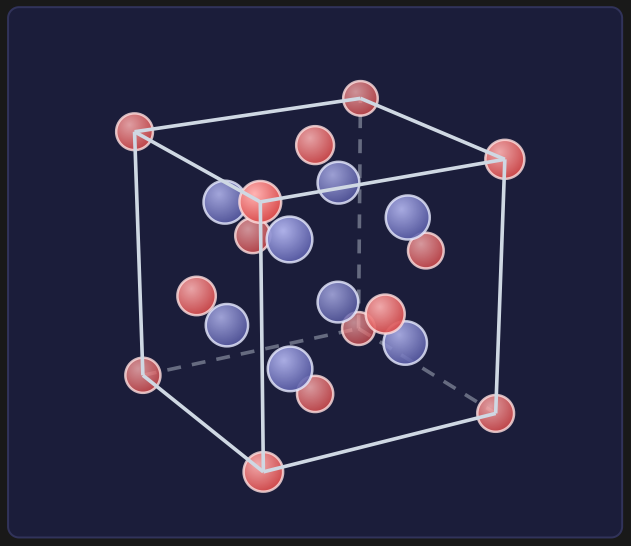
4 Ca on 4a

International Tables for Crystallography, Vol. A, entry No. 225, pp. 664, 666.

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



The fluorite cell. Four calcium per cell, red, on the face-centered sites and eight fluoride, blue, in the tetrahedral holes.

Ca on 4a: 4

F on 8c: 8

Z = 4, so 4 Ca + 8 F

The Wyckoff multiplicities give the cell contents.

Density is the mass of the atoms in the cell over the cell volume. From the Wyckoff multiplicities the cell holds four CaF_2: 4 Ca and 8 F.

$$\text{mass} = 4(40.08) + 8(19.00) = 312.32 \text{ amu} = \frac{312.32}{6.022 \times 10^{23}} \text{ g} = 5.186 \times 10^{-22} \text{ g}$$

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

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

Water is 1 g/cm^3 and the densest elements are near 20 g/cm^3, so 3.19 is a reasonable density for a mineral.

CRYSTAL STRUCTURE DRAWING PROGRAMS

VESTA free, and the program we use in this course

jp-minerals.org/vesta/en/

Diamond commercial

crystalimpact.com/diamond/

CrystalMaker commercial

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, and Wyckoff positions + fractional coordinates of unique atoms.

Case study: Calcium Fluoride (CaF_2)

Space group **Fm-3m (#225)**, cubic, a = 5.46 Å; Ca at Wyckoff 4a (0,0,0), F at 8c (¼,¼,¼).

Multiplicities & centering operations generate all atoms in the unit cell. Ca in a cubic (octahedral) environment; F in a tetrahedral environment.

Density and tools

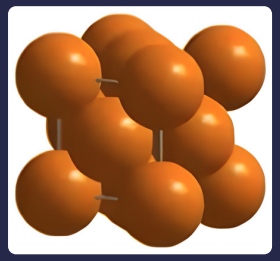
4 CaF_2 units per cell → 4 Ca + 8 F = 312.32 amu = 5.19×10^{-22} g; cell volume $(5.46 \times 10^{-8}\ \text{cm})^3 = 1.63 \times 10^{-22}\ \text{cm}^3$; density = **3.19 g/cm³**.

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

LEARNING OBJECTIVES

Three classes	sort an extended solid into the metallic, ionic, or covalent-network class from its bonding and its structure
Packing in a plane	explain the densest packing of atoms in one plane and how it extends into three dimensions
HCP versus CCP	tell hexagonal close packing from cubic close packing by the ABAB and ABCABC stacking sequences
Metallic unit cells	describe the FCC, BCC, and primitive cubic cells and compare their coordination numbers and packing efficiencies
Periodic trends	recognize how the preferred metal structure varies across the periodic table and how it follows bonding and band filling
Variations	identify other stackings such as ABAC, ordered compounds such as CsCl and Cu_3Au, and high-coordination structures such as $SmCo_5$

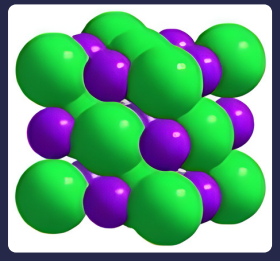
EXTENDED SOLIDS



Metallic Solids (Al, Fe, ...)

Bonding: Atoms held together by delocalized metallic bonding

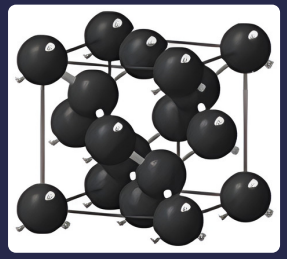
Structural Attributes: Closely packed atoms (large coordination numbers, symmetric structures)



"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

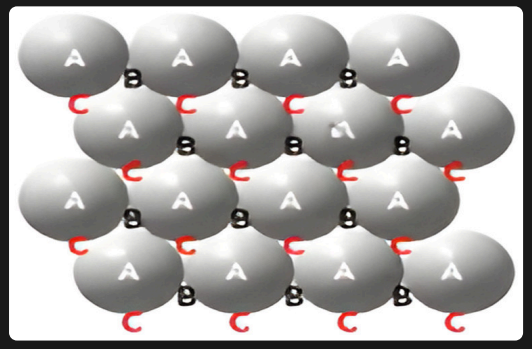


Covalent-Network Solids (WO_3, C, SiO_2, ...)

Bonding: Extended networks of atoms held together by covalent bonds

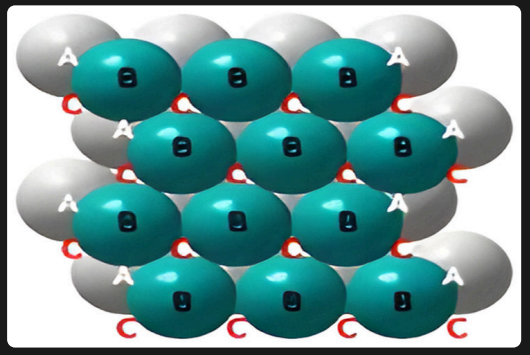
Structural Attributes: Lower coordination numbers and densities than metallic and ionic solids

