

# Chemistry and Physics of Solids – Lecture 6

## Pauling's principles of ionic structures, isomorphism and solid solution



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# After today?

- General construction principles of crystal structures of ionic compounds given by Pauling's laws.



- You will know that most of the solids are so-called solid solutions formed by the exchange of ions or atoms in ANM and metal alloys.



# Pauling's principles of ionic structures

Linus Pauling: *The Nature of the Chemical Bond*,  
J. Amer. Chem. Soc. 51, 1010 (1929)

1. Every cation is surrounded by a polyhedron of anions, the cation-anion distance being determined by the radius sum and the coordination number of the cation by the radius ratio.
2. The total strength of the valency bonds which reach an anion from all the neighbouring cations is equal to the charge of the anion.
3. The existence of edges, and particularly of faces, common to two anion polyhedra in a co-ordinated structure decreases its stability. This effect is large for cations with high valency and small co-ordination number, and is especially large when the radius ratio approaches the lower limit of stability of the polyhedron.
4. In a crystal containing different cations those of high valency and small co-ordination number tend not to share polyhedron elements with each other.
5. The number of essentially different kinds of constituent in a crystal tends to be small



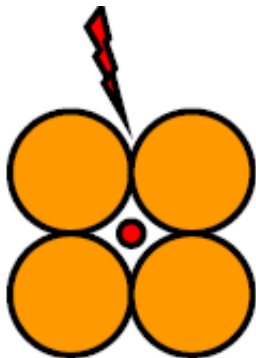
# 1. Pauling's principle

The anion-cation distance is determined from atomic radii.  
The coordination number of the cation is determined by the radius ratio.

## Radius ratio in 2D case

$r(\text{cation})/r(\text{anion})$   
< optimal value

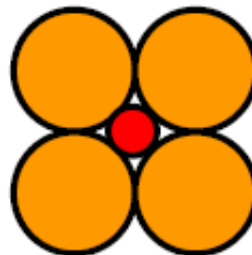
$$\rho = 0.26$$



unstable

$r(\text{cation})/r(\text{anion})$   
= optimal value

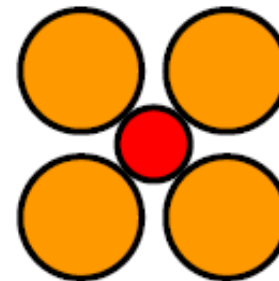
$$\rho = 0.41$$



Minimal radius  
ratio

$r(\text{cation})/r(\text{anion})$   
> optimal

$$\rho = \frac{r_+}{r_-} = 0.70$$



Stable, but it tends to  
transform to the higher co-  
ordination number

# 1. Pauling's principle

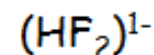
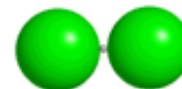
## Common coordination polyhedrons

cation-anion radius ratio  $r_c/r_a$  determines the coordination number CN

0.000-0.155

2

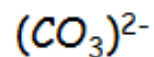
linear



0.155-0.225

3

triangular



0.225-0.414

4

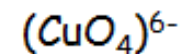
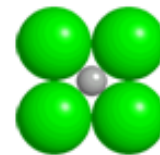
Tetrahedral



0.414-0.732

4

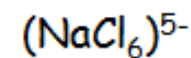
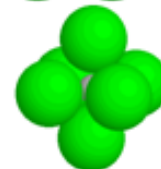
square



0.414-0.732

6

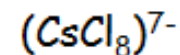
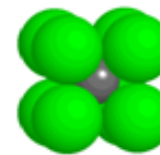
octahedral



0.732-1.000

8

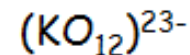
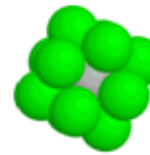
cube



1.000

12

Close packing



## 2. Pauling's principle. The electrostatic valency rule

This rule is an expression of the tendency of any structure to assume a configuration of minimum potential energy on which the ions strive as far as possible to surround themselves by neighbours of opposite sign so that electrical charges are neutralized locally.

For a given cation, Pauling defined the *electrostatic strength* to each coordinated anion as



$$s_{ij} = z/c$$

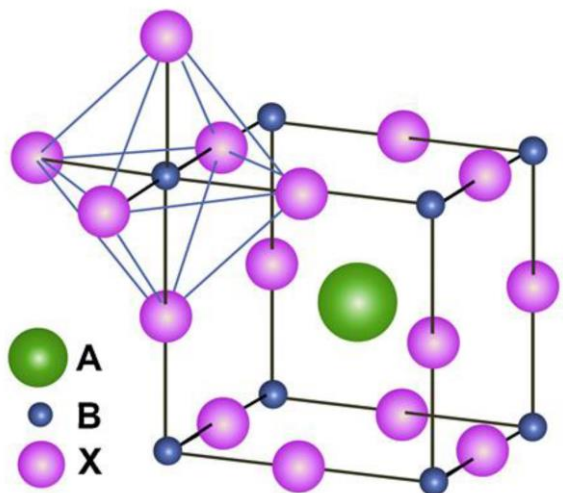
where  $z$  is the cation charge and  $c$  is the cation coordination number.

The valence of an ion ( $V_i$ , equal to the oxidation state of the ion) is equal to a sum of the valences of its bonds ( $s_{ij}$ ).

$$V_i = \sum(s_{ij})$$

The best way to illustrate this concept is to do some examples.

## 2. Paulingův zákon. Elektrostatická síla vazby



$$S_{ij} \text{ Ca-O} = 2/12 = 1/6$$

$$S_{ij} \text{ Ti-O} = 4/6 = 2/3$$

$$V_o = 2 \cdot s_{ij}(\text{Ti-O}) + 4 \cdot s_{ij}(\text{Ca-O}) = 2$$



	A	B	X
	Ca	Ti	O
CN	12	6	2(Ti), 4(Ca)
Oxidation state	2+	4+	2-

## 2. Pauling's principle. The electrostatic valency rule

What is this good for?

- checking the correctness of the crystal structure
  - predicting crystal structures and coordination
- calculating the formal charge or coordination number



### 3. Pauling's principle

The existence of edges,  
and particularly of faces, common to two anion polyhedra in a  
coordinated structure decreases its stability

This rule follows from a consideration of the Coulombic interactions in a crystal. To maximize such interactions we want to maximize the cation-anion interactions, which are attractive, and minimize the anion-anion and cation-cation interactions, which are repulsive. The cation-anion interactions are maximized by increasing the coordination number and decreasing the cation-anion distance. However, we know that if we bring ions too close together electron-electron repulsions become increasingly unfavorable. Thus optimal cation-anion distances are dictated either by ionic radii or quantitative use of the bond valence rule, which are elucidated in Pauling's first two rules.

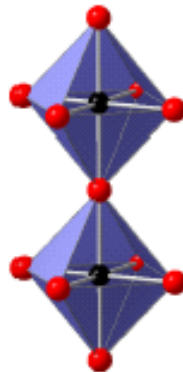
The basic concept behind this rule is to minimize the cation-cation interactions. To illustrate this consider the cation-cation distances in both tetrahedra and octahedra which share common corners, edges and faces, as a function of the cation-anion distance ( $M-X$ )

# 3. Pauling's principle

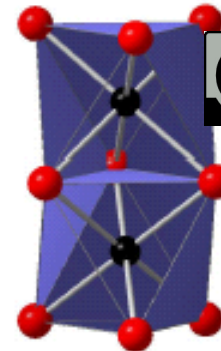
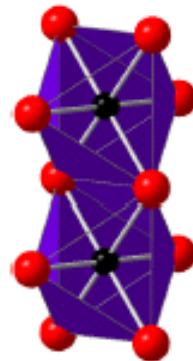
The existence of edges,  
and particularly of faces, common to two anion polyhedra in a  
coordinated structure decreases its stability

	<i>Cation-Cation Distance</i>		
	<i>Corner</i>	<i>Edge</i>	<i>Face</i>
Tetrahedra	2 M-X	1.16 M-X	0.67 M-X
Octahedra	2 M-X	1.41 M-X	1.16 M-X

cation-anion  
distance  
(M-X)



The most stable



The least stable

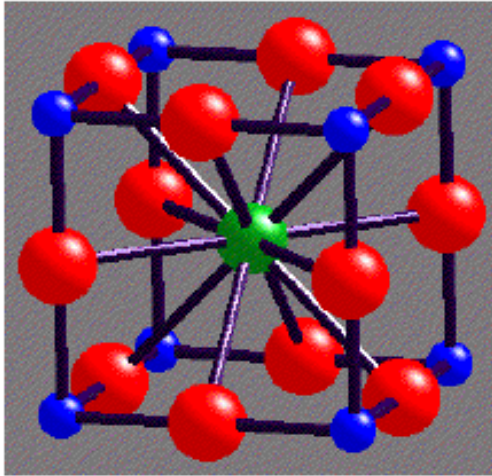


Stability:

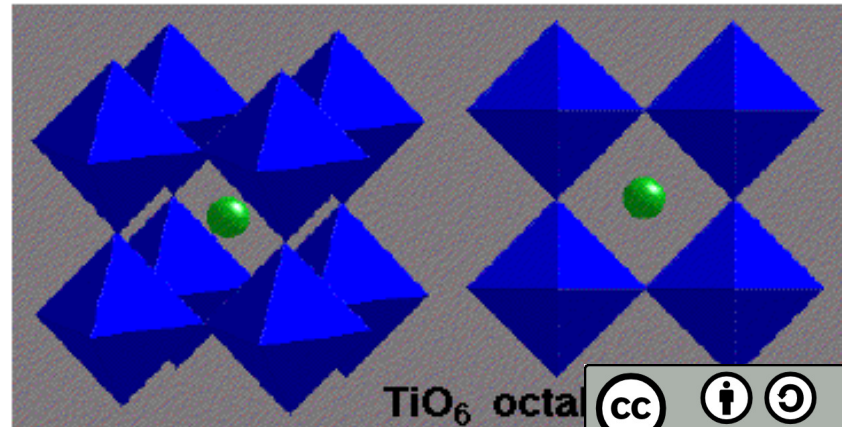
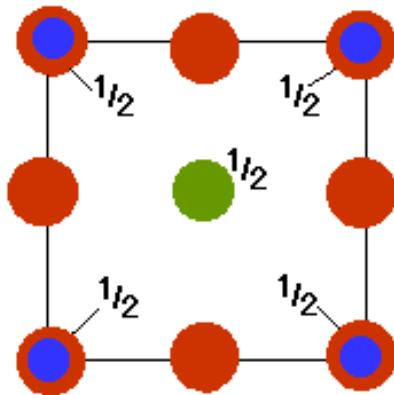
- degree of sharing decreases (corner < edge < face) .
- CN increases (cubic < octahedral < tetrahedral)
- cation oxidation state decreases (this leads to a stronger Coulomb repulsion)



## Closer look to the perovskite



A-Cell

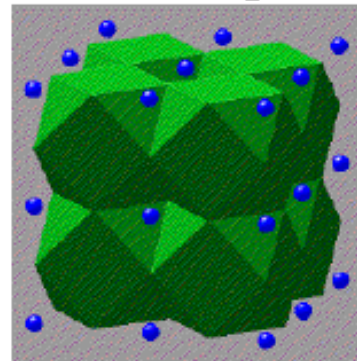


TiO<sub>6</sub> octa

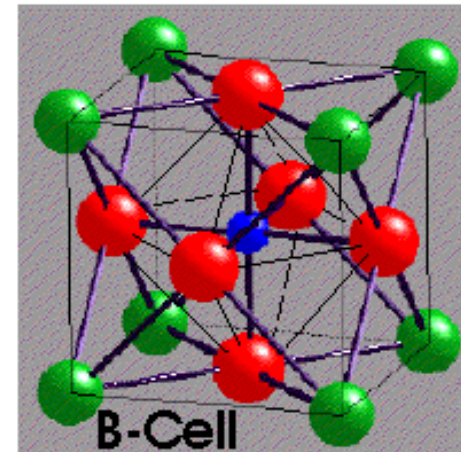


● Ca ● Ti ● O

Perovskite  
CaTiO<sub>3</sub>

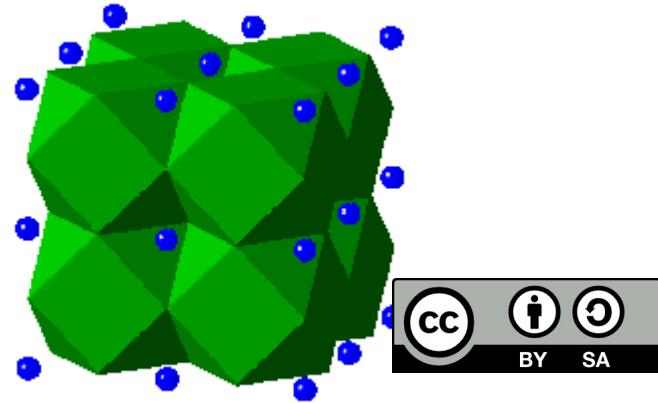
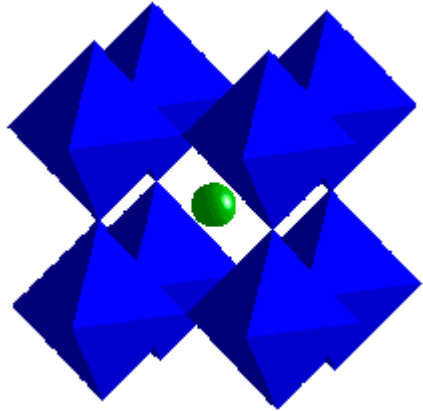


CaO<sub>12</sub> cuboctahedra



B-Cell

$\text{CaO}_{12}$  shares faces



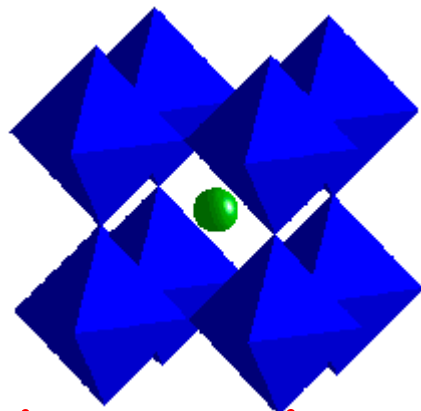
$\text{TiO}_6$  shares only corners

# 4. Pauling's principle.

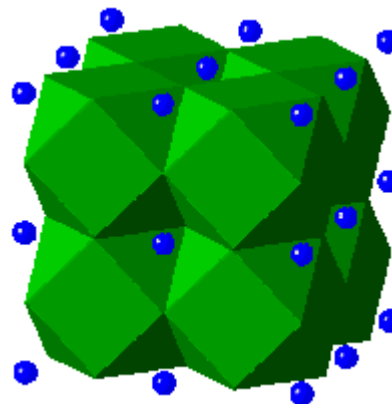
In a crystal containing different cations those of high valency and small coordination number tend not to share polyhedron elements with each other

This is a consequence of the 3rd principle, and follows from similar arguments.

Let's show it on the perovskite again:



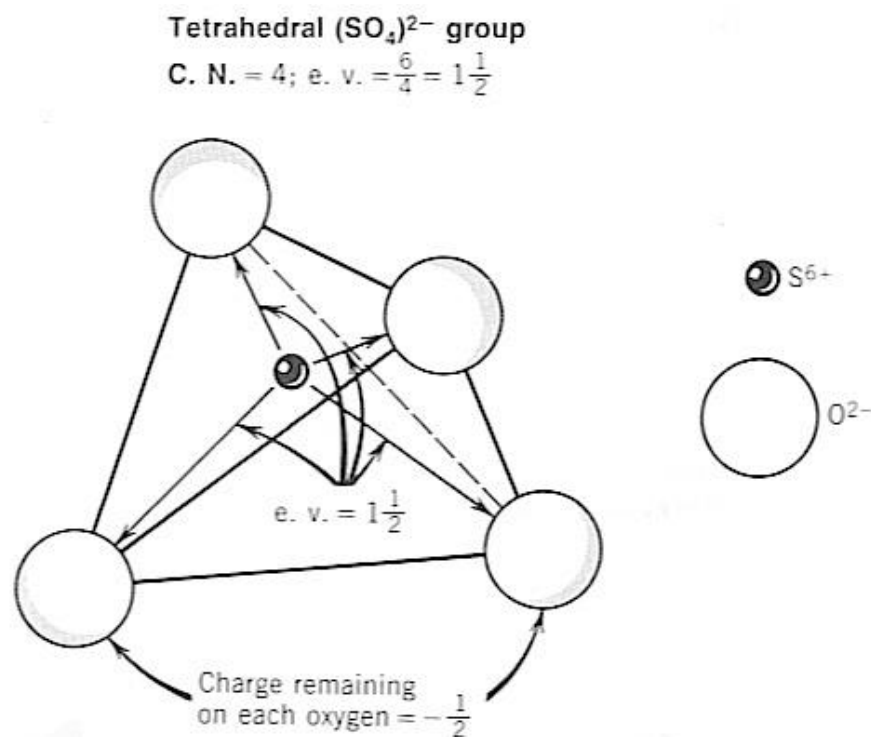
$\text{TiO}_6$  shares only corners  
 $\text{CN} = 6, V = 4$



$\text{CaO}_{12}$  shares faces  
 $\text{CN} = 12, V = 2$

# 4. Pauling's principle.

In crystals containing different cations with high valencies and low coordination numbers, there is no mutual sharing of polyhedral elements

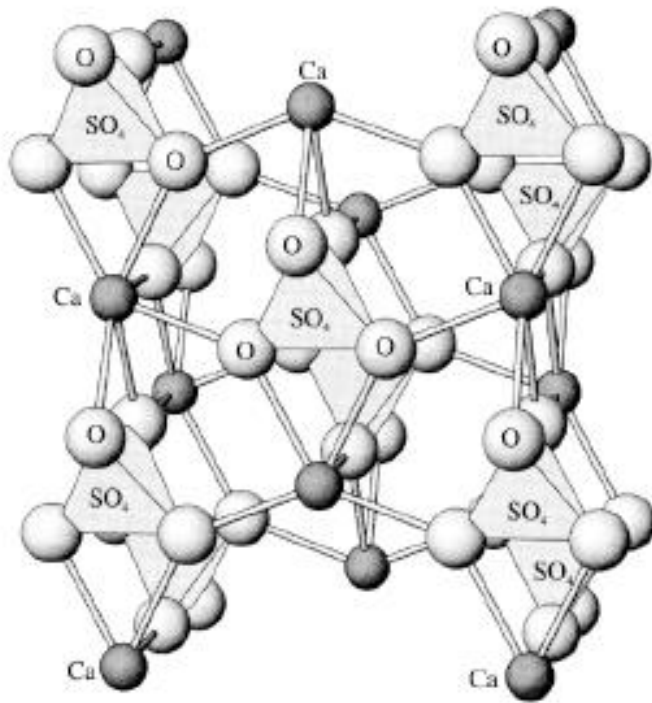


"Calculations" based on 4. Pauling of the principle lawermine that groups  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$  etc. must be discrete groups that do not share the vertex together  $\text{O}^{2-}$ .

For example, bond strength S-O in  $\text{SO}_4^{2-}$  is  $3/2$ . Valence O is 2. Remaining valence  $\frac{1}{2}$  je insufficient to join another S  $\Rightarrow \text{SO}_4^{2-}$  is a discrete ionic group.

# 4. Pauling's principle.

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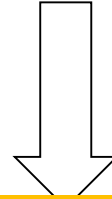


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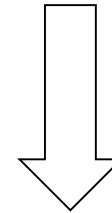
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# 5. Pauling's principle.

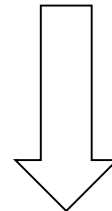
Relatively few types of cation and anion sites



The number of essentially different kinds of constituents in a crystal tends to be small



In structures with complex chemical compositions, a number of different ions can occupy the same structural position (site)



Solid solution

# Bond types based on electrostatic valence

- All bonds have the same strength  
(isodesmic) -  
Coordination compounds

$$V_i = Z_A / \text{CN}_A < 1/2Z_X$$



- Groups with exactly half of the anion charge: silicates (mesodesmic)  
 $V_i = Z_A / \text{CN}_A = 1/2Z_X$
- small, highly charged cations make compact groups  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$   
(anisodesmic)  
 $V_i = Z_A / \text{CN}_A > 1/2Z_X$



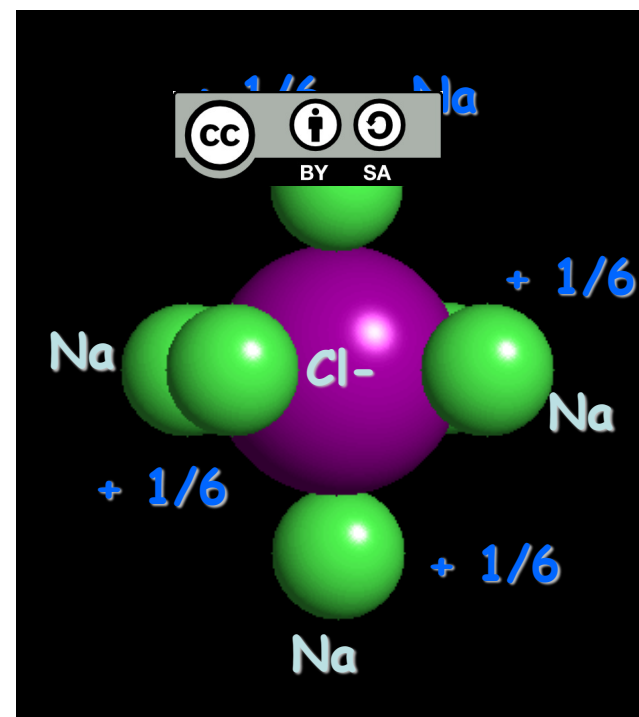
# Pauling's Laws for Ionic Crystals

Determination of bond-type from the 2nd Pauling's principle  
Isodesmic bond

$6 ( + 1/6 ) = +1$  (sum by Na)  
Charge -1

Charges are equal => stable  
crystal structure

Oxides, hydroxides





# Pauling's Laws for Ionic Crystals

Determination of bond-type from the 2nd Pauling's principle  
Isodesmic bond

...from the second side:

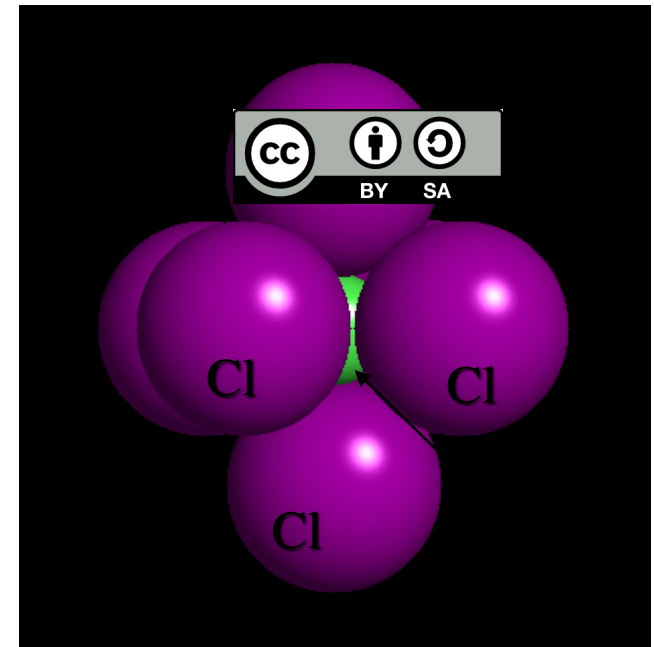
$\text{Na}^+$  in the structure of  $\text{NaCl}$  is also  
in the octahedral coordination =>  
surrounded by 6  $\text{Cl}^-$

Each of the  $\text{Cl}$  atoms contributes  
 $1/6$  negative charge

$$\Sigma (\text{Cl}) = 6 \left( -\frac{1}{6} \right) = -1$$

charge  $\text{Na} = +1$

The final charge is again neutral



# Pauling's Laws for Ionic Crystals

## - mesodesmic bond

The case occurs when e.v.s. cation corresponds to  $\frac{1}{2}$  charge of anion. An example is  $\text{Si}^{4+}$  in tetrahedral coordination of  $\text{O}^{2-}$ . E.v. Si is  $4/4 = 1$ . Each O has an uncompensated charge of -1. Charge -1 corresponds exactly to  $\frac{1}{2}$  charge on  $\text{O}^{2-}$ . Oxygen in the  $\text{SiO}_4^{4-}$  anion are connected by the same force to the outer groups as the central Si. In this case, the link is referred to as mesodesmic.

