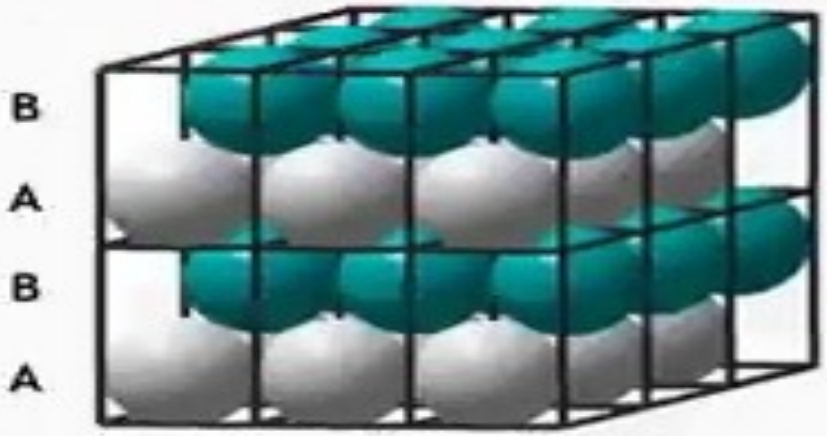
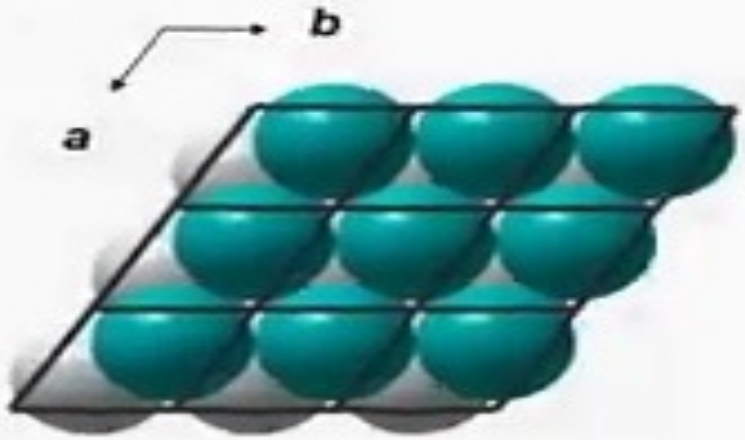
Hexagonal Close Packed Metal



Layer packing view



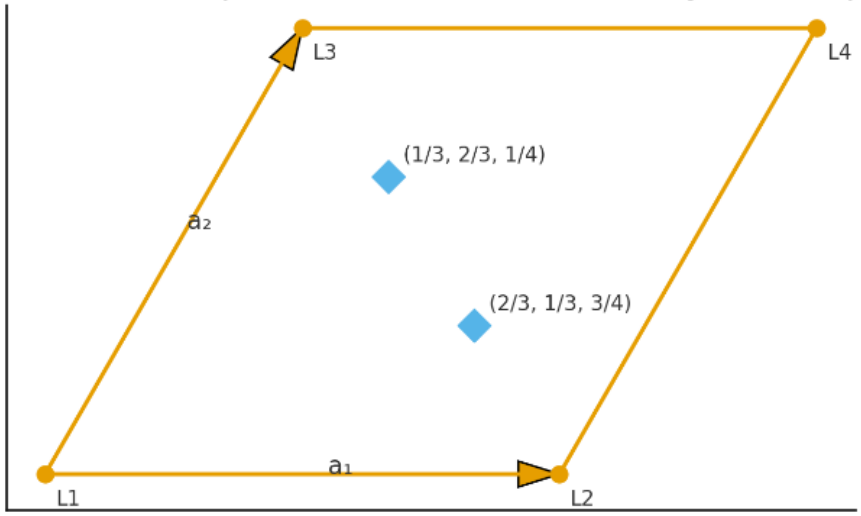
top view

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

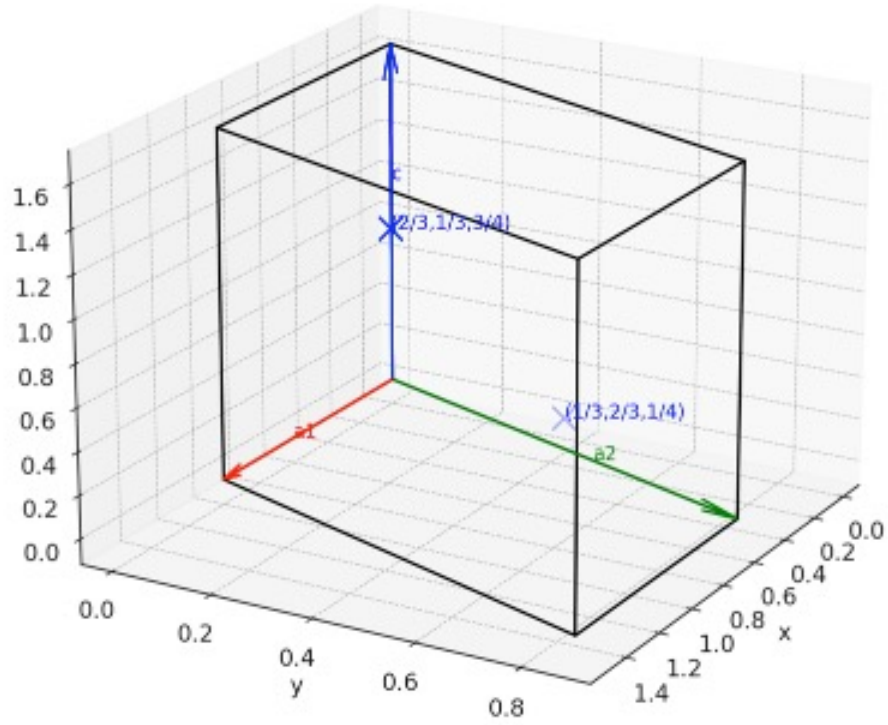
	Wyckoff Site	x	y	z
Mg	2a ($\bar{6}m2$)	1/3	2/3	1/4

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

hcp ($P6_3/mmc$) basal plane: standard a_1,a_2 and Wyckoff 2c positions



hcp unit cell ($P6_3/mmc$) with Wyckoff 2c sites



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

2	*c*	$\bar{6}m2$	$\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$	$\frac{2}{3}, \frac{1}{3}, \frac{3}{4}$
2	*b*	$\bar{6}m2$	$0, 0, \frac{1}{4}$	$0, 0, \frac{3}{4}$
2	*a*	$\bar{3}m.$	$0, 0, 0$	$0, 0, \frac{1}{2}$

How does the screw move point

$\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$

To point:

$\frac{2}{3}, \frac{1}{3}, \frac{3}{4}$

60° Rotation in Hex Coordinates

Rule:

$$(x, y) \mapsto (x - y,\ x)$$

Apply to $(\frac{1}{3}, \frac{2}{3})$:

$$x' = \frac{1}{3} - \frac{2}{3} = -\frac{1}{3}, \quad y' = \frac{1}{3}$$

So $(x', y') = (-\frac{1}{3}, \frac{1}{3})$.

Since fractional coords are modulo 1:
$(-1/3, 1/3) \equiv (2/3, 1/3)$.

And ½ translation along c

Ionic Structures

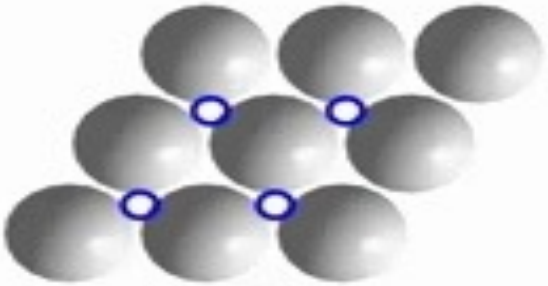
Many ionic structure types can be described as a close packing of anions with cations filling voids or holes in the structure. Generally we will consider two types of holes (for the cations)

- 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

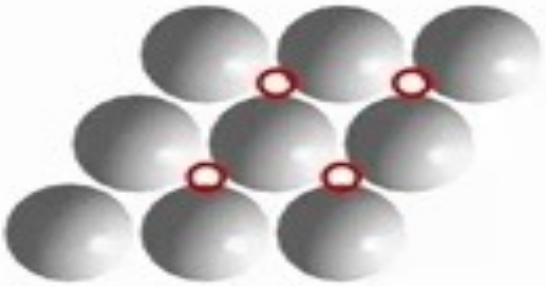
Why would anions want to close pack?

