

Solids

Solid structures, packing, metallic bond, ionic and covalent lattices & energy considerations



Solids

- **Crystalline:** high internal order (i.e. NaCl, diamond)
- **Amorphous:** no internal order (i.e. glass)
- Solids can be composed of atoms (for example metallic elements), molecules (for example, SF₄) and ions (again, NaCl).
- Different forces keep these constituents together in the solid state: metallic bond in metallic elements, ionic bond in ionic crystals and non-bonding interactions in molecular crystals (hydrogen bonds, van der Waals forces and similar)
- **Crystals** are characterized by a rigid, repeating geometrical pattern known also as a crystal lattice.
- **Crystal lattice** is considered to be infinite array of atoms, molecules or ions and is described with **unit cell**, its smallest building block.

Unit cells, crystal lattices and crystal systems

Some definitions:

The smallest repeating unit in a crystal lattice is *unit cell*. It contains all chemical and symmetry information of the whole crystal

All crystalline structures can be simplified to only 14 lattices (known as Bravais lattices): a 3D arrays of points (called lattice points). Structural elements are held at or around lattice points (do not worry, we'll see some examples)

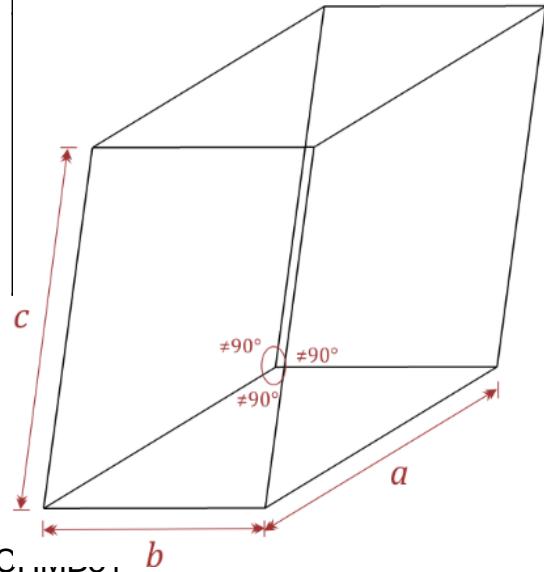
These 14 Bravais lattices can be further grouped into seven crystal systems based on the shapes (and symmetry) of the unit cell.

Crystal structure is known when we know: crystal system, dimensions of unit cell, (symmetry), lattice type and positions of atoms inside unit cell (crystal structure \neq molecular structure)

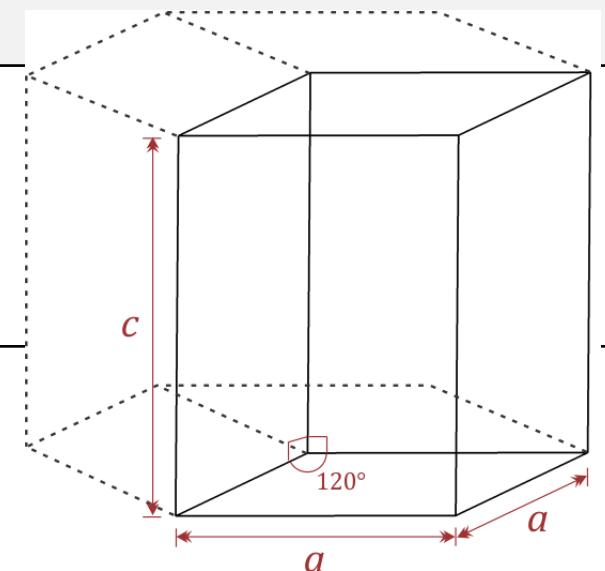
Crystal systems

Cubic	Tetragonal	Hexagonal
$a = b = c (= a)$, $\alpha = \beta = \gamma = 90^\circ$	$a = b (= a) \neq c$, $\alpha = \beta = \gamma = 90^\circ$	$a = b (= a) \neq c$, $\alpha = \beta = 90^\circ; \gamma = 120^\circ$
Rhombohedral	Orthorhombic	Monoclinic
$a = b = c (= a)$, $\alpha = \beta = \gamma \neq 90^\circ$	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta > 90^\circ$

Triclinic



$a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma$

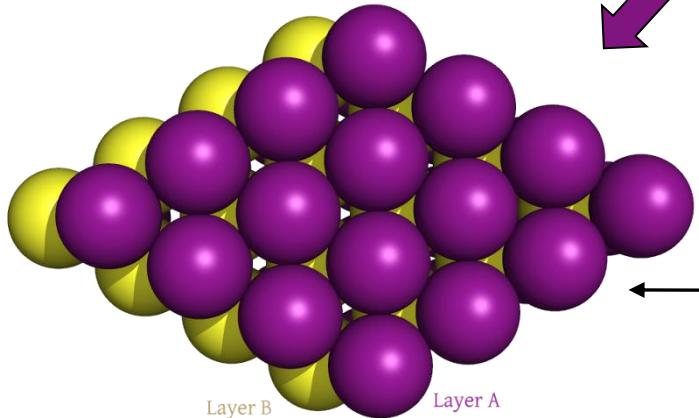
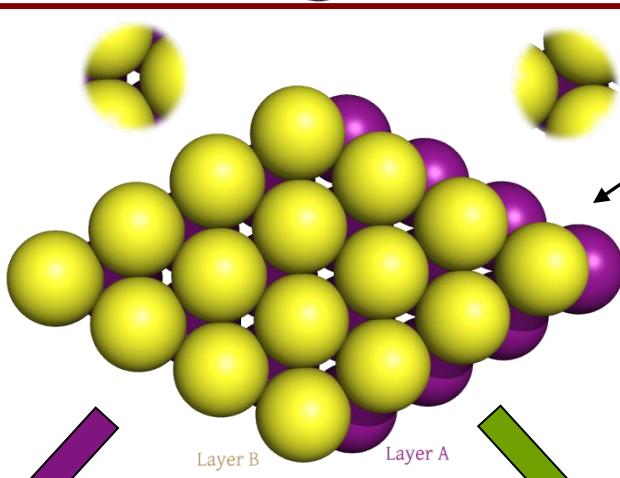
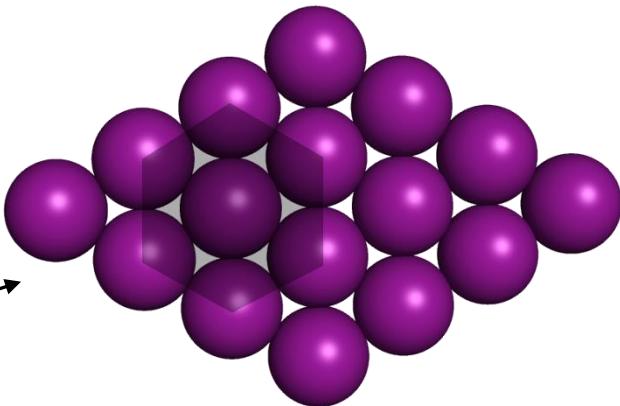


Metallic structures

Metallic structures can be described as packing of the atoms as spheres.

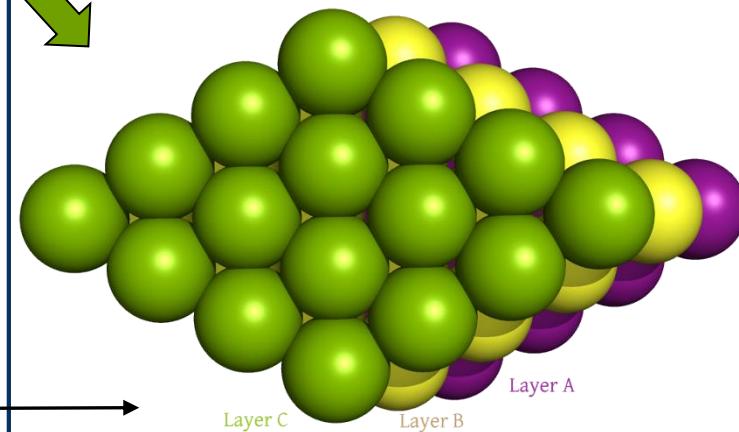
The densest packing of the spheres is based on hexagonal layers.

Note that even in this dense packing, there is still empty space.

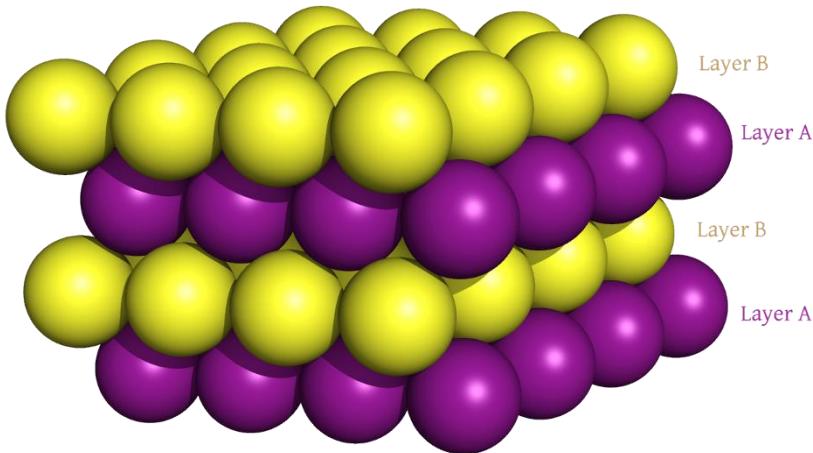


Depending where the atoms of the next layer 'land' we have hexagonal close packing (left, ABAB.. pattern) or cubic close packing (right, ABCABC... pattern).