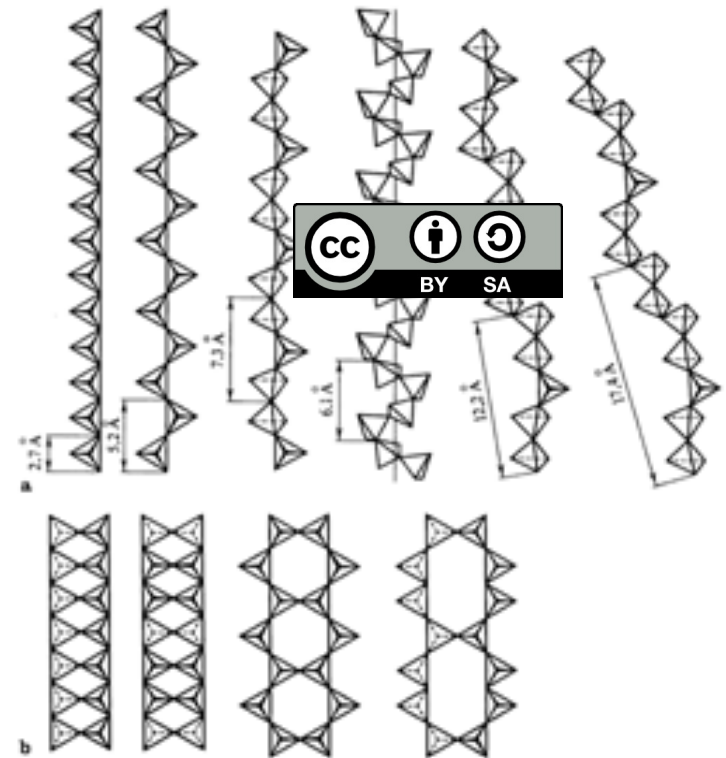
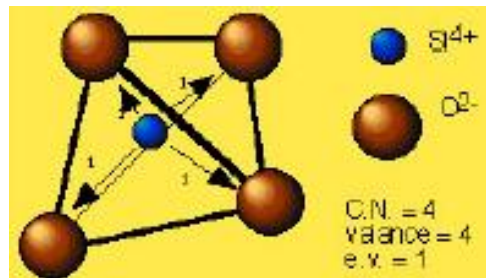
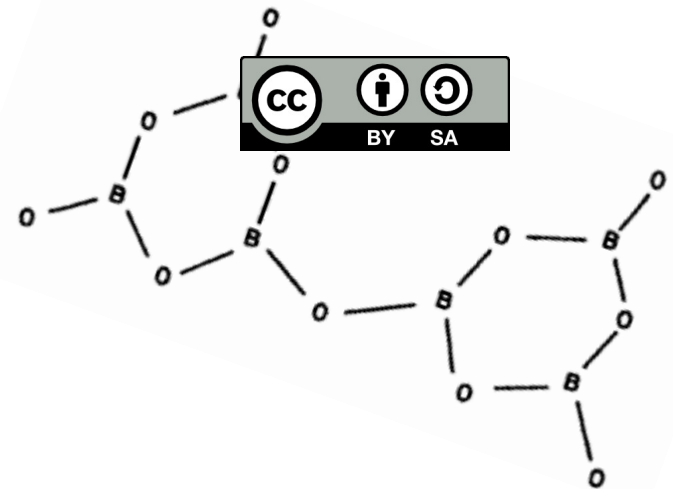
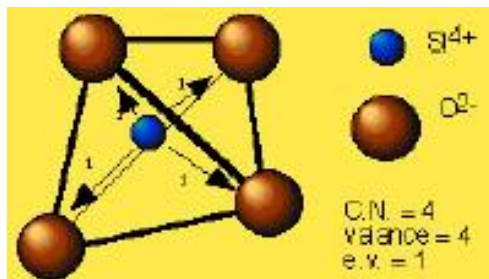


Fig. 2.30a, b. Various types of simple (a) and complex (b) chains in silicates

# Pauling's Laws for Ionic Crystals

## - mesodesmic bond

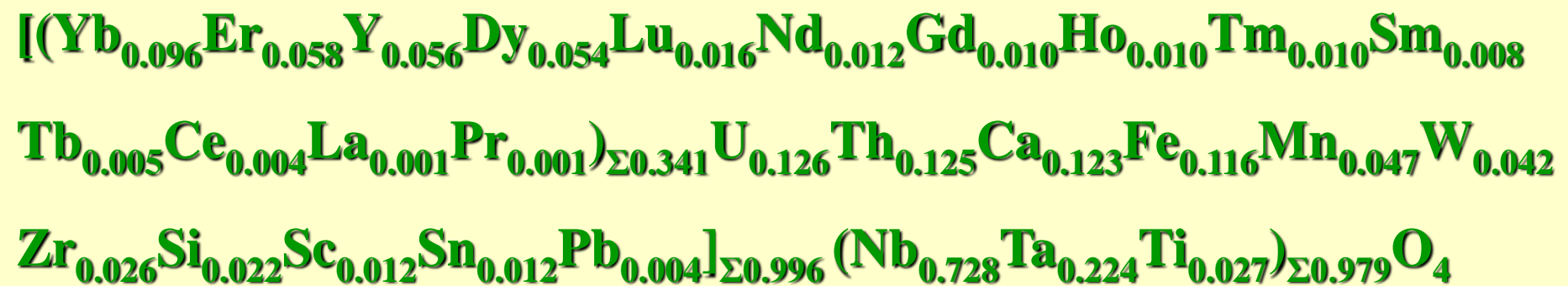
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Chain binding is also characteristic for borates, chaining occurs also in  $\text{ReO}_3$  (octahedral coordination)

## Samaraskite-(Yb)

- $ABO_4$
- Both sites are octahedrally coordinated, but they have different sizes





# Isomorphism

Solid solutions, inorganic non-metallic materials and metallic alloys



rules of isomorphic substitutions

# Isomorphism

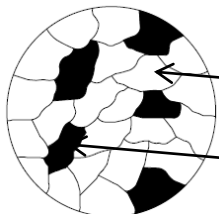
**Isomorphism** -mutual substitution of atoms or groups of different chemical elements in equivalent positions of the crystal structure

New properties



Mixture of crystals  
Mechanical mixtures

Isomorphous mixture,  
Solid subst. solutions



Crystals of A

Crystals of B

Microstructure of the  
mixture of crystals

# Solid solutions

impurities occurred in crystal structures in quantities between 0.1 – 1 %  
Are called as defects of impurities

If the content is higher than 1%?



**Solid solution**



## Definition:

a solid phase with more than one type of atoms in the structure regularly distributed in the structural positions

# 1st Goldschmidt's law

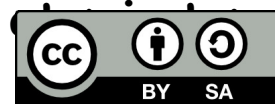
Goldschmidt tolerance factor:

atom A  
↑  
minority atomic type

## replaces

the atom B

↑  
major



Lets define the difference of radii between A and B as:

$$\% \Delta \mathbf{r}_{A/B} = \left( \frac{\mathbf{r}_A - \mathbf{r}_B}{\mathbf{r}_B} \right) \times 100$$

The lower value of  $|\% \Delta r|$ , the greater possible substitution

If  $|\% \Delta r|$  lower then **15%** (e.g. alloys), then the ions of one element extensively replace the others.

If  $|\% \Delta r|$  is higher than 15%, then only limited substitution occurs (15-30%). With a difference greater than 30% the substitution is impossible.



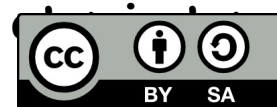
# 1st Goldschmidt's law

Goldschmidt tolerance factor:

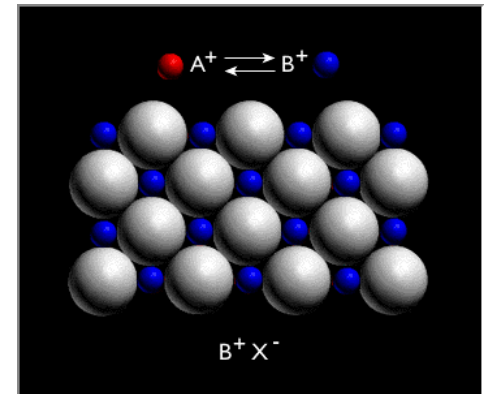
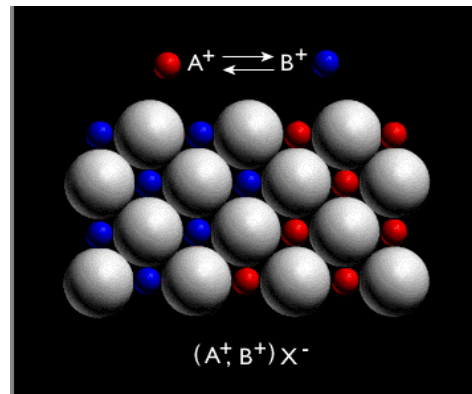
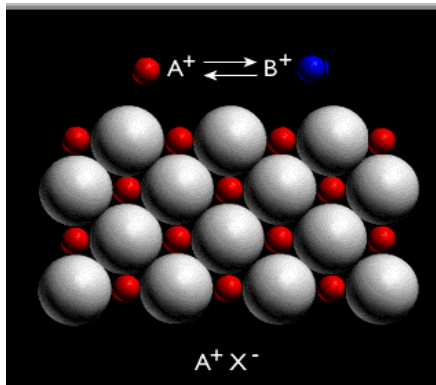
atom A  
↑  
minority atomic type

replaces

the atom B  
↑  
major



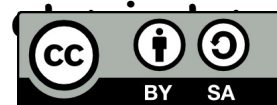
Continuous solid solution



# 1st Goldschmidt's law

Goldschmidt tolerance factor:

atom A replaces the atom B  
 ↑  ↑  
 minority atomic type  major

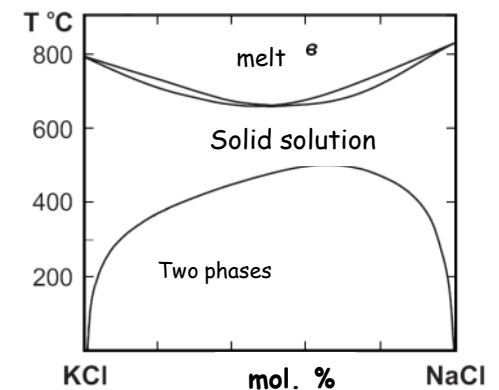


$$\% \Delta r_{A/B} = \left( \frac{r_A - r_B}{r_B} \right) \times 100$$

KBr a KCl  $\% \Delta r_{Br/Cl} = \frac{r_{Br} - r_{Cl}}{r_{Cl}} \times 100 = 8\%$  Continuous solid solution

KCl a KJ  $\% \Delta r_{Cl/J} = \frac{r_J - r_{Cl}}{r_{Cl}} \times 100 = 21\%$  Limited solid solution

KCl a NaCl  $\% \Delta r_{K/Na} = \frac{r_K - r_{Na}}{r_{Na}} \times 100 = 35\%$  Solid solution is impossible



# 1st Goldschmid's law

The ions of one element can be replaced indefinitely in ion crystals by others if they do not differ in their radii by more than 15%

The substitution is dependent on the concentration, compatibility of the bonds, structural types, the electronegativity difference and the coordination numbers.



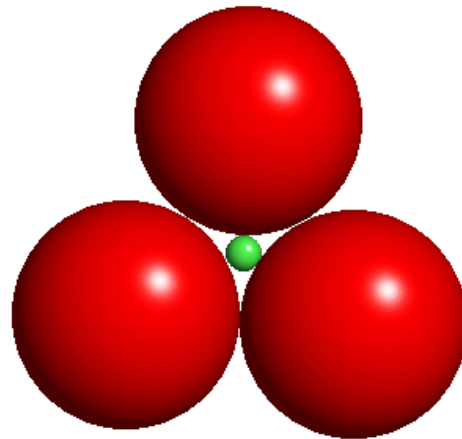
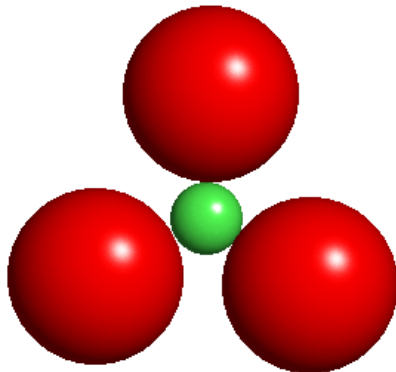
The difference in the electron structure of the atoms and the different character of the chemical bonds of the atoms in the respective compounds can be explained by bounded or no isomorphism of atoms very similar in their size, but the differing electronegativity of the pairs:  $K^+$  a  $Ag^+$  ( $\Delta r = 18\%$ ,  $\Delta \chi = 1,1$ ),  $Ca^{2+}$  a  $Cd^{2+}$  ( $\Delta r = 5\%$ ,  $\Delta \chi = 0,6$ ),  $Ca^{2+}$  a  $Hg^{2+}$  ( $\Delta r = 8\%$ ,  $\Delta \chi = 0,9$ ),  $Mg^{2+}$  a  $Zn^{2+}$  ( $\Delta r = 12\%$ ,  $\Delta \chi = 0,4$ ).

Tolerance to isomorphism increases with increasing temperature.

At high temperatures, broad or continuous isomorphous rows of compounds are formed  $Na^+$  a  $K^+$  ( $\Delta r = 36\%$ ,  $\Delta \chi = 0,1$ ),  $K^+$  a  $Rb^+$  ( $\Delta r = 12\%$ ,  $\Delta \chi = 0,0$ ),  $Ca^{2+}$  a  $Sr^{2+}$  ( $\Delta r = 16\%$ ,  $\Delta \chi = 0,1$ ),  $Sr^{2+}$  a  $Ba^{2+}$  ( $\Delta r = 15\%$ ,  $\Delta \chi = 0,1$ ),  $Zn^{2+}$  a  $Cd^{2+}$  ( $\Delta r = 19\%$ ,  $\Delta \chi = 0,1$ ) with a lower or high difference in the size of the ions, but with a lower difference  $\Delta \chi$ .

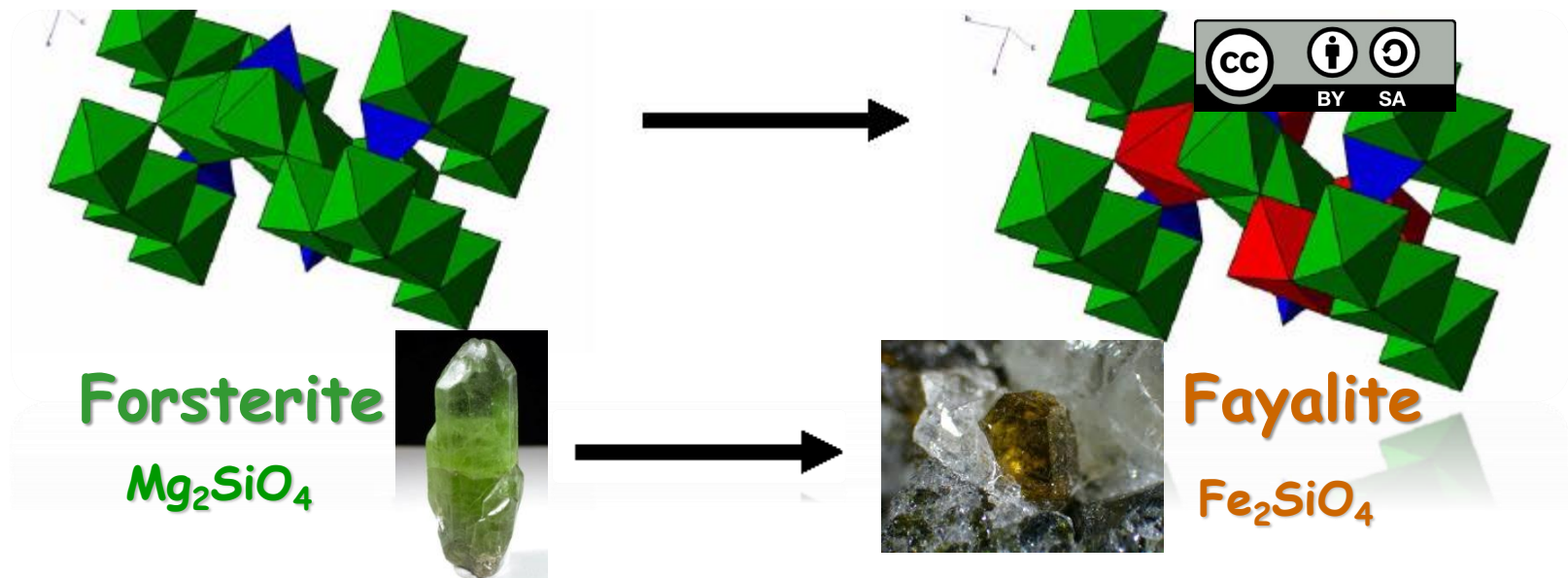
## 2nd Goldschmidt's law

If two cations have the same charge, but a different size, then the smaller of them will enter the structure more readily. The smaller ion causes a smaller distance between the cation and the anion, and therefore the ionic theory results in a stronger bond.



# 2nd Goldschmidt's law

If two cations have the same charge, but a different size, then the smaller of them will enter the structure more readily. The smaller ion causes a smaller distance between the cation and the anion, and therefore the ionic theory results in a stronger bond.



$\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  in octahedral sites of olivine  $(\text{Mg,Fe})_2\text{SiO}_4$

Their sizes are similar  $\text{Fe}^{2+}$  0.61 Å,  $\text{Mg}^{2+}$  0.57 Å

When crystallizing from the melt what will crystallize at the beginning?

$\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$  olivine?

# 3rd Goldschmidt's law

Ion with the same radius, but with higher charge will preferably be incorporated by the growing crystal

## Influence of the charge (z)

The following criteria are valid only when the charge neutrality of the crystal is achieved:

$$|\Delta z_{A/B}| = 0$$

very good substitution

$$|\Delta z_{A/B}| = 1$$

substitution is possible



$$|\Delta z_{A/B}| > 1$$

very bad substitution

both laws result from ensuring a minimum of attractive and repulsive forces in ionic bonds and the distance of ion cores:

$$U = \frac{-N |z^+ z^-| A e^2}{r_o} \left(1 - \frac{1}{n}\right)$$

# Goldschmidt laws of isomorphic substitutions

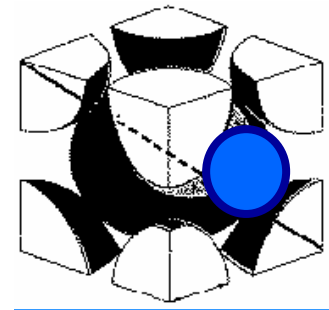
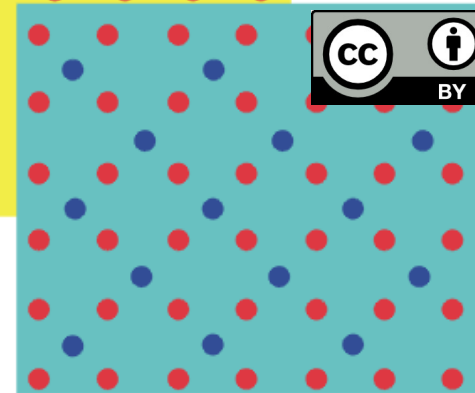
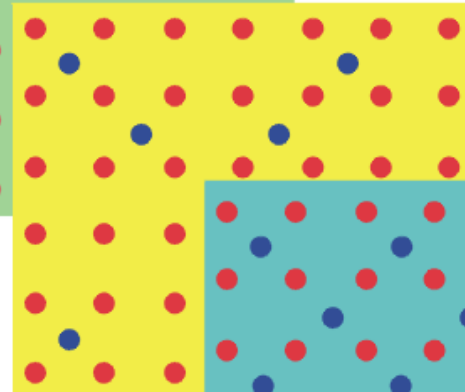
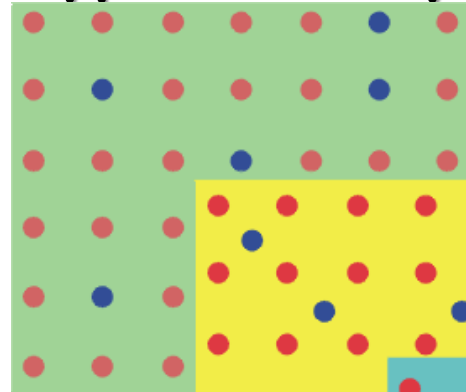
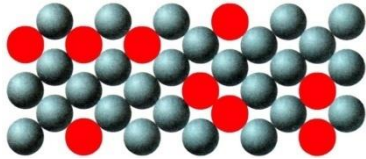
Common substitutions:

<i>Ion</i>	<i>KČ</i>	<i>r<sup>+</sup></i>	<i>Ion</i>	<i>KČ</i>	<i>r<sup>+</sup></i>
<i>Mg<sup>2+</sup></i>	6	0.57	<i>Fe<sup>2+</sup></i>	6	
<i>Al<sup>3+</sup></i>	4	0.39	<i>Si<sup>4+</sup></i>	4	0.39
<i>Ba<sup>2+</sup></i>	8 nebo 9	1.42-1.47	<i>K<sup>+</sup></i>	8 nebo 9	1.51-1.55
<i>Sr<sup>2+</sup></i>	6 nebo 8	1.18-1.26	<i>Ca<sup>2+</sup></i>	6 nebo 8	1.0-1.18
<i>Na<sup>+</sup></i>	8	1.18	<i>Ca<sup>2+</sup></i>	8	1.12
<i>Na<sup>+</sup></i>	8	1.18	<i>K<sup>+</sup></i>	8	1.51
<i>Hf<sup>4+</sup></i>	8	0.84	<i>Zr<sup>4+</sup></i>	8	0.83



# Solid solutions in systems of metal-alloys

## Types of alloys



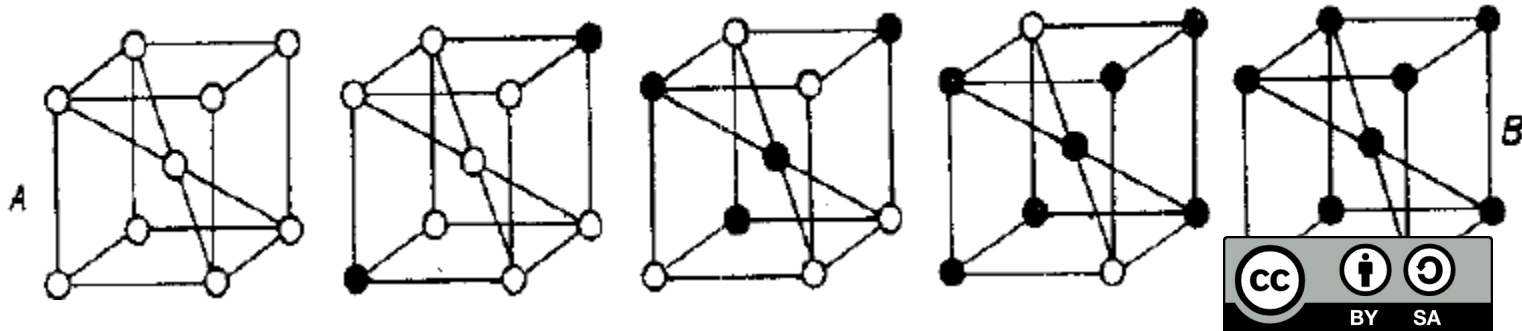
- (a) Substitute
- (b) Interstitial
- (c) Intermediate,  
intermetallic



# Solid solutions of metals

## Substitutional solid solutions

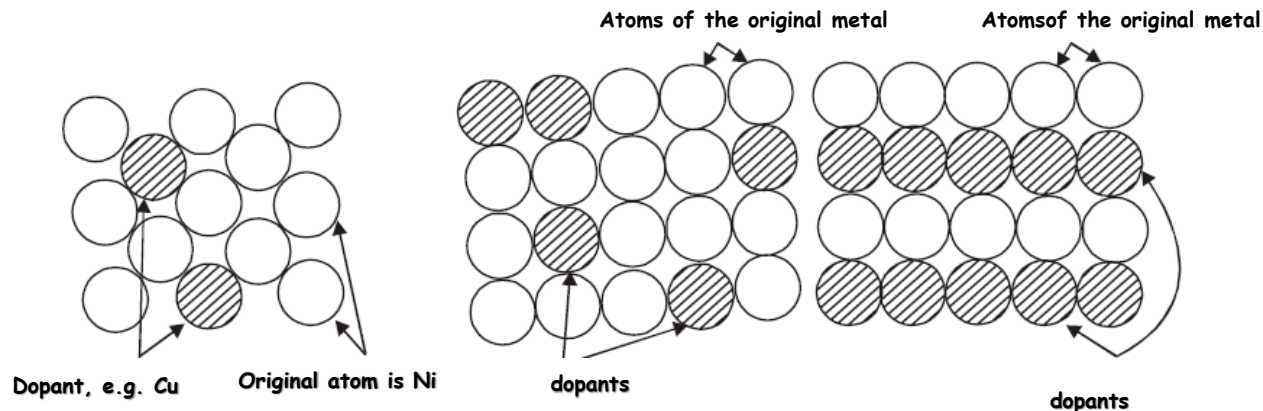
atoms of dopant elements may successively occupy all the sites of the original metal structure (unlimited solubility) or a limited number of sites



Homogeneous solid crystalline phase consisting of at least two components A and B

A - Base metal (solvent)

B - dopant(dissolving element)



Substitutional solid solution

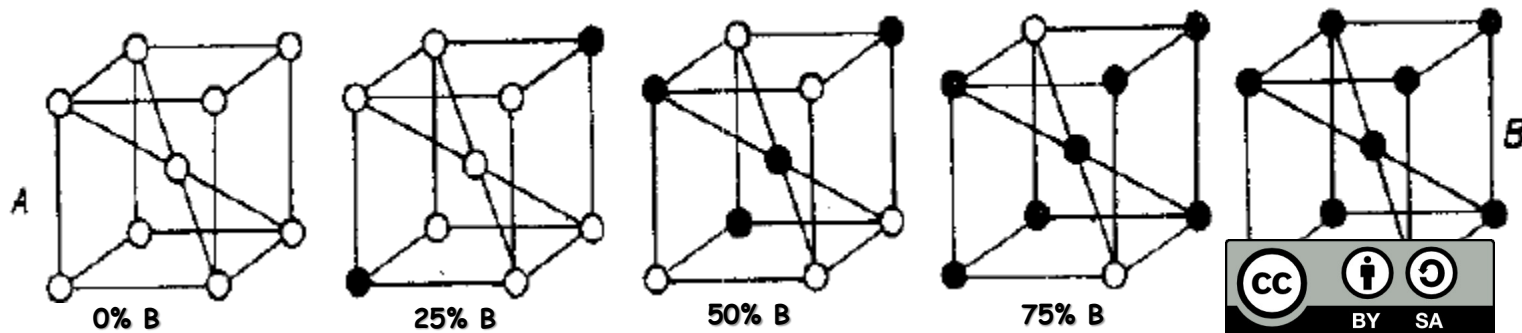
disordered substitutional solid solution

ordered solid solution

# Solid solutions of metals

## Substitutional solid solutions

atoms of dopant elements may successively occupy all the sites of the original metal structure (unlimited solubility) or a limited number of sites



Their crystal structure is identical to that of the original metal. The formation and range of substitutional solid solutions is governed by the Hume-Rothery rules:

1. **Size factor** - The radii of the atoms of the original metal and the dopant must be roughly the same,  $r_A - r_B = \Delta r \leq 8\%$  **soluble**

$\Delta r \geq 15\%$  **insoluble**

2. **Electrochemical behavior of the elements** - For the formation of a solid solution, it is necessary for the elements to have approximately the same electronegativity ( $\pm 0.4$ )

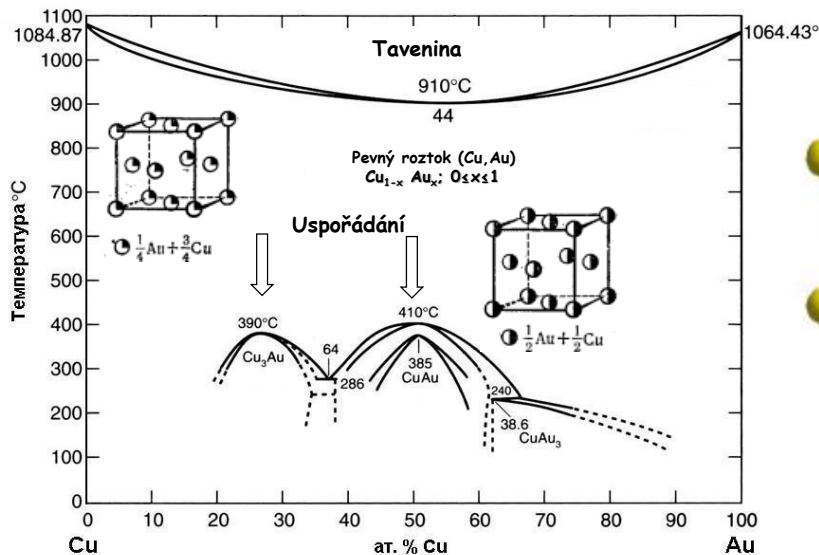
(when one is strongly electropositive and the other strongly electronegative, the more difficult to form solid solutions and intermediate phases are formed).