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

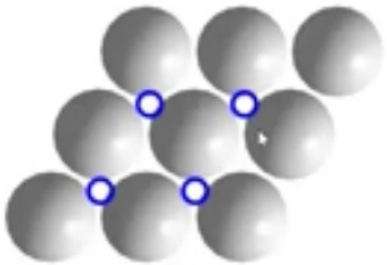
Octahedral Holes

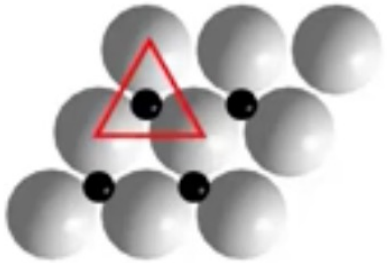


Tetrahedral (+) Holes

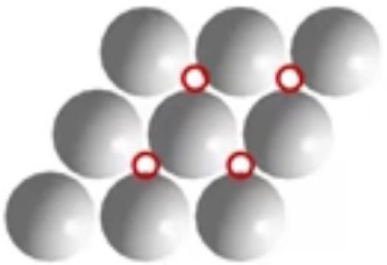


Octahedral Holes

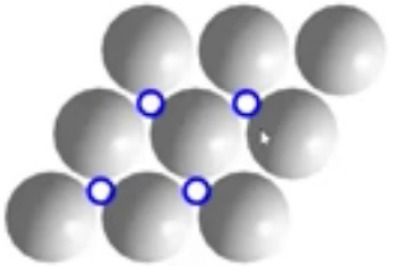


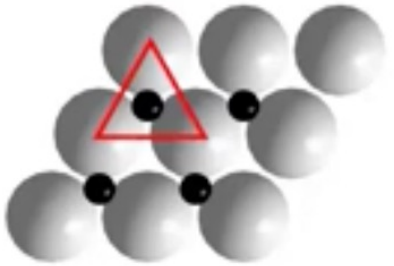


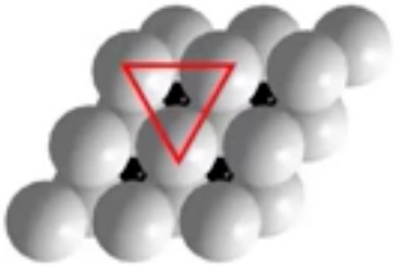
Tetrahedral (+) Holes



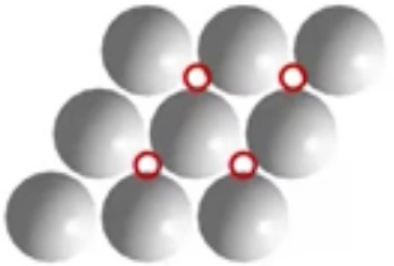
Octahedral Holes



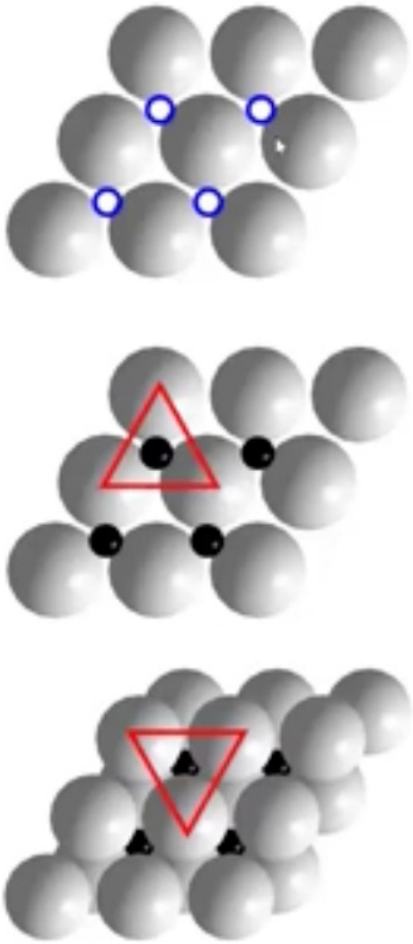




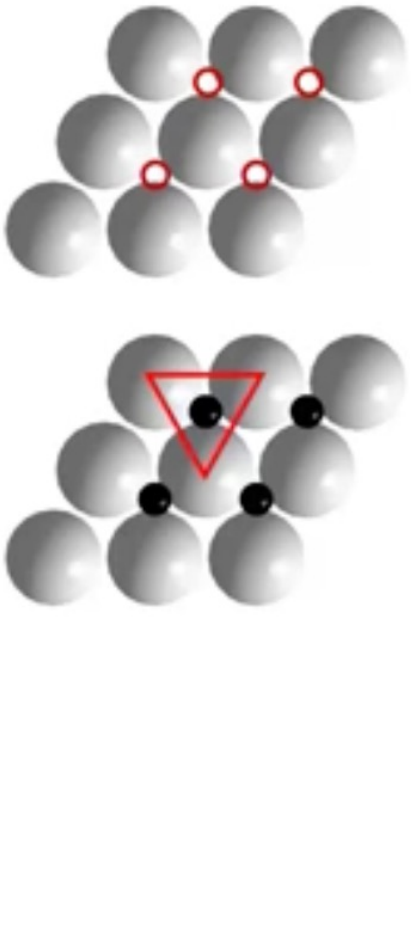
Tetrahedral (+) Holes

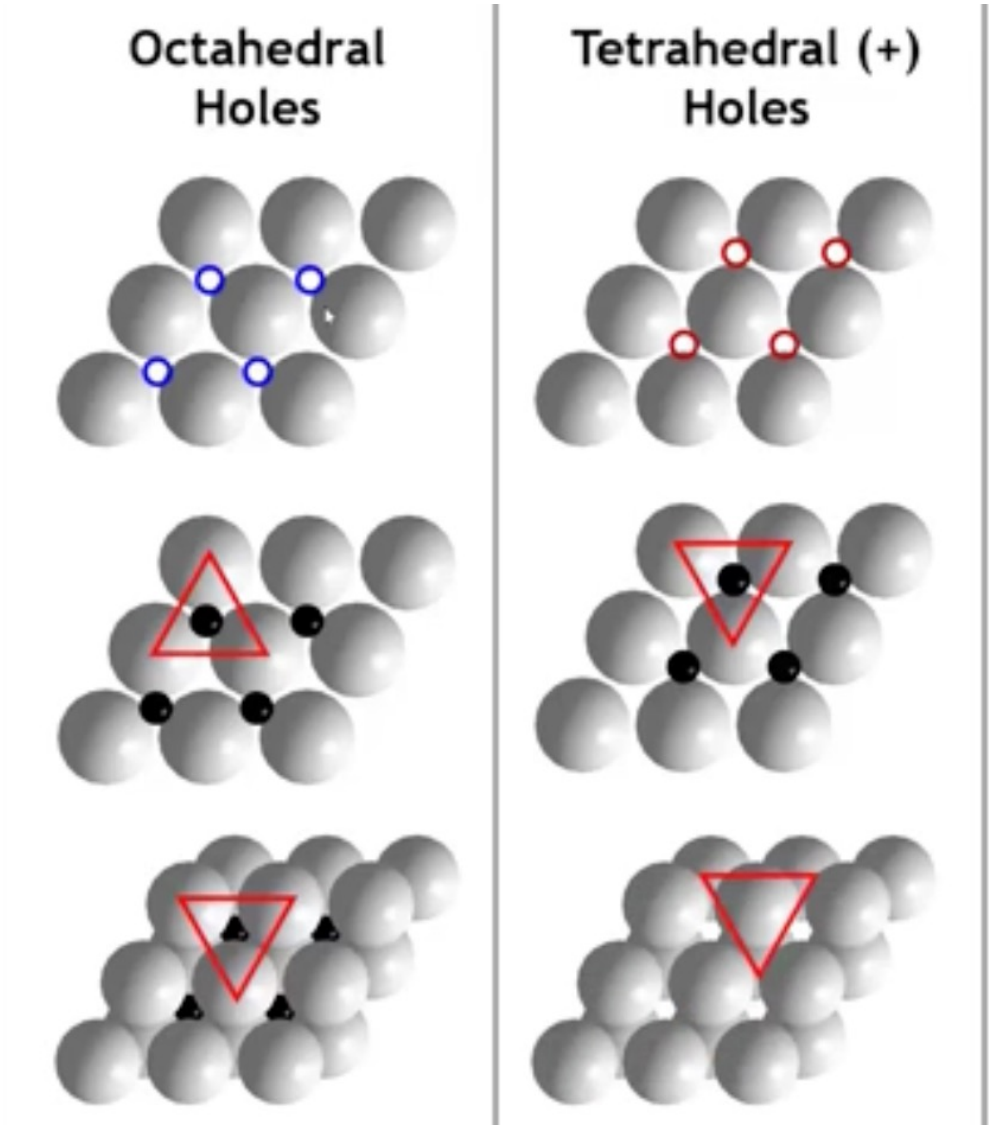


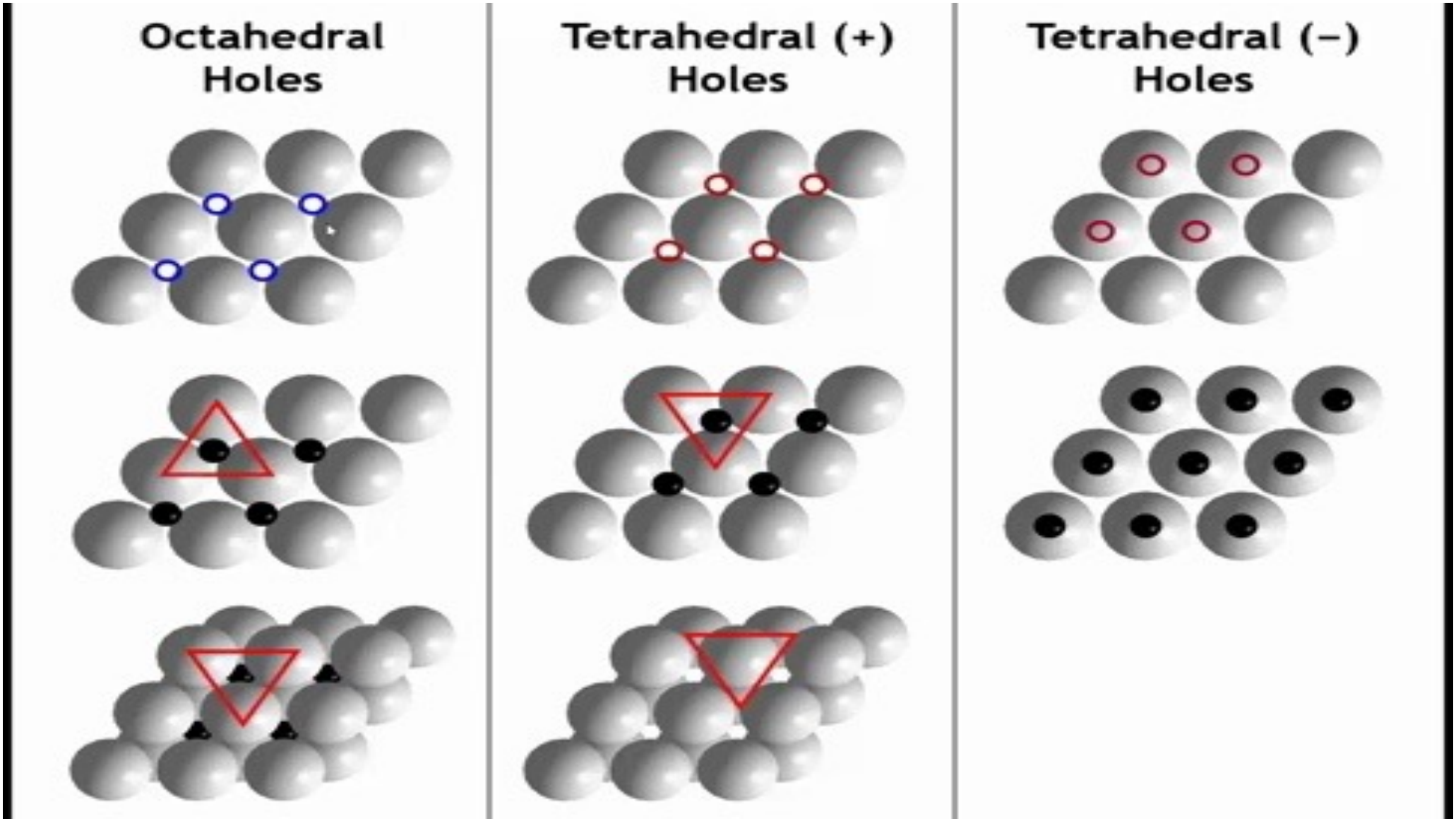
Octahedral Holes

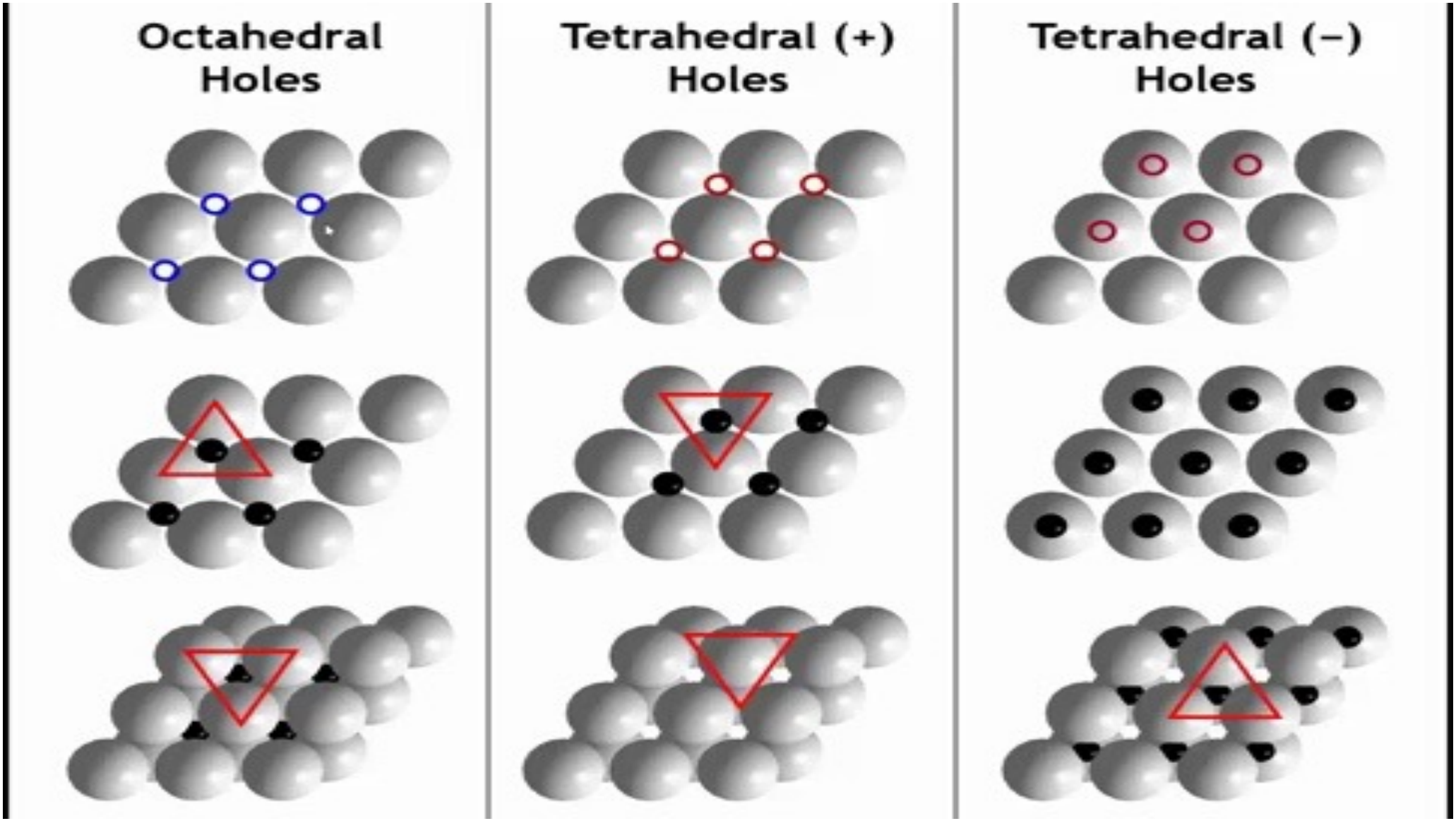


Tetrahedral (+) Holes




Octahedral Holes
Tetrahedral (+) Holes

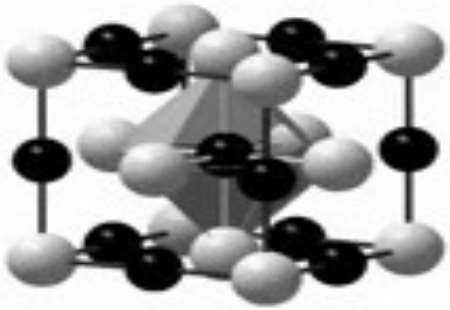
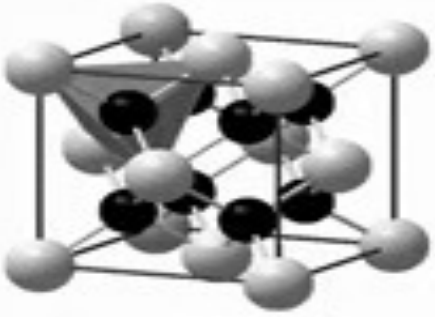