CLOSE PACKED STRUCTURES

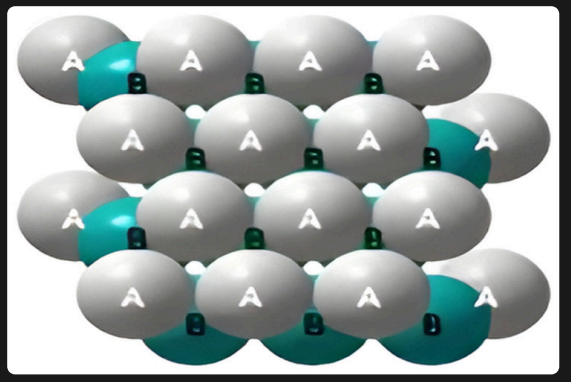


Spheres form a close packed hexagonal layer

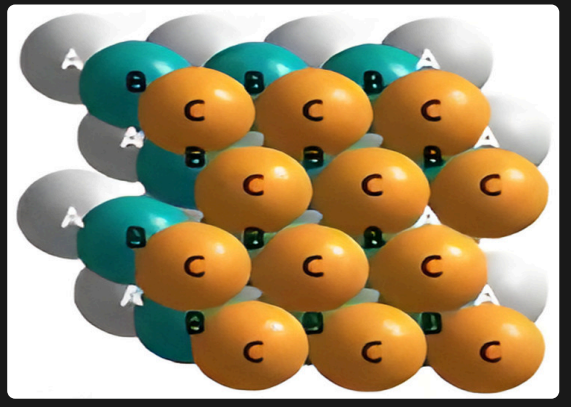
→



Second layer sits in the depressions marked B

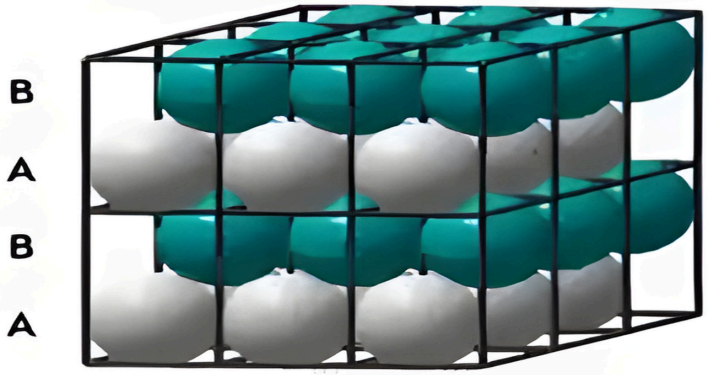


Hexagonal close packing (ABAB…)
third layer directly over the first

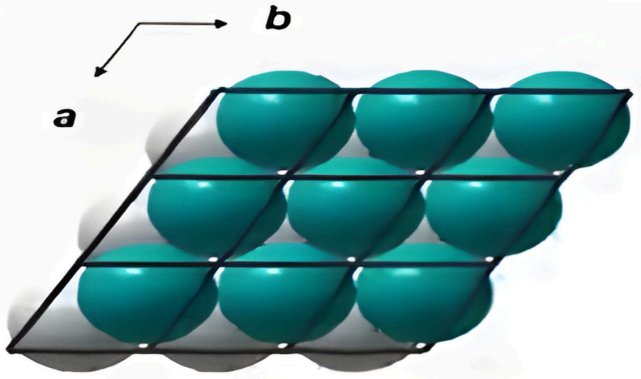


Cubic close packing (ABCABC…)
third layer in the depressions marked C

Hexagonal Close Packed Metal



Layer packing view



top view

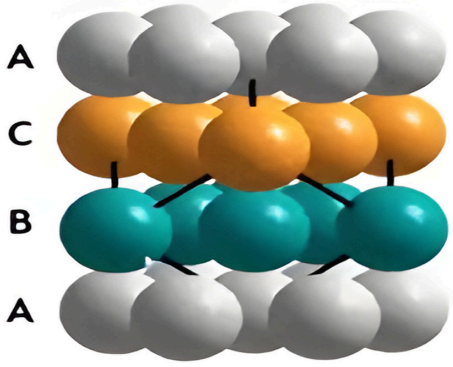
Example: Mg
Space Group: $P6_3/mmc$ (#194)
Unit Cell: a = 3.21 Å, c = 5.21 Å

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

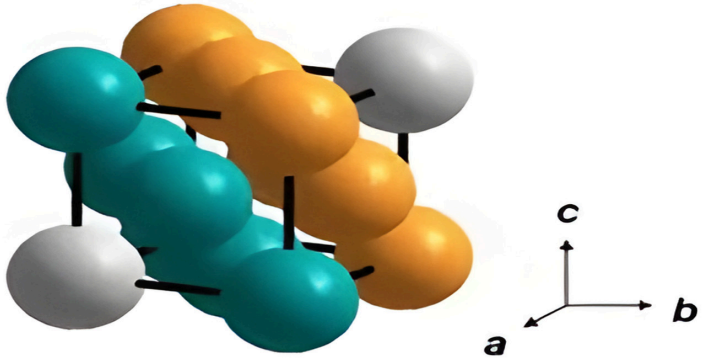
Note: Different colors are used to show layers, all atoms are equivalent

CN 12 · 74% packed

Cubic Close Packed Metal



Layer packing view



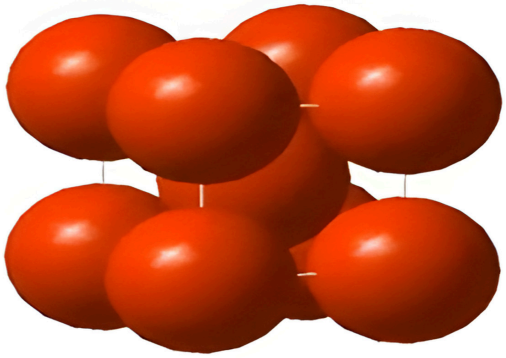
Example: Cu
Space Group: $Fm\bar{3}m$ (#225)
Unit Cell: a = 3.62 Å

	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

CN 12 · 74% packed

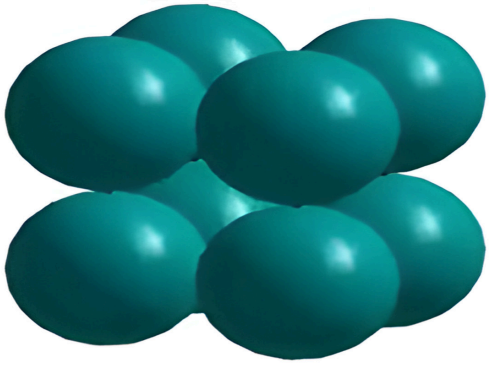
Body-centered cubic metal



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

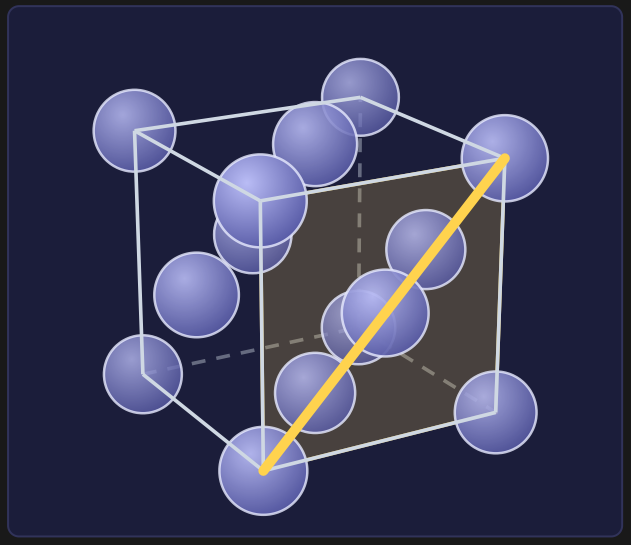
	Wyckoff Site	x	y	z
Po	1a ($m\bar{3}m$)	0	0	0

CN 8 · 68% packed

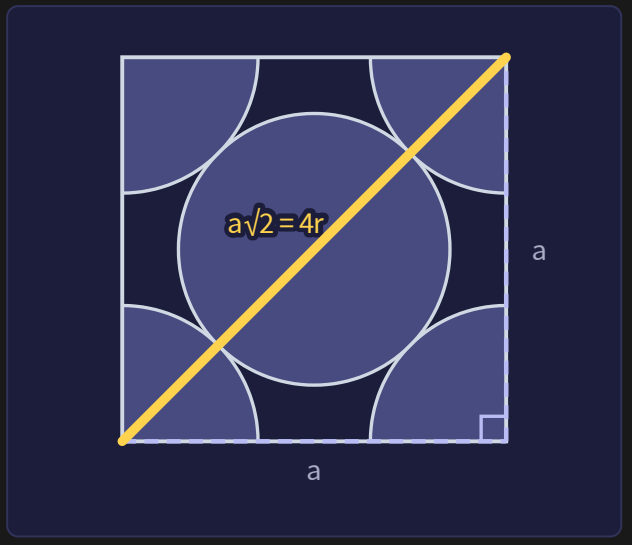
CN 6 · 52% packed

Structure	Nearest neighbors	Space filled
Cubic close packed	12	74%
Hexagonal close packed	12	74%
Body-centered cubic	8	68%
Primitive cubic	6	52%

HOW FULL IS CUBIC CLOSE PACKING?



The face-centered cubic cell with the atoms drawn small. The gold plane is the face shown at the right.



The face at true size. The corner atoms touch the face-center atom.

The face is a square of side a, so the diagonal is $d^2 = a^2 + a^2 = 2a^2$ and $d = a\sqrt{2}$.

The atoms touch along the diagonal, so $4r = a\sqrt{2}$ and $r = a\sqrt{2}/4$. The cell holds four atoms.