3. **Electron concentration** - the ratio of the number of valence electrons. Metal with fewer valence electrons more easily dissolves the metal with multiple valence electrons

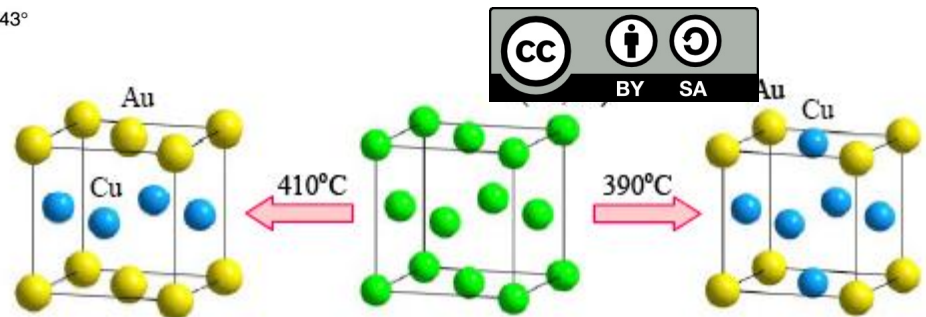
# Solid solutions

## Arrangement

- a) Non-ordered (random, statistical occurrence)
- b) ordered (superstructure - superlattice)



Phase diagram of the system Cu-Au



Arrangement of solid solution Cu-Au  
a) structure of the CuAu compound; b)  
Structure of solid CuAu solution; c);  
Structure of Cu<sub>3</sub>Au.

# Substitutional solid solutions of metals - examples of unlimited solubility

system		Crystal structure	Atomic radii (Å)	Valence	Electronegativity
Ag-Au	Ag	FCC	1.44	1	1.9
	Au	FCC	1.44	1	2.4
Cu-Ni	Cu	FCC	1.28	1	1.9
	Ni	FCC	1.25	2	1.9
Ge-Si	Ge	DC	1.22	4	1.8
	Si	DC	1.13	4	1.8

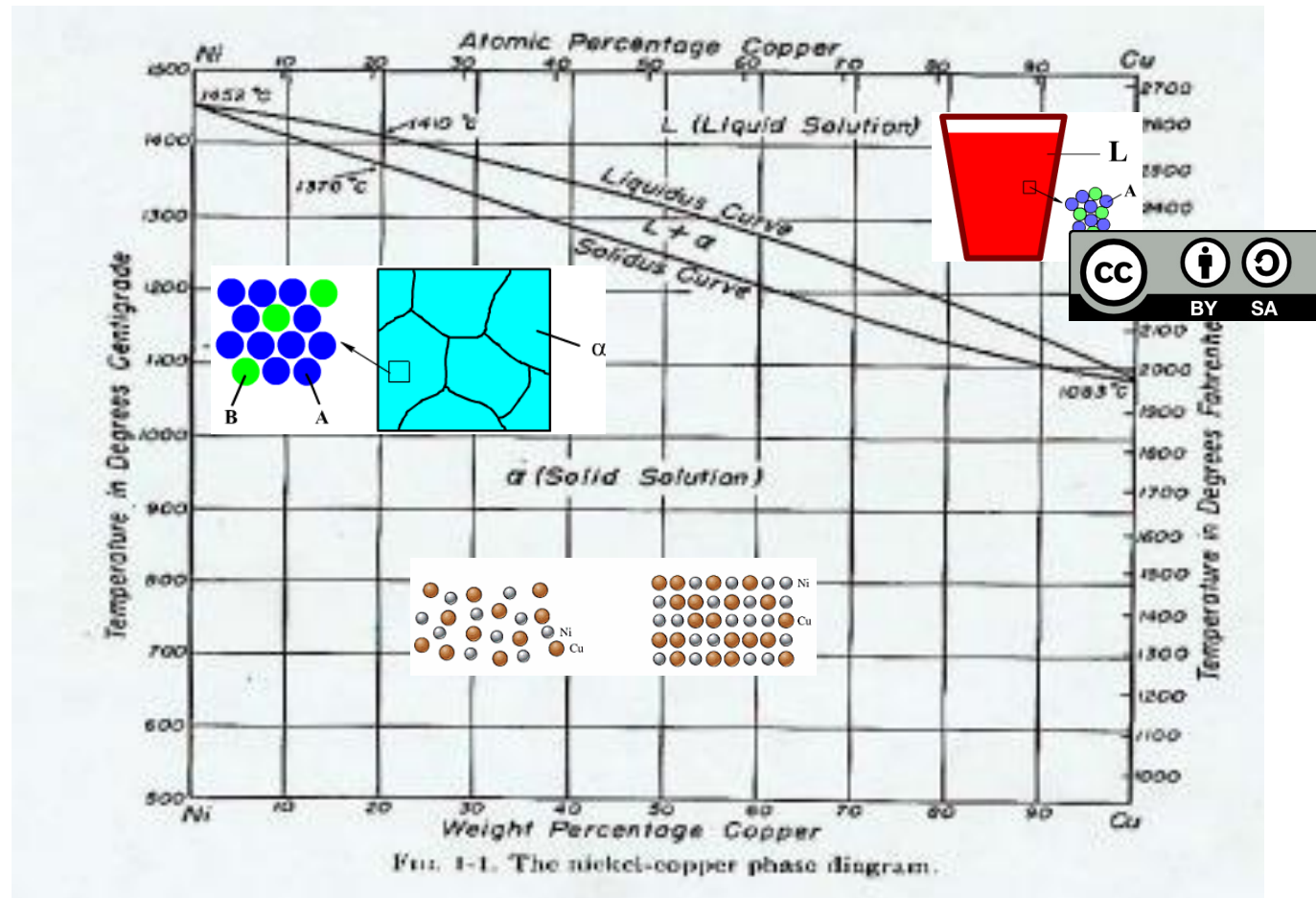


Unlimited solubility: The solvent and the solute are unlimitedly soluble in each other.

The requirements meet Hume-Rothery's laws  
"Single-phase alloys"

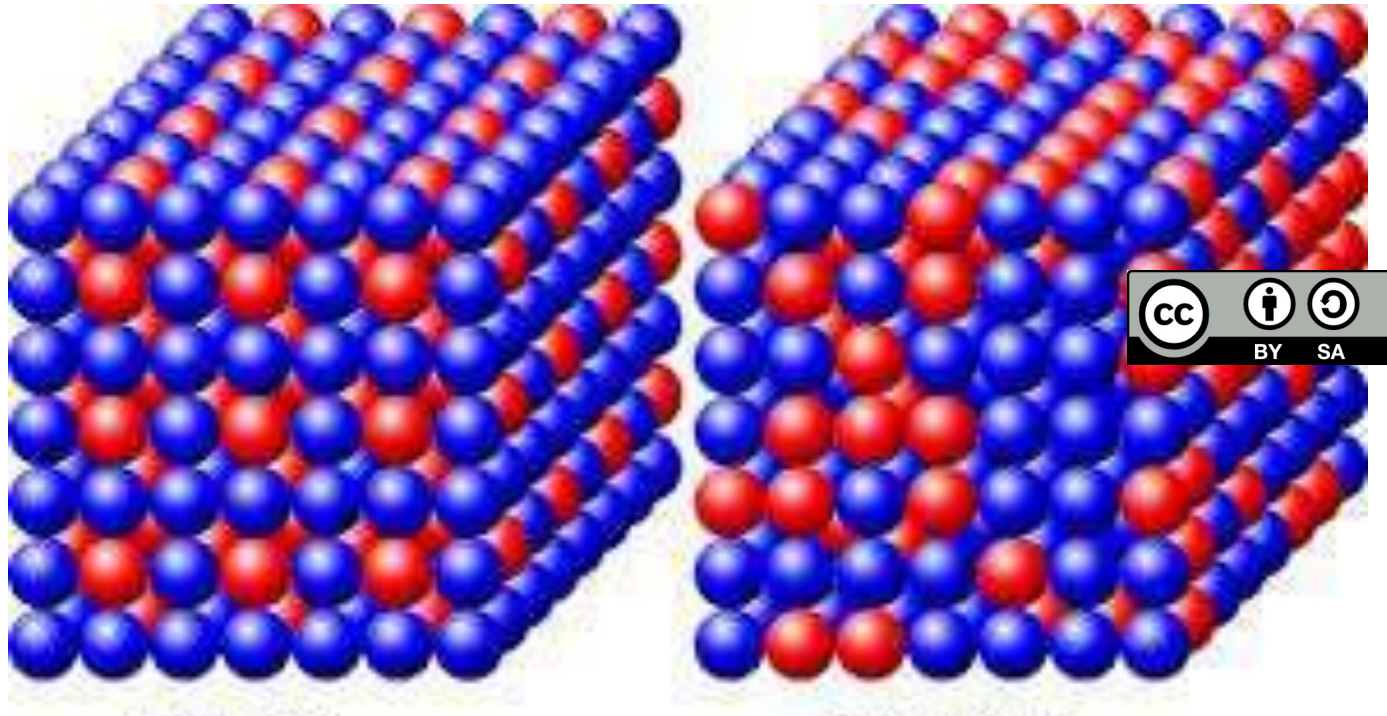
# Solid solution

## The phase diagram of Ni-Cu





# Intermetallic compounds



Intermetallic compound

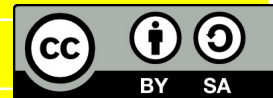
Common alloy

Unlike solid alloy solutions, intermetallic compounds have a crystalline structure different from the original metals.

Two metals can form several compounds ;  
For example  $\text{NaSn}_3$ ,  $\text{NaSn}_2$ ,  $\text{NaSn}$ ,  $\text{Na}_4\text{Sn}_3$ ,  $\text{Na}_2\text{Sn}$ ,  $\text{Na}_4\text{Sn}$  and other.

# Intermetallic (intermediate) phases arise from breaking of Hume-Rothery laws. Substitution solid metal solutions, limited solubility

System		Crystal structure	Atomic radius (Å)	Valence	Electronegativity
Cu-Zn	Cu	FCC	1.28	1	1.9
	Zn	HCP	1.21	2	1.9
Cu-Sn	Cu	FCC	1.28	1	1.9
	Sn	FCC	1.41	2	1.9
Cu-Ag	Cu	FCC	1.28	1	1.9
	Ag	FCC	1.44	1	1.9
Ag-Bi	Ag	FCC	1.44	1	1.9
	Bi	trigonální	1.58	3	2.0



Limited or partial solubility: There is a solubility limit of the substance in the solvent until "saturation", for example Cu-Sn. Most of the other systems do not meet the requirements of Hume-Rothery's laws to create "multi-phase alloys"

Intermetallic (intermediate) phases arise from breaking of Hume-Rothery laws. Substitution of solid metal solutions, limited solubility

## Intermetallic compounds:

(a) Electronic compounds. In these, metals do not exhibit their oxidation levels. Their composition is determined not by the properties of the interacting components but by the formal electron concentration (FEC), i.e. the ratio of the valence electrons to the number of interacting atoms in the formula. Most known electronic alloys can be divided into three types with specific structures. **FEC of the first type is equal to  $3/2$  (CuZn), of the second type is equal to  $21/13$  (Cu<sub>5</sub>Zn<sub>8</sub>) and of the third type to  $7/4$  (CuZn<sub>3</sub>).**

**b) Laves phases** - unfulfilled size factor

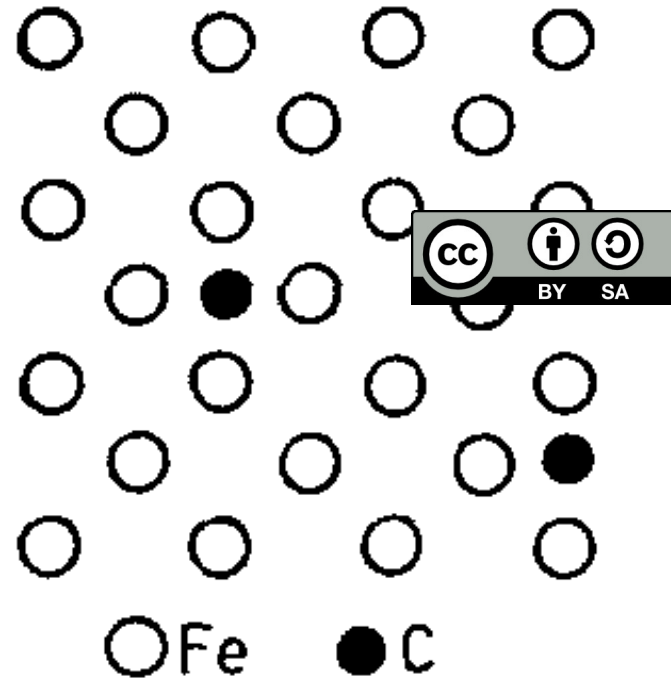
**c) valence** - they are formed by metals with significantly different electronegativity. The formulas correspond to the usual valency of the elements

**Na<sub>2</sub>Sn, Na<sub>4</sub>Sn, Mg<sub>2</sub>Ge, Mg<sub>2</sub>Sn, Mg<sub>3</sub>Sb<sub>2</sub>, Mg<sub>3</sub>Al<sub>2</sub>**

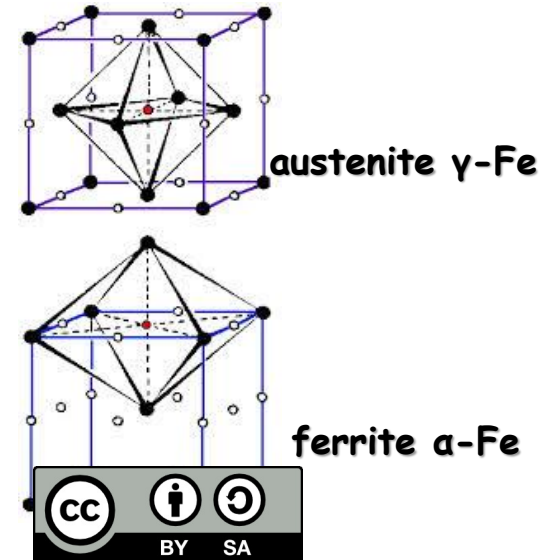
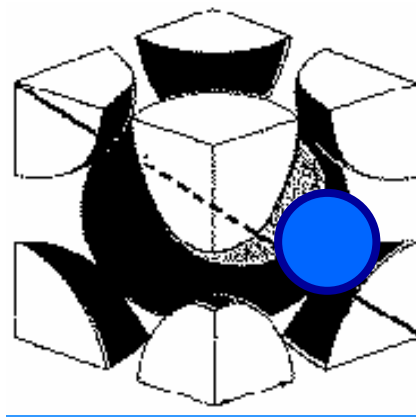
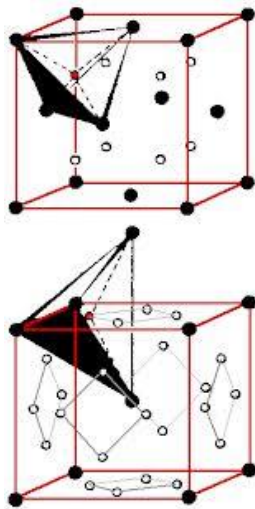


# Interstitial solid solutions

Solid interstitial solutions - solutions to form dissolved particles - non-metallic elements with low atomic volumes (carbon, nitrogen, hydrogen and others) occupy vacant positions in the parent metal structure and do not expel the atoms or ions of the initial structure



# Interstitial solid solutions



Admixture atoms enter into interstitial positions,  
and only a limited number of additive atoms can enter.

Solubility is always limited

The ratio of the atomic size of the additive and the original atom must be less than:

$$\frac{r_B}{r_A} \leq 0,59$$

# Solid solutions of metals

## Interstitial solid solution

- 1) For the ratio of the size of the atoms of the additive B and the parent metal A, the Hume-Rothery relationship must be fulfilled:

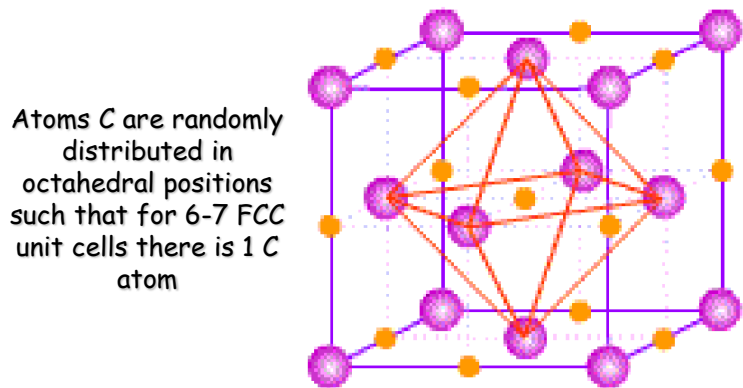
$$\frac{r_B}{r_A} \leq 0,59$$

- 2) The size of the interstitial position is not suitable for C:  $\frac{r_{aC}}{r_{aFe}} = \frac{0,08 \cdot 10^{-9}}{0,124 \cdot 10^{-9}} = 0,645$

For N, the interstitial cavity is optimal:

$$\frac{r_{aN}}{r_{aFe}} = \frac{0,07 \cdot 10^{-9}}{0,124 \cdot 10^{-9}} = 0,565$$

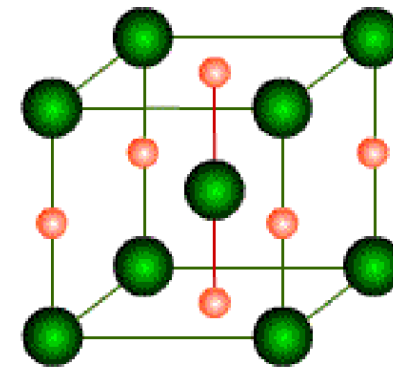
The most important of interstitial solid solutions, although according to the Hume-Rothery's rules should not have been formed are:



$\gamma$ -Fe (C) -austenite, FCC, solubility up to 8.9% C ~ 0.8% (727 ° C) (the main component of most of the stainless steel)

At high concentrations of C, the structural type  $\gamma$ -Fe (FCC) changes to the structural type NaCl (FCC). The carbon atoms occupy octahedral positions

Low content C does not change the structural type of  $\alpha$ -Fe. Only the unit cell parameter changes



$\alpha$ -Fe (C) -ferrite, BCC, the highest solubility of 0.1 at% C ~ 0.02% (the major component of most common structural steels)

# Chemistry and Physics of Solids – Lecture 7

## Amorphous compounds



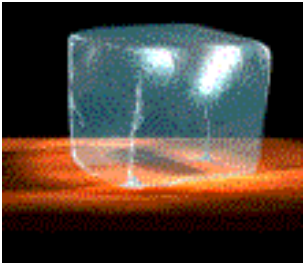
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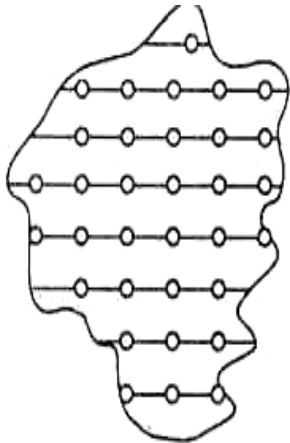


# Amorphous compounds

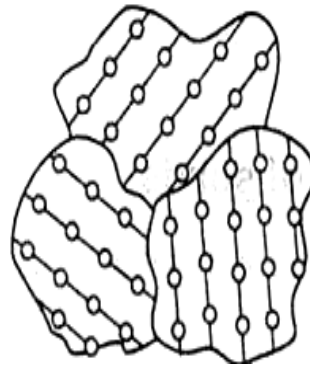
In addition to



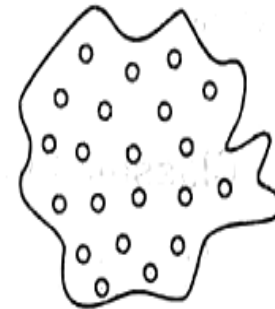
Single-crystals and polycrystalline compounds, there are non-crystalline or **amorphous substances**



Single-crystal



polycrystalline

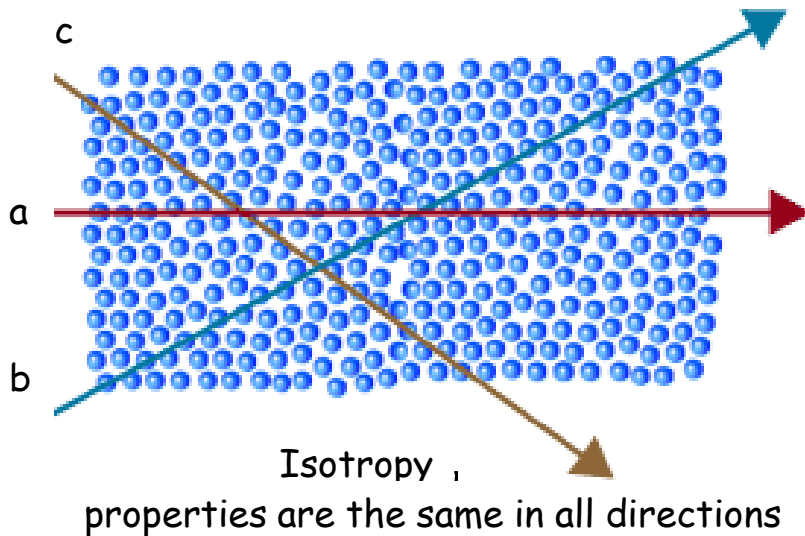


amorphous

*The solid non-crystalline substance in the amorphous state is formed by cooling the melt at such a rate as to prevent crystallization.*

# Amorphous compounds

## Characteristic properties



There is no precise melting point



supercooled liquid

# Amorphous compounds

## Characteristic properties



supercooled liquid

Perhaps the longest physical experiment in the world was made at a university in the Australian city of Brisbane. In 1927 Prof. Thomas Parnel put the tar in a glass funnel:

1938 the first drop showed

1947 the second drop showed

1948 professor Parnel died



### Other drops:

1954

1962

1970

1988

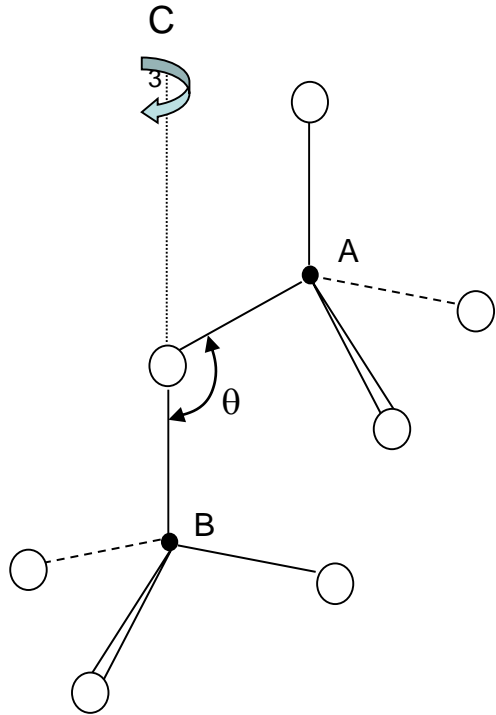
2000

The experiment is far from complete, but it is clear that tar is 100 million times more viscous than water.



# Principle of the glass order

Consider two of the network's tetrahedra



- The rotation of tetrahedron A around the  $C_3$  through the tetrahedron B that occurs in the melt by breaking the linkages to the oxygen anions
- During cooling, bonds are re-created in random orientations and the system freezes. Reverse linkages must be re-created
- Non-ordered system occurs within an angle  $\theta$   $120^\circ - 180^\circ$ .