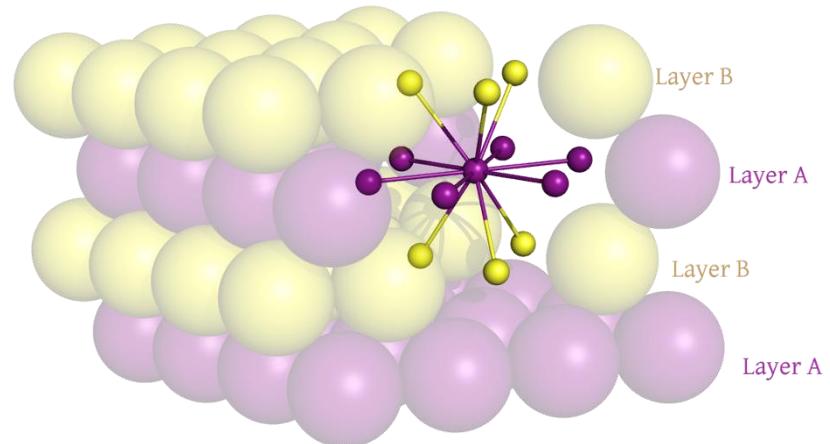
Lecture 6: Solid State



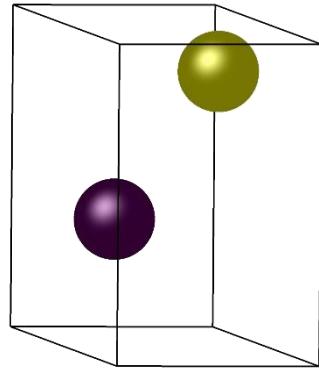
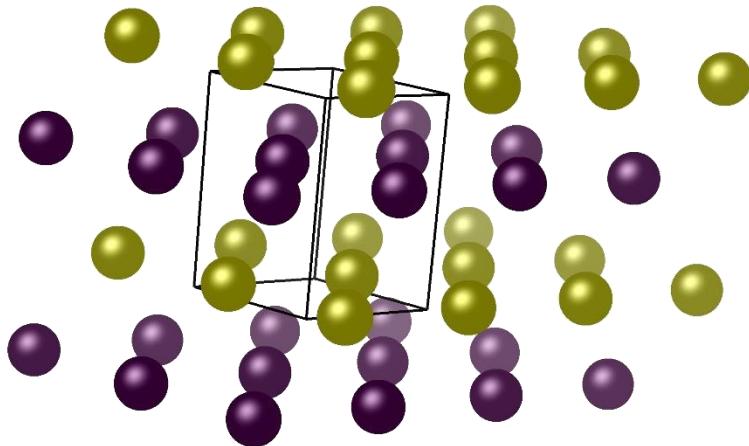
Hexagonal close packing (HCP)



Four layers of hexagonal close packing (hcp)

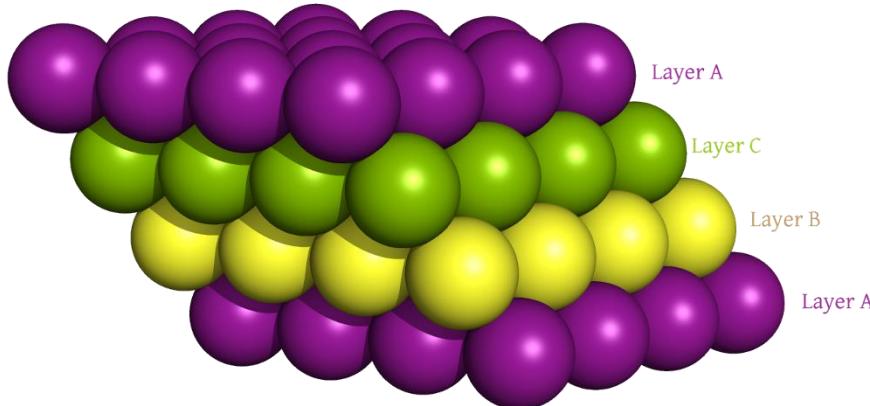


Each atom is surrounded by 12 nearest neighbors (called coordination number); the pair of three yellow atoms is eclipsed

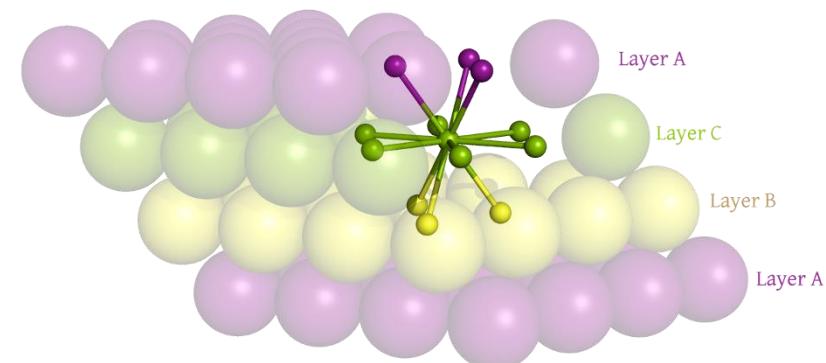


The unit cell of hexagonal close packing is also hexagonal. It contains only two atoms.

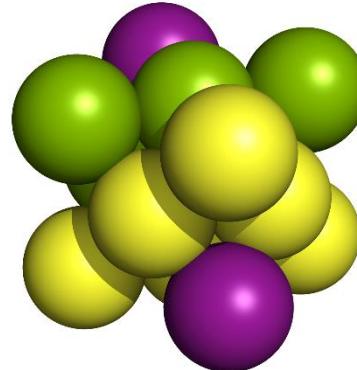
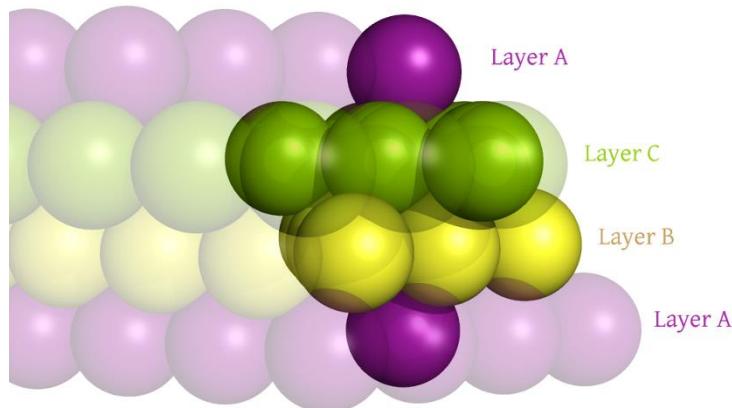
Cubic close packing (ccp)



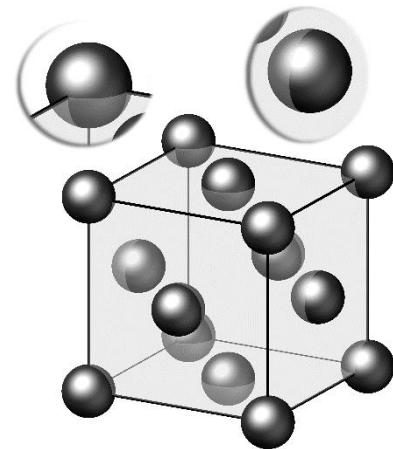
Four layers of cubic close packing (hcp)



Each atom is surrounded by 12 nearest neighbors again; the pair of three atoms are staggered



The unit cell is a cube with atoms at each corner and middle of each face of the cube (face centered cubic structure, fcc)

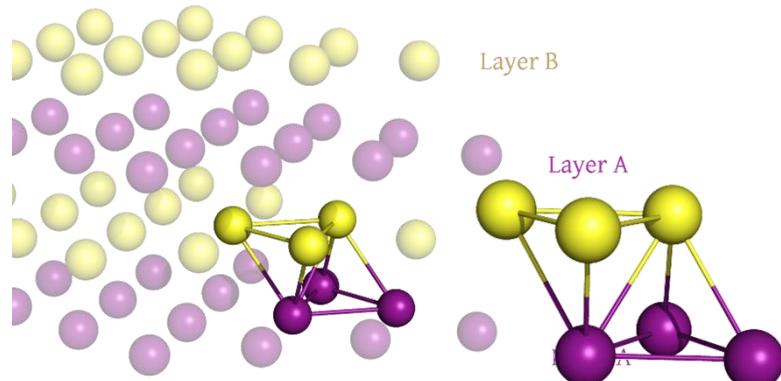


Unit cell content:

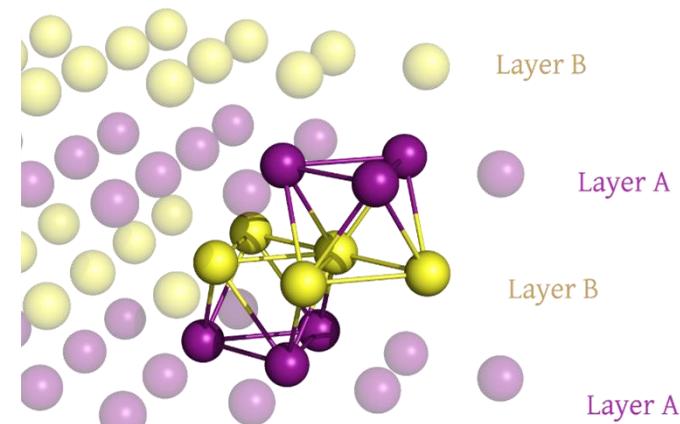
$$8 \times \frac{1}{8} \text{ (corners)} + 6 \times \frac{1}{2} \text{ (faces)} = 4 \text{ atoms}$$

Close-packing but...