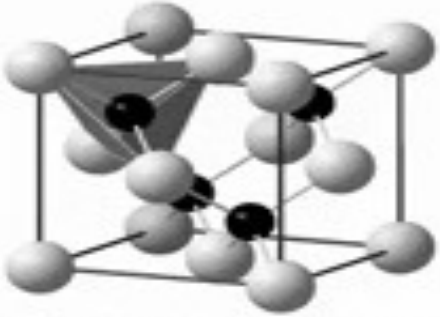
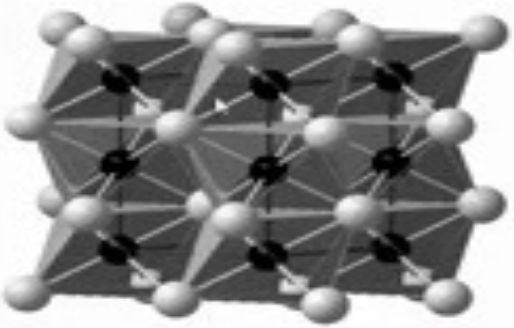
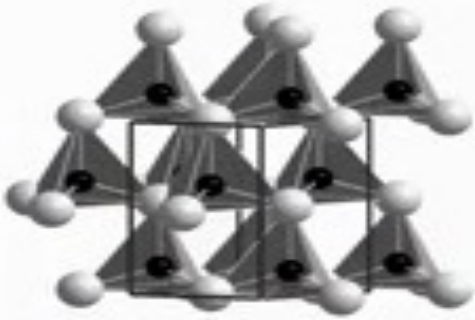

Octahedral Holes
Tetrahedral (+) Holes
Tetrahedral (–) Holes


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

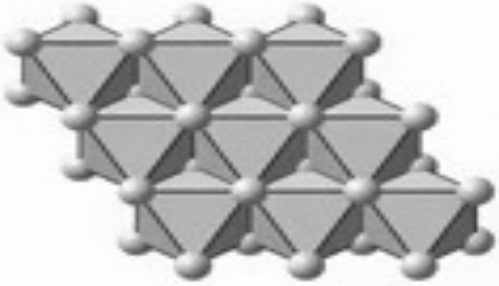
	octahedral holes filled	tetrahedral holes filled	50% of tetrahedral holes filled
ccp anion array	 NaCl ($Fm\bar{3}m$)	 Li_2O ($Fm\bar{3}m$)	 Sphalerite ($F\bar{4}3m$)
hcp anion array	 NiAs ($P6_3/mmc$)	This combination leads to face sharing tetrahedra, which are highly unfavorable.	 Wurtzite ($P6_3mc$)

Eutactic Structures

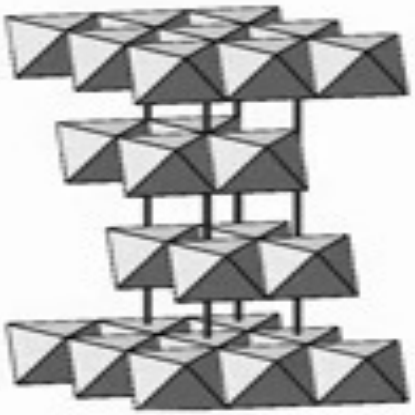
Hole filling in total	*General formula*	*Structure type hcp of anions*	*Structure type ccp of anions*	*The plane-filling sequence*
all octahedral	CA	NiAs	NaCl	all full
½	CA_2	CdI_2	$CdCl_2$	empty and full
½	CA_2	$CaCl_2$		all ½ full