**SHORT RANGE ORDER (SRO)**

Tetrahedral

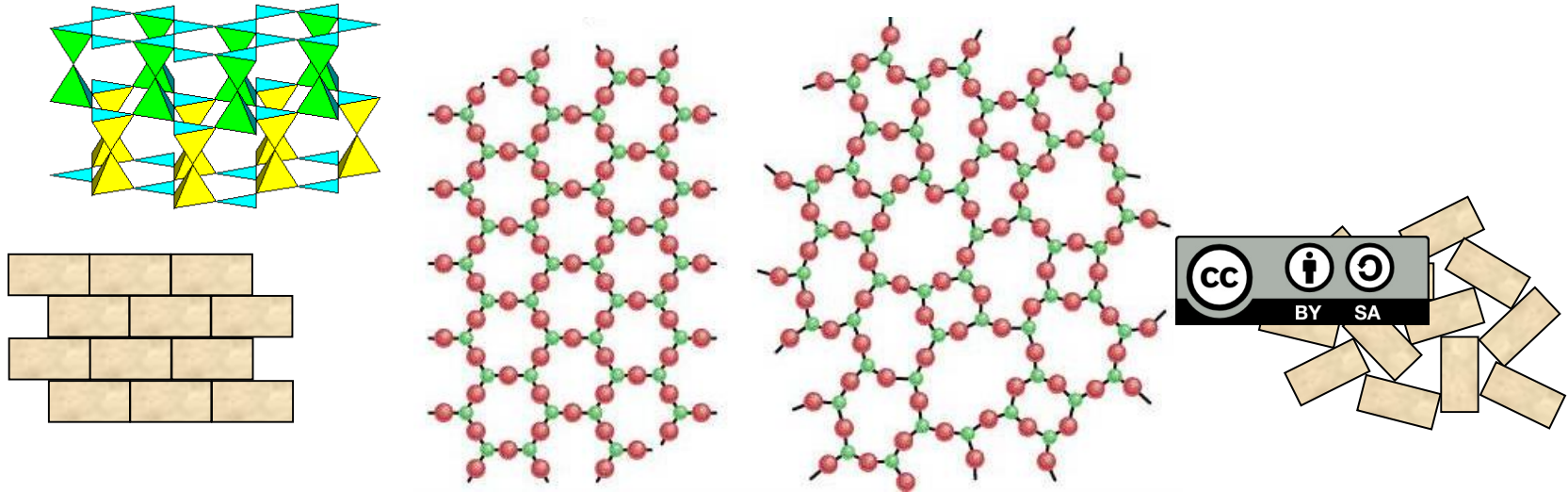
no

**LONG RANGE ORDER (LRO)**



***The amorphous compound is characterized by the absence of a defined long range order:***

**random order of atoms, absence of periodic symmetry and crystalline structure**



**Crystalline solid  
cristobalite ( $\text{SiO}_2$ )**

**Amorphous glass**

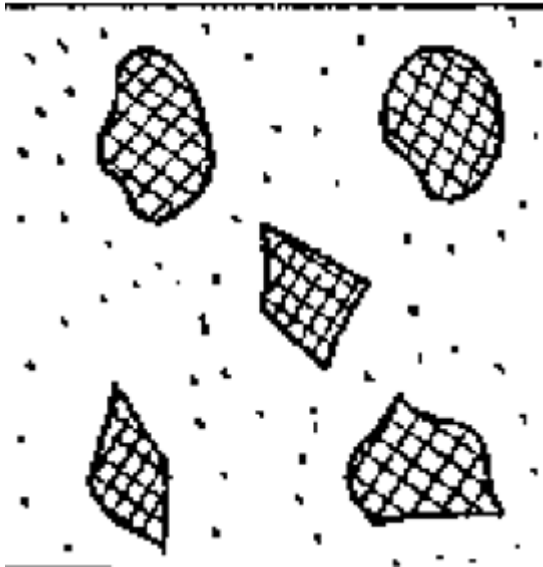
Slow heating of quartz gradually generates high temperature modifications of tridymite and then cristobalite, which passes over. With rapid quenching of quartz above  $1500^\circ\text{C}$ , it can melt without the formation of high temperature forms. The amorphous mass in the range of  $1000\text{--}1500^\circ\text{C}$  is unstable and slightly reverts back to crystalline modification of cristobalite. For this reason, in the production of quartz glass, the crystalline raw material is heated to temperatures higher than  $1700^\circ\text{C}$  (cristobalite melting point).

**In amorphous solids, the arrangement of atoms is limited to the nearest neighbors - it is a so-called short range order**

# Glass - theory of the structure

- Irregular Network Model - Oxidized Glass
- Bernal model (sphere arrangement) - amorphous metals

Crystalline hypothesis: Glass is an aggregate of highly dispersed crystals dissolved in a substance or phase of an unordered structure. When glazing a polymorphic transformation occurs in crystallinity.



The theory satisfies the glass-forming processes in spontaneous solidification, characteristic of semiconductor and metallic glass.



In silicate systems, crystalline theory was not confirmed. Crystals include a number of 1-2 unit cells so deformed that it is not relevant to describe the glass state.

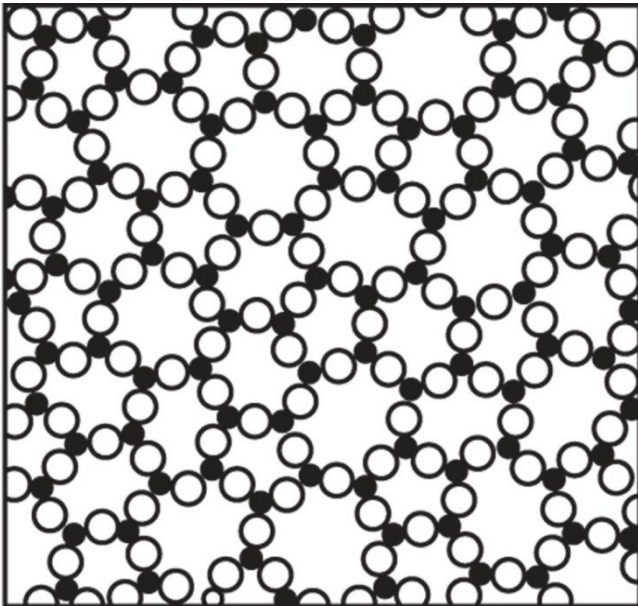
# Glass - theory of the structure

- Irregular Network Model - Oxidized Glass
- Bernal model (sphere arrangement) - amorphous metals

## Zachariasen's rules of glass formation ( $A_nO_y$ )

An oxygen atom is linked to not more than two glass-forming atoms. ( $CN\ O \leq 2$ ).

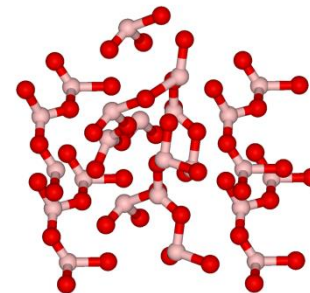
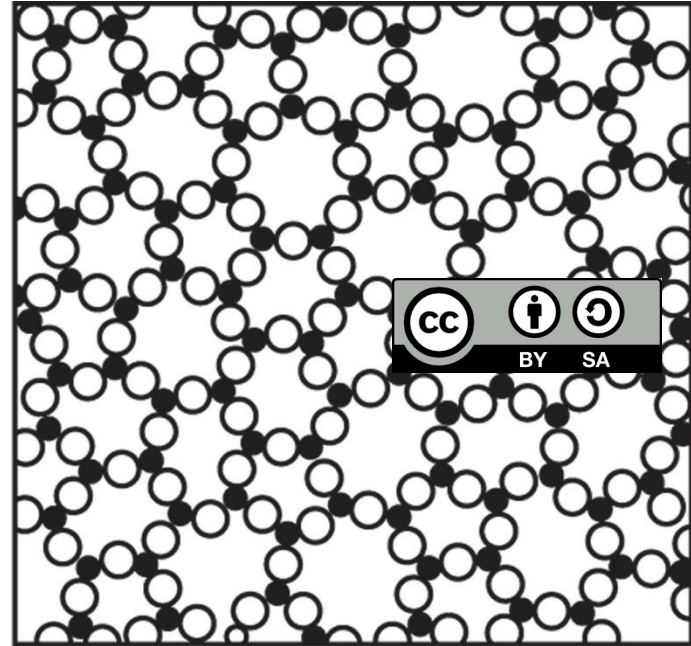
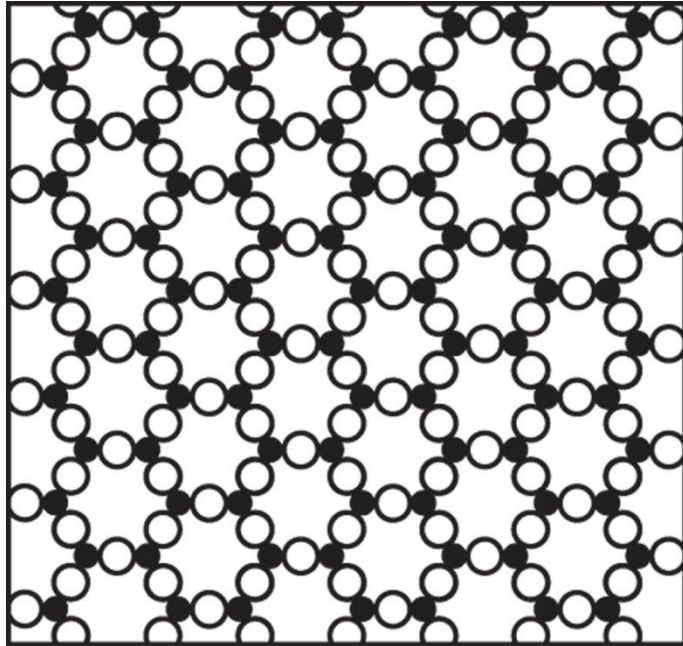
- The coordination number of the glass-forming atoms is small (3,4)
- The oxygen polyhedra share corners with each other, not edges or faces.
  - The polyhedra are linked in a three-dimensional network.



Oxides  $A_2O$  or  $AO$ , where  $A$  is a metal atom, do not meet any of the laws

Oxides  $A_2O_3$  meet the laws if oxygen atoms form triangular coordination around each atom of  $A$ . Similarly,  $AO_2$  or  $A_2O_5$  meet these laws if the oxygen atoms form a tetrahedron around each atom  $A$

# Oxides formed as glasses:- $B_2O_3$





# Oxides formed as glasses:

1. Glass-forming oxides - can produce glass; for example  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{GeO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{As}_2\text{O}_5$ . Silicon directional covalent bonds. Bond strength with oxygen is higher than 80 kcal / mol

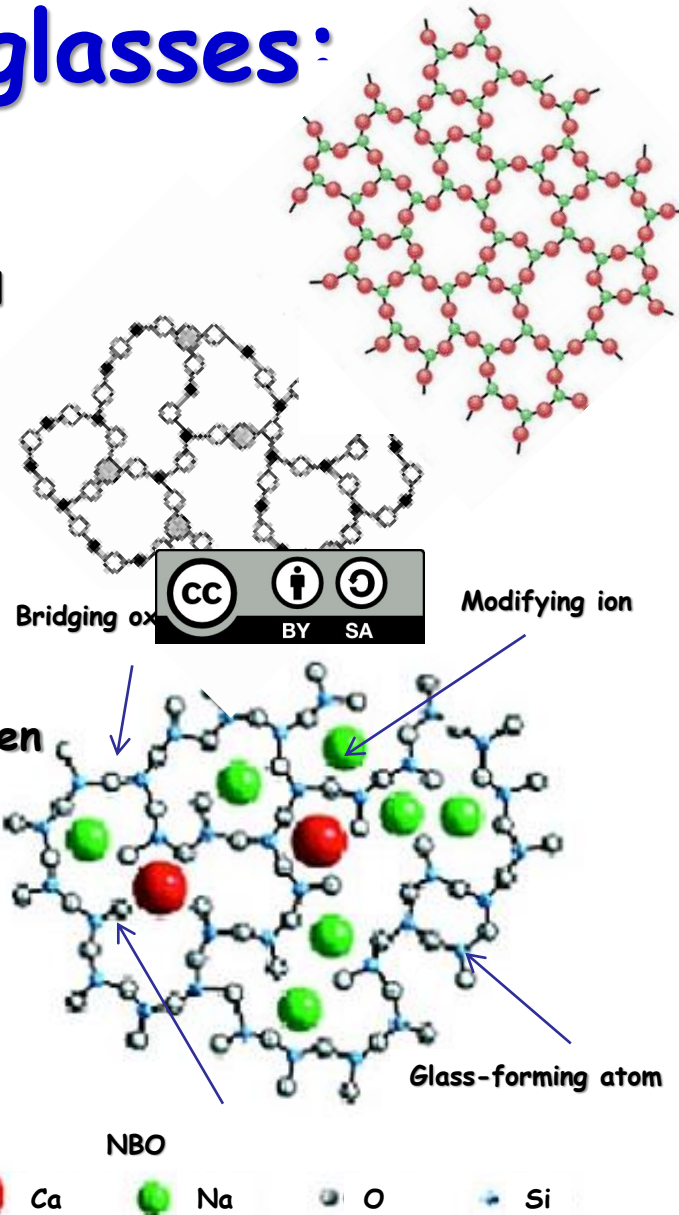
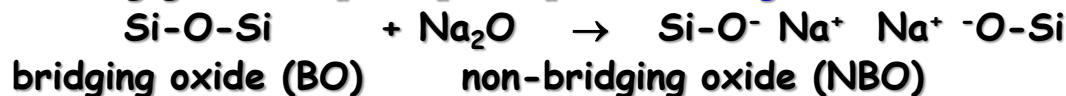
2. Intermediate oxides - can replace the network builder, but can not independently form glass, for example  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ . Fixed broken networks. Bond strength with oxygen between 60-80 kcal / mol



3. Network modifiers - interrupt bindings between polyhedrons in the network - alkali oxides and alkaline earth oxides. Bond strength with oxygen lower than 60 kcal / mol



If a large number of links are broken, then it does not happen to form the grid and the melt will rather crystallize without Creating glass-  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Li}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$

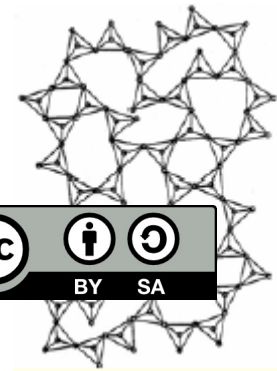


# Amorphous in the meaning of X-ray diffraction

## Structure of glass

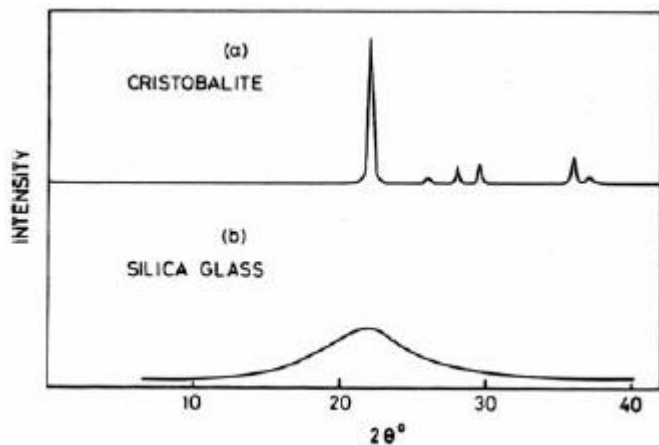
$\text{SiO}_2$  is composed of corner-shared tetrahedra into a 3D infinite network.

Powder diffraction: "diffuse wide peak" - shows distances over long distances - reflects only typical glass distances, ie, short distance arrangements.

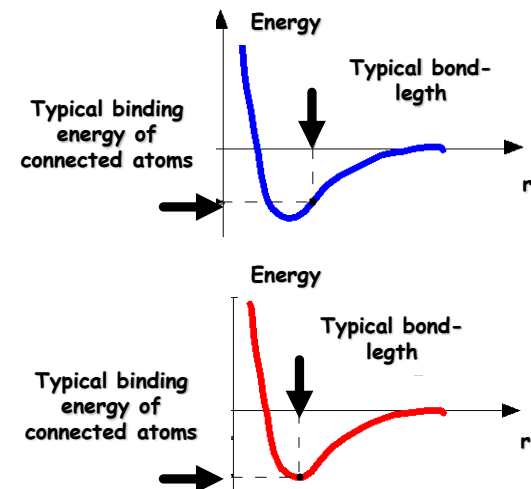
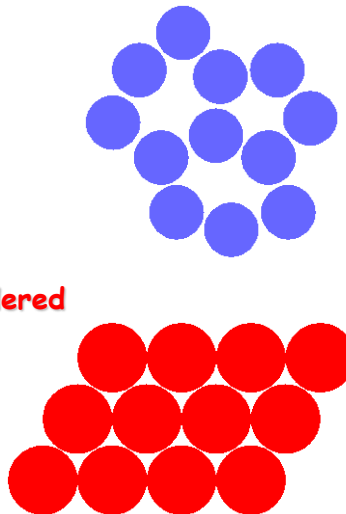


## Radial distribution function

Random order



ordered

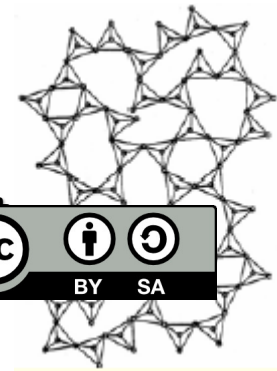


# Amorphous in the meaning of X-ray diffraction

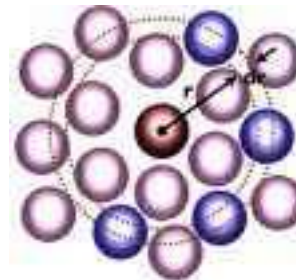
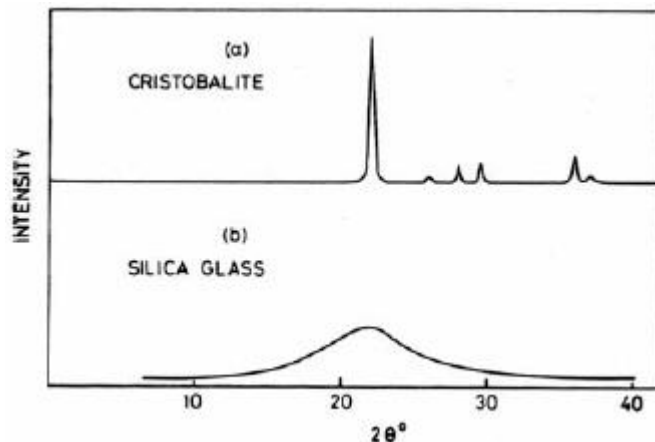
## Structure of glass

$\text{SiO}_2$  is composed of corner-shared tetrahedra into a 3D infinite network.

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## Radial distribution function

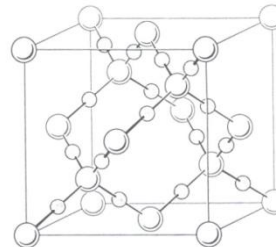


Volume of the layer

$$V = \frac{4}{3}\pi(r + \delta r)^3 - \frac{4}{3}\pi r^3 \approx 4\pi r^2 \delta r.$$

The number of atoms in the spherical layer between  $r_1$  and  $r_2$ :

$$\int_{r_1}^{r_2} 4\pi r^2 \rho(r) dr$$



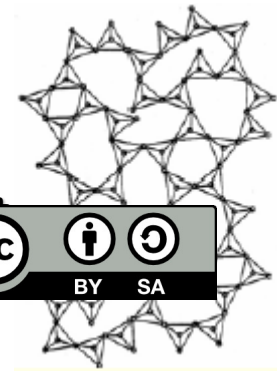
Crystal structure of cristobalite

# Amorphous in the meaning of X-ray diffraction

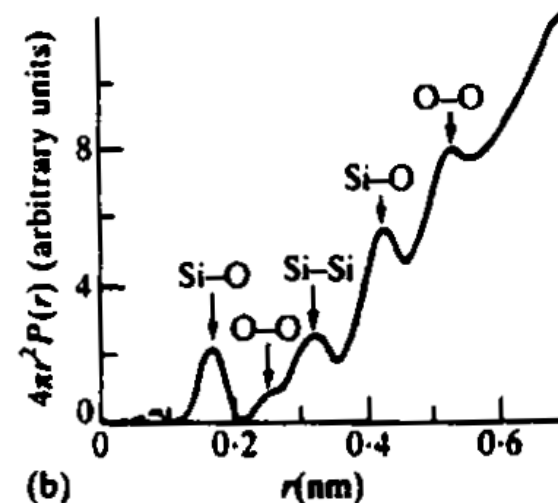
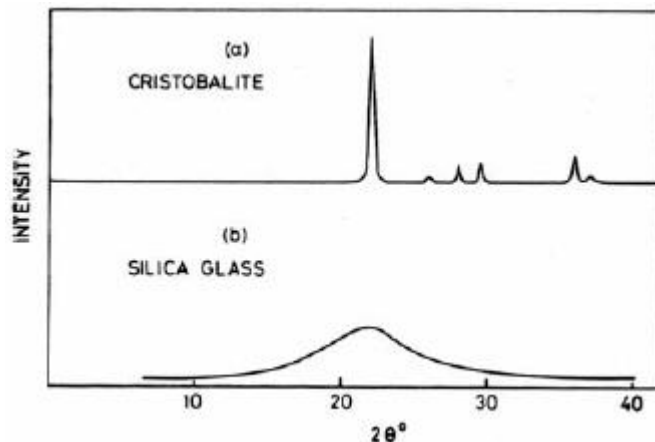
## Structure of glass

$\text{SiO}_2$  is composed of corner-shared tetrahedra into a 3D infinite network.

Powder diffraction: "diffuse wide peak" - shows distances over long distances - reflects only typical glass distances, i.e., short distance arrangements.

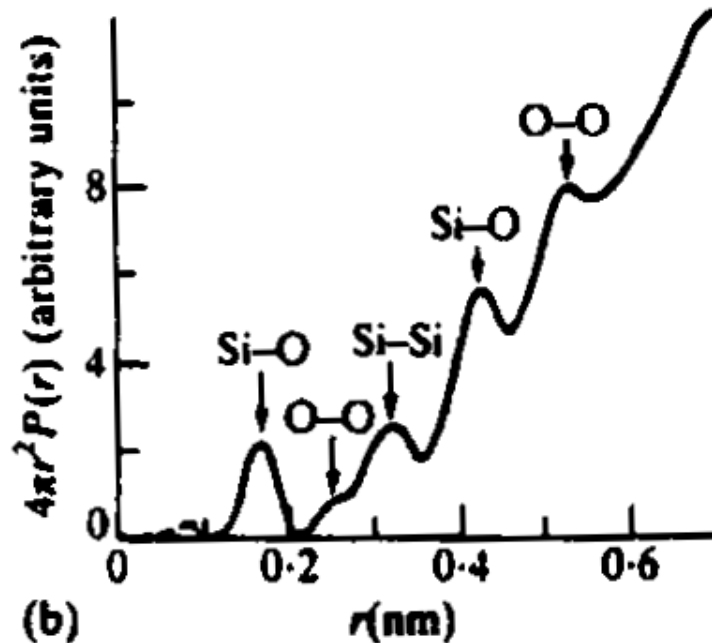


## Radial distribution function





# Measurement



Si-O distance in the first coordinate sphere:  $\sim 0.16$  nm

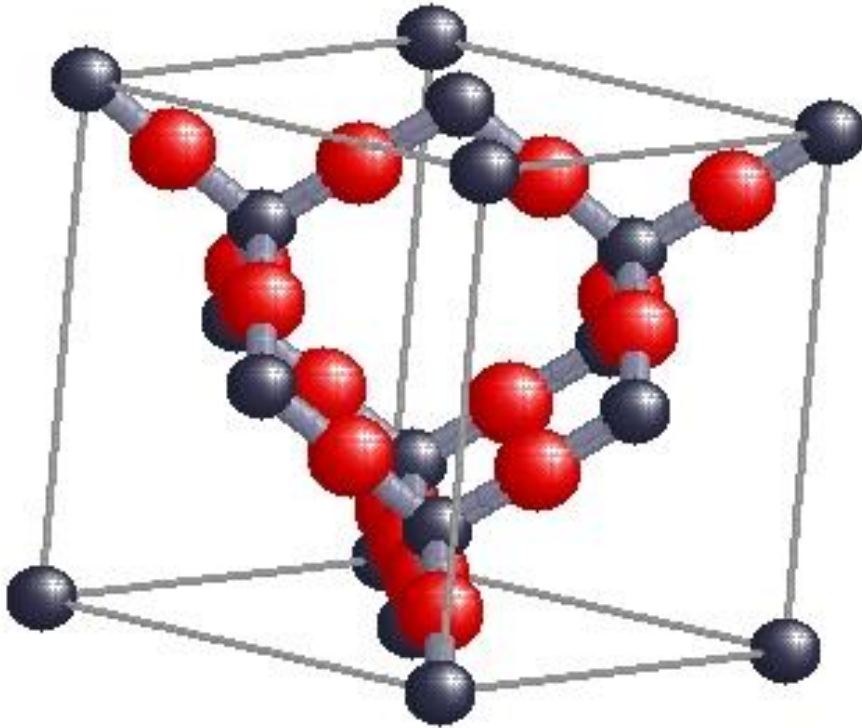
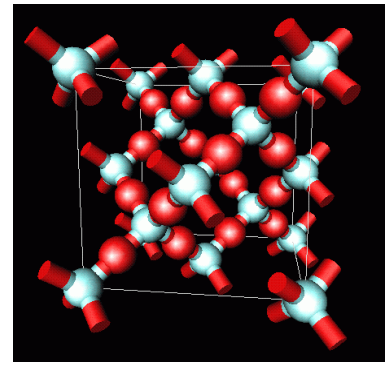
The Si-O bond length in silicates corresponds to 0.162 nm. The calculated bond length corresponds to the ratio:

$$\frac{(\text{Si-O})}{(\text{O-O})} = \frac{(\sqrt{3})}{2} = 0.162/x$$

(2)

$x = 0.265$  nm - the value corresponds to the detected distance O-O (second co-ordinating sphere)  $\sim 0.27$  nm

# Measurement



Si-O distance in the first coordinate sphere:  $\sim 0.16$  nm

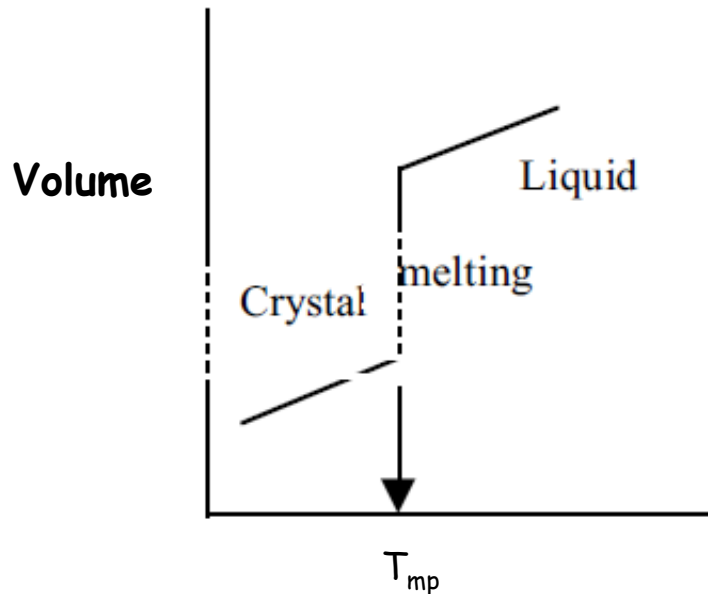
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$x = 0.265$  nm - the value corresponds to the detected distance O-O (second co-ordinating sphere)  $\sim 0.27$  nm