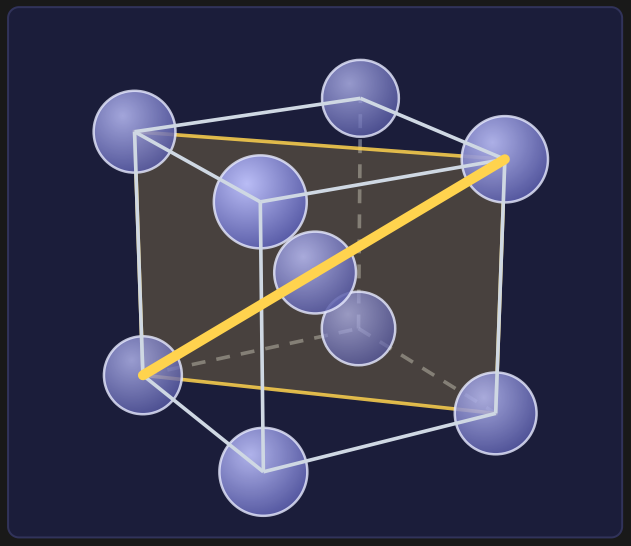
Cube the radius: $r^3 = \left(\frac{a\sqrt{2}}{4}\right)^3 = \frac{2\sqrt{2}}{64}\,a^3 = \frac{\sqrt{2}}{32}\,a^3.$

$$\frac{4 \cdot \frac{4}{3}\pi r^3}{a^3} = \frac{4 \cdot \frac{4}{3}\pi \cdot \frac{\sqrt{2}}{32}\cancel{a^3}}{\cancel{a^3}} = \frac{\pi\sqrt{2}}{6} = 74\%$$

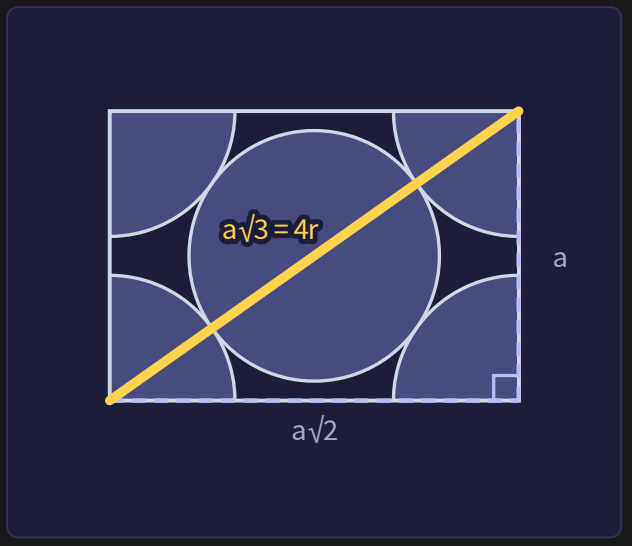
Hexagonal close packing has the same contacts and also gives 74%.

cubic close packed · 74% | body-centered | primitive

HOW FULL IS BODY-CENTERED CUBIC?



The body-centered cubic cell. The gold plane is the diagonal section shown at the right.



The section at true size, $a\sqrt{2}$ by a. The corner atoms touch the center atom.

The face diagonal is $f^2 = a^2 + a^2 = 2a^2$. The body diagonal is the hypotenuse of the triangle with legs f and a, so $d^2 = 2a^2 + a^2 = 3a^2$ and $d = a\sqrt{3}$.

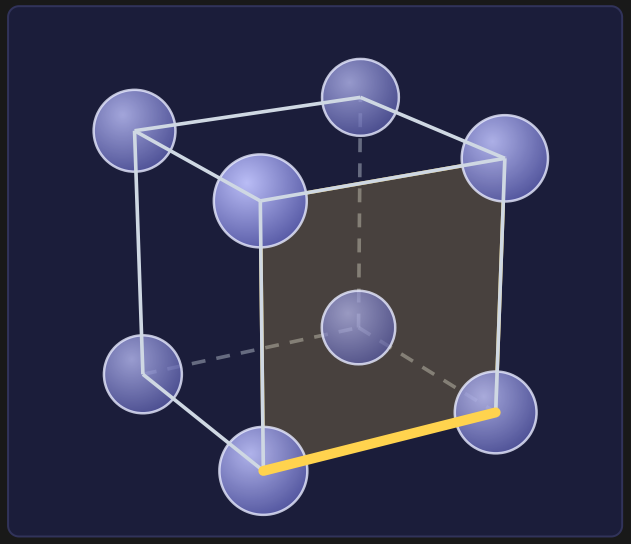
The atoms touch along the body diagonal, not across the face, so $4r = a\sqrt{3}$ and $r = a\sqrt{3}/4$. The cell holds two atoms.

Cube the radius: $r^3 = \left(\frac{a\sqrt{3}}{4}\right)^3 = \frac{3\sqrt{3}}{64}\,a^3$.

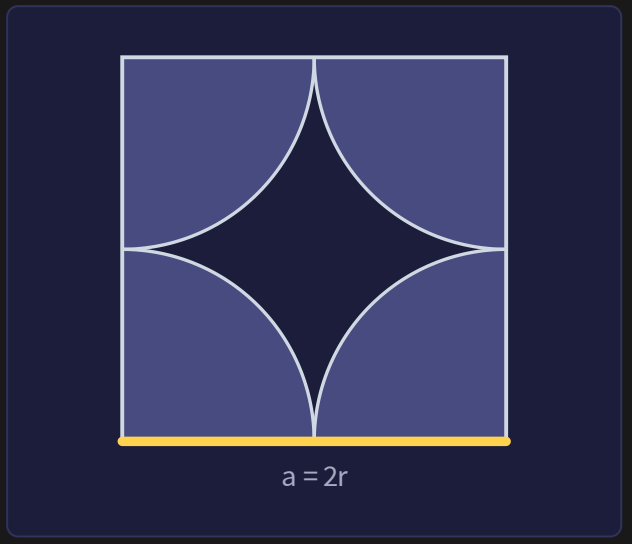
$$\frac{2 \cdot \frac{4}{3}\pi r^3}{a^3} = \frac{2 \cdot \frac{4}{3}\pi \cdot \frac{3\sqrt{3}}{64}\cancel{a^3}}{\cancel{a^3}} = \frac{\pi\sqrt{3}}{8} = 68\%$$

cubic close packed · 74% | body-centered · 68% | primitive

HOW FULL IS PRIMITIVE CUBIC?



The primitive cubic cell, corner atoms only. The gold plane is the face shown at the right.



The face at true size. The corner atoms touch along the edge.

The atoms touch along the cell edge, so there is no triangle to solve.

The edge is two radii, so $2r = a$ and $r = a/2$. The cell holds one atom.

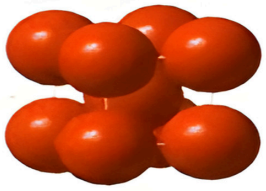
Cube the radius: $r^3 = \left(\frac{a}{2}\right)^3 = \frac{a^3}{8}$.

$$\frac{1 \cdot \frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi \cdot \frac{1}{8}\cancel{a^3}}{\cancel{a^3}} = \frac{\pi}{6} = 52\%$$

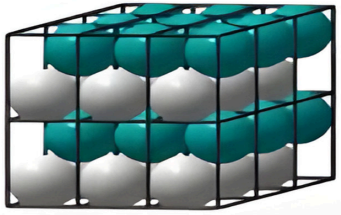
cubic close packed · 74% | body-centered · 68% | primitive · 52%

Structures of Elemental Metals

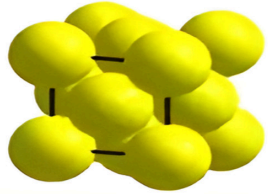
Li	Be											Al
Na	Mg											
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl



Body Centered Cubic

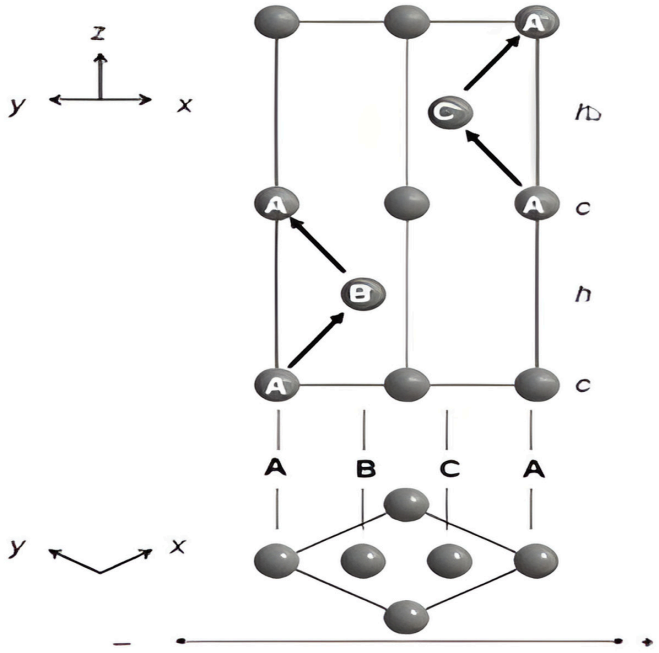


Hexagonal close packing



Face Centered Cubic

Mixed Hexagonal-Cubic Stacking



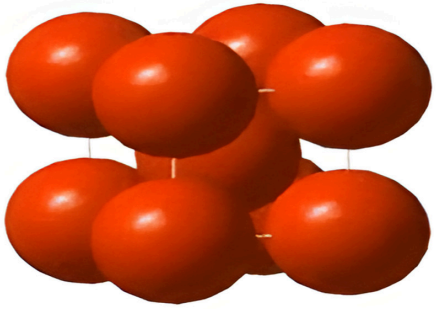
Ramsdell symbol: 4H
Jagodzinski–Wyckoff notation: $(hc)_2$

ICSD #102655
P6₃/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

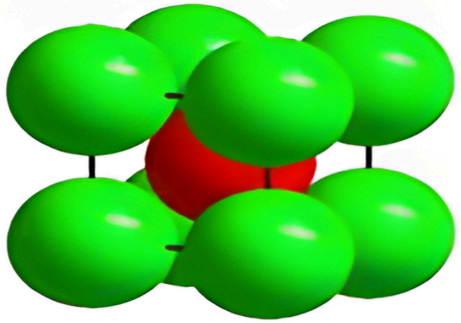
Intermetallic Compounds

ordered variants



Body-centered cubic metal

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

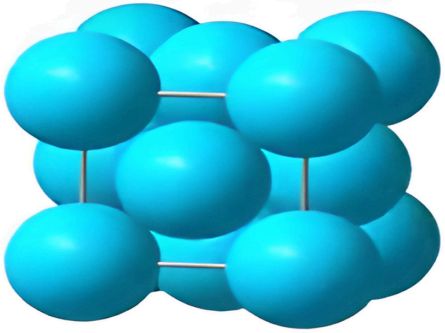


CsCl Structure

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

Examples

CuZn
LaAg
MgAu
CoAl
PdIn
CdPr



Face-centered cubic metal

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



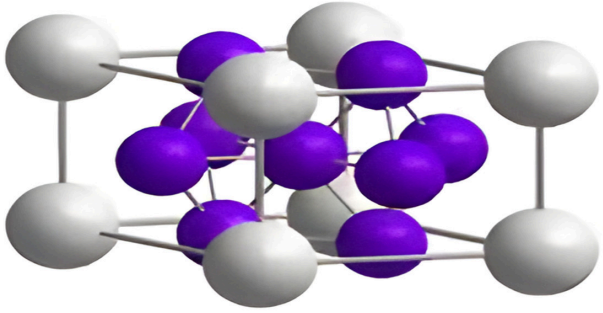
Cu_3Au Structure

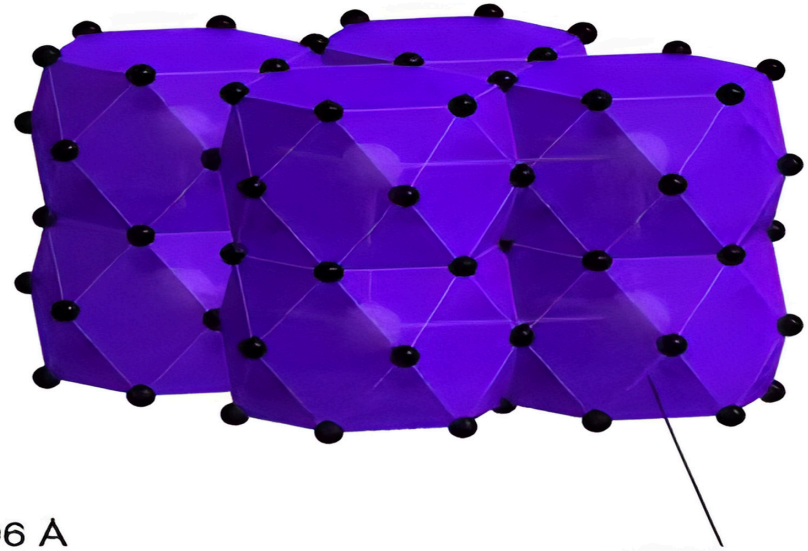
Space Group: $Pm\bar{3}m$

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 SOLIDS

Three classes

Metallic, ionic, and covalent-network solids differ in what holds the atoms together, and that bonding sets the structure. Delocalized electrons pack atoms densely at high coordination numbers, electrostatic attraction builds symmetric structures that keep like charges apart, and localized covalent bonds give the lowest coordination numbers and densities.

Metallic unit cells

Structure	Stacking	Nearest neighbors	Space filled
Cubic close packed (FCC)	ABCABC	12	74%
Hexagonal close packed	ABAB	12	74%
Body-centered cubic	not close packed	8	68%
Primitive cubic	not close packed	6	52%

Variations and intermetallics

Lanthanum and other rare earths stack ABAC, as densely as either simple sequence: Ramsdell symbol 4H, Jagodzinski-Wyckoff notation $(hc)_2$. Ordering two metals on one framework gives CsCl-type PdIn and MgAu from BCC, and Cu_3Au from FCC. $SmCo_5$ puts 18 cobalt neighbors around each samarium.

What decides the structure

Band filling and the details of metallic bonding decide it, not packing efficiency alone. BCC is about as common among the elements as either close packing.

IONIC STRUCTURES

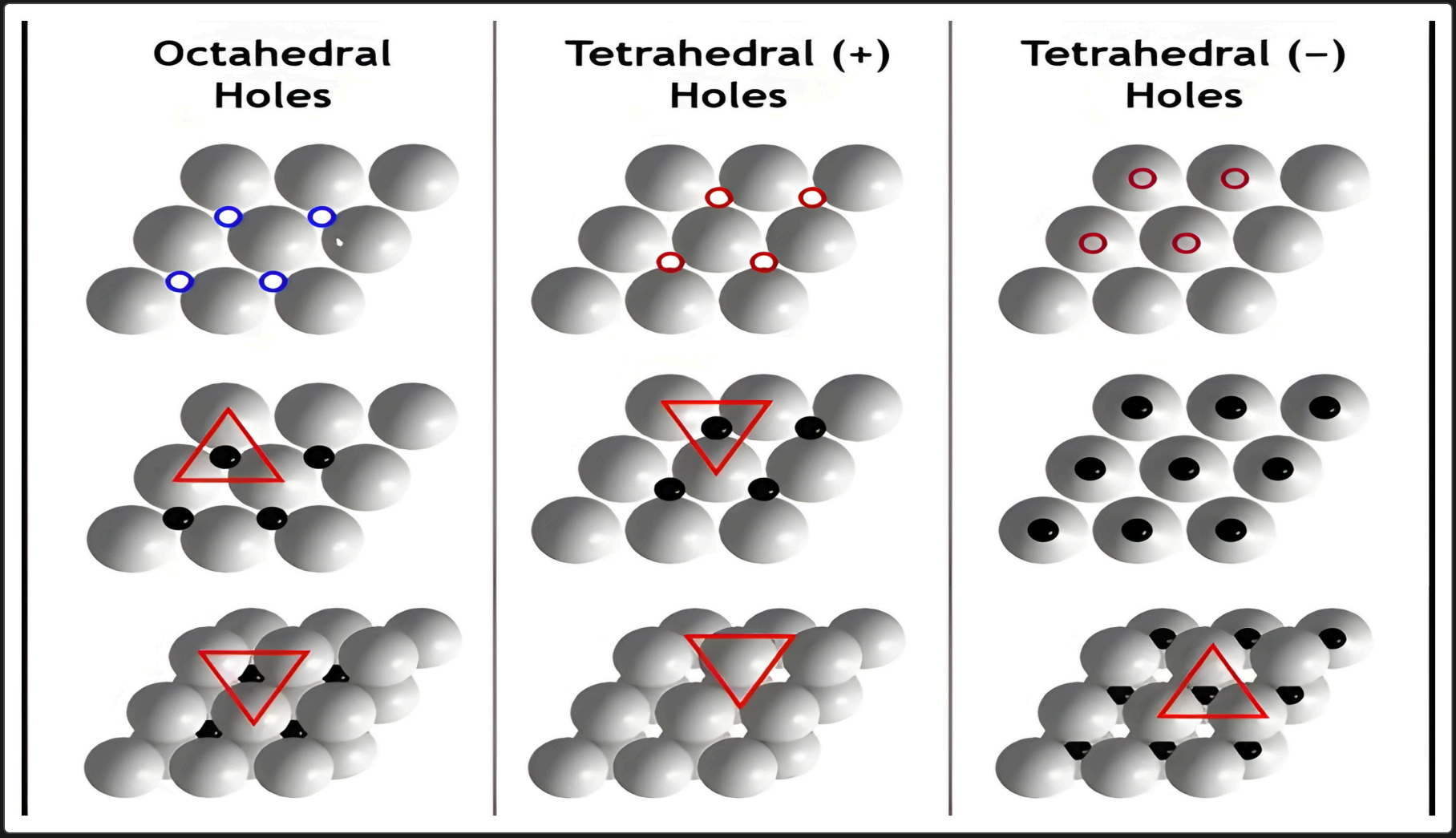
Many ionic structure types can be described as a close packing of anions with cations filling voids or holes in the structure. Generally we will consider two types of holes (for the cations)