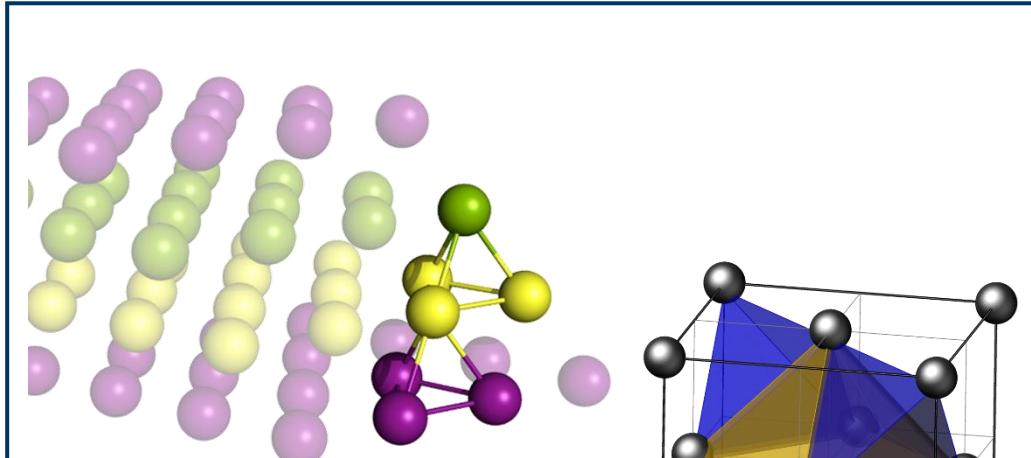
- Close-packing of the spheres has the most efficient use of space, **but** there is still ~26% of empty space
- Close packings have two types of holes: octahedral & tetrahedral



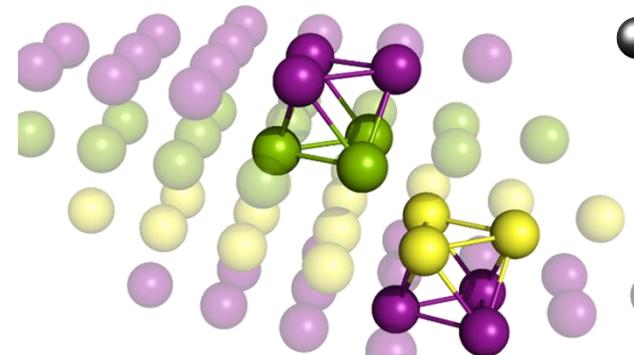
Tetrahedral holes in hcp



Octahedral holes in hcp



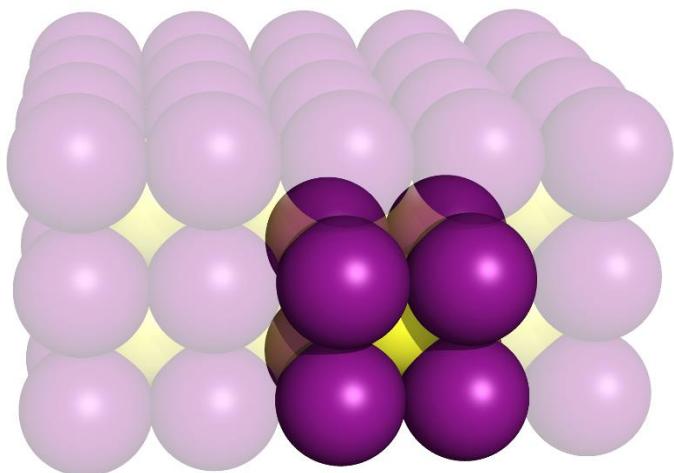
Tetrahedral holes in ccp



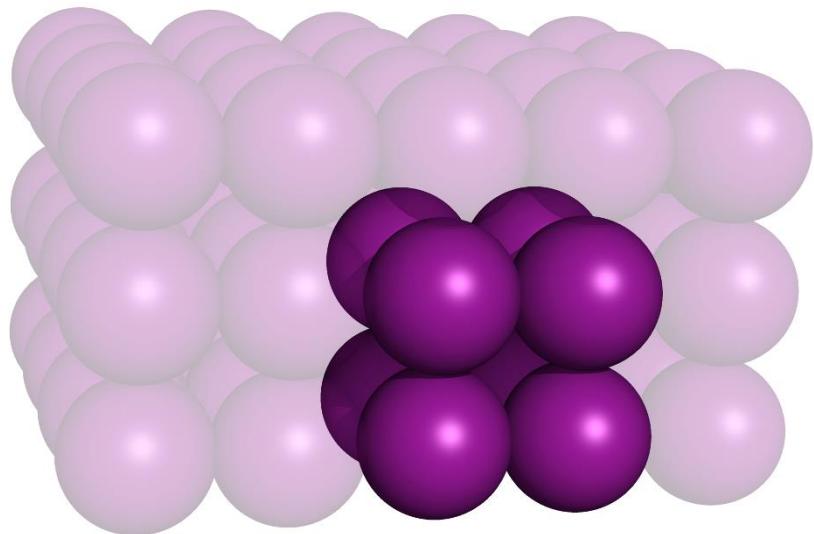
Octahedral holes in ccp

Non-close packing

- Non-close packing arrangements have lower space economy: they have more than 26% of empty space.
- Two examples are simple cubic and body-centered cubic lattice



Body-centered cubic lattice (bcc): corners and center of the cube

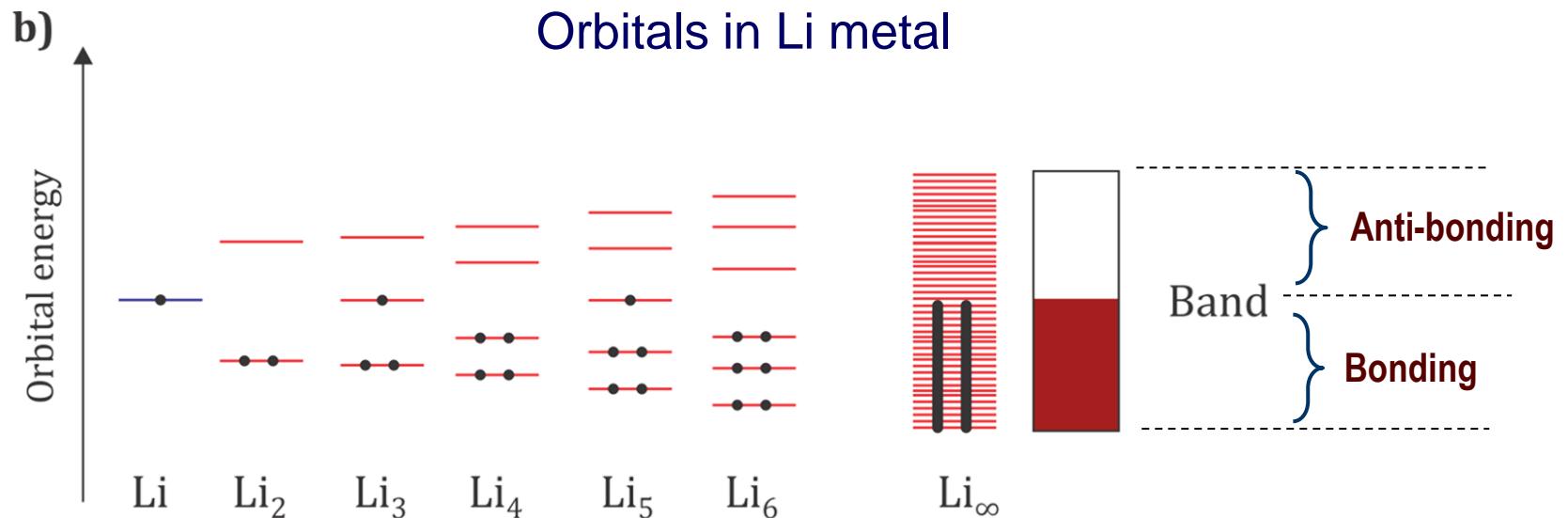
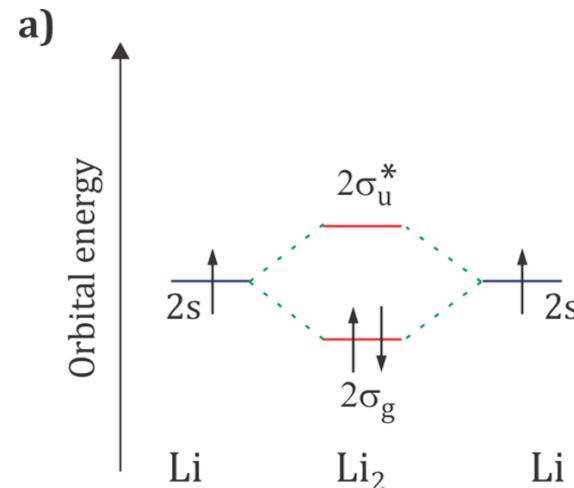


Simple cubic lattice (sc): spheres only on the corners of the cube

Practice: determine the cell content and coordination numbers for simple and body-centered unit cells!