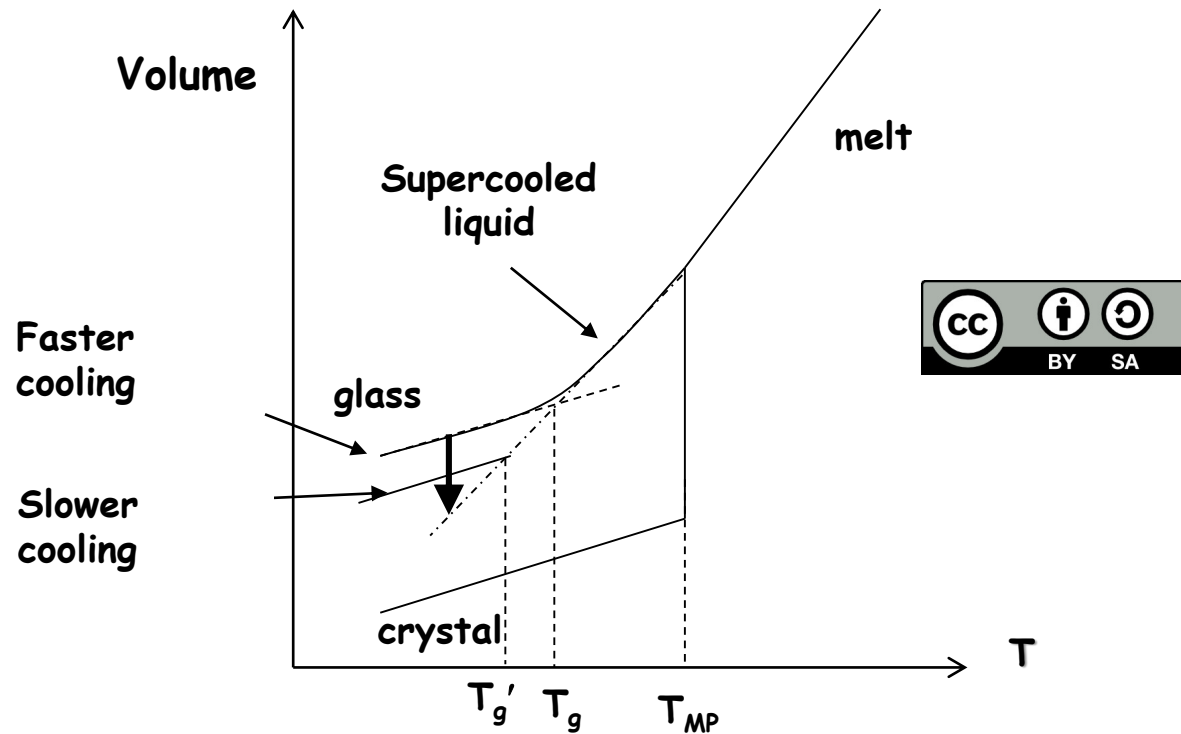
# Differences between crystalline and amorphous substances

1. Amorphous substances always have isotropic properties
2. Differences can be observed when heating



Dependence of the molar volume on the temperature during melt cooling or heating of the crystalline solid

# Different modes of melt cooling to glass state



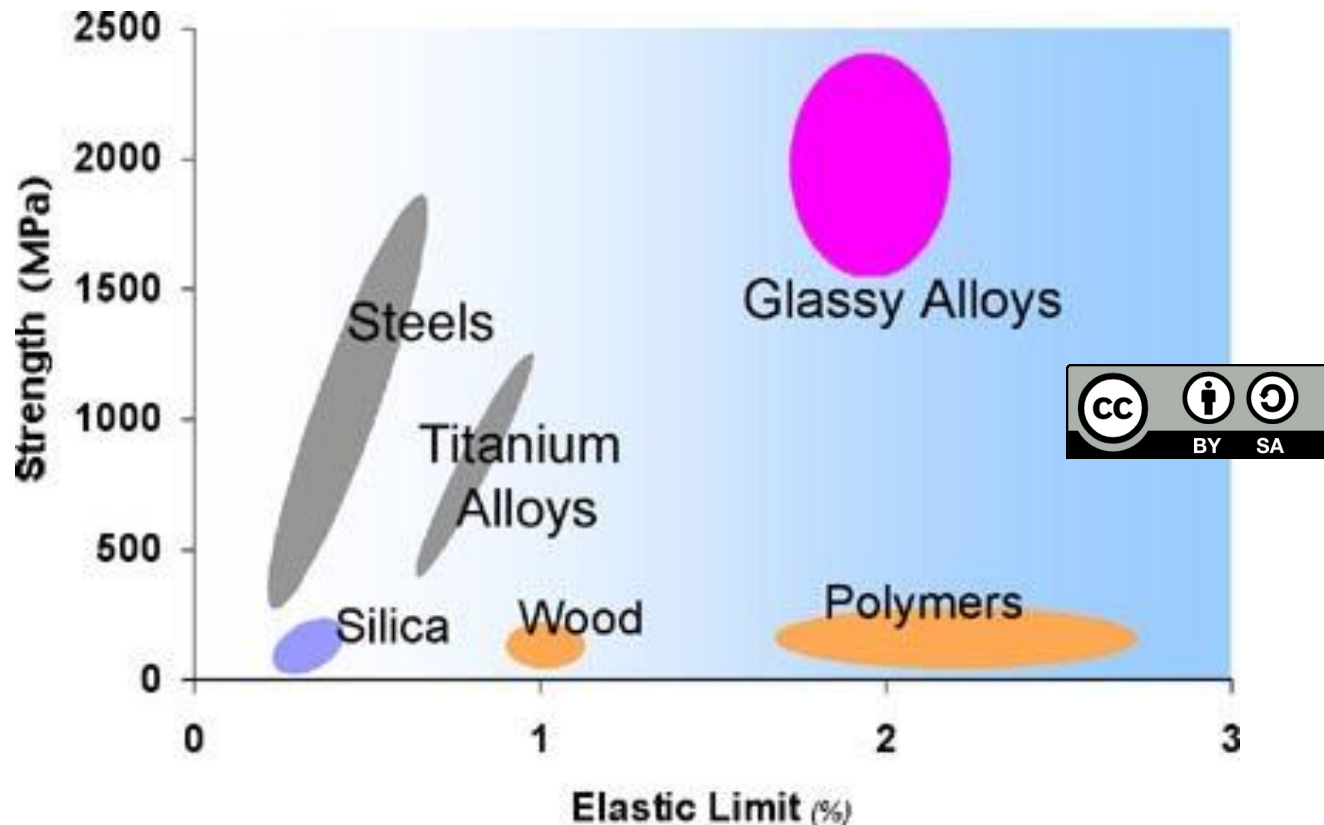
Dependence of the molar volume on the temperature during melt cooling or heating  
(a) crystalline substances; (b) amorphous solids

# Properties of oxide glasses

- Optically transparent
  - non-conductive
- Strong but fragile
  - Chemically inert
- High melting point



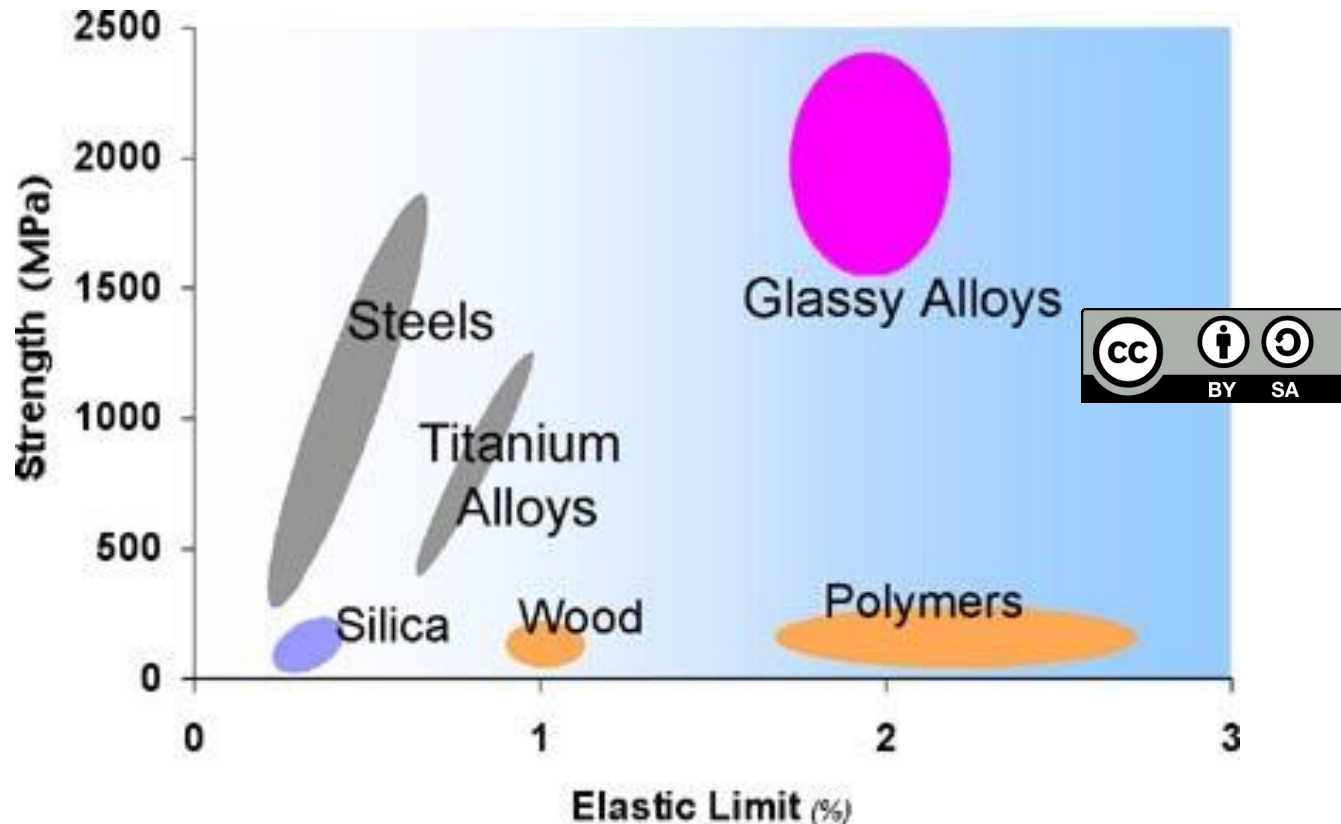
# Metal glasses



These are metal alloys - Mn, Fe, Co, Ni, Pt, Mo ... and metalloids (B, Si) and non-metallic elements N, C. Glasses containing only one metal element are known. They are formed by extremely rapid cooling of the melt to suppress crystallization. The structure remains glassy.

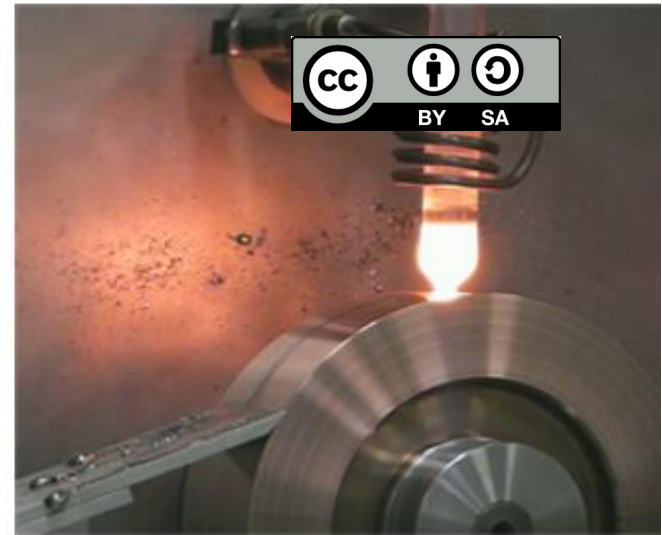
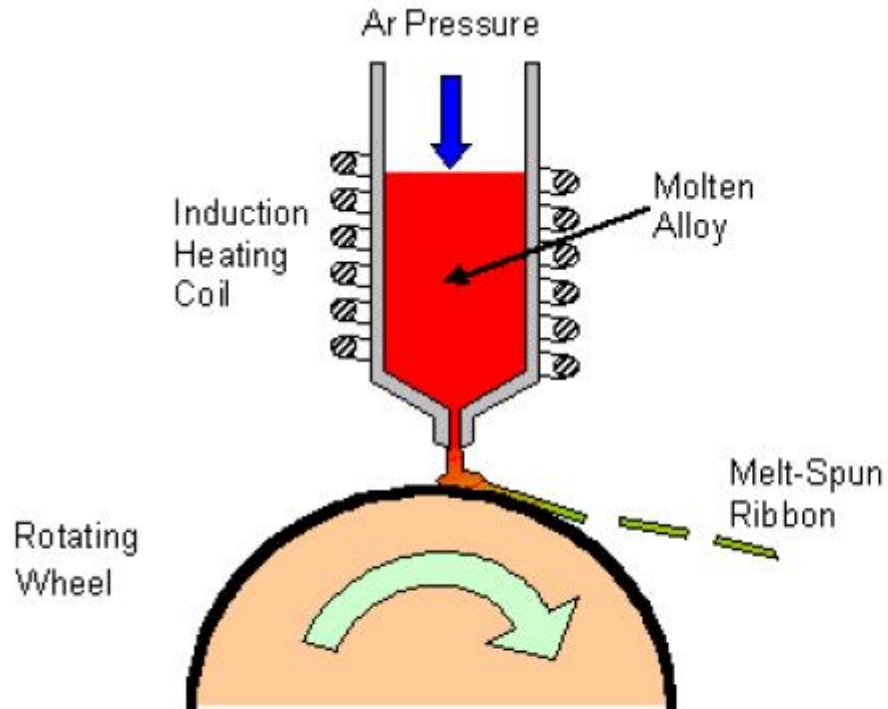
# Metal glasses

<http://www.youtube.com/watch?v=wiMFxOU7tAU>



**Features of metal glass - high strength, resistance against abrasion, toughness, ductility, excellent corrosion resistance**

# Production of metal glasses



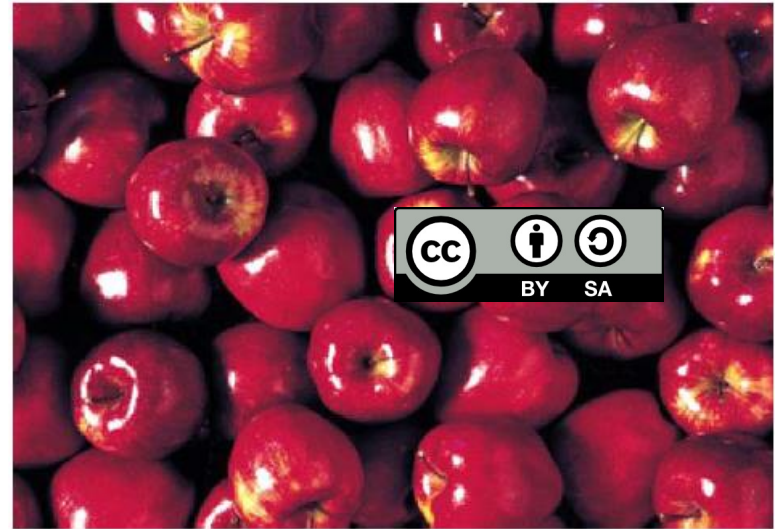
**Metal glass** - Requires cooling speeds  $> 10^6 \text{ K s}^{-1}$   
**Na-Ca glass** - cooling  $\sim 10 \text{ K s}^{-1}$   
**SiO<sub>2</sub>** - cooling  $0.1 \text{ K s}^{-1}$   
**B<sub>2</sub>O<sub>3</sub>** - does not crystallize under normal pressures



# ordered and dis-ordered packing



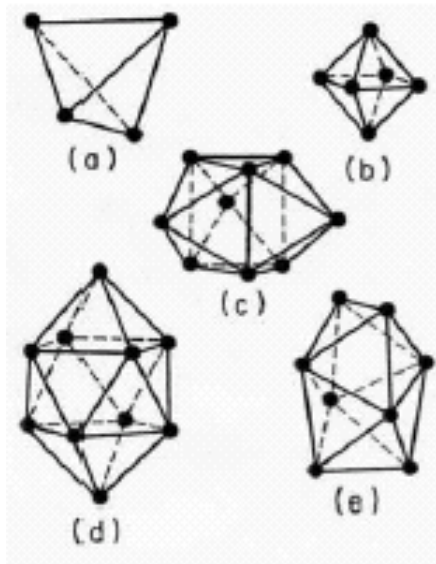
Kepler's estimate - it is not possible to beat the balls more densely than the bulk fraction  $\pi/\sqrt{18} = 0.7405$



Disordered packing of balls with lower density around 0.64 (Bernal's packing)

# Models of amorphous state

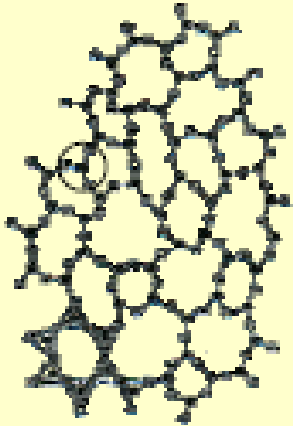
Bernal - the local atomic arrangement in the amorphous alloys is not random and is related to a local atomic arrangement that is similar to any of its named polyhedrons.



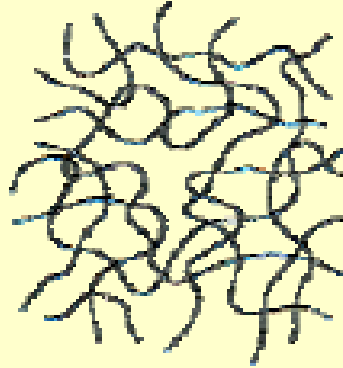
The five "canonical" cavities described by Bern: a) tetrahedron; (b) octahedron; c) a trigonoidal prism (covered by three polookapters); d) Archimedean anti-border (ended with two semi-cents); e) tetragonal dodecahedron

# Glass types

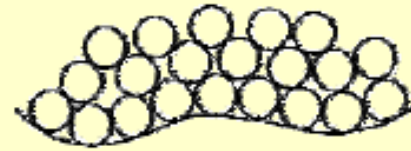
Oxide glasses/  
silicate glasses



Polymeric glasses



Metallic glasses



	Building blocks	Bonds inside the building block	Bonds between building blocks
Oxide glasses	tetrahedral (3D)	covalent (ionic)	covalent (ionic)
Polymeric glasses	Curved lines (1D)	covalent	van der Waals bonds and H-bonds
Metallic glasses	Atoms (0D)	-	metallic

# Thermodynamic stability of glasses

- There are no conditions under which the glass would be thermodynamically stable
- Still, glasses in nature last for the entire geological epoch
- glass is thermodynamically metastable

## Gravity Analog:



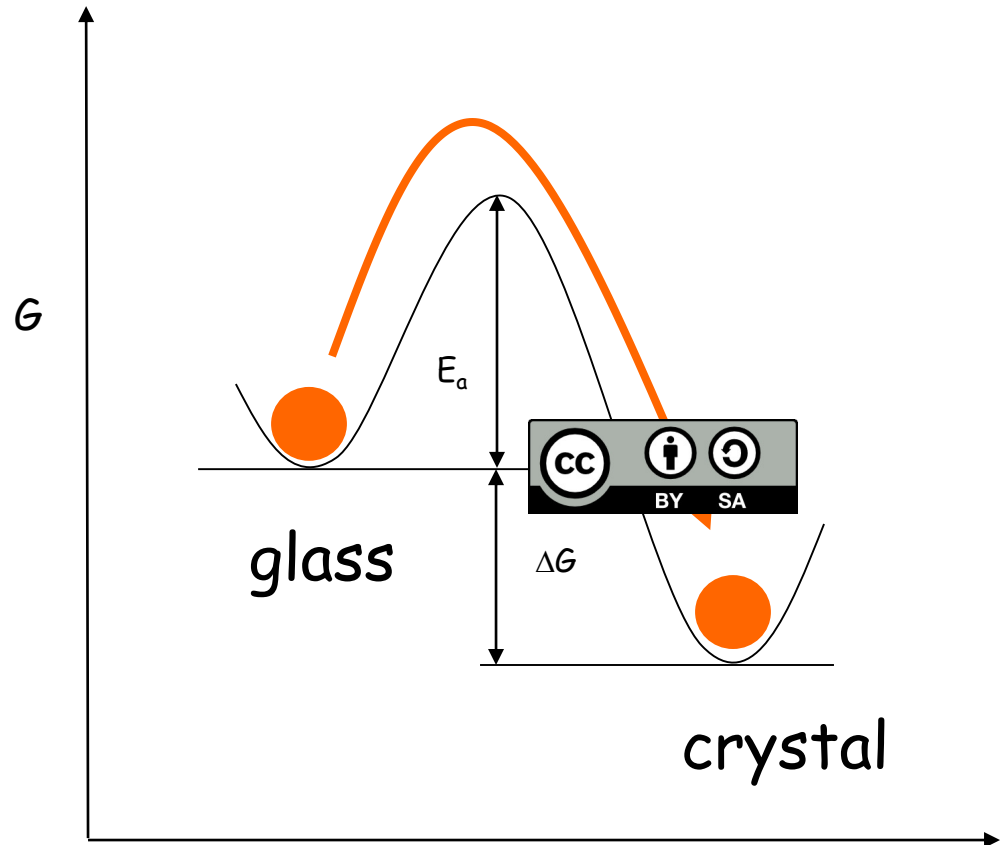
Stable position - lowest point



An unstable position - usually at the highest point - any change means shifting to a stable position

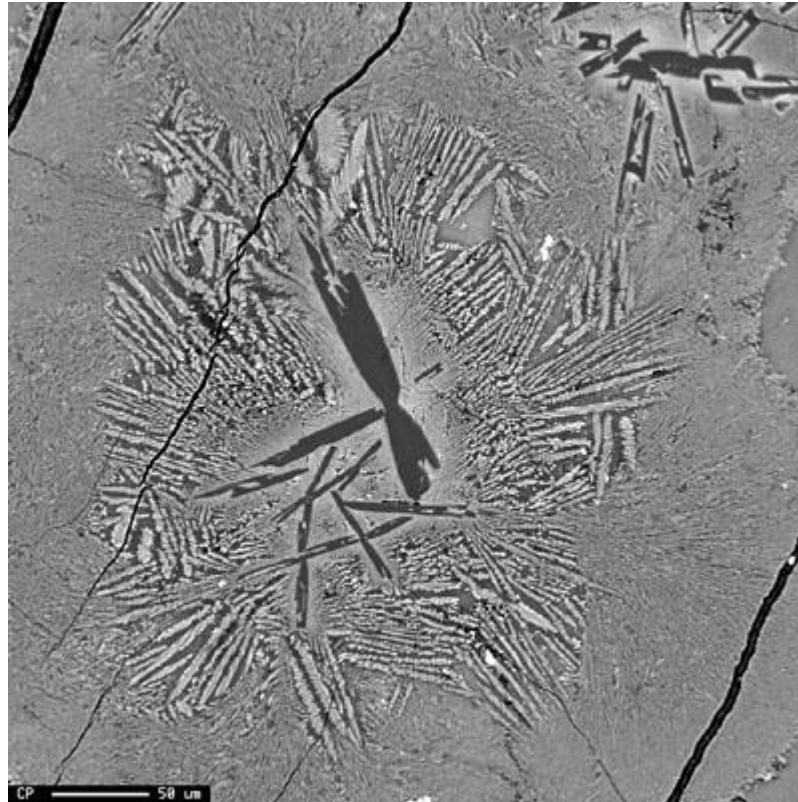


Metastable position - must move before falling

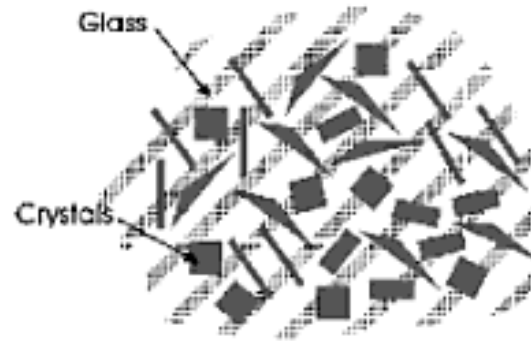


The glass is in a state of relatively high Gibbs' free energy. High activation energy is required to change the structure  $E_a$ .