- **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)]

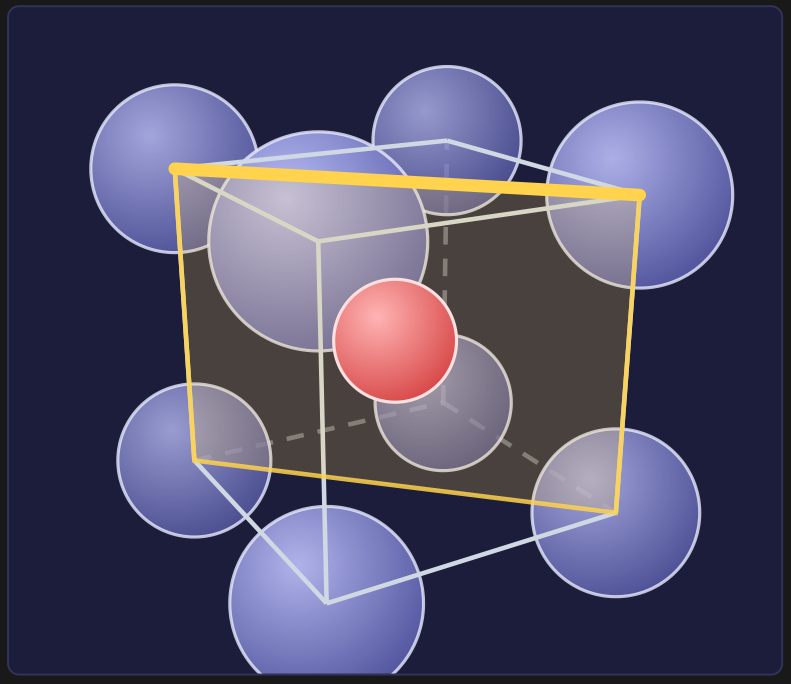
OCTAHEDRAL AND TETRAHEDRAL HOLES



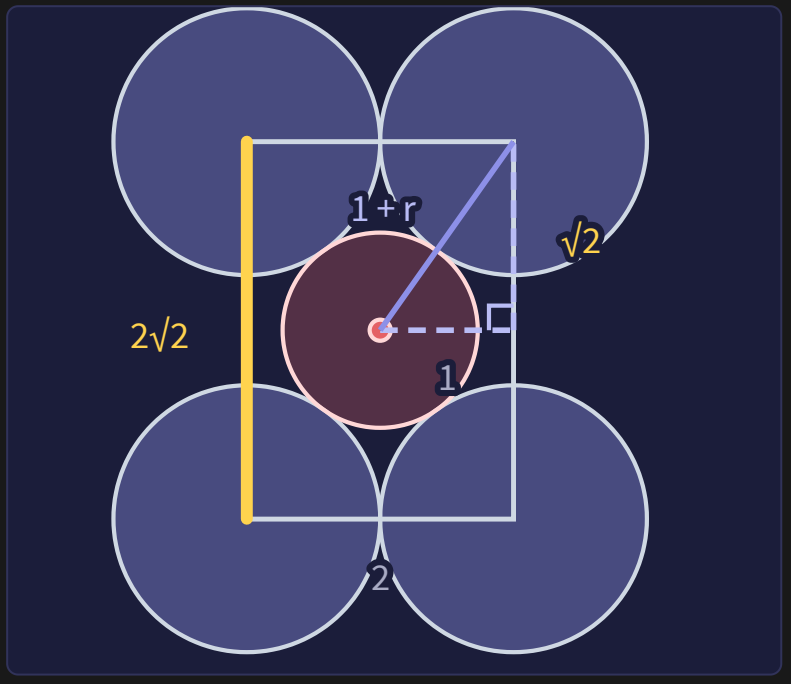
Every anion has **two** tetrahedral holes, one pointing up and one pointing down, against **one** octahedral hole.

HOW BIG A CATION FITS A CUBE OF 8?

Anion radius = 1. All lengths run between ion centers.



Cut vertically through the gold face diagonal.



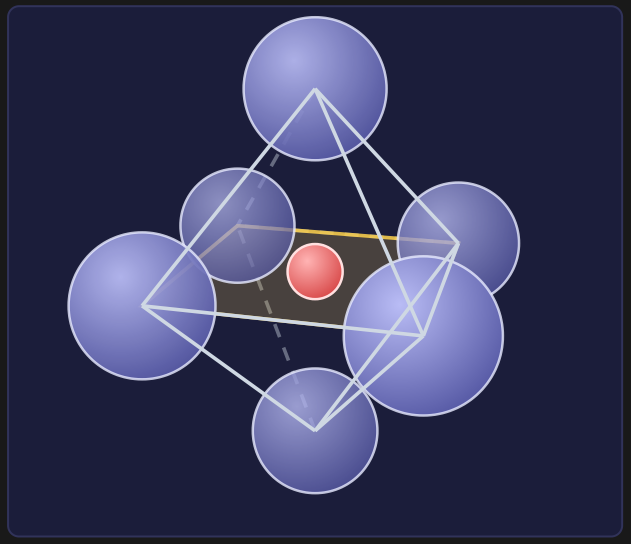
At contact, the center-to-corner distance is 1 + r.

$$1 + r = \sqrt{1^2 + (\sqrt{2})^2} = \sqrt{3}$$

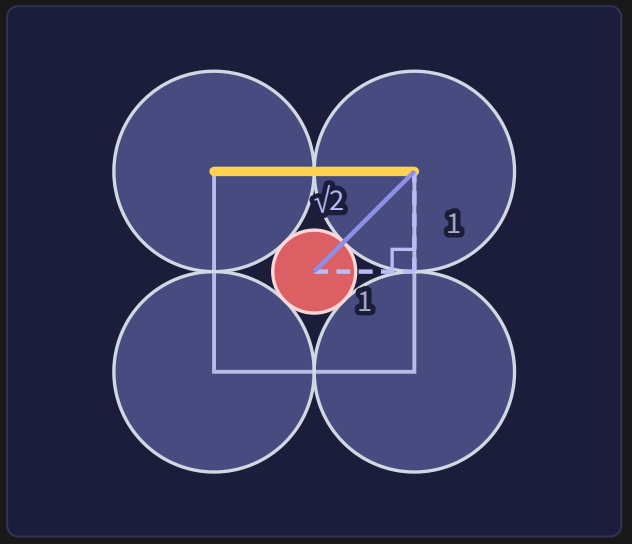
$$r = \sqrt{3} - 1 = 0.732$$

cube of 8 | octahedron of 6 | tetrahedron of 4

HOW BIG A CATION FITS AN OCTAHEDRON OF 6?



Six anions at the corners of an octahedron with the cation at the center.



The square of four anions at true size. The other two sit above and below the plane.

Four of the six anions form a square of edge 2. From the cation to a corner is half an edge across, 1, and half an edge up, 1, so the distance is $\sqrt{1^2 + 1^2} = \sqrt{2}$.