⅓	CA_3	BiI_3	YCl_3	empty and ⅔ full
⅓	CA_3	$RuBr_3$		all ⅓ full
⅔	C_2A_3		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

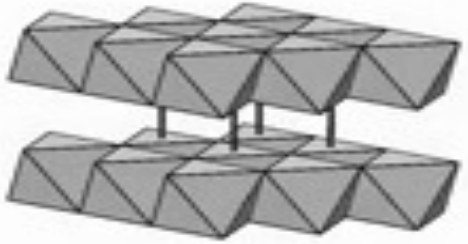


A layer with all of the octahedral holes filled



ccp anion array

hcp anion array



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

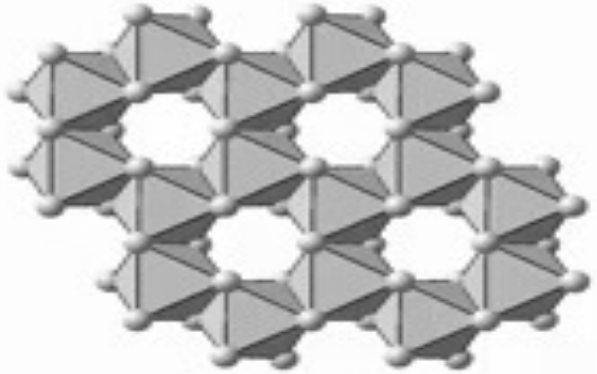
alternating layers of filled and empty octahedral holes

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

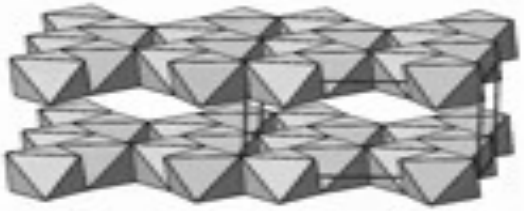
alternating layers of filled and empty octahedral holes

Layered Structures

alternating 2/3-filled and empty layers

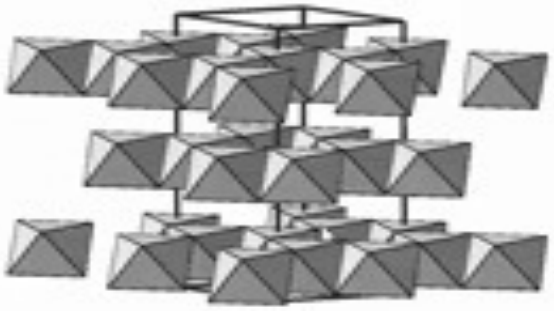


A layer with 2/3 of the octahedral holes filled



ccp anion array

hcp anion array



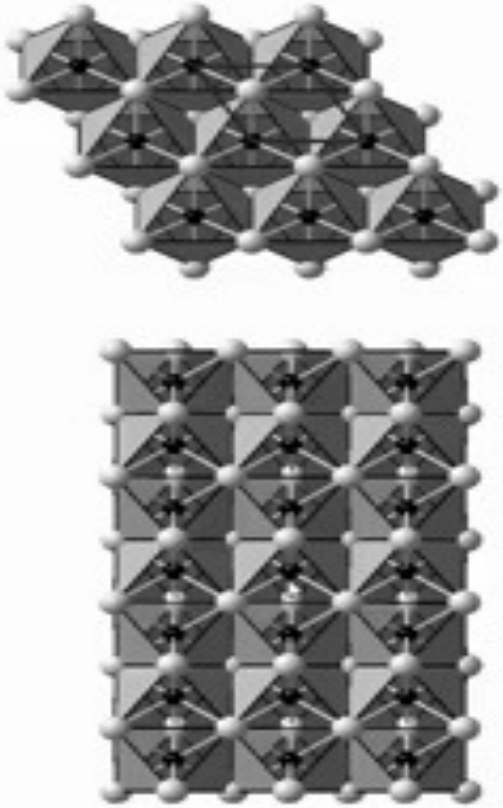
YCl_3 $(C2/m)$
alternating layers of 2/3-filled and empty octahedral holes