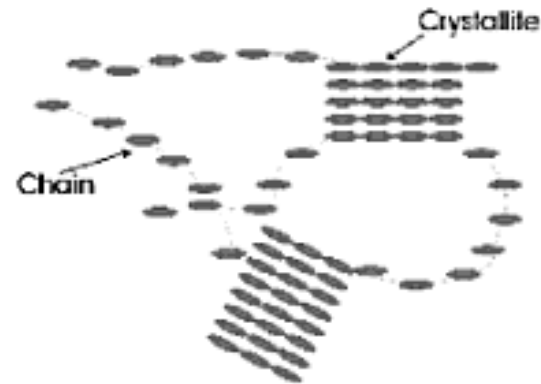
# Partially crystalline substances



# Partially crystalline substances



(a)



(b)



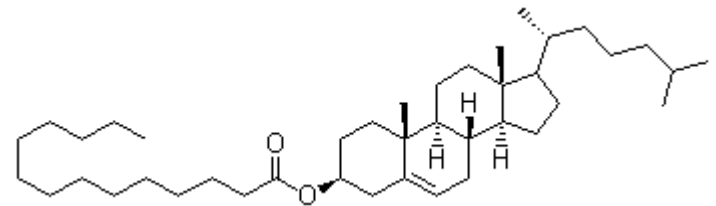
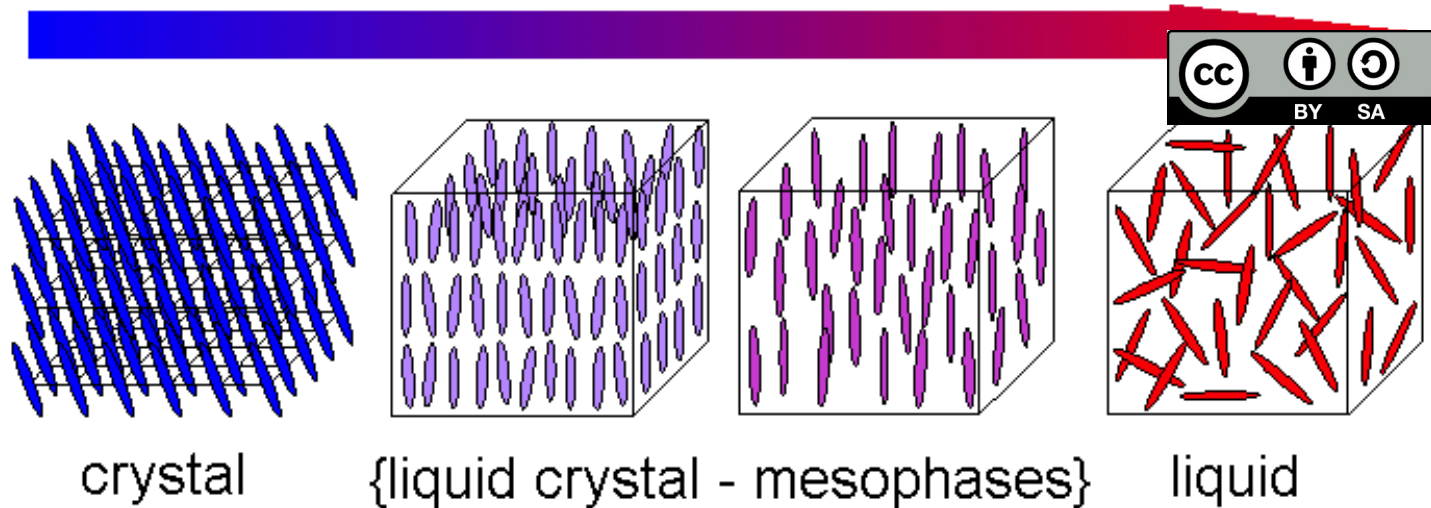
Partially crystalline solids

a) glass ceramics, b) a partially crystalline polymer



# Non-crystalline solid phase - mesophase

With increasing temperature the reduction of the order can be observed

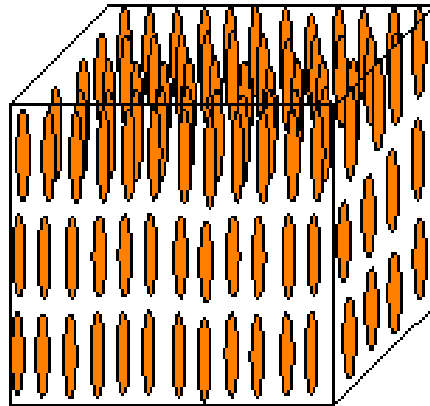




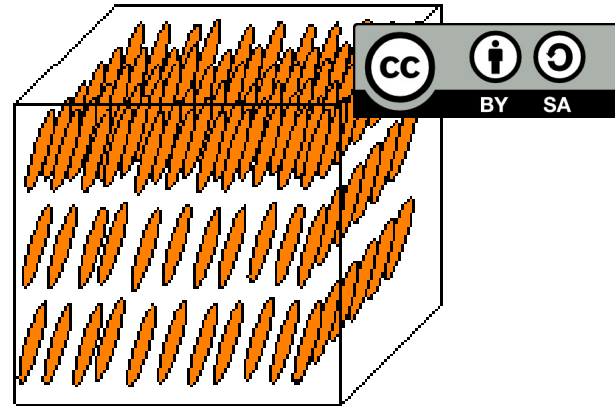
# Mesophase

(a) smectic phase - from the Greek name for soap

A



C

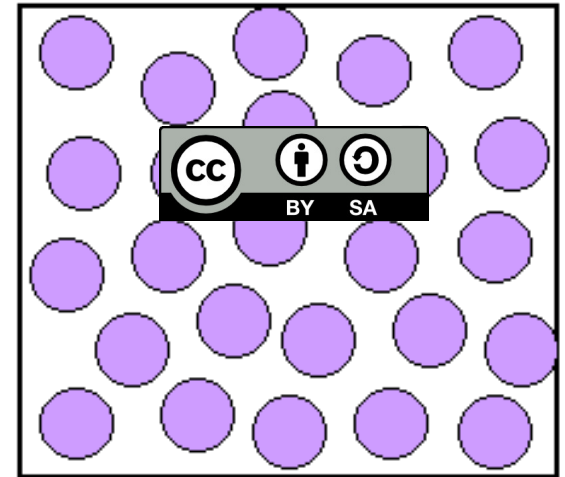
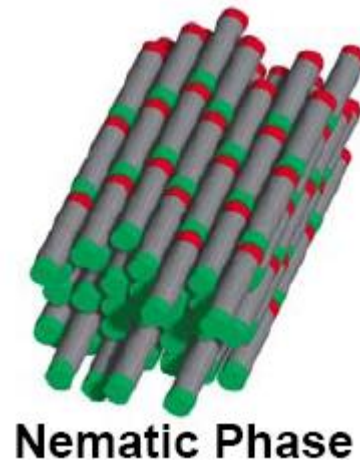
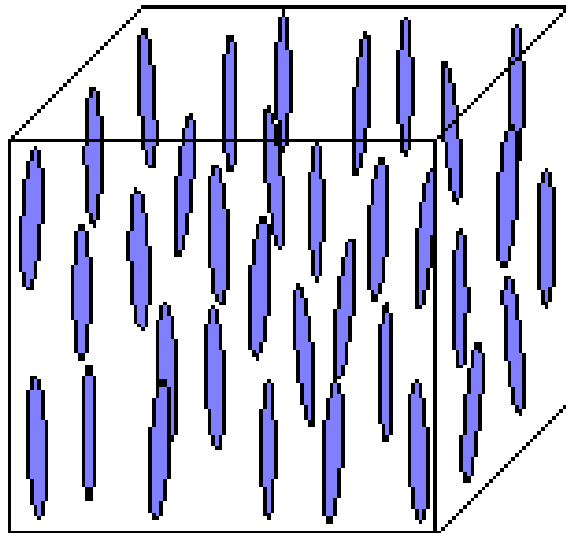


The layers are preserved, but the arrangement between them is lost

# Mesophase

(b) Nematic phase from the Greek word for thread

νεμωσ



Layering lost, but the molecules remain stacked  
- looking at the ends of the molecules - there  
is an obvious fluid-like disorder

# Chemistry and Physics of Solids – Lecture 8

## Ionic bond



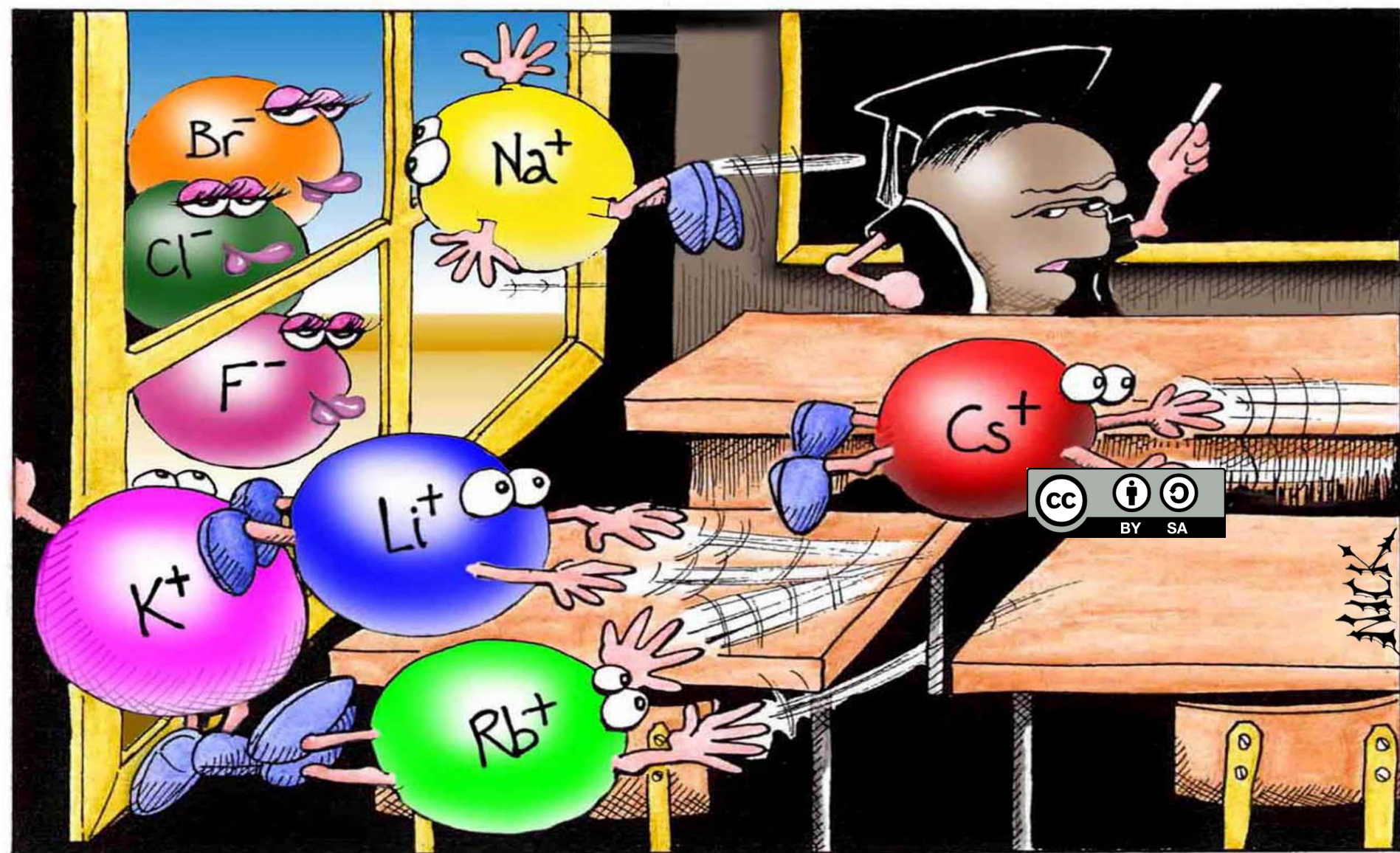
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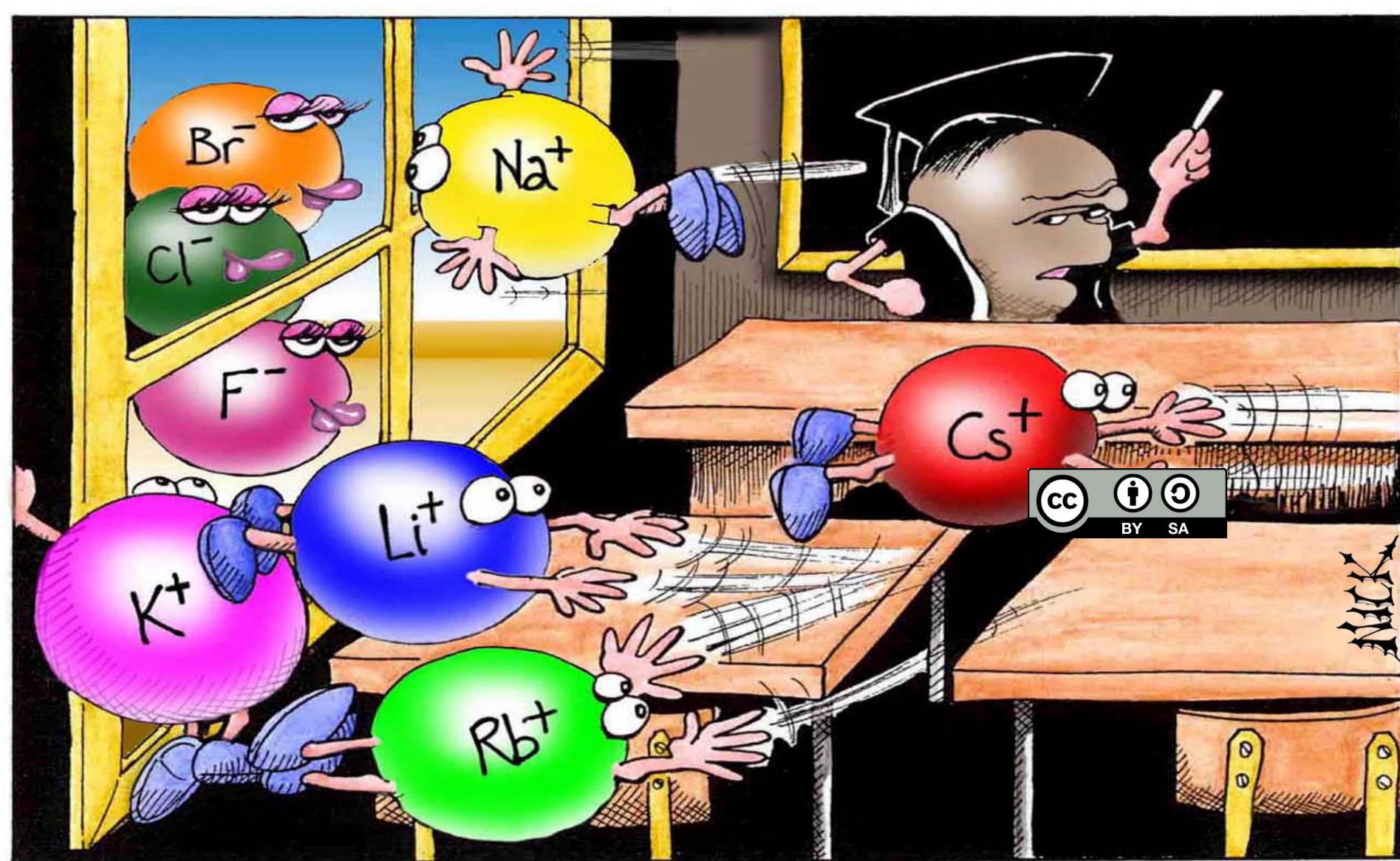




# Bonds in solid compounds

What kinds of forces are holding them together? 2





*“Perhaps one of you gentlemen would mind telling me just what it is outside the window that you find so attractive..?”* 3

# Classification of solids

based on realized bonds

- **Ionic** = transmission of electrons, ion formation, coulomb's attractive forces between oppositely charged ions

Bond's energy 50 -1000 kJ/mol

- **Covalent** = electron sharing between several atoms (2, 3, 4....)



Bond's energy 200 -1000 kJ/mol

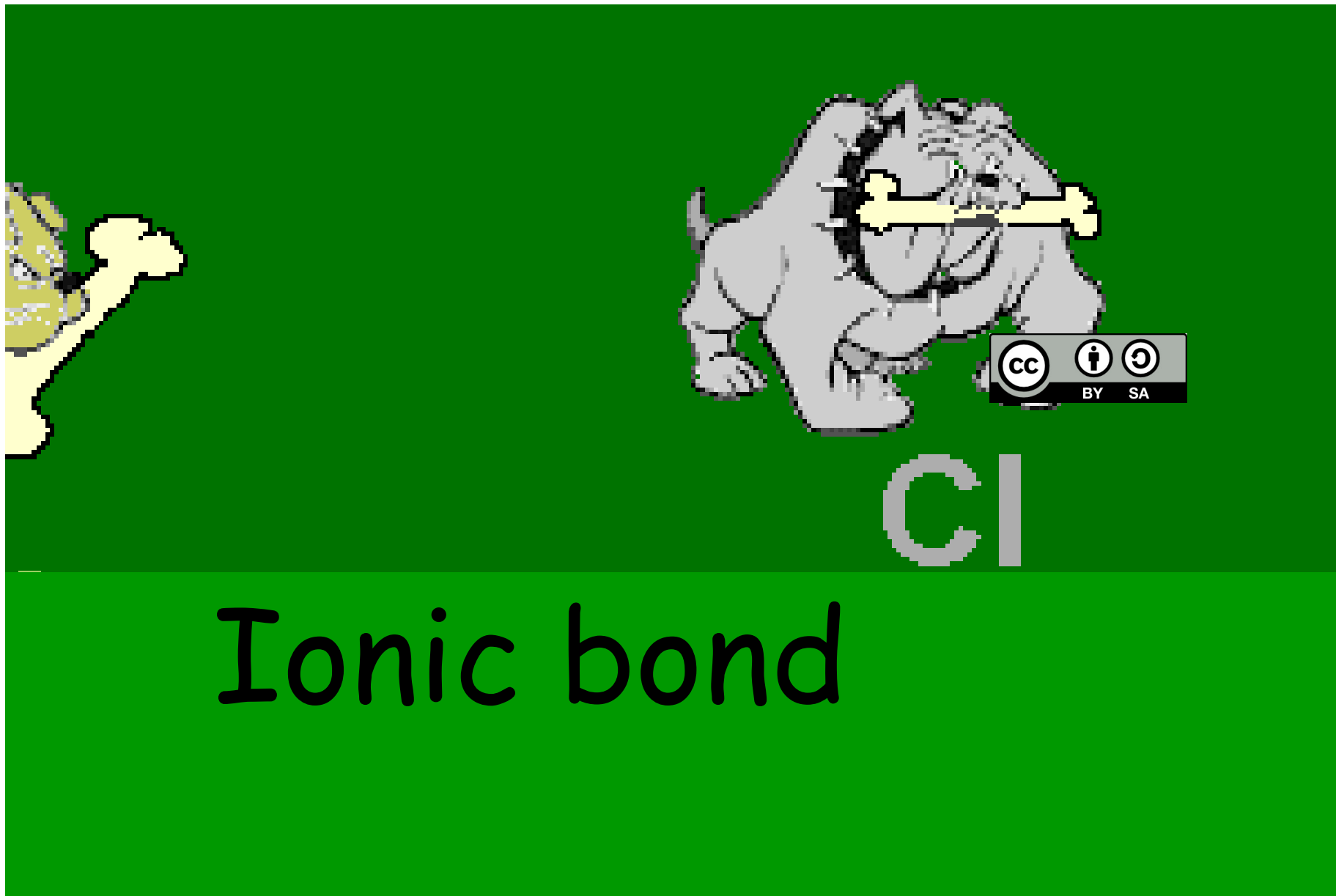
- **Metallic** = electron sharing between many atoms

Bond's energy 50 -1000 kJ/mol

- **Van der Waals** = attractive forces between temporary poles (dipoles)

Bond's energy 4-42 kJ/mol

Ionic bond: anion is a big, greedy thief dog



Cl

Ionic bond



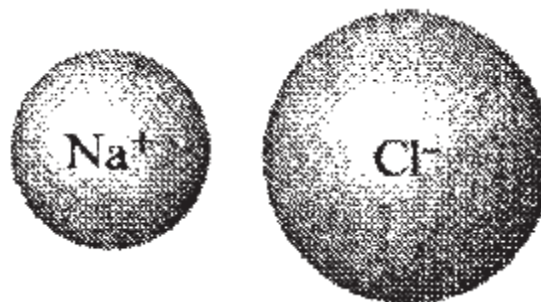
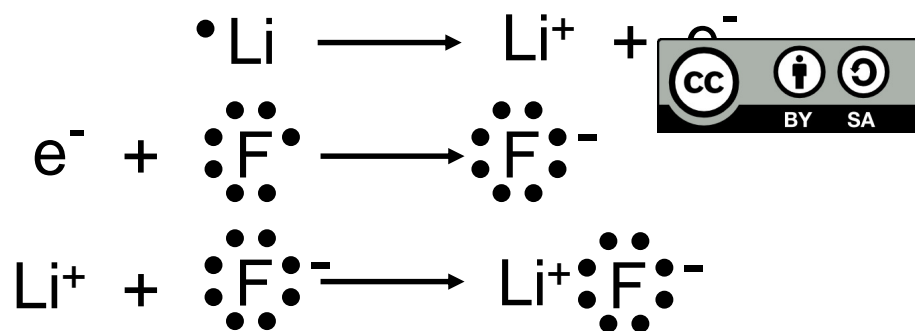
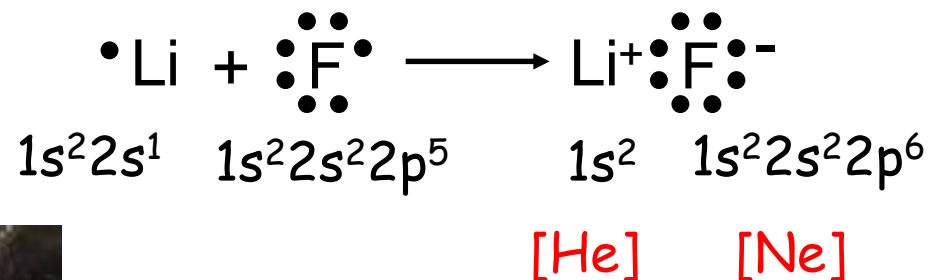
# Ionic bond is characterized by:

- 1) non-directional (any ion in any direction is capable of attracting an ion of the opposite charge).
- 2) each ion that interacts with the counter ion does not compensate the force fields in all directions.



# Ionic bond

Kossel's description:




Model of ionic bond according to Kossel (1916)

# General ideas



- There must be attractive forces between cations and anions
  - An obvious candidate for explaining the attraction forces will be coulombic forces

$$F = -\frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^2}$$


- where  $r$  is the distance between the atoms (ions) forming the solid

However, it is preferable to consider the potential energies between two ions instead of forces.

Mathematically, energy ( $E$ ) and force ( $F$ ) are combined by:

$$E(r) = \pm \frac{q_1 q_2}{4\pi\epsilon_0 r}$$

$$E(r) = \int F dr$$


# Ionic bond

The ions have repulsive forces, van der Waals forces (the same as for neutral molecules), and Coulomb forces.

Potential energy between pairs of isolated ions of the charge  $e$  in the distance  $r$ :

$$E(r) = -\frac{A}{r^m} + \frac{B}{r^n} \pm \frac{z_A z_B e^2}{4\pi\epsilon_0 r}$$

$m \approx 6, n \approx 5$  a.u.



1st van der Waals member. 2nd member is repulsive, 3. Coulombic member

VDW contribution is negligible compared to Coulombic ( $\sim 0.01 - 0.1 \text{ eV}$  versus  $10 \text{ eV}$ ).

$$E(r) \approx +\frac{B}{r^n} - \frac{e^2}{4\pi\epsilon_0 r}$$

Attraction  
(decreasing energy)

$$E(r) \approx +\frac{B}{r^n} + \frac{e^2}{4\pi\epsilon_0 r}$$

Repulsion  
(increasing energy)

# Ionic bond

The minimum value of  $U_0$  is called the ionic cohesive energy of the solid.

It represents the energy needed to separate the solid into a set of isolated cations and anions

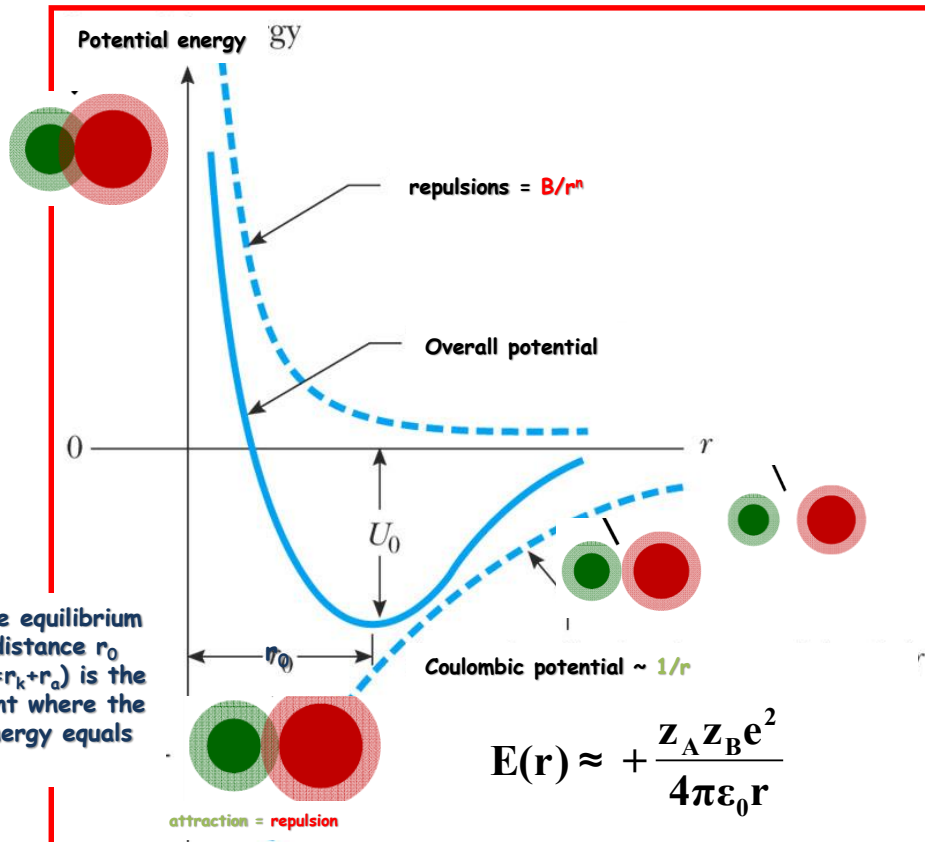
Repulsive potential:  $B / r^n$

  $n$  - Born's exponent dependent on electrostatic configuration of layers of ions

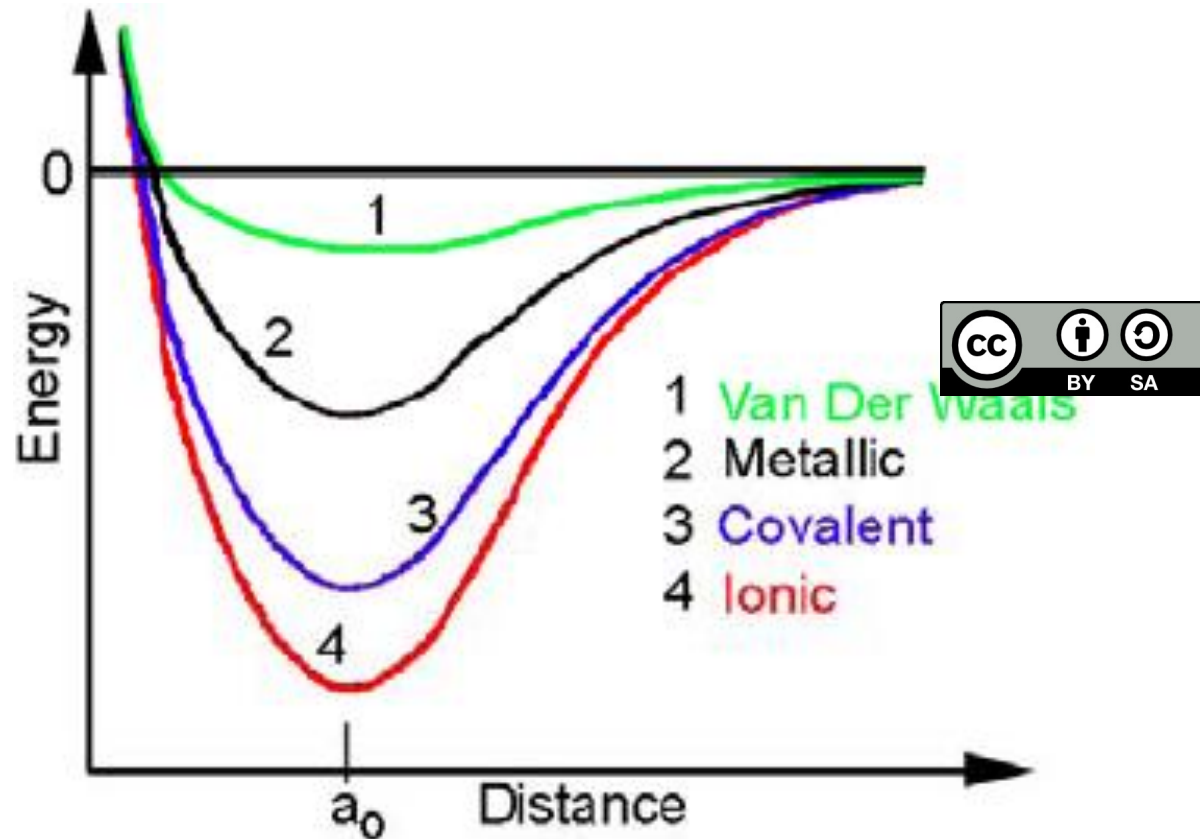
configuration	$n$
He	5
Ne	7
Ar, Cu <sup>+</sup>	9
Kr, Ag <sup>+</sup>	10
Xe, Au <sup>+</sup>	12

For example  $\text{Na}^+\text{Cl}^- = [\text{Ne}][\text{Ar}] \rightarrow (7+9)/2 = 8$

The more compressible the ion is, the higher the value of Born's exponent



# Relative bond strength of every bonds types





# Calculation of the unit cell energy of NaCl

## Bond energy of NaCl

- What is the energy of electron transition from Na to Cl to form a "molecule" of NaCl?
  - To remove the electron from Na (ionisation energy IE), it is necessary to "release" 5.14eV



- If Cl catches an electron then it releases 3.62eV (electron affinity EA):





# Bonding energy of NaCl

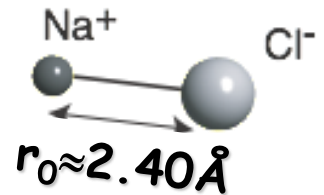
where is the energy gain?