Molecular orbitals and metallic bond: Band formation

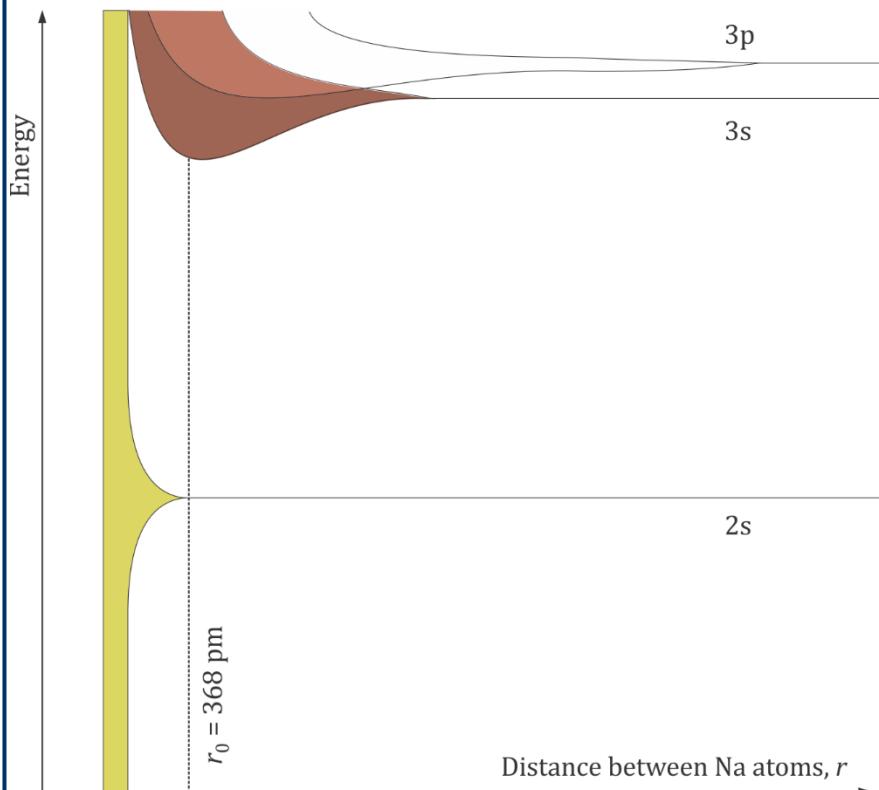
MO diagram for Li_2 molecule



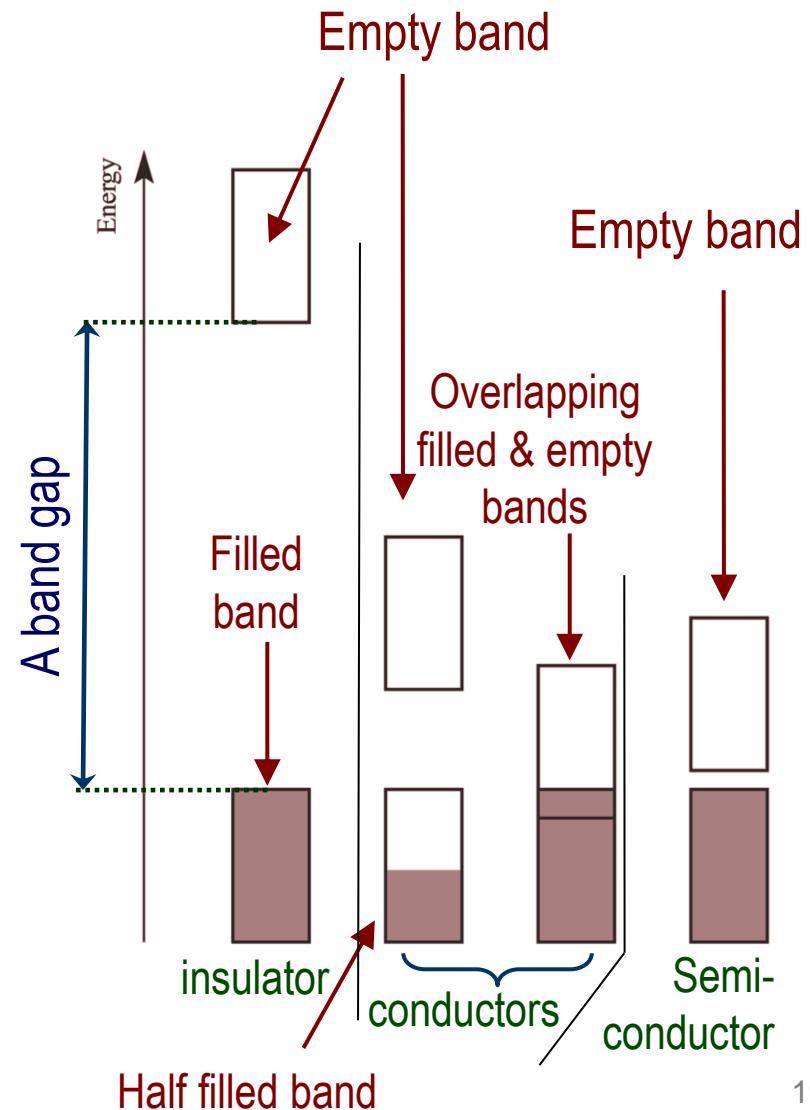
A group of MOs with really, really small differences in energy between them constitute a *band*.

Bands, gaps, conductors...

Bands formed from different atomic orbitals can overlap



Schematic presentation of bands in sodium as a function of distance.
The equilibrium distance coincides with the minimum in energy

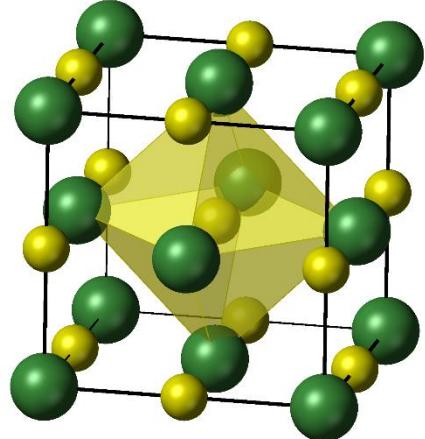
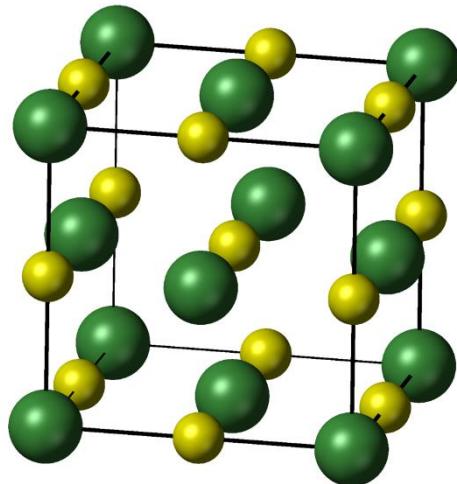


Ionic structures

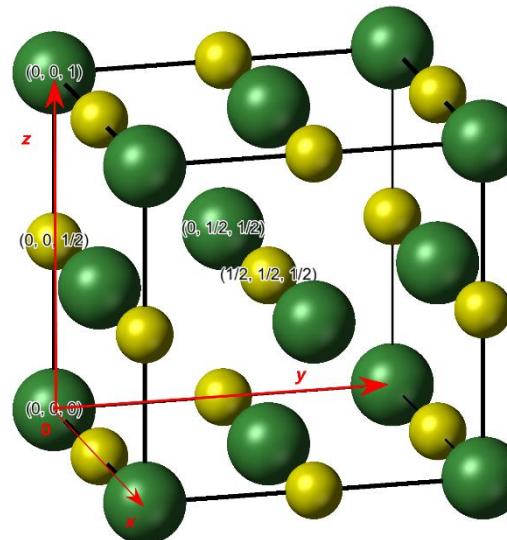
- If we focus on monoatomic ions or very symmetrical polyatomic ions, we can use the same ‘packing of the spheres’ approach keeping in mind electrostatic interactions
 - For ions that cannot be taken as spheres (for example, planar CO_3^{2-}) the descriptions are different and a bit more difficult to systematize
- All compounds with the same distribution of atoms in space are grouped together and their structure is given by a prototype:
 - For example, all structures with the same distribution of ions as found in NaCl have NaCl-type structure and their prototype is NaCl
- The structures are described in terms of locations of cations or anions in the unit cell and coordination numbers, this time it is the number of closest neighbours of opposite charge.

AX Structures: Rock salt (halite) structure, NaCl

- Each cation is coordinated with 6 anions and vice versa
- Note the relation with fcc: Cl⁻ ions form an fcc packing and Na⁺ ions reside in octahedral holes.

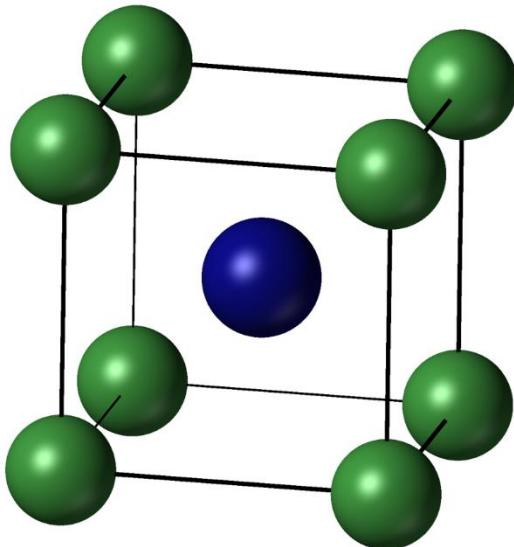


Na⁺ - yellow; Cl⁻ - green



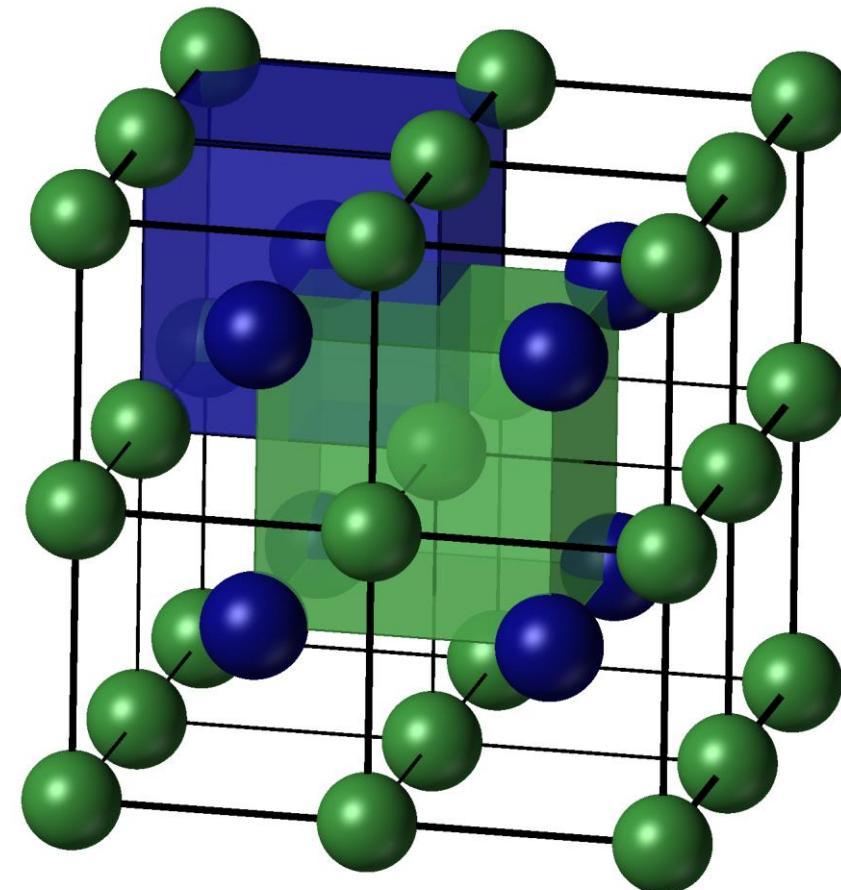
Halite (rock salt) crystal

AX structures: Caesium chloride (CsCl)