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

NiAs Structure

Space Group: $P6_3/mmc$

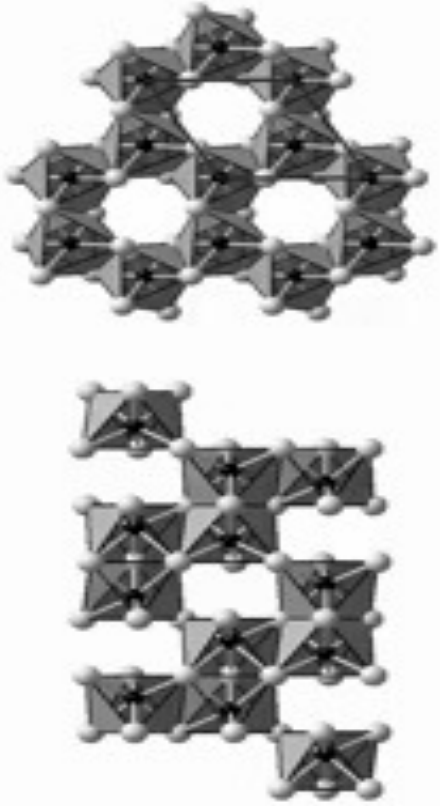
hcp anion array with 100% of the octahedral holes filled



Corundum Structure

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

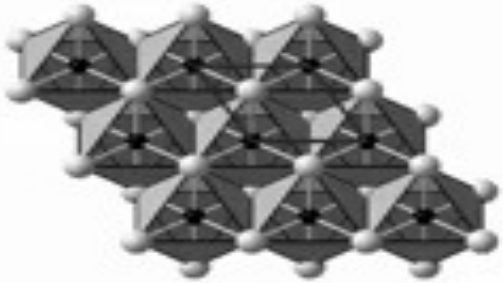
hcp anion array with 2/3 of the octahedral holes filled

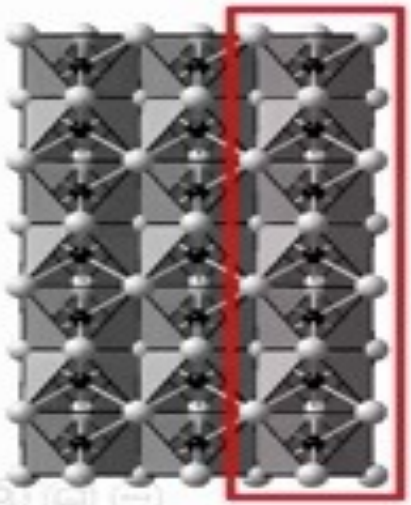


NiAs Structure

Space Group: $P6_3/mmc$

hcp anion array with 100% of the octahedral holes filled



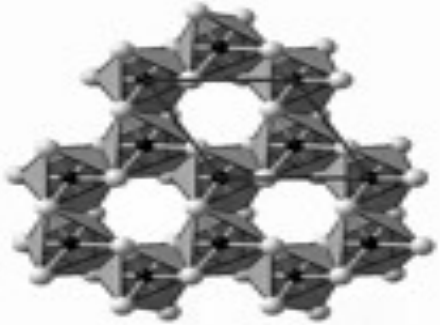


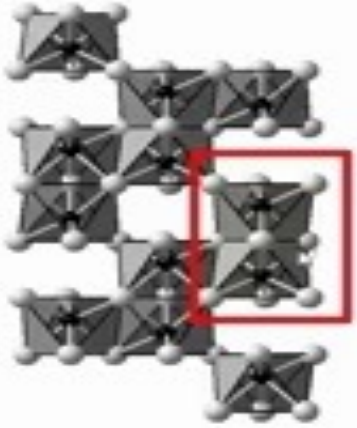
Infinite chains of face-sharing octahedra

Corundum Structure

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

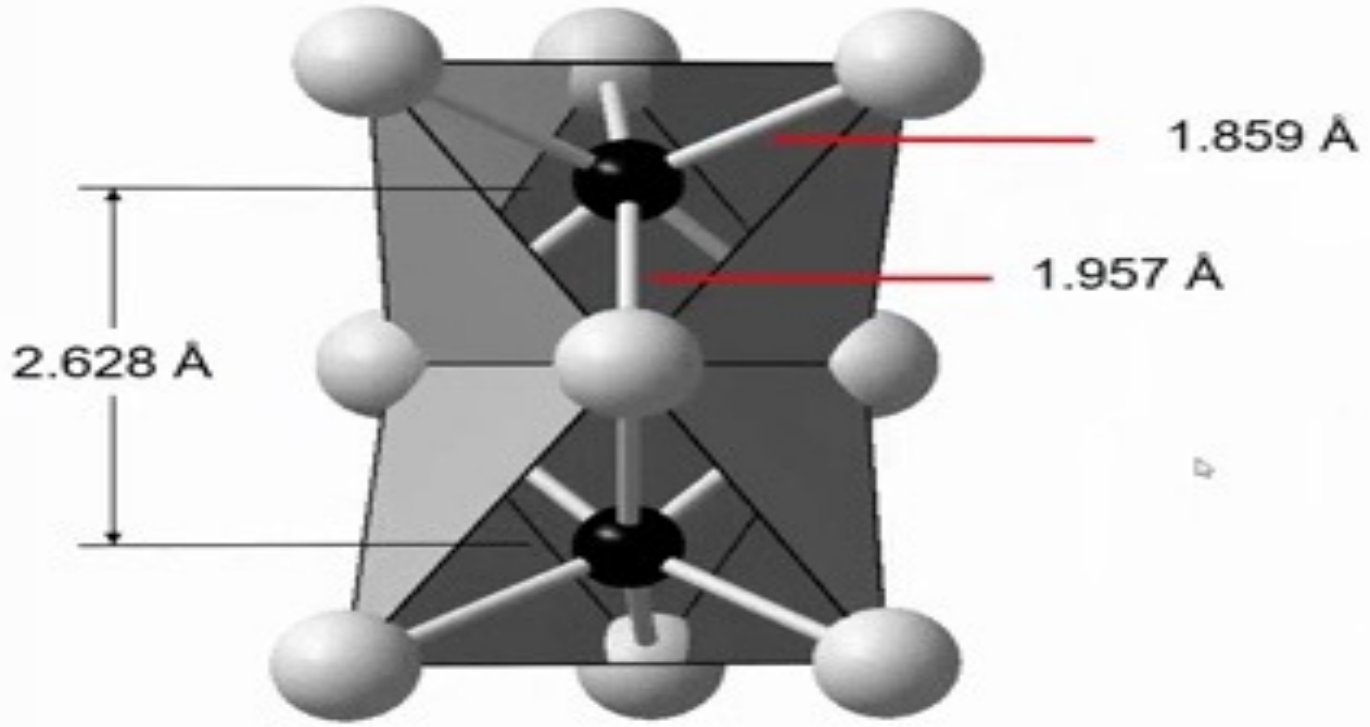
hcp anion array with 2/3 of the octahedral holes filled





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.