- If  $\text{Na}^+(\text{g})$  and  $\text{Cl}^-(\text{g})$  reach the distance of  $r_0 \approx 2.40 \text{ \AA}$  [ $\text{\AA} = 10^{-10} \text{ m} = 0.1 \text{ nm}$ ] a "molecule" of NaCl occurs. Released energy:

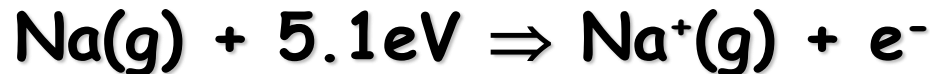
**6 eV** (Coulomb's potential)

$$\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

$$\begin{aligned} (V) &= \frac{-[1.6 \times 10^{-19}]^2}{4 \times \frac{22}{7} \times 8.85 \times 10^{-12} \times 2.4 \times 10^{-10}} \text{ J} \\ &= \frac{-[1.6 \times 10^{-19}]^2}{4 \times \frac{22}{7} \times 8.85 \times 10^{-12} \times 2.4 \times 10^{-10} \times 1.6 \times 10^{-19}} \text{ eV} \cong -6 \text{ eV} \end{aligned}$$



- Energy of "molecular unit" NaCl formation :



# Ionic solid forms

- Energy gain of the „molecule“ formation of NaCl(s) is  **$\sim 4.5 \text{ eV}$** 
  - It is the cohesive energy needed to disrupt a "molecule" of NaCl and to rebuild neutral Na and Cl atoms.
  - This energy is enormous-  $E_{\text{disp}} = E_{\text{CC}} + E_{\text{BY}} + E_{\text{SA}}$  :  
 $4.5 \times 1.6 \times 10^{-19} \text{ (Joul/pair)} \times 6.023 \times 10^{23} \text{ (pairs)} = 433.7 \text{ kJ/mol}$
  - For a much more accurate calculation of total electrostatic energy, it is necessary to take into account the interactions of each ion with all others in the crystal

$$4.5 \times 1.6 \times 10^{-19} \text{ (Joul/pair)} \times 6.023 \times 10^{23} \text{ (pairs)} = 433.7 \text{ kJ/mol}$$

$$433.7 \times A = 433.7 \times 1.7476 = 757.9 \text{ kJ/mol}$$

# Ionic solid compounds

## Energy of the unit cell of NaCl

We considered only the molecule of NaCl, but what is the electrostatic gain of the solid?

Unit cell energy (enthalpy)  $E$ : 1 mole of ionic matter is the released energy given by approaching the oppositely charged gaseous ions from the infinite distance to the equilibrium at OK.

We start from the central ion  $\text{Cl}^-$

Energy gain from other 6  $\text{Na}^+$  :

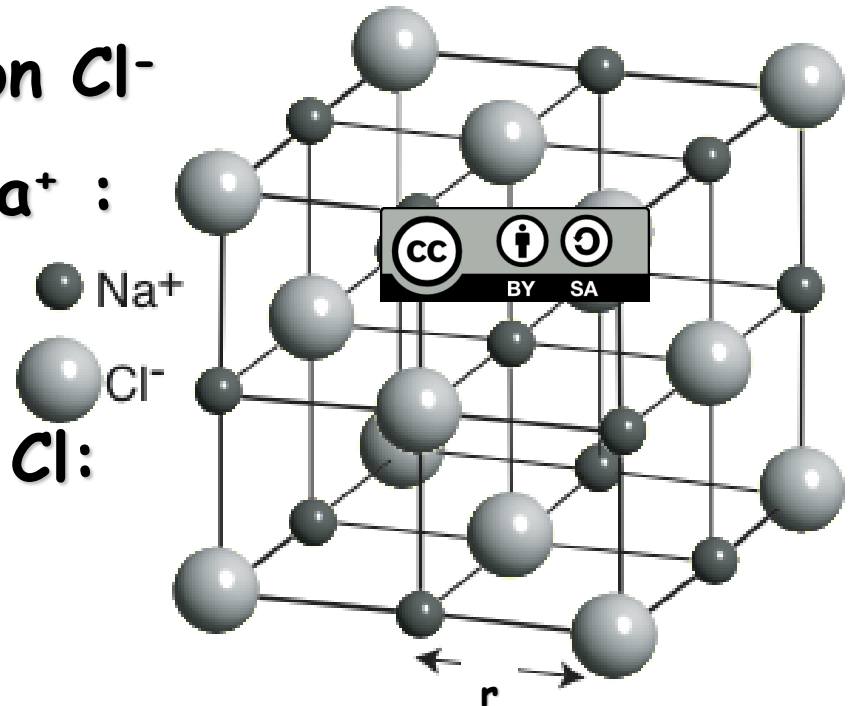
$$E = -6 \frac{e^2}{4\pi\epsilon_0 r}$$

Energy loss from other 12  $\text{Cl}^-$ :

$$E = +12 \frac{e^2}{4\pi\epsilon_0 r \sqrt{2}}$$

Energy gain from another 8 ions of  $\text{Na}^+$  and together:

$$E = -\frac{e^2}{4\pi\epsilon_0 r} \times \left( 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} \right)$$



# Ionic solid compounds

## Energy of the unit cell of NaCl

We considered only the molecule of NaCl, but what is the electrostatic gain of the solid?

Unit cell energy (enthalpy) E: 1 mole of ionic matter is the released energy given by approaching the oppositely charged gaseous ions from the infinite distance to the equilibrium at OK.

We start from the central ion  $\text{Cl}^-$

1. coordination sphere

3. coordination sphere

7. coordination sphere

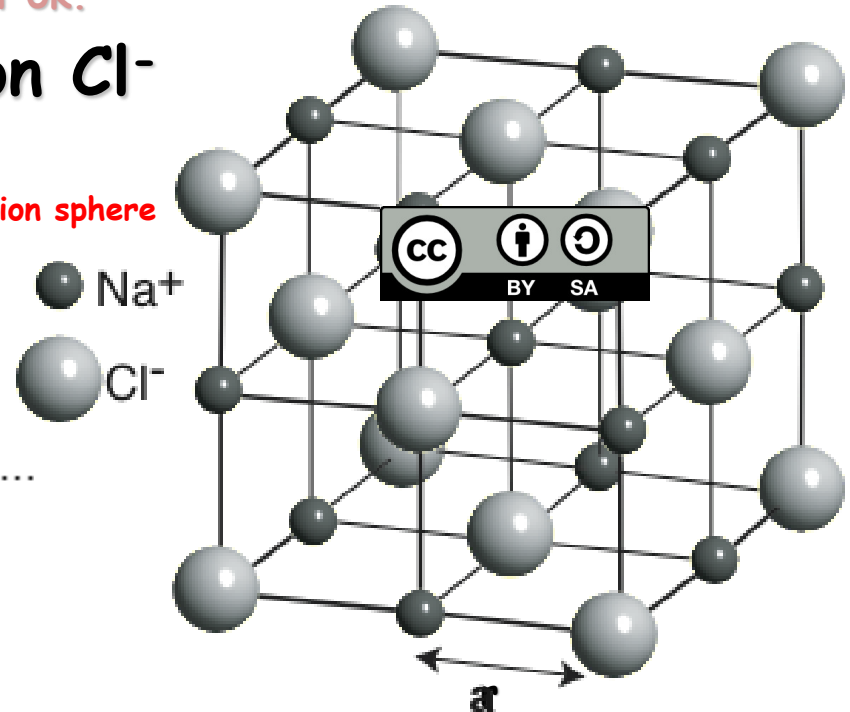
5. coordination sphere

4. coordination sphere

2. coordination sphere

6. coordination sphere

$$A = \frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} + \frac{12}{\sqrt{7}} \dots$$



# Ionic solid forms

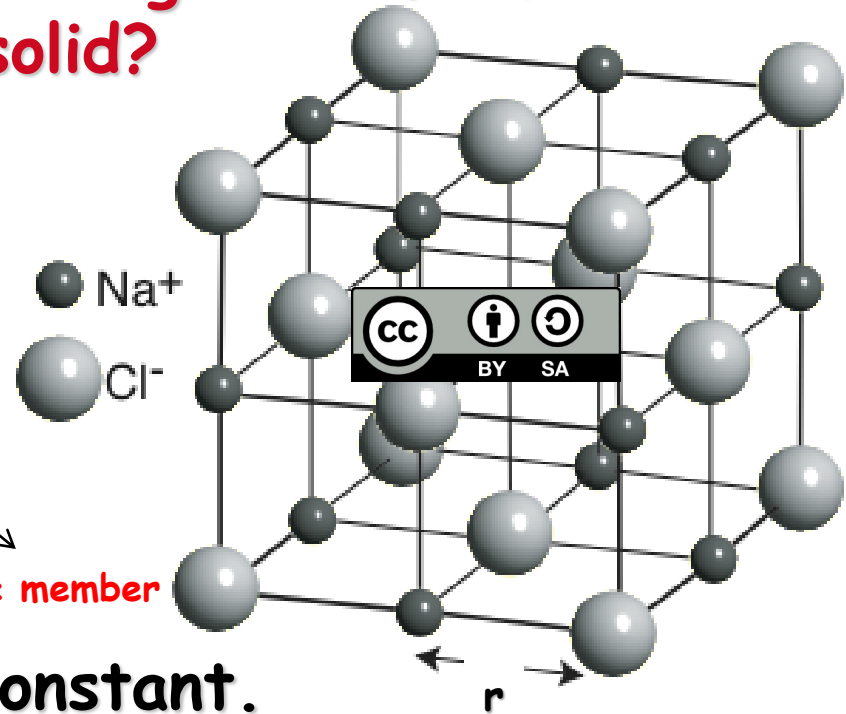
Example: NaCl

How high is the electrostatic gain to form the ordered solid?

A lot (70 000 members!):

$$E = -1.748 \frac{e^2}{4\pi\epsilon_0 r} = -A \frac{e^2}{4\pi\epsilon_0 r}$$

Atomic arrangements      Electrostatic member



$A$  - Madelung's constant.

Its value is characteristic of a particular structure

# Values of Madelung's constant

CN are coordination numbers (cation, anion) and n are the total number of ions in the empirical formula.

Why are some of the substances given the highest coordination?

**Answer**  
Higher Madelung Potential

lattice	A	CN	A <sub>n</sub> B <sub>m</sub>	A / n
CsCl	1.763	(8,8)	AB	0.882
NaCl	1.748	(6,6)	AB	0.874
Zinc blende	1.638	(4,4)	AB	0.819
wurtzite	1.641	(4,4)	AB	0.821
fluorite	2.519	(8,4)	AB <sub>2</sub>	0.840
rutile	2.408	(6,3)	AB <sub>2</sub>	0.803
CdI <sub>2</sub>	2.355	(6,3)	AB <sub>2</sub>	0.785
Al <sub>2</sub> O <sub>3</sub>	4.172	(6,4)	A <sub>2</sub> B <sub>3</sub>	0.834



**Erwin Madelung**

The value of Madelung constant A is constant for each of the stoichiometries, and the values for A / n are approximately similar for each of the structures.

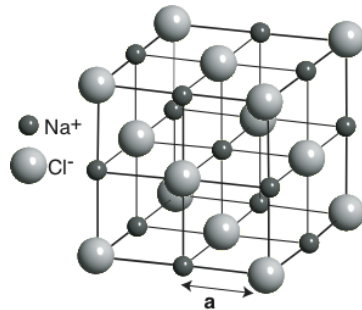
$$E_{\text{disp}} = E_{\text{mr}} / A$$

# Ionic solid compounds

example: NaCl

$$E_{Cl} = -1.748 \frac{e^2}{4\pi\epsilon_0 r} = -A \frac{e^2}{4\pi\epsilon_0 r}$$

Total lattice energy per mole of NaCl



$$E_{tot} = \frac{2E_{Cl} \text{ CC BY SA } 0^{23}}{2}$$

Two ions - Na a Cl

Every pair needs to be included only once

$$E_{tot} = -AN \frac{e^2}{4\pi\epsilon_0 r}$$

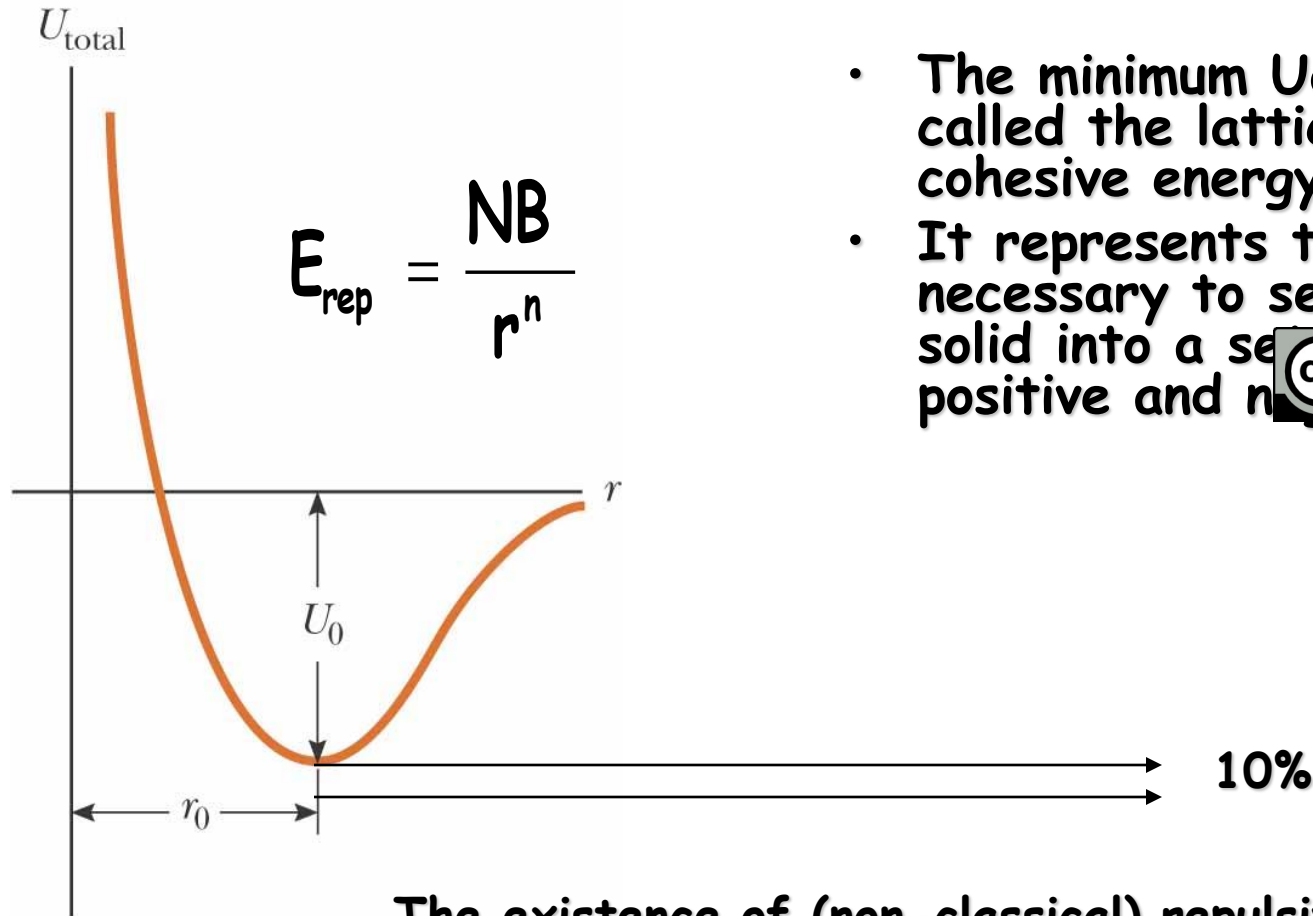
calculation: 861 kJmol<sup>-1</sup>.

Experiment: 786 kJmol<sup>-1</sup>

Grid energy is calculated, but incorrectly: there are repulsive forces, otherwise the crystal would immediately become a black hole. <sup>19</sup>



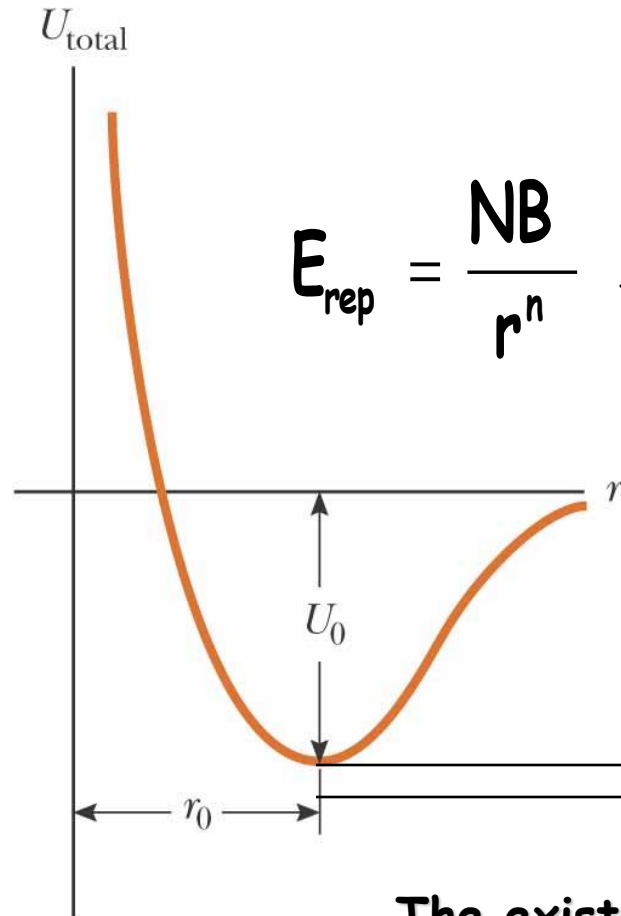
# Total energy of crystalline solid



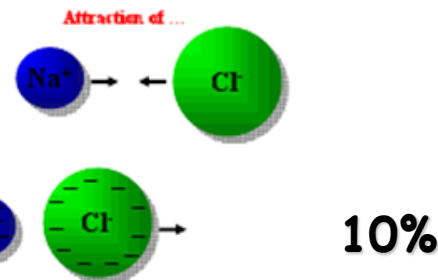
- The minimum  $U_0$  value is called the lattice or ion cohesive energy of the solid
- It represents the energy necessary to separate the solid into a set of separated positive and negative ions.

The existence of (non-classical) repulsive forces causes real cohesive energies to be about 10% lower than the values calculated by Coulomb's potential.

# Total energy of crystalline solid

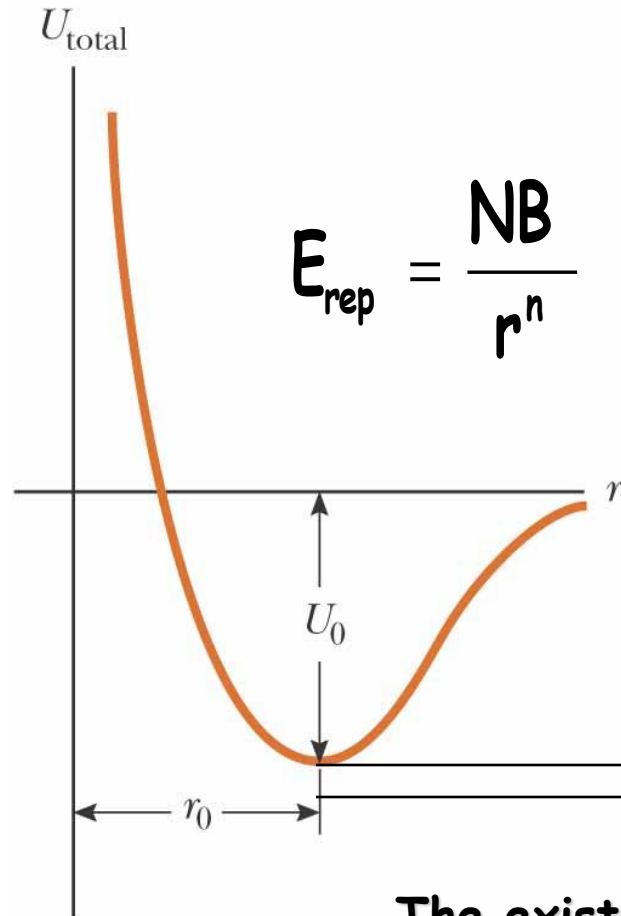


- The minimum  $U_0$  value is called the lattice or ion cohesive energy of the solid
- It represents the energy necessary to separate the solid into a set of isolated positive and negative ions.



The existence of (non-classical) repulsive forces causes real cohesive energies to be about 10% lower than the values calculated by Coulomb's potential.

# Total energy of crystalline solid



- The minimum  $U_0$  value is called the lattice or ion cohesive energy of the solid
- It represents the energy necessary to separate the solid into a set of separated positive and negative ions.

$$E_{\text{coul}} + E_{\text{rep}} = - \frac{NAz_Az_Be^2}{4\pi\epsilon_0 r} + \frac{NB}{r^n}$$

10%

How to find this term?

The existence of (non-classical) repulsive forces causes real cohesive energies to be about 10% lower than the values calculated by Coulomb's potential.

# Born-Landé equation

$$U = -\frac{NAz_Az_Be^2}{4\pi\epsilon_0r} + \frac{NB}{r^n}$$

In equilibrium distance ( $r = r_0$ )  $\frac{dU}{dr} = 0$

$$B = \frac{Az_Az_Be^2r^{n-1}}{4\pi\epsilon_0n}$$



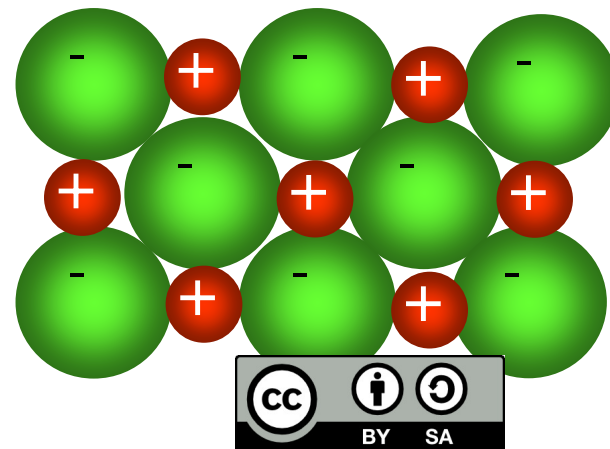
In general  
(lattice energy):

$$U = -\left(\frac{NAz_Az_Be^2}{4\pi\epsilon_0r_0}\right)\left(1 - \frac{1}{n}\right)$$

$$U = -1389\left(\frac{z_Az_BA}{r_0}\right)\left(1 - \frac{1}{n}\right) \quad (\text{kJmol}^{-1})$$

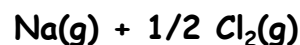
# Born-Haber cycle

The lattice enthalpy of any ionic compound is a change in enthalpy to produce 1 mol of solids in the standard state from the ions in the gaseous state



Grid enthalpy can not be measured directly and hence counts from other known enthalpies that join in the cycle.