CsCl unit cell

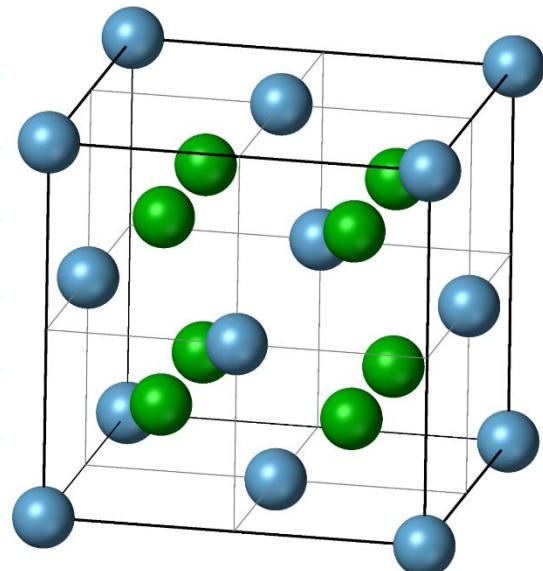
Careful! Easily described as body centered cubic structure, which is *wrong!!*



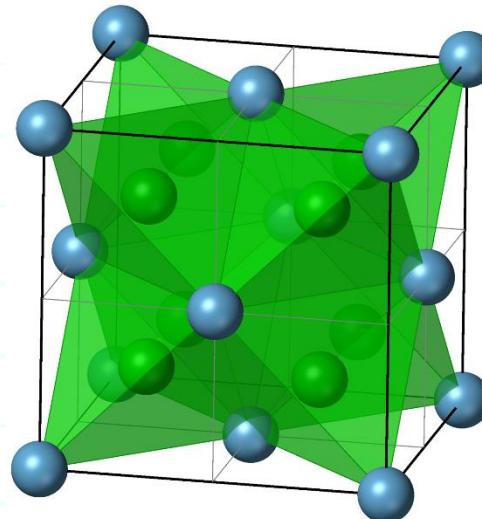
CNs: $\text{Cs}^+ = \text{Cl}^- = 8$

Cs^+ - yellow; Cl^- - green

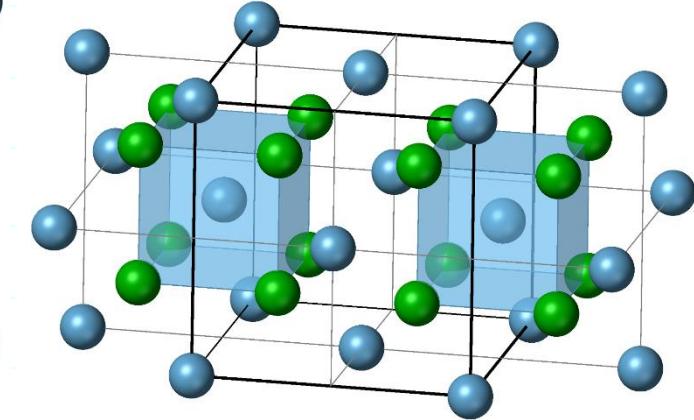
AX_2 Structures: Fluorite (CaF_2) and antifluorite



CaF_2 unit cell (Ca^{2+} blue)



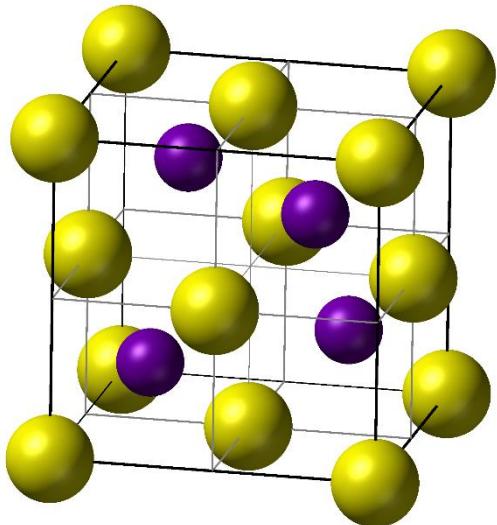
Coordination numbers (CNs):, $\text{F}^- = 4$, $\text{Ca}^{2+} = 8$



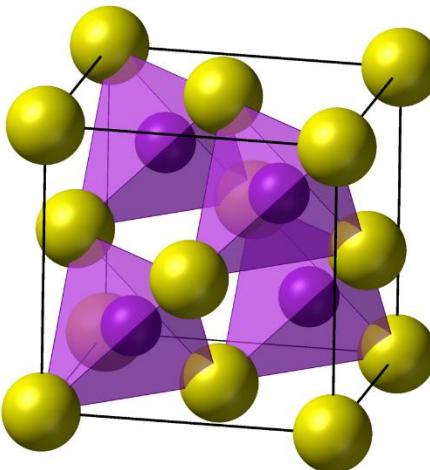
Red fluorite (CaF_2) on albite ($\text{NaAlSi}_3\text{O}_8$)

- Note similarity with ccp: put Ca^+ where the spheres are in ccp structure and F^- in each tetrahedral hole.
- If cations and anions exchange places then the structure is called *antifluorite* structure and compound has a general formula M_2X .

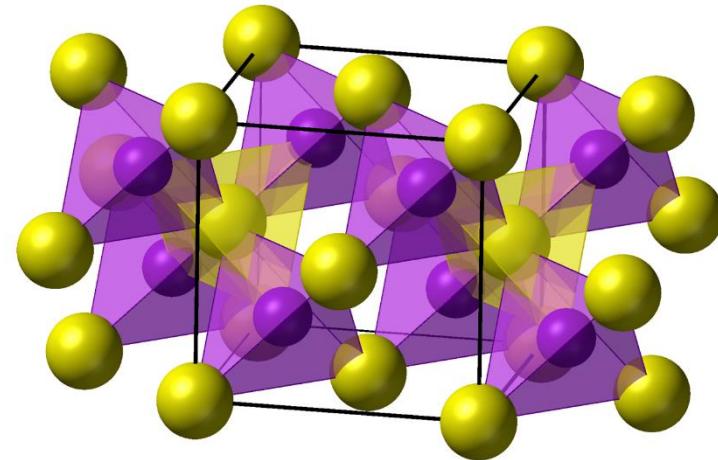
AX Structures: Zinc-sulfide (ZnS) Structure I: Sphalerite (zincblend)



Sphalerite unit cell
(Zn^{2+} purple)



Coordination numbers (CNs): $\text{Zn}^{2+} = \text{S}^{2-} = 4$



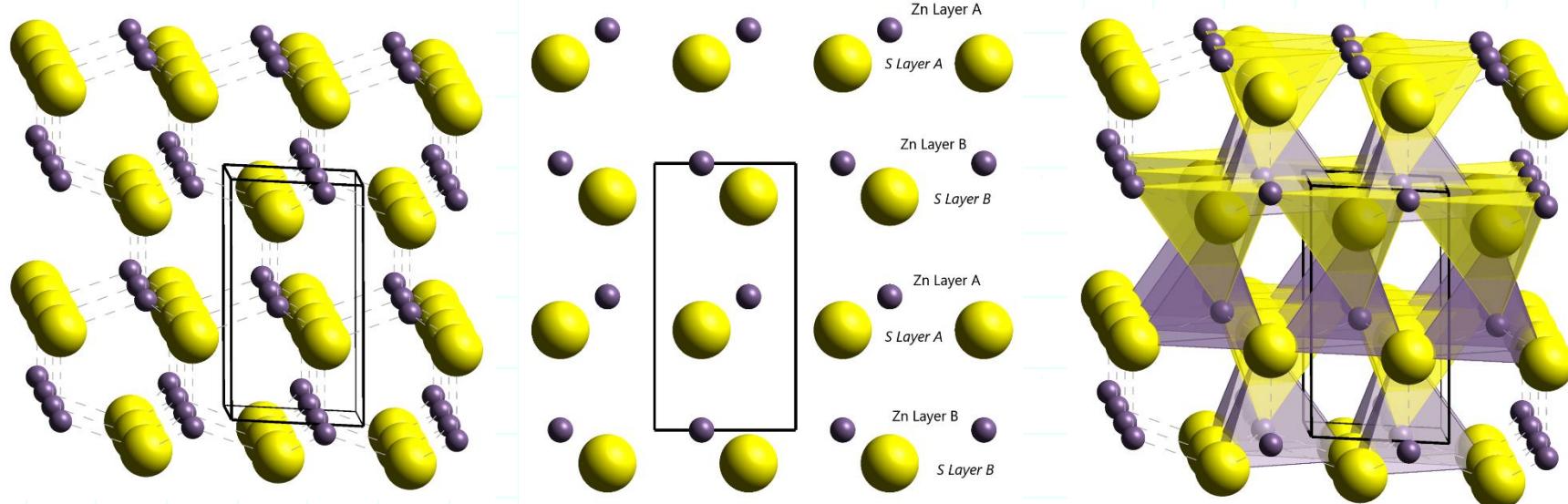
- Note similarity with fluorite structure: every second anion from fluorite structure has been removed to balance the charge.