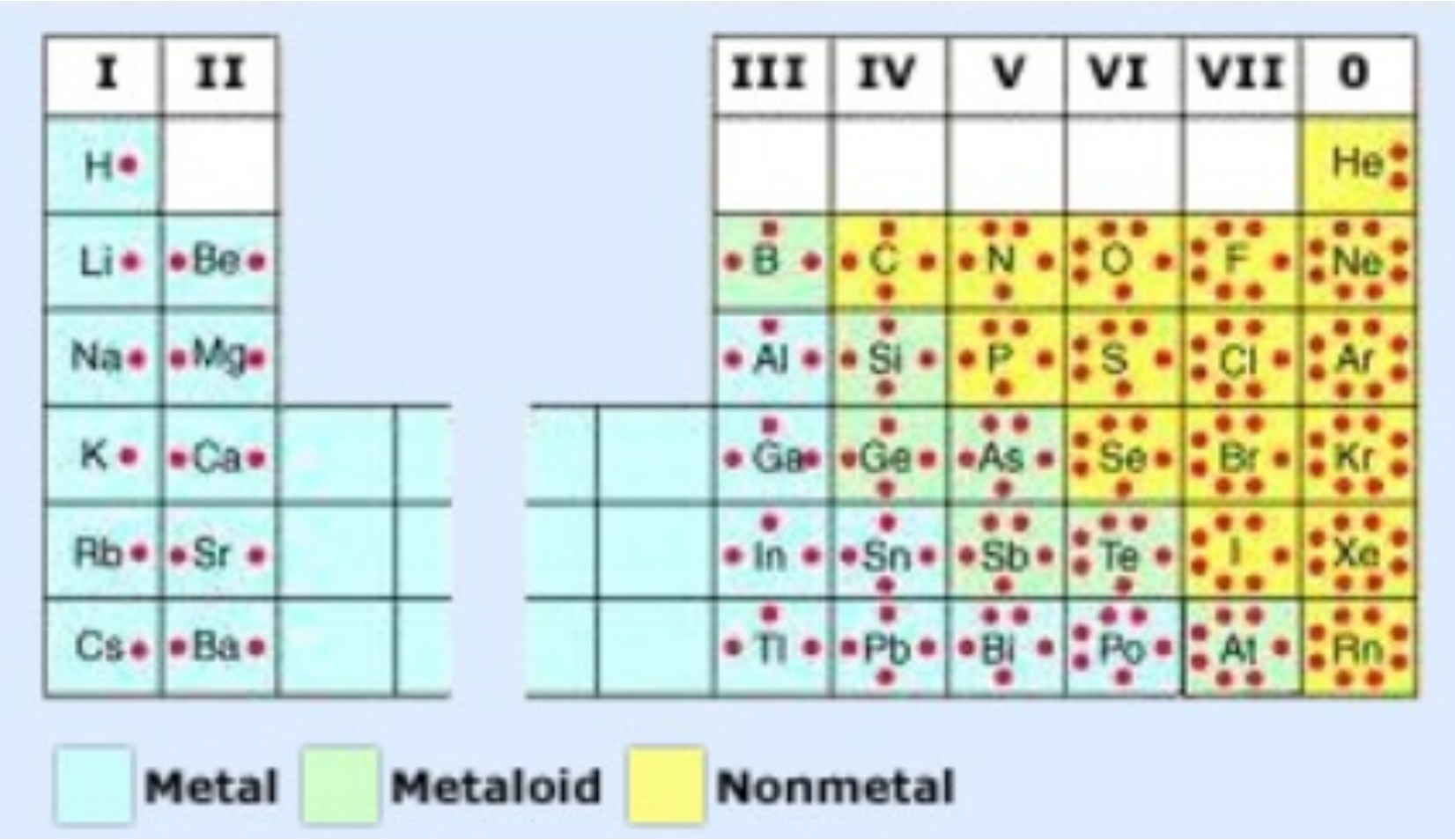
1.17 From unit-cell parameters in figures in this chapter, calculate the following shortest distances: (a) Na–Cl and Na–Na in NaCl, (b) Ni–Ni in NiAs, (c) Ca–F in CaF_2, (d) C–C in diamond, (e) Ti–Ti in TiO_2 (rutile), and (f) Ti–O, Sr–O, and O–O in the cubic perovskite $SrTiO_3$ (a = 3.90 Å).

Learning Objectives

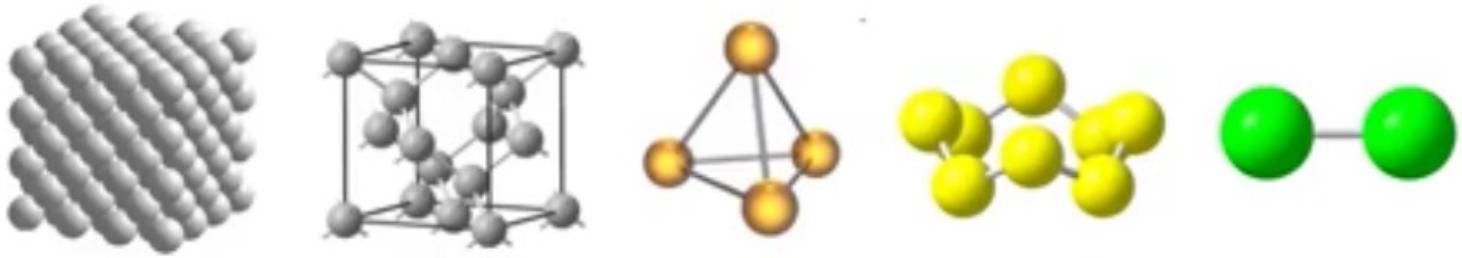
By the end of this lecture, you should be able to:

- Explain how covalent bonding satisfies the octet rule through directional bonding.
- Use Lewis structures and periodic trends (Groups 7A → 4A) to predict bond counts.
- Distinguish covalent, metallic, and ionic bonding by electron availability.
- Apply the *valence electron count per anion (VEC/A)* method.
- Use the **generalized 8–N rule** to predict when:
  - anion–anion bonds form
  - cation–cation bonds form
  - cation lone pairs remain.
- Recognize Zintl phases and explain how electropositive metals donate electrons to form covalent networks or dimers.

Octet Rule: Main-group atoms form bonds until they have **8 valence electrons**, like a noble gas.



Electron count and covalent bonds



3A	4A	5A	6A	7A
Al	Si	P_4	S_8	Cl_2
12 nearest neighbors	4 bonds per atom	3 bonds per atom	2 bonds per atom	1 bond per atom

← Metallic bonding

→ Covalent bonding

Valence Electron Count per Anion

For a binary compound with stoichiometry C_mA_n where C is the more electropositive element ("cation") and A is the more electronegative element ("anion"). We can use the following equation to determine the valence electron count per anion to see if the octet rule is obeyed (i.e. $VEC_A = 8$)

Valence electrons per C

Valence electrons per A

$$VEC_A = \frac{e_C \cdot m + e_A \cdot n}{n}$$

Electron count per anion

Generalized Octet Rule

SiO_2

Generalized Octet Rule

SiO_2

$$VEC_A = \frac{e_C \cdot m + e_A \cdot n}{n}$$

$$VEC_A = \frac{4 \cdot 1 + 6 \cdot 2}{2} = \frac{16}{2} = 8$$

Generalized Octet Rule

SiO_2

$$VEC_A = \frac{e_C \cdot m + e_A \cdot n}{n}$$

$$VEC_A = \frac{4 \cdot 1 + 6 \cdot 2}{2} = \frac{16}{2} = 8$$

The octet rule is obeyed

NaTl

$$VEC_A = \frac{e_C \cdot m + e_A \cdot n}{n}$$

$$VEC_A = \frac{1 \cdot 1 + 3 \cdot 1}{1} = 4$$

Generalized 8−N Rule

When the octet rule is not obeyed ($VEC_A \neq 8$) we must have either cation-cation bonds ($VEC_A > 8$), cation lone pairs ($VEC_A > 8$) or anion-anion bonds ($VEC_A < 8$). To predict the number we can use the generalized octet rule:

$$VEC_A = 8 + CC(^m/_n) - AA$$

Number of electrons left behind on the cation

Number of anion-anion bonds

Generalized 8−N Rule

NaTl

$$VEC_A = \frac{e_C \cdot m + e_A \cdot n}{n}$$

$$VEC_A = \frac{1 \cdot 1 + 3 \cdot 1}{1} = 4$$

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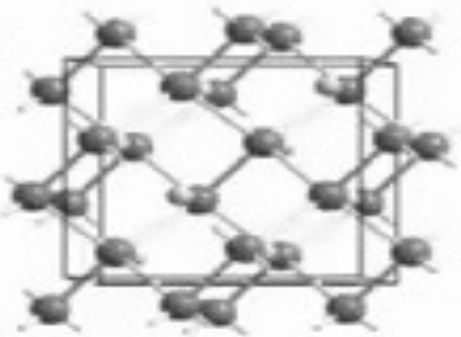
$$VEC_A = 8 + CC(^m/_n) - AA$$

$$4 = 8 + CC(^m/_n) - AA$$

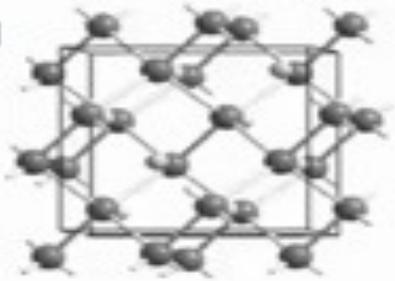
$$AA = 4$$

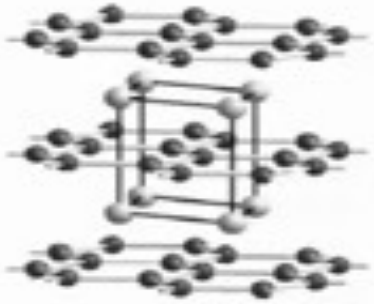
NaTl



Zintl Phases

Follow the Zintl-Klemm concept: the electropositive metal donates its electrons to the electronegative metal(s)