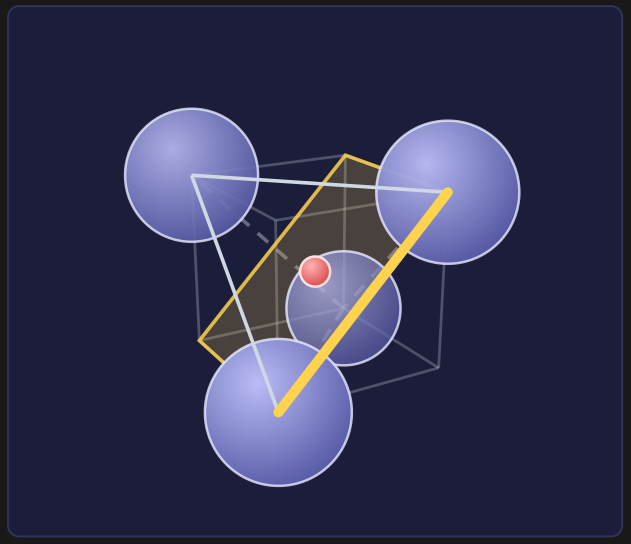
The anion takes 1 of that $\sqrt{2}$ and the cation takes the rest.

$$r = \sqrt{2} - 1 = 0.414$$

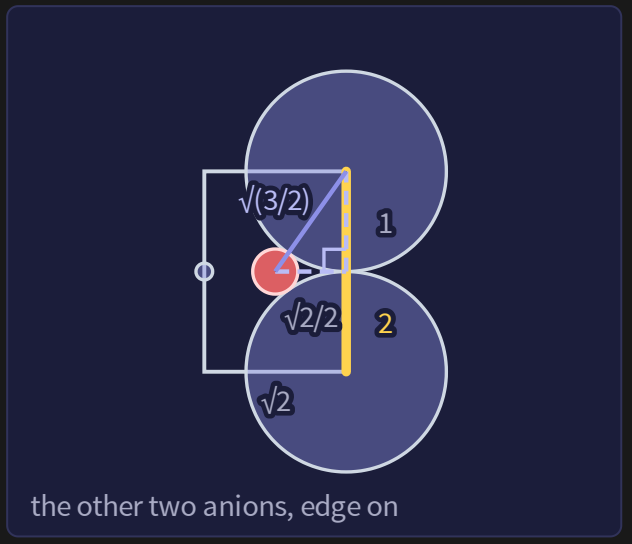
sodium in the NaCl structure

cube of 8 · 0.732 | octahedron of 6 · 0.414 | tetrahedron of 4

HOW BIG A CATION FITS A TETRAHEDRON OF 4?



Four anions on alternate corners of a cube. The gold plane is the diagonal section shown at the right.



The gold diagonal section at true size, √2 by 2. Two anions and the cation lie in it. The other two anions touch it at the dot.

The anions sit on alternate corners of a cube and touch along its face diagonals, so the face diagonal is 2 and the cube edge follows from $e^2 + e^2 = 2^2, e = \sqrt{2}$.

In the diagonal section, from the cube centre to an anion centre is half a cube edge across, $\sqrt{2}/2$, and half a face diagonal up, 1, so the distance is $\sqrt{(\sqrt{2}/2)^2 + 1^2} = \sqrt{3/2}$.

The anion takes 1 of that $\sqrt{3/2}$ and the cation takes the rest.

$$r = \sqrt{3/2} - 1 = 0.225$$

zinc in sphalerite

These are the largest cations the three holes hold. Charge and ionicity also decide the structure.

cube of 8 · 0.732 | octahedron of 6 · 0.414 | tetrahedron of 4 · 0.225

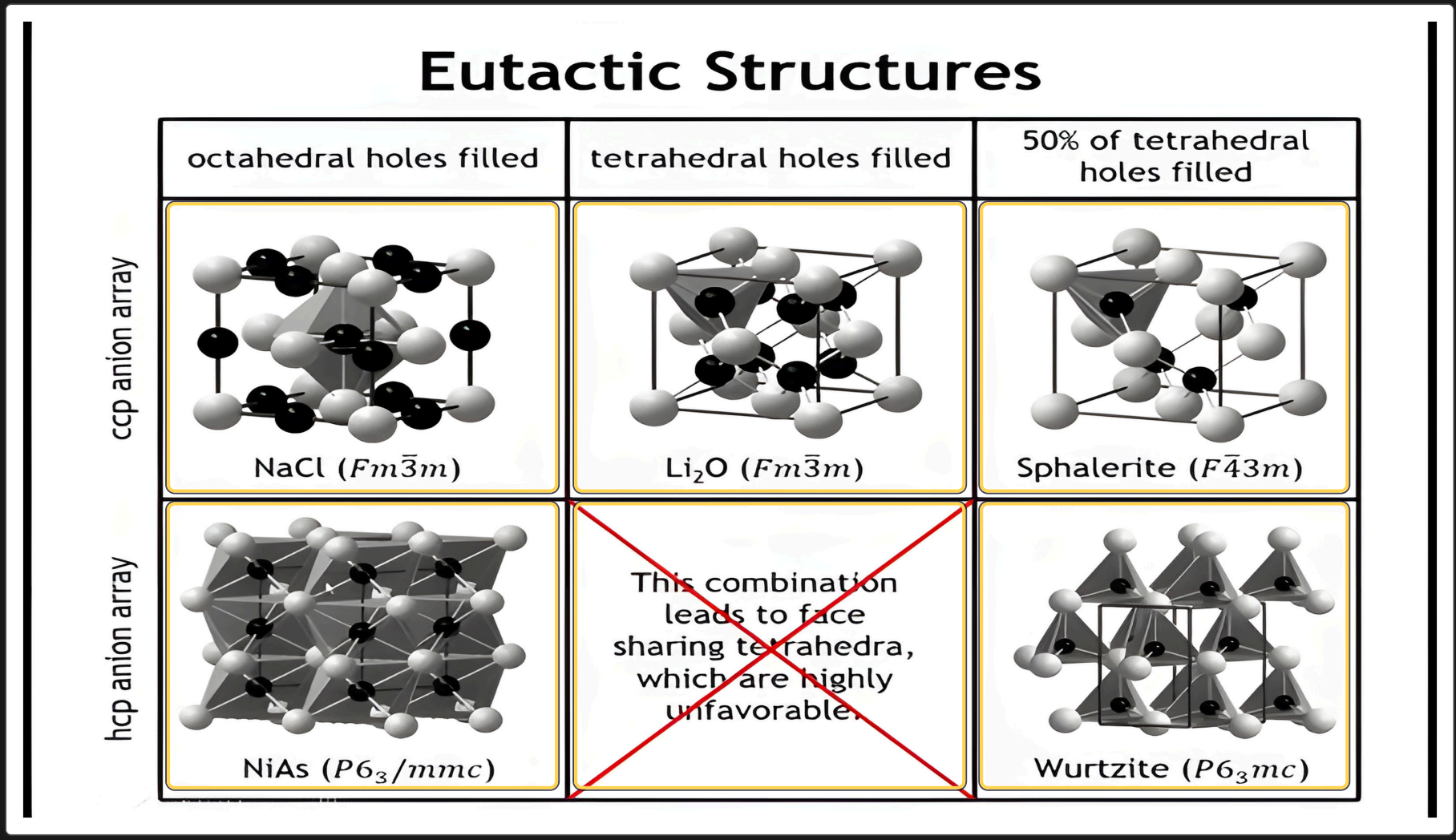
HOLE FILLING AND STRUCTURE TYPE

Two sets of holes to fill, two ways to pack the anions.

Hole filling in total	General formula	Structure type hcp of anions	Structure type ccp of anions	The plane-filling sequence
all octahedral	CA	NiAs nickel arsenide	NaCl sodium chloride	all full
½	CA_2	CdI_2 cadmium iodide	$CdCl_2$ cadmium chloride	empty and full
½	CA_2	$CaCl_2$ calcium chloride		all ½ full
⅓	CA_3	BiI_3 bismuth iodide	YCl_3 yttrium chloride	empty and ⅔ full
⅓	CA_3	$RuBr_3$ ruthenium bromide		all ⅓ full
⅔	C_2A_3		La_2O_3 lanthanum oxide	empty, full, full
⅔	C_2A_3	Al_2O_3 aluminum oxide		all ⅔ full
all tetrahedral	C_2A	not possible	Li_2O lithium oxide	all full
½	CA	ZnS zinc sulfide wurtzite	ZnS zinc sulfide sphalerite	all ½ full

EUTACTIC STRUCTURES

The same structures as unit cells, including the one no compound takes.