Dark red sphalerite (ZnS)
on calcite (CaCO_3)

AX Structures: Zinc-sulfide (ZnS) structure II: wurtzite

- Sphalerite and wurtzite are *polymorphs* of ZnS: polymorphs have the same formula but different structures



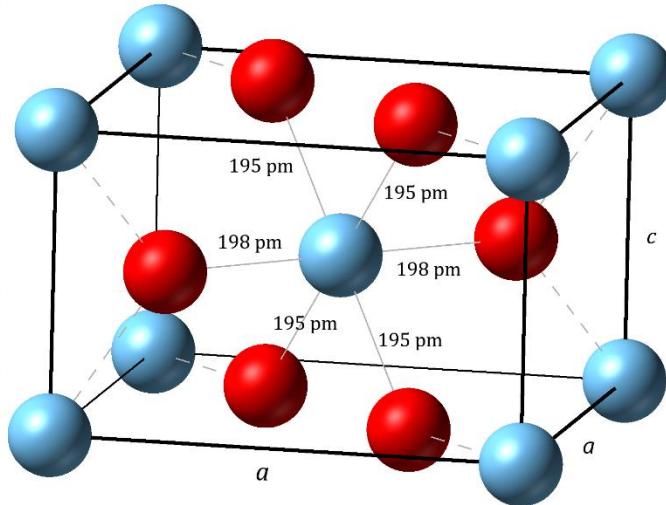
Wurtzite structure is composed of two intermeshed hexagonal close packed structures: one defined with S²⁻ the second with Zn²⁺. The unit cell is hexagonal

Zn²⁺ - purple; S²⁻ - yellow

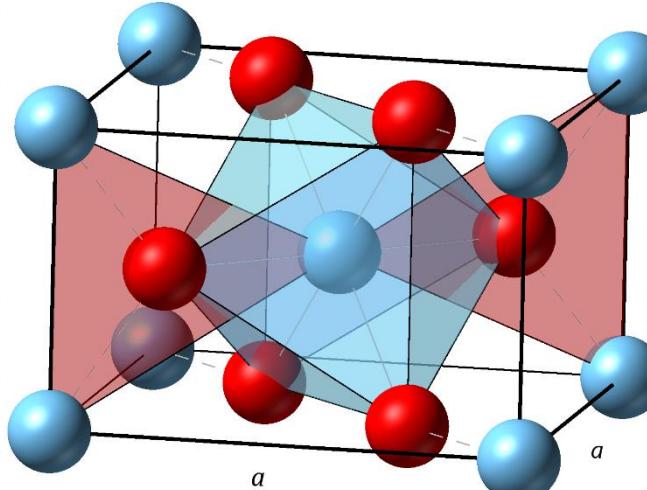
Coordination Numbers (CNs):
Zn²⁺ = S²⁻ = 4

AX_2 Structures: Rutile (TiO_2) structure

- Rutile is one of the TiO_2 polymorphs
- Rutile unit cell is *tetragonal*: $a=b\neq c$, $\alpha, \beta, \gamma=90^\circ$



Rutile unit cell



CNs: $\text{Ti}^{4+} = 6$; $\text{O}^{2-} = 3$

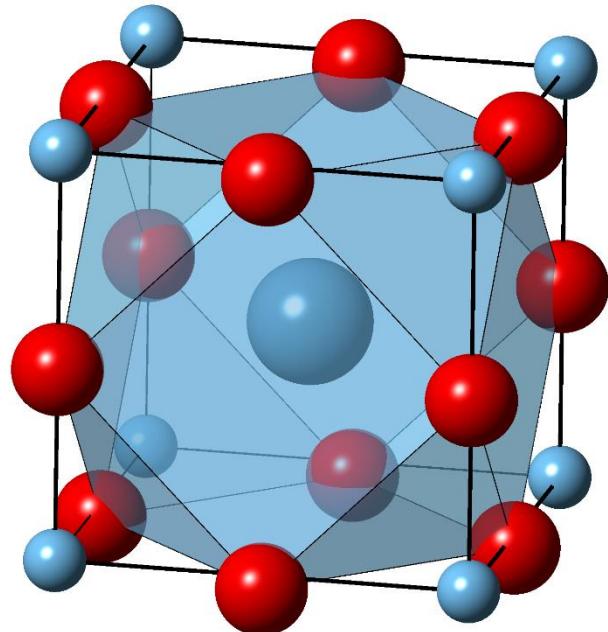
Ti^{4+} - light blue;
 O^{2-} - red



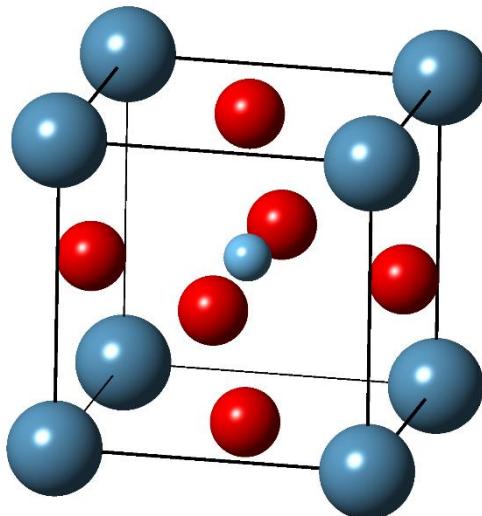
Golden-yellow rutile (TiO_2)
with dark hematite (Fe_2O_3)

A More Complex Structure: Perovskite (CaTiO_3)

- Perovskite is a double oxide: a ‘mixed’ Ca^{2+} (CaO) and Ti(IV) oxide (TiO_2)



Perovskite unit cell with
 Ca^{2+} coordination
emphasized



Alternative unit cell
showing coordination
of Ti(IV)

Ca^{2+} - large sphere; Ti(IV) – small, blueish; O^{2-} - red

Where do we find these, then?

- Some examples:

Ions	Halides				Ions	Group 16			
	F	Cl	Br	I		O	S	Se	Te
Li	Rock salt (NaCl)				Be	W	Sphalerite (S)		
Na	Rock salt (NaCl)				Mg	NaCl			S
K	Rock salt (NaCl)				Ca	Rock salt (NaCl)			
Rb	Rock salt (NaCl)				Sr	Rock salt (NaCl)			
Cs	NaCl	CsCl			Ba	Rock salt (NaCl)			
Cu	?	Sphalerite (S)			Zn	W	W or S		
Ag	NaCl			W	Cd	NaCl	W/S	W	S
					Hg	other	S	S	S

- W = wurtzite, S = sphalerite

Ionic radii in action

- We can predict the likely structure if we know the ratio:

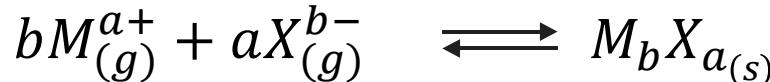
$$\rho = \frac{r_{\text{small}}}{r_{\text{large}}} \left(= \frac{r_+}{r_-} \right)$$

Cation, r_+ /pm	Li ⁺ , 76	Na ⁺ , 102	K ⁺ , 138	Rb ⁺ , 149	Cs ⁺ , 170
Anion, r_- /pm	F ⁻ , 133	Cl ⁻ , 181	Br ⁻ , 196	I ⁻ , 220	

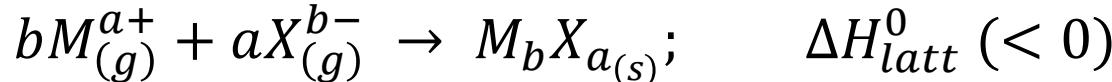
Radius ratio	CN for AB & AB ₂	AB type	AB ₂ type
1	12	None (metals)	
0.732-1	8:8 & 8:4	CsCl	CaF ₂
0.414-0.732	6:6 & 6:3	NaCl	TiO ₂
0.225-0.414	4:4	ZnS	-

The Lattice Enthalpy

- A ionic compound adopts the lattice that corresponds to the lowest Gibbs energy for the process:



- If we take $T = 0\text{K}$ as a standard condition, then for the above reaction $\Delta G^0 = \Delta H^0$
- This ΔH^0 , called the lattice enthalpy, is defined as standard molar enthalpy change accompanying the formation of the lattice starting from the constituent ions in a gas phase:

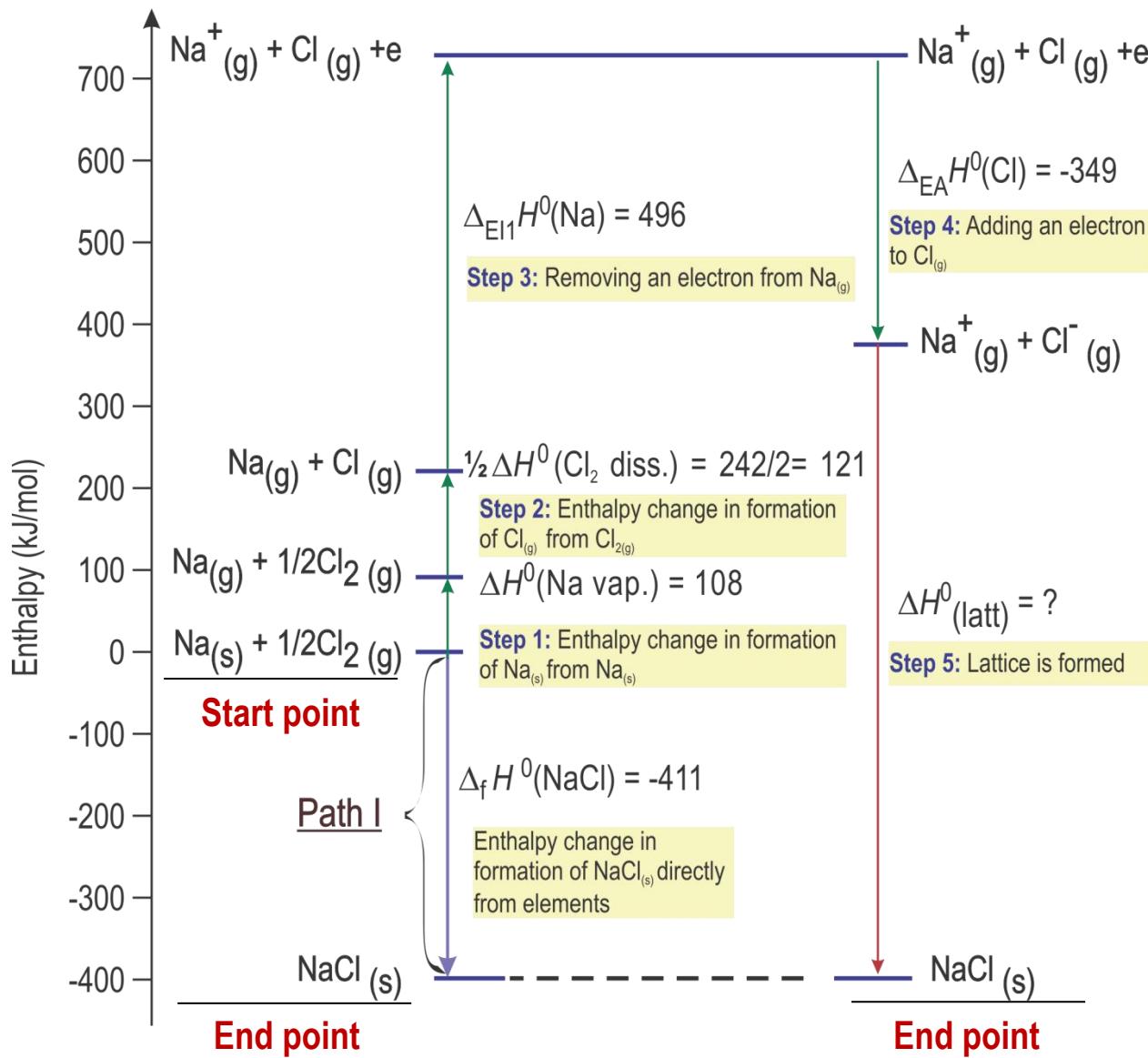


- Your textbook however defines the lattice energy in opposite direction: energy required to break up the lattice into its constituent ions. The absolute value for energy is the same in both cases, but the signs differ: the above definition will give negative while your textbook definition will give positive values for ΔH_{latt}^0 .

Measuring ΔH_{latt}^0 : The Born- Haber Cycle

- The ΔH_{latt}^0 values are difficult to measure directly as per chemical equations give before
- Instead, it is more convenient to use the **Born-Haber cycle** to determine ΔH_{latt}^0
- The cycle is based on the Hess' Law: the overall change in energy for a stepwise process equals the sum of energy changes of each step and it does not matter which path we take as long as the start point and end point of each path are equal.
- For calculating ΔH_{latt}^0 , the steps involved are dependent on the given reaction but are always logical steps that must take place during the reaction
- Two paths are taken: direct formation of our lattice from the elements and stepwise analysis of the whole process

The Born- Haber cycle: An Example NaCl



$$\begin{aligned}\Delta H (\text{Path I}) &= \Delta H (\text{Path II}) \\ \Delta_f H^0 (\text{NaCl}_{(s)}) &= \Delta H^0 (\text{Na vap.}) \\ &\quad + \frac{1}{2} \Delta H^0 (\text{Cl}_2 \text{ diss.}) \\ &\quad + \Delta_{\text{EI}1} H^0 (\text{Na}) \\ &\quad + \Delta_{\text{EA}} H^0 (\text{Cl}) \\ &\quad + \Delta H^0 (\text{latt.})\end{aligned}$$

$$-411 \text{ kJ/mol} = 108 \text{ kJ/mol} + 121 \text{ kJ/mol} + 496 \text{ kJ/mol} + (-349 \text{ kJ/mol}) + \Delta H^0 (\text{latt.}) \text{ and}$$

$$\Delta H^0 (\text{latt.}) = -787 \text{ kJ/mol}$$

The NaCl Cycle: The Details

- Path I has only one step:
 1. $\text{Na}_{(s)} + \frac{1}{2} \text{Cl}_{2(g)} \rightleftharpoons \text{NaCl}_{(s)}$; $\Delta_f H^0(\text{NaCl})$
- Path II has five steps:
 1. Atomization of $\text{Na}_{(s)}$: $\text{Na}(s) \rightarrow \text{Na}(g)$; $\Delta H^0(\text{Na vap.})$
 2. Breaking of Cl–Cl bond: $\frac{1}{2} \text{Cl}_2(g) \rightarrow \text{Cl}(g)$; $\frac{1}{2} \Delta H^0(\text{Cl}_2 \text{ diss.})$
 3. Ionization of sodium atoms: $\text{Na}(g) \rightarrow \text{Na}^+(g) + e$; $\Delta_{EI} H^0(\text{Na})$
 4. Addition of an electron to Cl(g): $\text{Cl}(g) + e \rightarrow \text{Cl}^-(g)$; $\Delta_{EA} H^0(\text{Cl})$
 5. Formation of NaCl lattice: $\text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{NaCl}_{(s)}$; ΔH_{latt}^0
- Values 1 – 4 and $\Delta_f H^0(\text{NaCl})$ are known (they are taken from the tables), and ΔH_{latt}^0 is calculated
- Keep in mind that all units are in kJ/mol (!) and that the number of moles used must be considered (hence $\frac{1}{2} \Delta H^0(\text{Cl}_2 \text{ diss.})$)
 - The equations are generally balanced so that they give one mole of product: i.e. $\text{Na}(s) + \frac{1}{2} \text{Cl}_2(g) \rightleftharpoons \text{NaCl}(s)$ and not $2\text{Na}(s) + \text{Cl}_2(g) \rightleftharpoons 2\text{NaCl}(s)$

Calculating ΔH_{latt}^0 : The Born-Mayer Equation

- ΔH_{latt}^0 can be theoretically estimated using the Born- Mayer equation:

$$\Delta H_{lat} = -\frac{N_A \cdot |z_+| \cdot |z_-| \cdot e^2}{4\pi\varepsilon_0 d} \left(1 - \frac{d^*}{d}\right) A$$

where: ΔH_{lat} – lattice enthalpy, N_A = Avogadro's constant, A – the **Madelung constant** (no units), z_+ and z_- - charges on cation and anion, e – electron charge, ε_0 – permittivity of vacuum ($8.854 \times 10^{-12} \text{ F m}^{-1}$), d – internuclear distance between ions (m) and d^* is usually 34.5 pm

- The equation shows two important facts:
 1. With increase in d , ΔH_{lat} decreases (for example, $\Delta H_{lat}(\text{LiF}) = -1030 \text{ kJ/mol}$ vs. $\Delta H_{lat}(\text{LiI}) = -757 \text{ kJ/mol}$)
 2. With increase in charge ΔH_{lat} increases (for example, $\Delta H_{lat}(\text{NaCl}) = -787 \text{ kJ/mol}$ vs. $\Delta H_{lat}(\text{MgO}) = -3795 \text{ kJ/mol}$)

Calculating ΔH_{latt}^0 : The Madelung constant

- The Madelung constant accounts for all Coulombic interactions in the crystal lattice.
- The constant values depend on the lattice type and coordination numbers (CN):

Structure type	CN (cation, anion)	A
Sodium chloride (NaCl)	6,6	1.7476
Caesium chloride (CsCl)	8,8	1.7627
Wurtzite (ZnS)	4,4	1.6413
Sphalerite (ZnS)	4,4	1.6381
Fluorite (CaF_2)	8,4	2.5194
Rutile (TiO_2)	6,3	2.408
Cadmium Iodide (CdI_2)	-	2.355

Calculating ΔH_{latt}^0 : The Kapustinskii equation

- A general equation for estimating lattice energies
- More simple but not as precise as the Born-Meyer equation:

$$\Delta H_{latt}^0 = - \frac{(1.07 \cdot 10^5) v |z_+| |z_-|}{r_+ + r_-}$$

where: v – the number of ions in salt's formula unit, r_+ and r_- - radii for cation and anion, z_+ and z_- - cation and anion charges (absolute value is taken)

- The Kapustinskii equation can be used to determine *thermodynamic radii* of cations and anions
 - The thermodynamic radius is a radius calculated based on thermodynamic values: if we know ΔH_{latt}^0 (from, for example, Born-Haber cycle) we can use the Kapustinskii equation to calculate r values for ions that are not necessary spherical (i.e. linear, planar etc.)