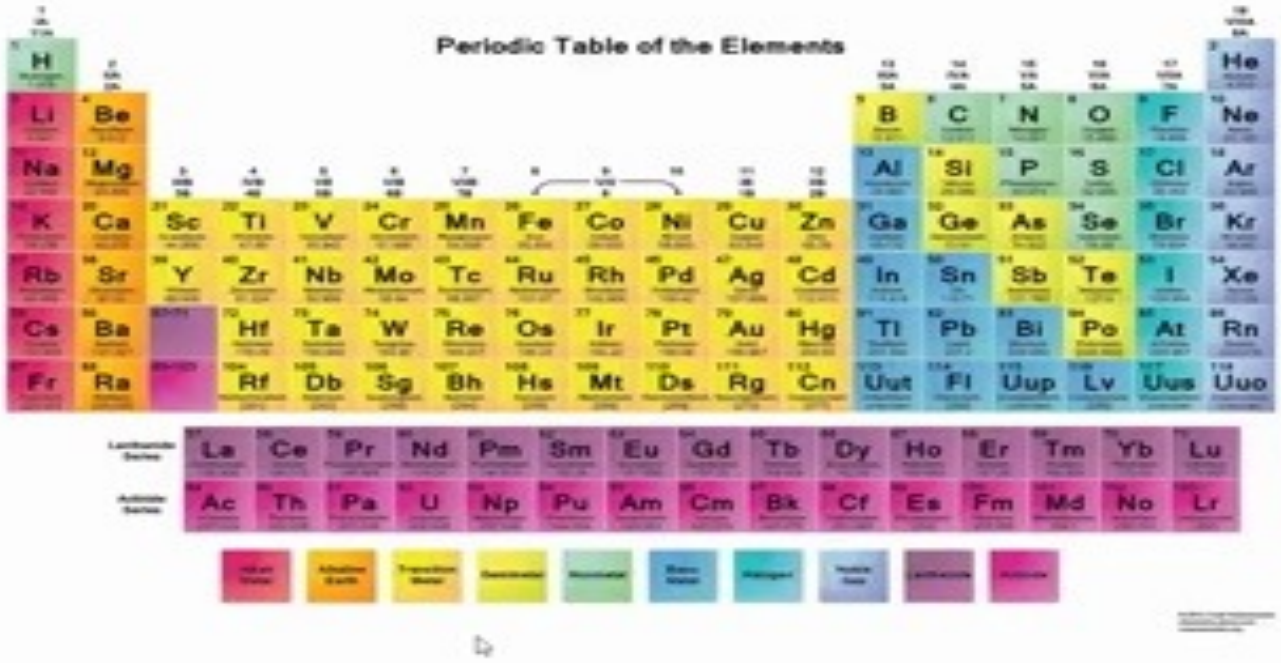
NaTl 

$SrGa_2$ 

- Fixed stoichiometry
- Diamagnetic, brittle, and exhibit low electrical conductivity

Apply the generalized 8−N rule

- $SnCl_2$
- CaSb



Generalized Octet Rule

$SnCl_2$

$$VEC_A = \frac{4 \cdot 1 + 7 \cdot 2}{2} = \frac{18}{2} = 9$$

$$VEC_A = 8 + CC(^m/_n) - AA$$

$$9 = 8 + CC(^1/_2) - \cancel{AA}$$

$$CC = 2$$

There are 2 electrons localized on Sn^{2+} that form a lone pair

Generalized Octet Rule

CaSb

$$VEC_A = \frac{2 \cdot 1 + 5 \cdot 1}{1} = 7$$

$$VEC_A = 8 + CC(^m/_n) - AA$$

$$7 = 8 + CC(^1/_1) - AA$$

$$AA = 1$$

There is a Sb-Sb bond that leads to formation of Sb_2^{2-} dimers

Summary

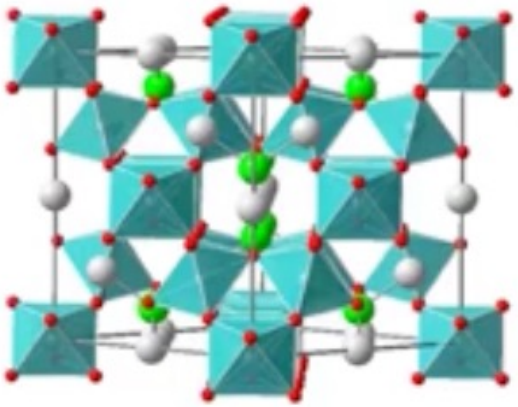
- Moving across the periodic table:
  - Halogens ($7e^-$) → 1 bond; Chalcogens ($6e^-$) → 2 bonds; Group 5A ($5e^-$) → 3 bonds; Group 4A ($4e^-$) → 4 bonds (diamond, Si, Ge).
  - Further left: metallic bonding via delocalized electrons.
- VEC/A framework: track electrons donated by cations and accepted by anions.
- Octet rule applies even in largely covalent solids (e.g., SiO_2).
- **Generalized 8–N rule:**
  - VEC/A < 8 → anion–anion bonds form (e.g., Tl–Tl in NaTl, Sb_2^{2-} in Ca_2Sb).
  - VEC/A > 8 → excess electrons stay on cations as lone pairs (e.g., Sn^{2+} in $SnCl_2$).
- Zintl phases: electropositive metal donates electrons; electronegative element forms covalent structures (e.g., NaTl diamond-like, $SrGa_2$ graphite-like sheets).

Homework

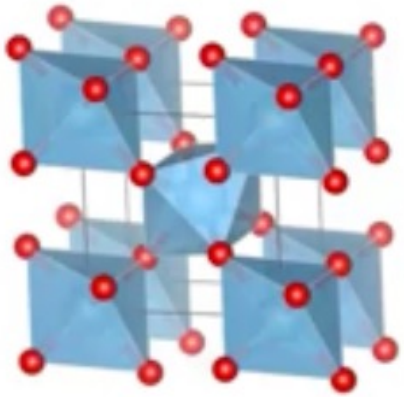
1.13 Use the generalized 8−N rule to identify whether anion–anion or cation–cation bonds are present for the following compounds (assume no cation-localized nonbonding electron pairs): (a) Na_2Tl, (b) $SrSb_2$, (c) $BaTe_2$, (d) InSe.

1.14 Suggest the anion bonding that might occur in MgB_2 and MgC_2.

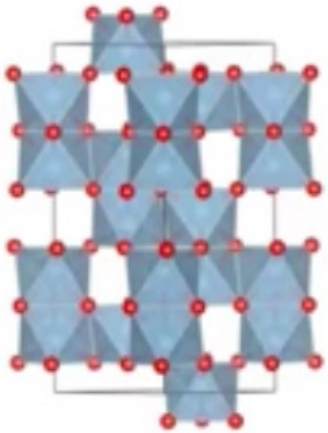
$La_2Zr_2O_7$



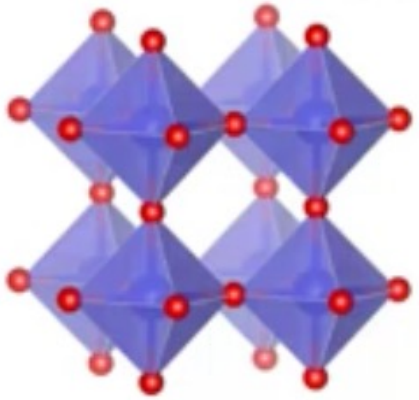
TiO_2



Al_2O_3



ReO_3



Learning Objectives

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

- Explain how **stoichiometry** constrains crystal structures.
- Define and apply the **crystal chemical formula**.
- Use three key balances to analyze compounds:
  - **Electroneutrality balance** (charge neutrality).
  - **Connectivity balance** (coordination numbers).
  - **Bond valence balance** (bond order = oxidation state ÷ coordination number).
- Construct and interpret a **bond graph**.
- Apply **Pauling's Rule of Parsimony** and **Brown's Rule of Maximum Symmetry** to evaluate structures.
- Predict coordination numbers and bond valences in real compounds (e.g., **SiO_2, TiO_2, CaF_2, Al_2O_3, Na_3N**).

Stoichiometry Constraints

Consider a binary compound formed between 2 elements, one being more electronegative (the "anion" of charge a−) than the other (the "cation" of charge c+). Assume that all atoms of a given element are in identical surroundings. This compound must obey three balances:

Coordination # of C

Coordination # of A

$$\mathrm{C}_m^{c+}\,[N]\,\mathrm{A}_n^{a-}\,[M]$$

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$$\mathrm{C}_m^{c+}[N]\,\mathrm{A}_n^{a-}[M]$$

Electroneutrality balance: $m \times c = n \times a$

Connectivity balance: $m \times N = n \times M$

Bond valence balance: $c/N = a/M$

Stoichiometry Constraints

What is the stoichiometry of the binary compound that forms between silicon and oxygen? Given that silicon usually adopts a tetrahedral coordination what is the coordination number of oxygen? What is the valence of the bonds between Si and O?