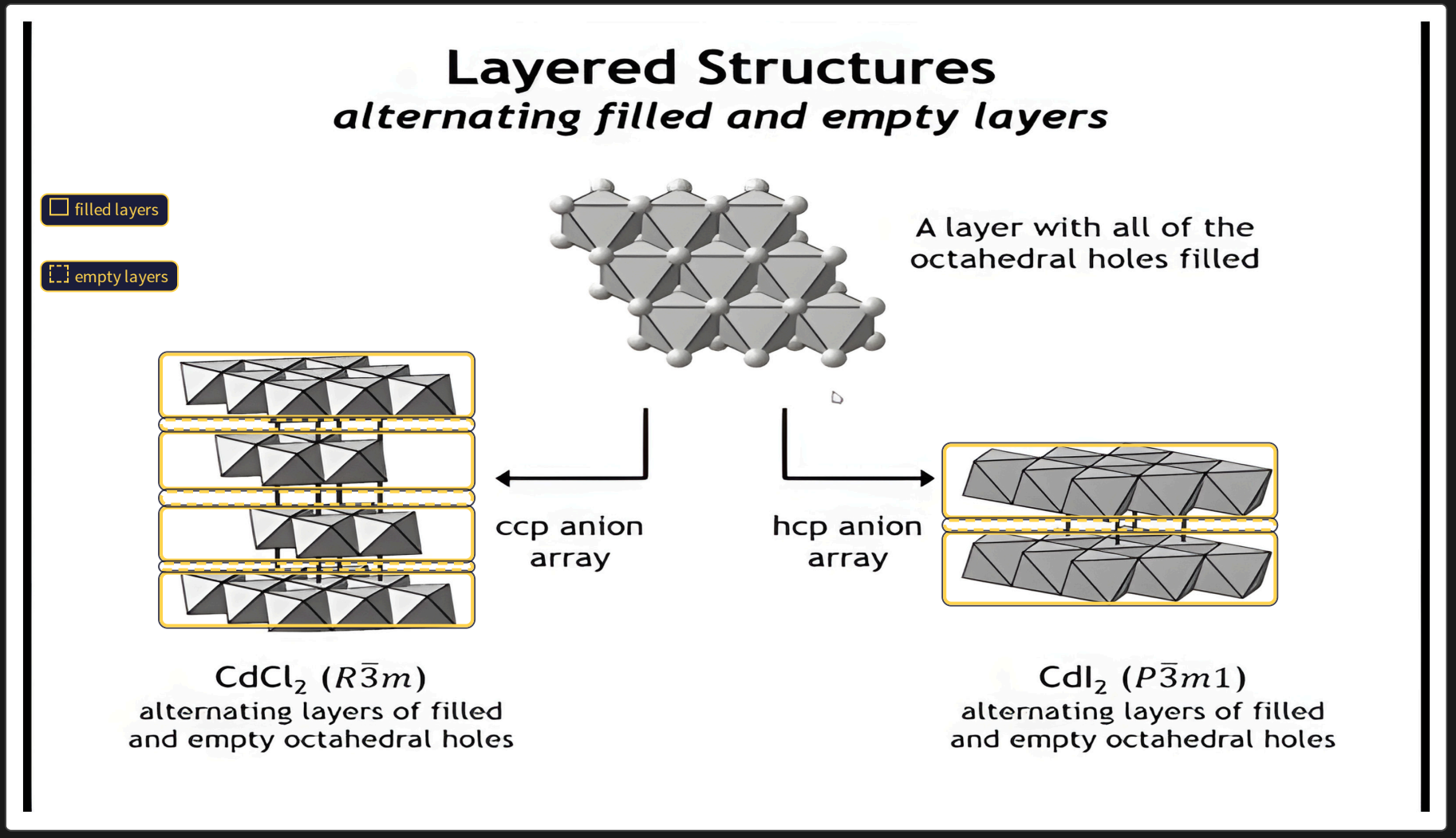


FILLING ONLY SOME OF THE HOLES

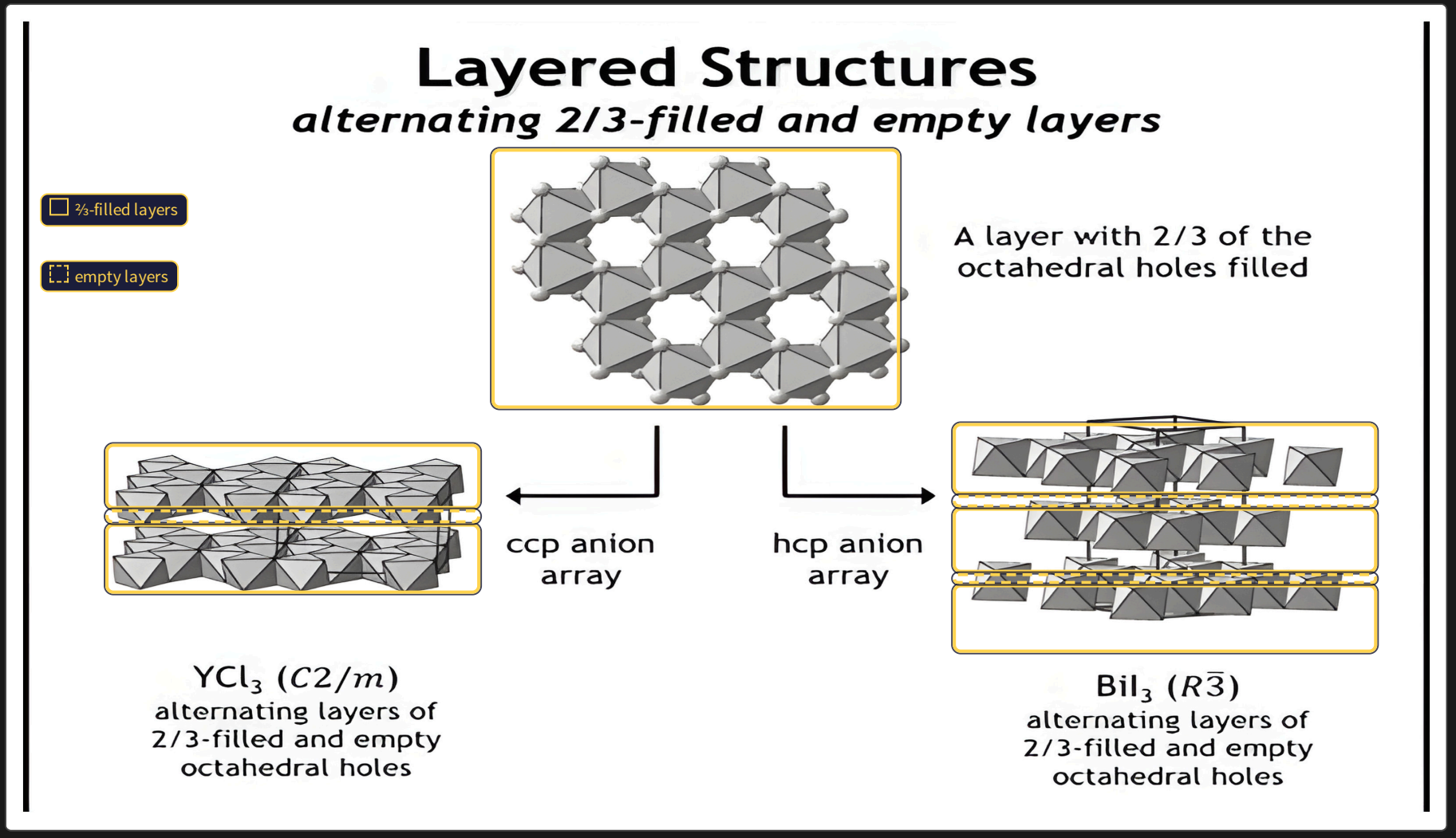
The same total fraction, reached two ways: evenly through every plane, or whole planes on and off.