The “gray area” between ionic and covalent

- Covalent character of ionic bond *and* ionic (polar) character of covalent bond
- The Lewis-Langmuir equation is used to estimate the partial charges on bonded atoms:

$$\delta_{LL} = \frac{\text{Number of valence electrons on X}}{\text{Number of lone electrons on X}} - 2 \times \sum_{\text{bonds}} \left(\frac{\chi_x}{\chi_x + \chi_y} \right)$$

- Where χ is Pauling electronegativity and X and Y are bonded atoms.
- This can be used to calculate the dipole moment of the bond:

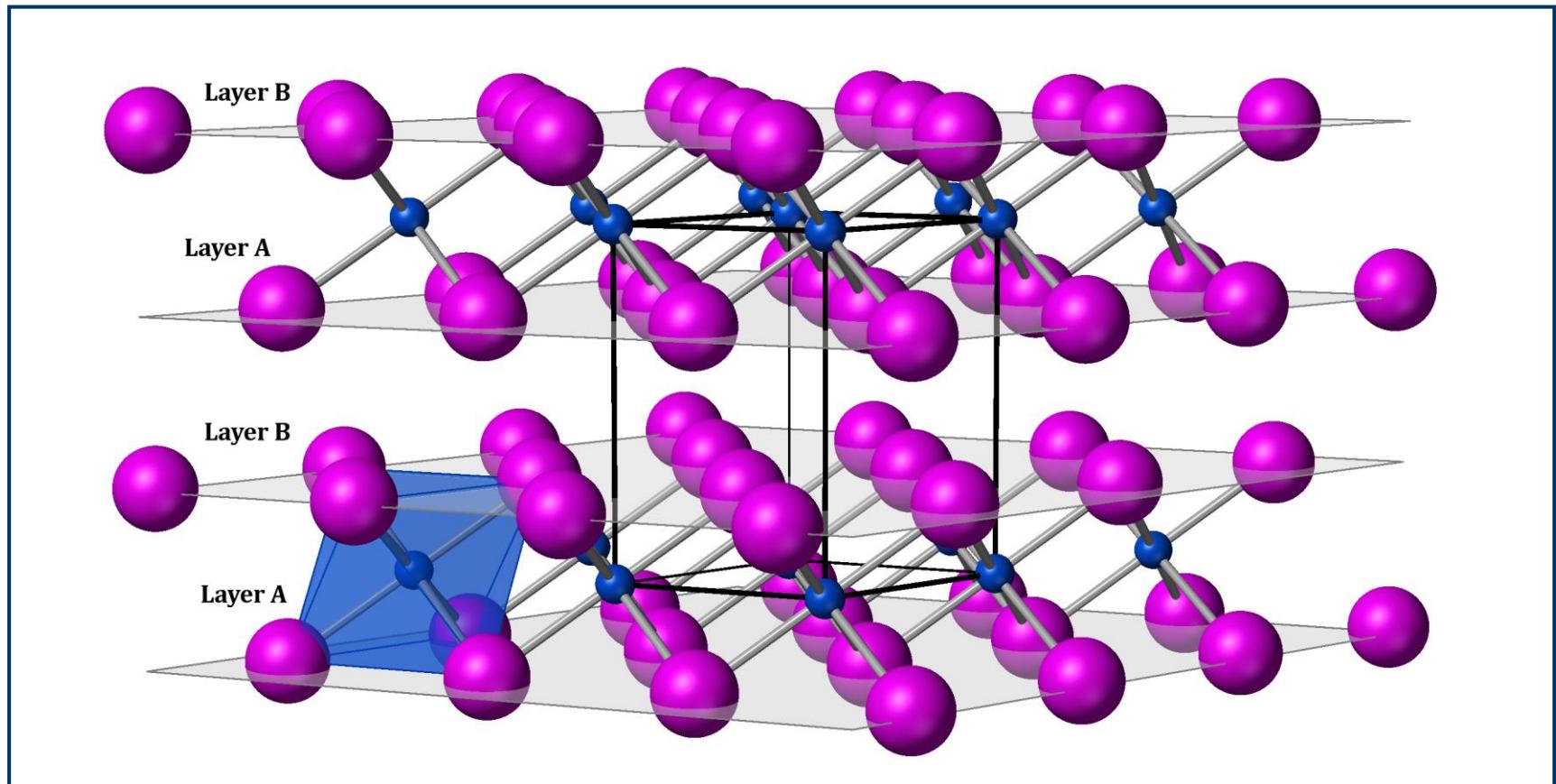
$$\mu = d \times \delta.$$

- Where μ is the dipole moment, d is the internuclear distance (bond length) and δ is the partial charge
- And the ionic character of a covalent bond is given by:

$$\% \text{ ionic character} = \frac{\mu(\text{experiment})}{\mu(\text{ionic, calc})} \times 100\%$$

Some consequences: Layered structures

- In a layered structure two different types of forces keep the structure together
- For example, CdI_2 has a high covalent bonding character:



Some consequences: Physical properties

- Changes in bonding and structure result in changes in physical properties
- Recall that ionic solids have higher melting and boiling points in comparison to covalent solids
 - And this is a consequence of weak, non-bonding interactions holding covalent molecules in the solid state
- For example:

Compound	CdF_2	CdCl_2	CdI_2
Melting point ($^{\circ}\text{C}$)	1075	568	388
Boiling point ($^{\circ}\text{C}$)	1750	964	744

Overview

- The concepts of:
 - Crystalline and amorphous solids;
 - Crystal lattice and unit cell;
 - Coordination number;
 - Lattice energy.
- Simple solids:
 - Hexagonal and cubic close packing;
 - Simple cubic and volume-centered cubic.
- Ionic and covalent structures:
 - AB type structures: sodium-chloride (NaCl), caesium-chloride (CsCl), zinc-sulfate (ZnS);
 - AB₂ and A₂B structures: calcium-fluoride (CaF₂), titanium(IV) oxide (TiO₂);
 - Perovskite (CaTiO₃).
- Ionic radii and structure: predicting a likely structure and estimating the lattice energy (the Born-Mayer and Kapustinskii equations).
- The Born-Haber cycle and lattice energies.

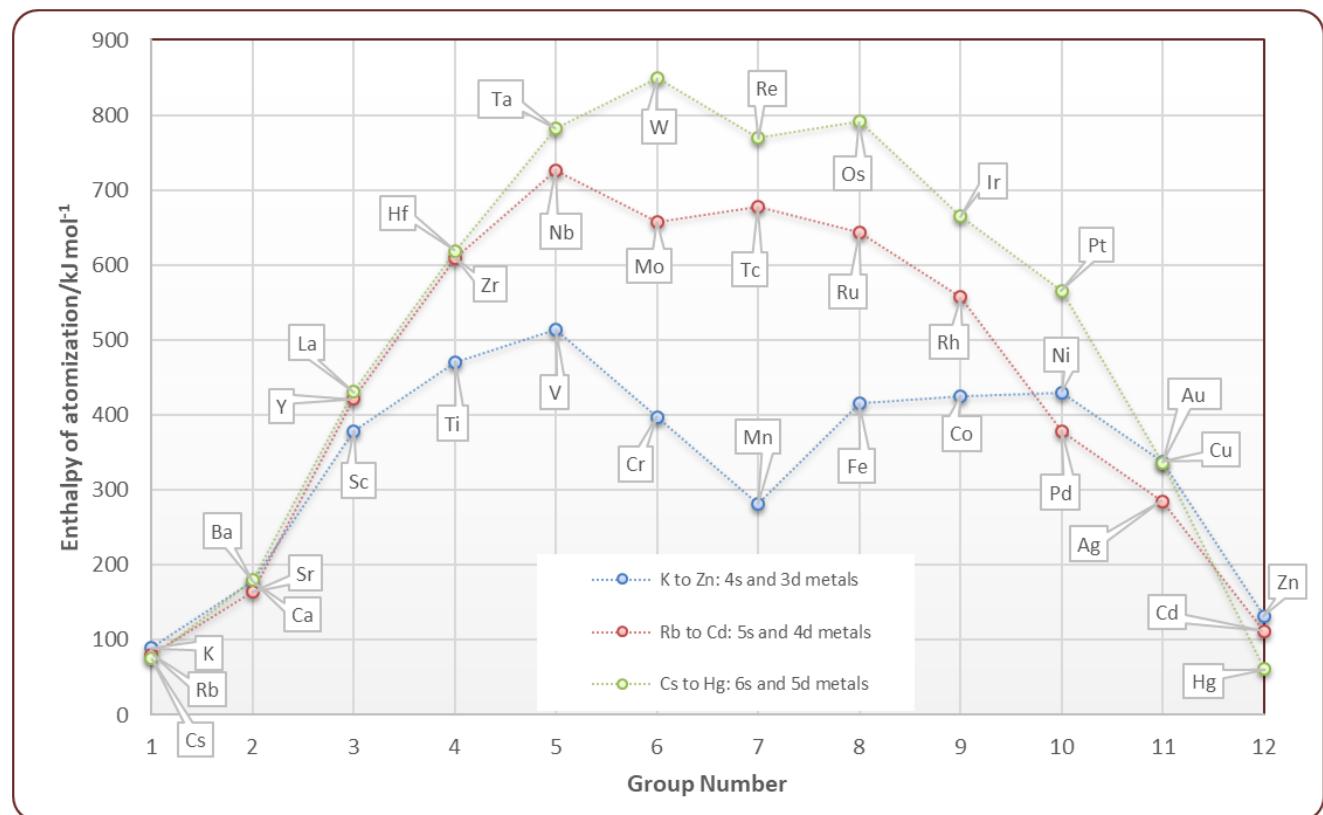
Readings and problems

- Readings:
 - **6th ed.** Chapter 3 “The Structures of Simple Solids” up to “Consequences of lattice enthalpies”; you can also skip section 3.10 “The rationalization of structures”
 - **7th ed.** As above, just Chapter 4
- Problems:
 - Worked examples and self-tests: 3.2, 3.6, 3.9, 3.11, 3.12
 - End-of-chapter exercises: 3.2, 3.7, 3.8, 3.13, 3.14, 3.17
 - End-of-chapter problems: 3.2, 3.5 and 3.15
 - For 7th edition as above, but from Chapter 4

Enthalpies of atomization

- Enthalpy of atomization is the change in enthalpy for the sublimation of metal (an equivalent of bond dissociation energy for covalent bond)

From Group 1 to right, electrons are occupying bonding region of bands resulting in steady increase in ΔH_a ; the energy decreases from the middle further to right because the antibonding regions are being filled.



Note sharp drops for Cr and Mn – trend breakers!