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Coordination # of Si

Coordination # of O

$$\mathrm{Si}_m^{4+}\,[4]\,\mathrm{O}_n^{2-}\,[M]$$

Electroneutrality balance: $m \times 4 = n \times (2)$

Stoichiometry Constraints

What is the stoichiometry of the binary compound that forms between silicon and oxygen? Given that silicon usually adopts a tetrahedral coordination what is the coordination number of oxygen? What is the valence of the bonds between Si and O?

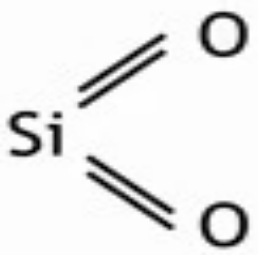
Coordination # of Si

Coordination # of O

$$\mathrm{Si}_m^{4+}\,[4]\,\mathrm{O}_n^{2-}\,[M]$$

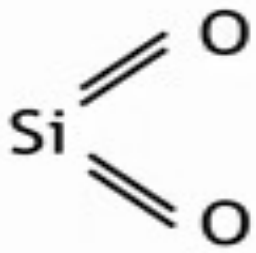
Electroneutrality balance:	$m \times 4 = n \times (2)$	$\mathrm{SiO_2}$
Connectivity balance:	$1 \times 4 = 2 \times M$	$M = 2$
Bond valence balance:	$c/N = a/M$	$4/4 = 2/2 = 1$

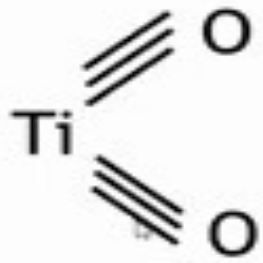
Bond Graphs



$Si^{[4]}O_2^{[2]}$

Bond Graphs



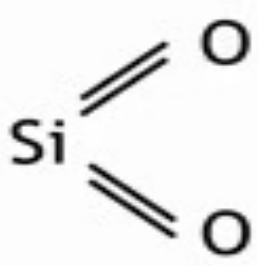


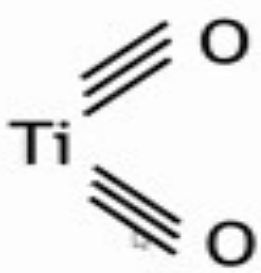
$Si^{[4]}O_2^{[2]}$

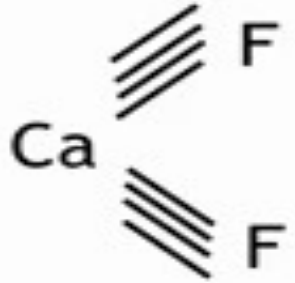
$Ti^{[6]}O_2^{[3]}$

bond valence
4/4 = 2/2 = 1

Bond Graphs







$Si^{[4]}O_2^{[2]}$

bond valence
4/4 = 2/2 = 1

$Ti^{[6]}O_2^{[3]}$

bond valence
4/6 = 2/3

$Ca^{[8]}F_2^{[4]}$

bond valence
2/8 = 1/4

All things equal nature favors symmetric structures

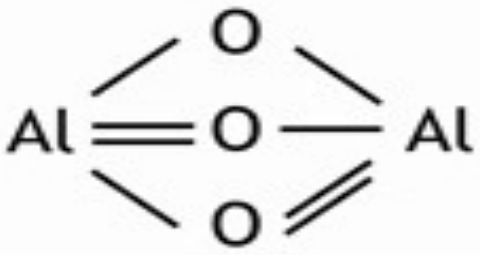
Pauling's Rule of Parsimony

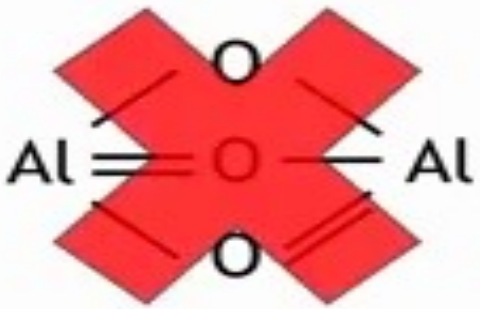
The number of chemically different coordination environments for a given ion in a crystal tends to be small.

Brown's Rule of Maximum Symmetry

The most stable structure is the most symmetric structure, consistent with the constraints acting on the system.

What can you tell me about the coordination numbers and bond valences in the aluminum oxide and sodium nitride? Assume the rule of parsimony is obeyed.


O
Al
O
Al
O


O
Al
O
Al
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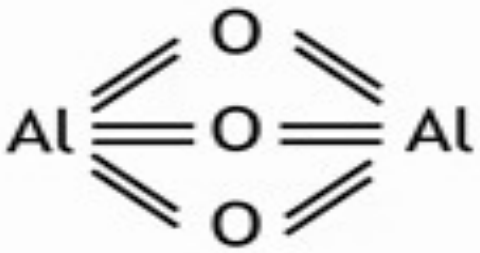
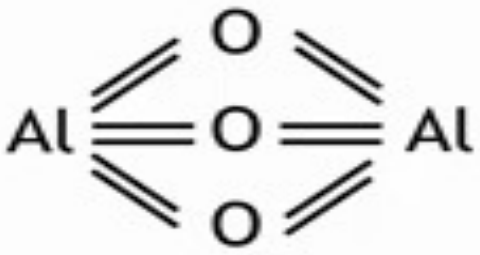
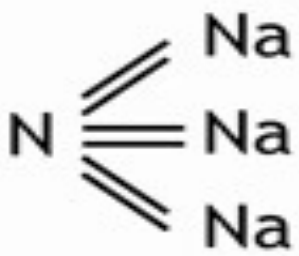
O
Al
O
Al
O



$Al_2^{[6]}O_3^{[4]}$

bond valence
3/6 = 2/4 = ½





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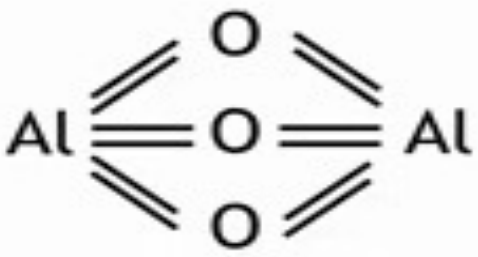
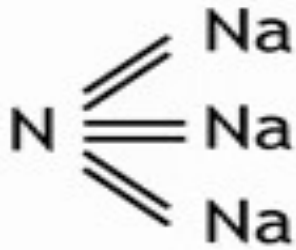
bond valence
3/6 = 2/4 = ½



$Al_2^{[6]}O_3^{[4]}$

bond valence
3/6 = 2/4 = ½



$Na_3^{[2]}N^{[6]}$

bond valence
1/2 = 3/6 = ½

Summary

- Crystal structures are not random — they reflect **stoichiometry and symmetry constraints**.
- **Crystal chemical formulas** allow us to track oxidation states, coordination numbers, and bonding.
- **Three balances** guide predictions:
  - Electroneutrality (charges balance).
  - Connectivity (total bonds balance).
  - Bond valence (bond strength balance, fractional values allowed).
- **Bond graphs** provide a simple visual tool for coordination analysis.
- **Rules of symmetry:**
  - Pauling's Parsimony → minimize distinct environments.
  - Brown's Maximum Symmetry → maximize symmetry consistent with stoichiometry.
- Case studies (SiO_2, TiO_2, CaF_2, Al_2O_3, Na_3N) show how these rules explain common structures and rare ones (e.g., Na_3N, only synthesized in 2002, unstable at 360 K).

Homework

1.8 Write down crystal-chemical formulas for two-site binary compounds CrN, Cr_2O_3, and CrO_2 with octahedrally coordinated chromium.

1.9 Write down the three balances expressed in the crystal-chemical formulas of the phases in the previous problem.

1.10 Draw the bond graph for the mineral spinel $MgAl_2O_4$ (Figure 1.47).

1.11 Convert the bond graphs in Figure 1.15 into crystal-chemical formulas.

1.12 Describe or sketch a structure for layered V_2O_5 that is consistent with the bond-graph representation in Figure 1.15.