Hole filling in total	General formula	Structure type hcp of anions	Structure type ccp of anions	The plane-filling sequence
all octahedral	CA	NiAs nickel arsenide	NaCl sodium chloride	all full
½	CA_2	CdI_2 cadmium iodide	$CdCl_2$ cadmium chloride	empty and full
½	CA_2	$CaCl_2$ calcium chloride		all ½ full
⅓	CA_3	BiI_3 bismuth iodide	YCl_3 yttrium chloride	empty and ⅔ full
⅓	CA_3	$RuBr_3$ ruthenium bromide		all ⅓ full
⅔	C_2A_3		La_2O_3 lanthanum oxide	empty, full, full
⅔	C_2A_3	Al_2O_3 aluminum oxide		all ⅔ full
all tetrahedral	C_2A	not possible	Li_2O lithium oxide	all full
½	CA	ZnS zinc sulfide wurtzite	ZnS zinc sulfide sphalerite	all ½ full

LAYERED STRUCTURES: FILLED AND EMPTY LAYERS



LAYERED STRUCTURES: TWO-THIRDS-FILLED LAYERS

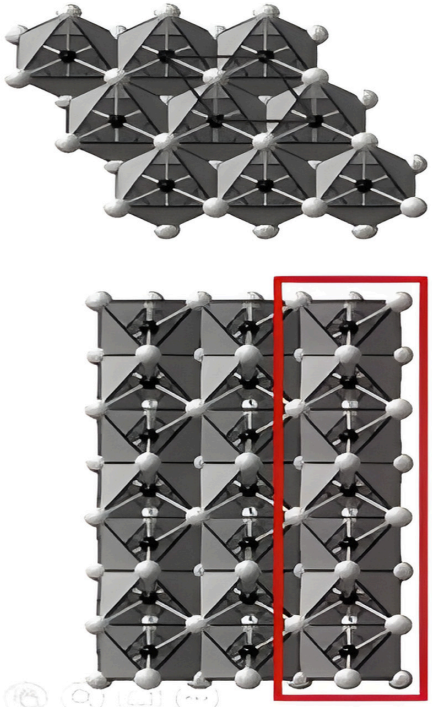


NIAS VERSUS CORUNDUM

NiAs Structure

Space Group: $P6_3/mmc$

hcp anion array with 100% of the octahedral holes filled

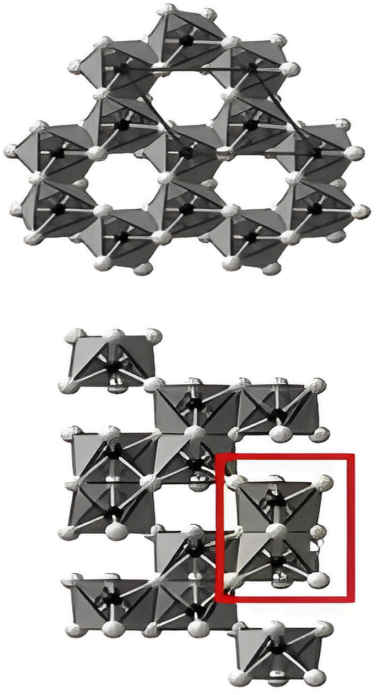


Infinite chains of face-sharing octahedra

Corundum Structure

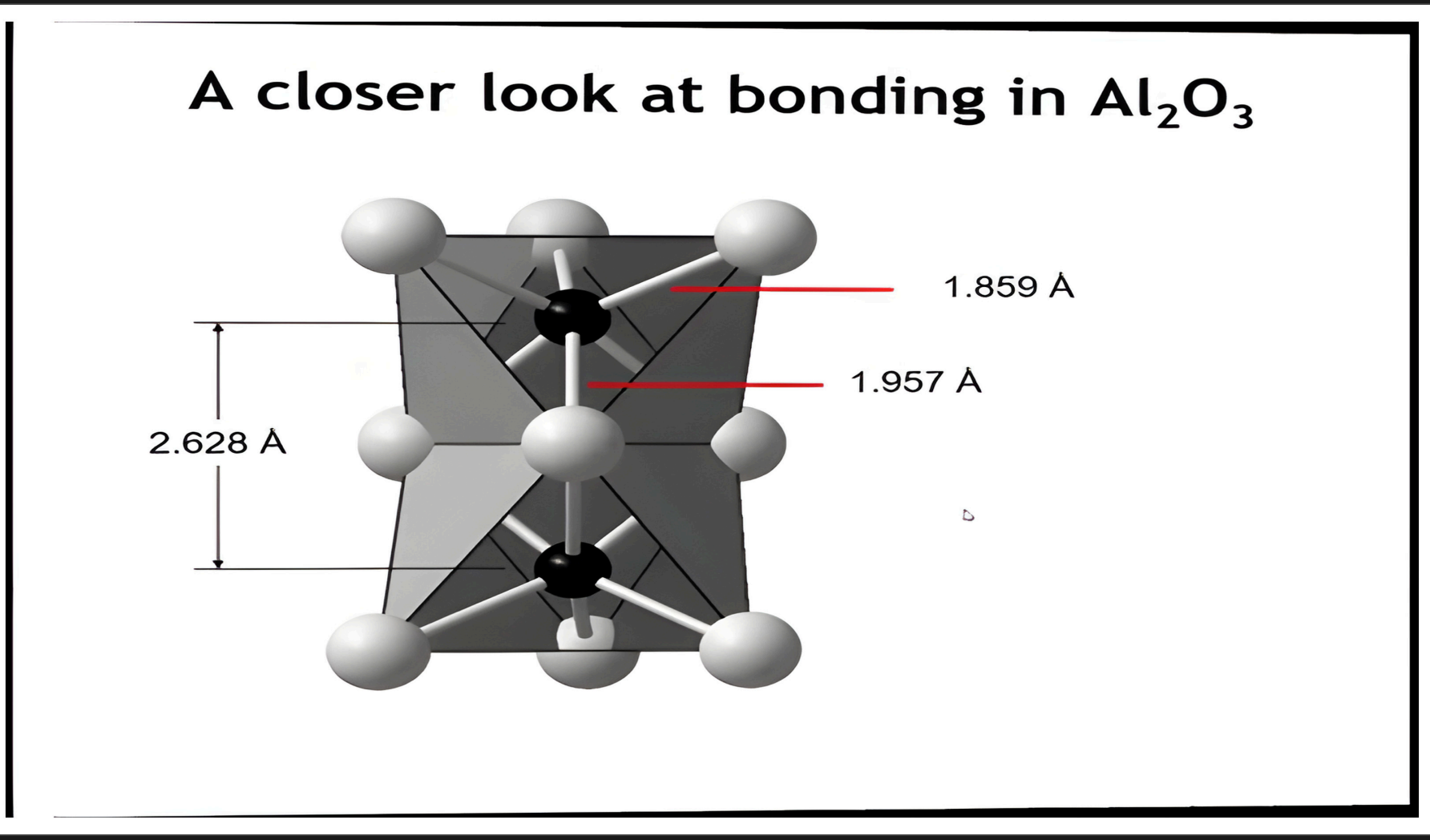
Space Group: $R\text{-}3c$

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

One question, asked once: which holes do the cations take, and how many of them?

Holes filled	Formula	hcp anion array	ccp anion array
all octahedral	CA	NiAs nickel arsenide	NaCl sodium chloride
½ octahedral, spread evenly	CA_2	$CaCl_2$ calcium chloride	—
½ octahedral, whole layers	CA_2	CdI_2 cadmium iodide	$CdCl_2$ cadmium chloride
⅔ of every filled layer	CA_3	BiI_3 bismuth iodide	YCl_3 yttrium chloride
⅔ octahedral	C_2A_3	Al_2O_3 aluminum oxide corundum	La_2O_3 lanthanum oxide
all tetrahedral	C_2A	not possible	Li_2O lithium oxide anti-fluorite
½ tetrahedral	CA	ZnS zinc sulfide wurtzite	ZnS zinc sulfide sphalerite

Which one a compound picks depends on cation size, charge, and ionicity: highly ionic systems avoid face-sharing polyhedra, layered and covalent ones tolerate them.

PRACTICE QUESTIONS

Work the Lecture 4 practice questions before the next class.

Open the Lecture 4 practice questions

Every question carries a worked explanation, so you can check your reasoning as you go.