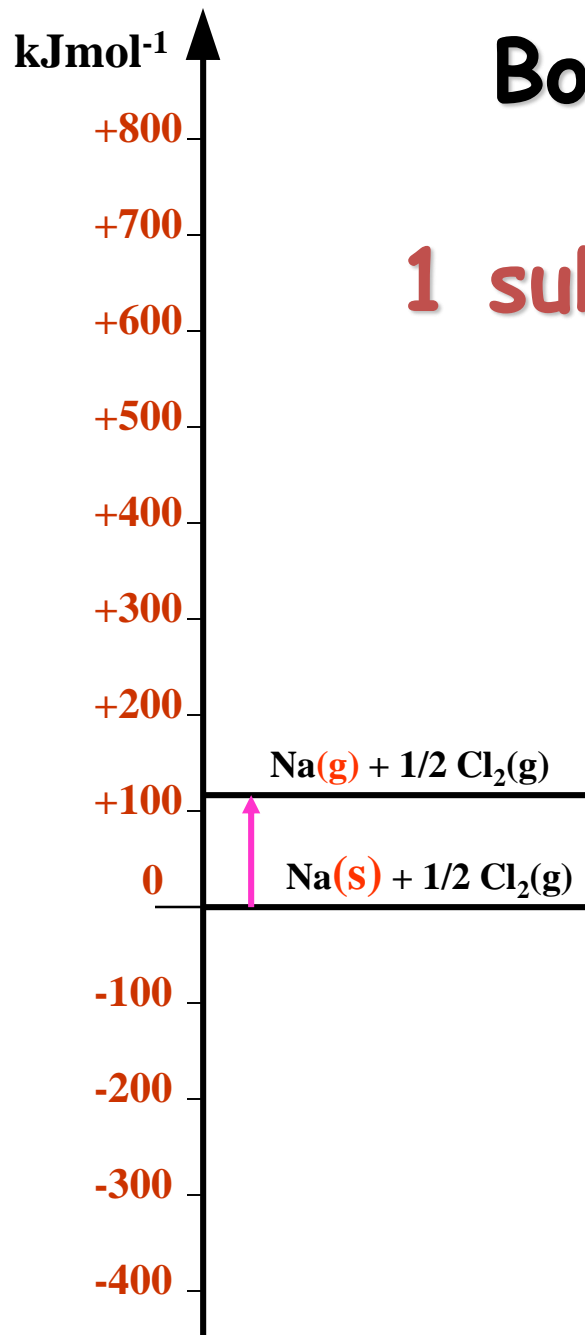
## Born-Haber cycle



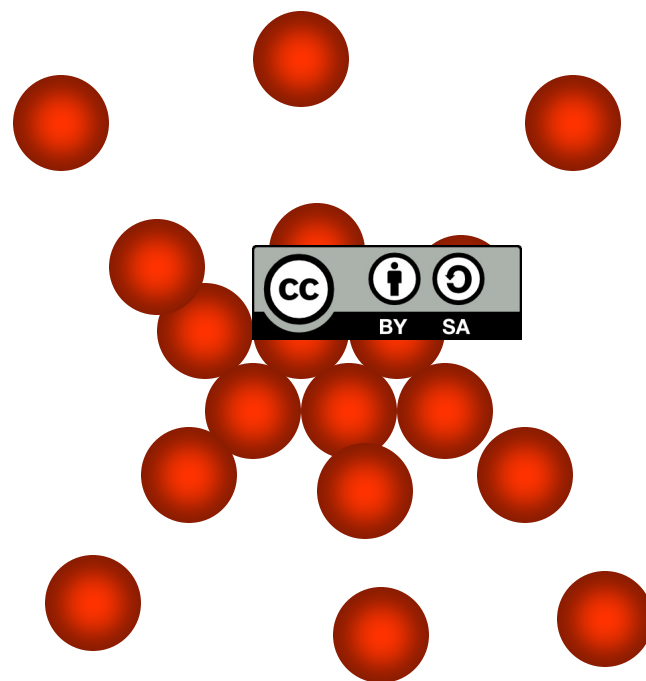
Madelung procedure

# Born-Haber cycle of NaCl

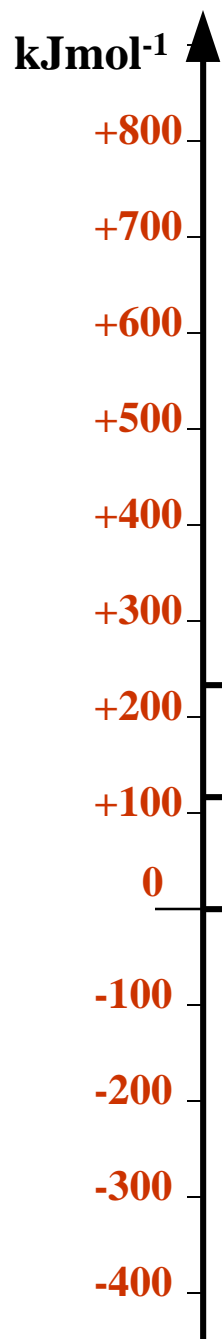
## 1 sublimation Na



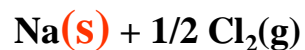
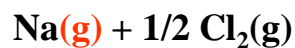
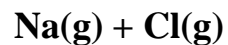
$$\Delta H_S^\theta = +107 \text{ kJmol}^{-1}$$



# Born-Haber cycle of NaCl



2 Dissociation of bonds of Cl

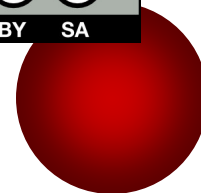
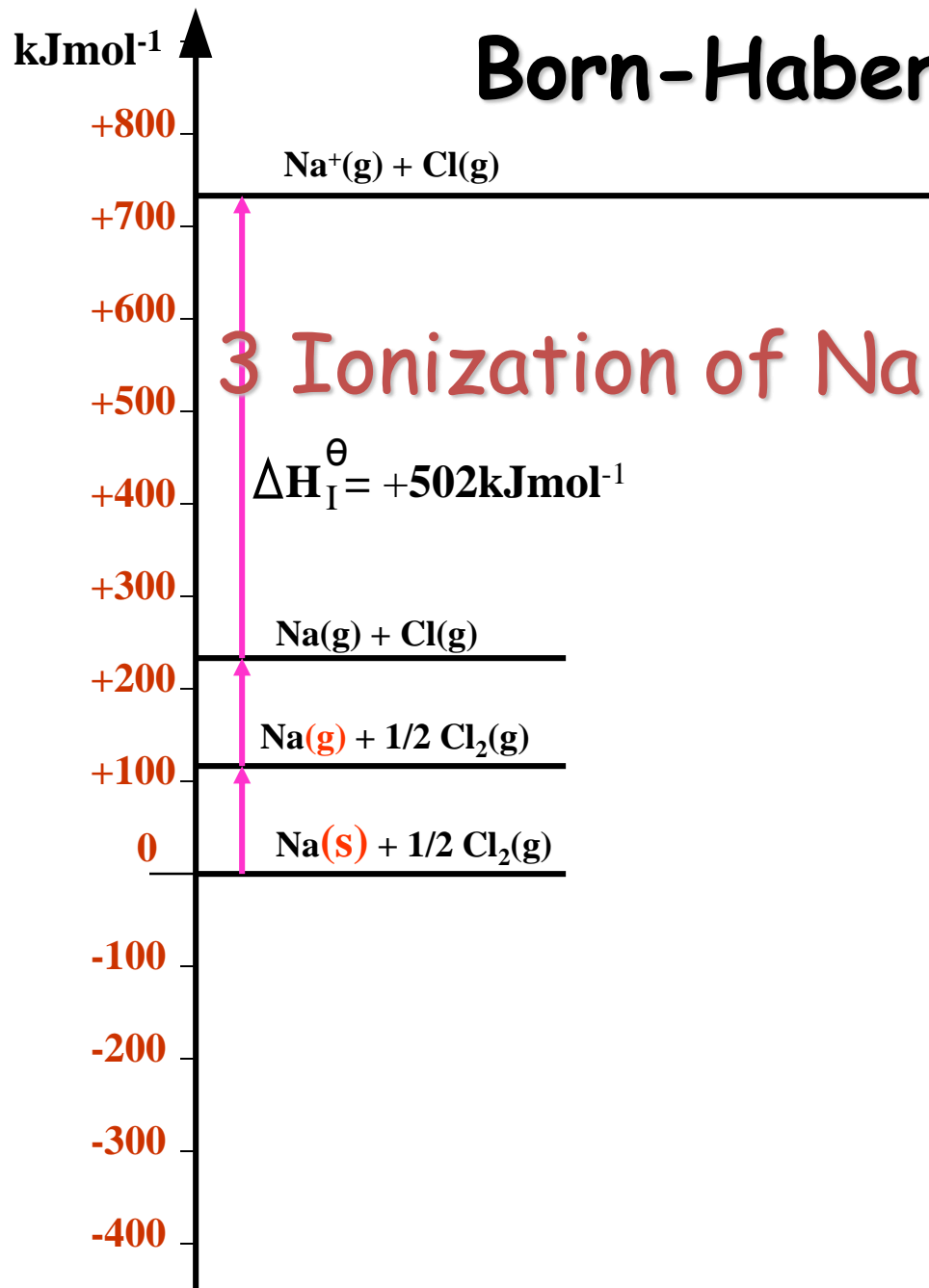


$$\frac{1}{2}\Delta H_D^\theta = +121\text{kJmol}^{-1}$$



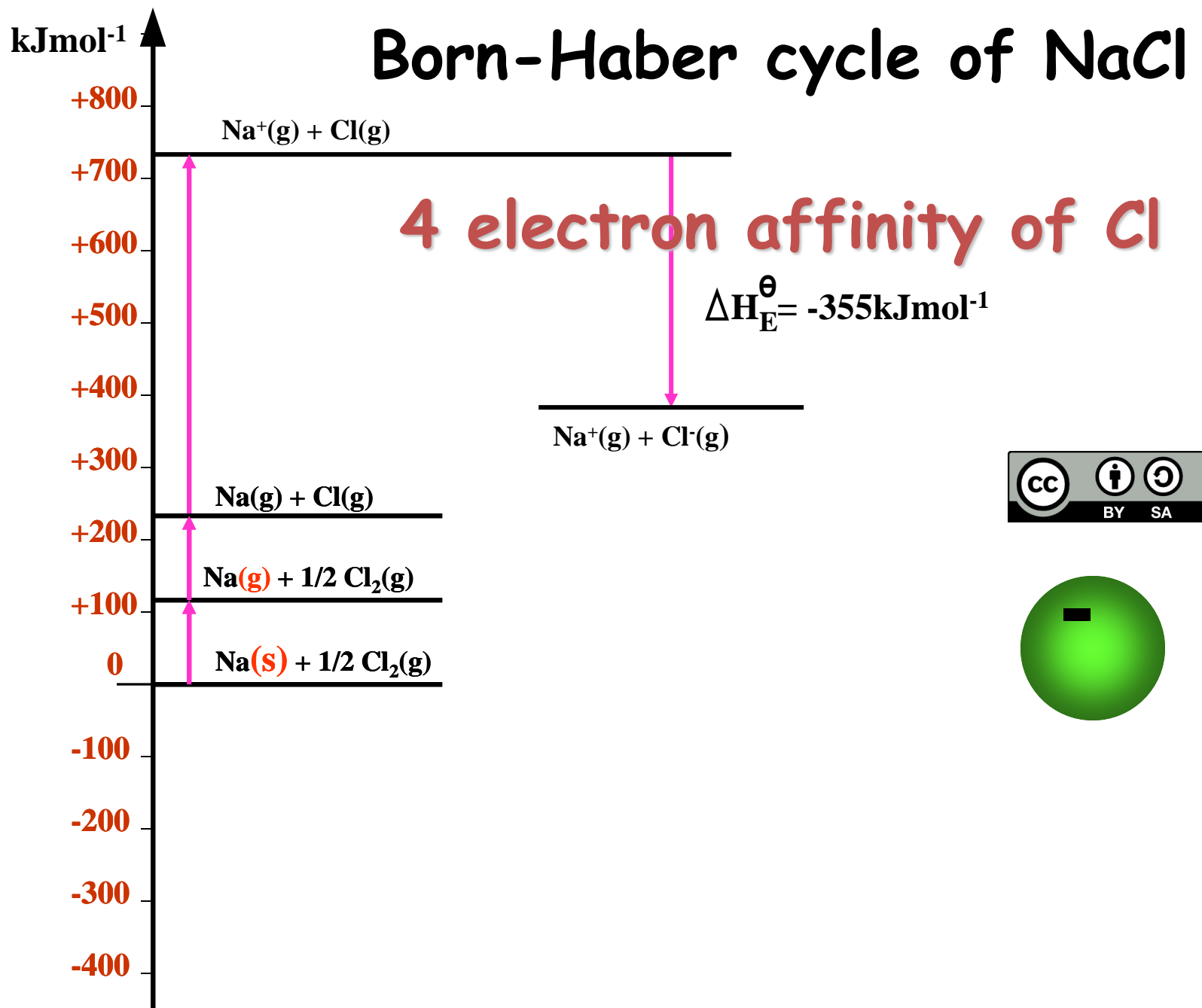


# Born-Haber cycle of NaCl

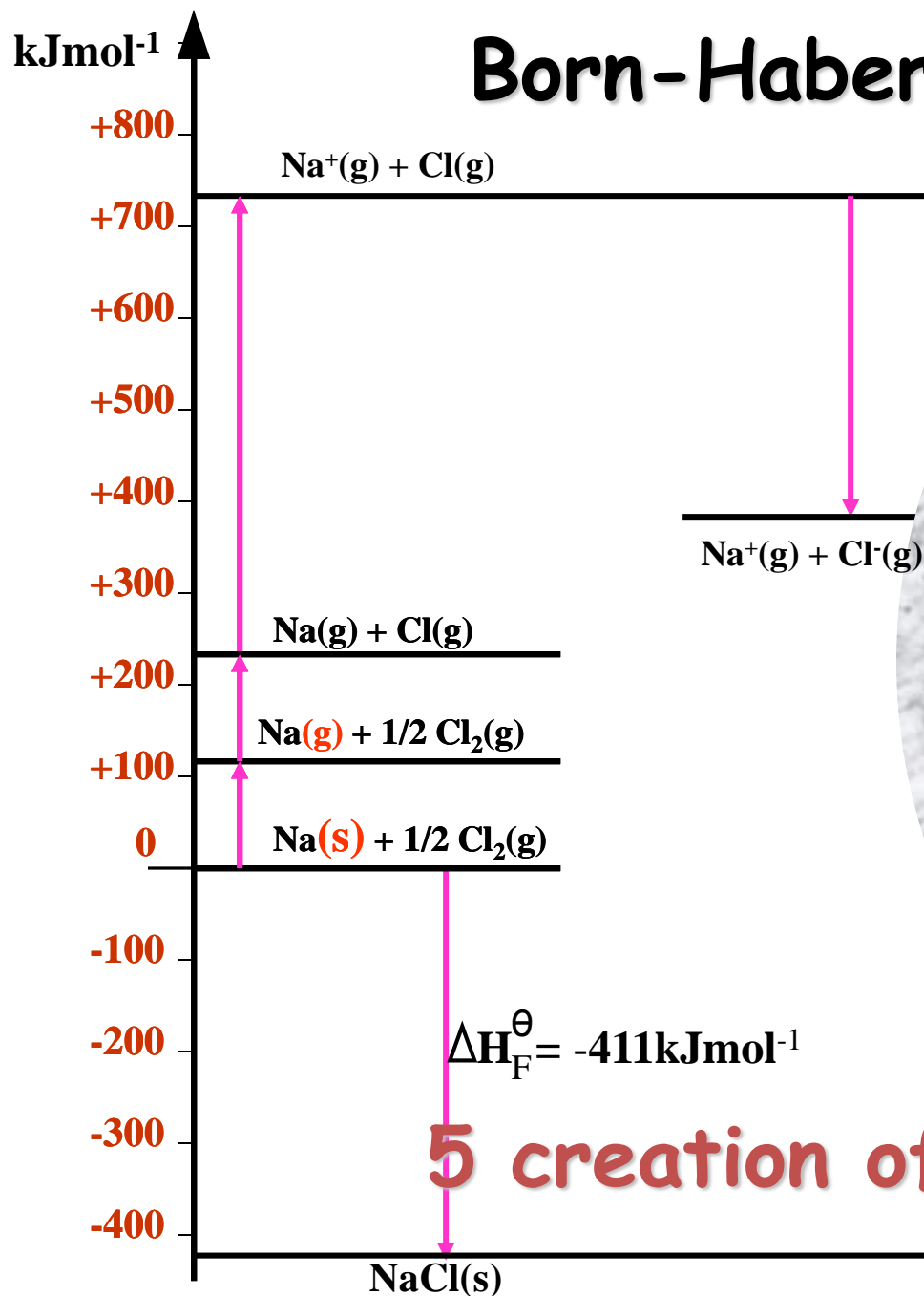


$\text{e}^-$   
 $\text{e}^-$   
 $\text{e}^-$   
 $\text{e}^-$   
 $\text{e}^-$

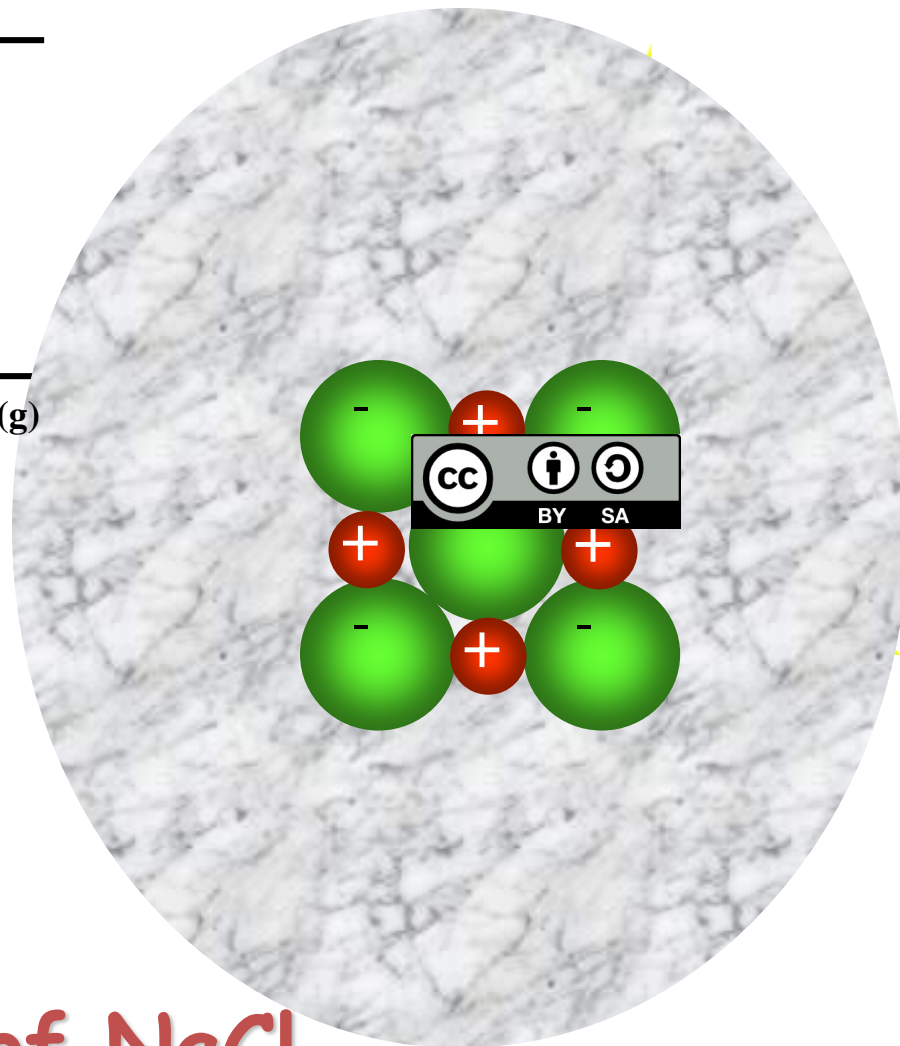
# Born-Haber cycle of NaCl



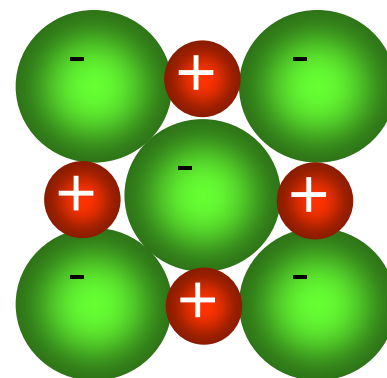
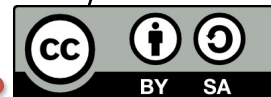
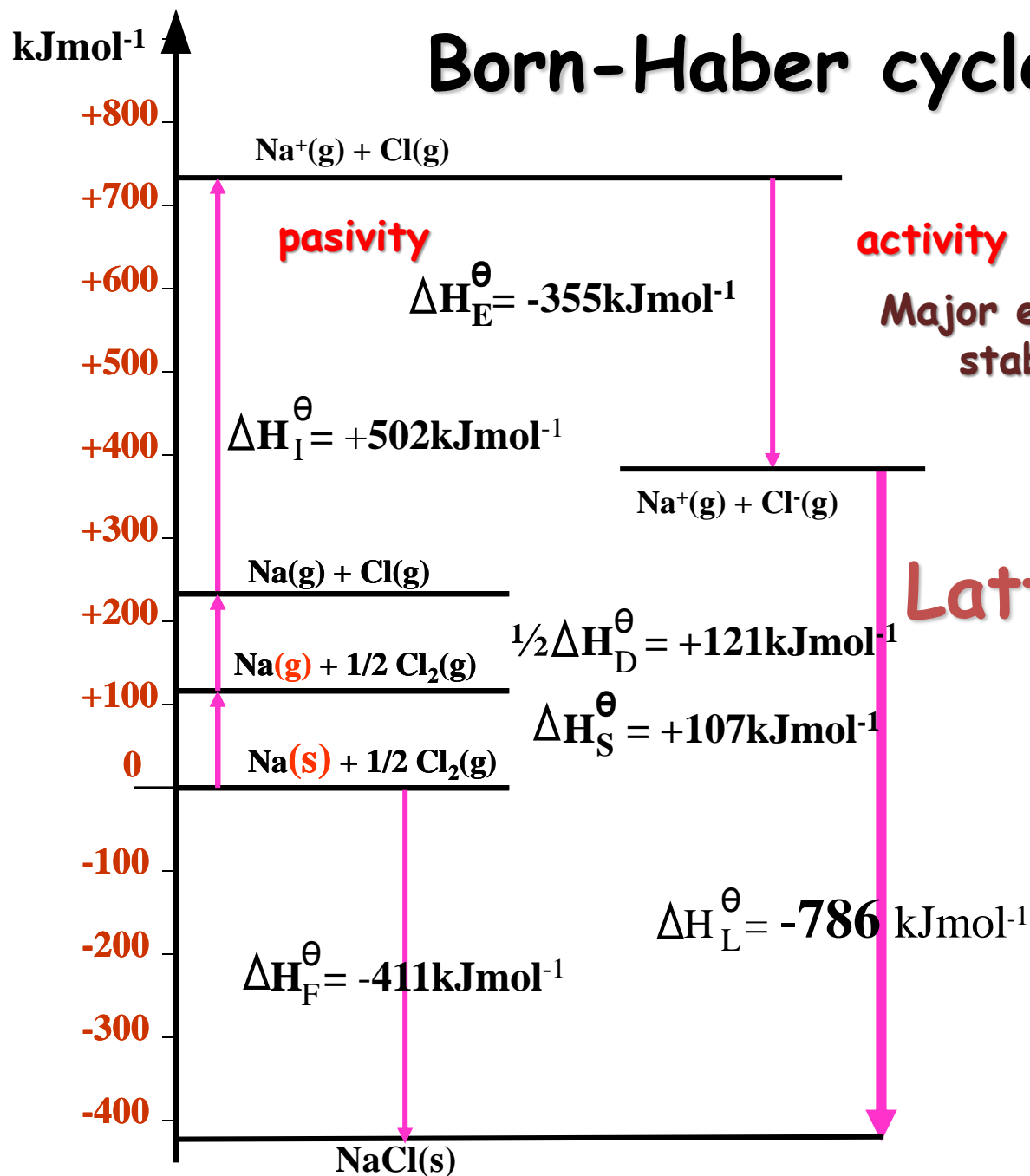
# Born-Haber cycle of NaCl



5 creation of NaCl



# Born-Haber cycle of NaCl



# Calculation of the lattice energy

Calculation of lattice enthalpy (direct measurement is impossible)  
is performed:

1

Theoretically  
Born-Landé  
Born-Meyer  
Kapustinsky

$$\Delta H_L^\theta = -762 \text{ to } -752 \text{ kJmol}^{-1}$$

lattice energy consists  
of an ionic contribution  
only

2

By experiment  
Born-Haber cycle

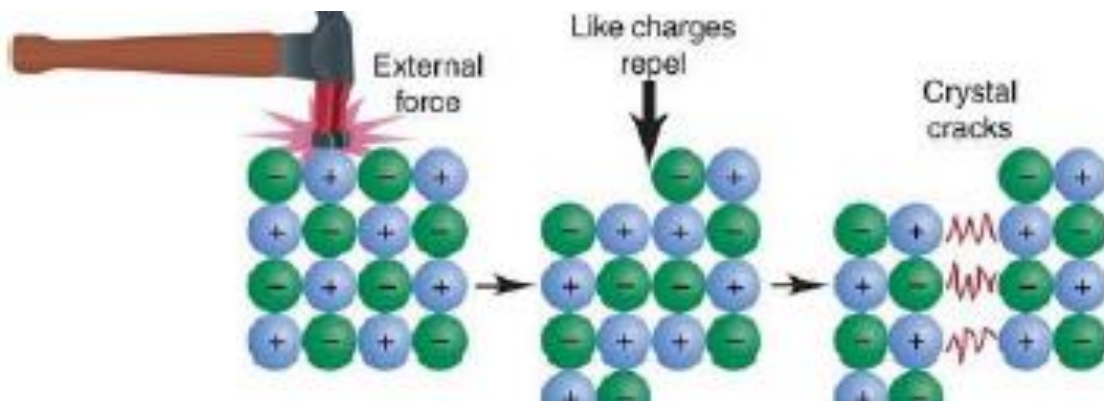


$$\Delta H_L^\theta = -786 \text{ kJmol}^{-1}$$

lattice energy consists  
of an ionic and covalent  
contribution

# Properties of ionic compounds

- Ionic solids are crystalline (arranged in a 3D set of ions)
- High melting points and boiling points - Very strong attraction between ions (difficult to separate)
    - Hard, rigid, but brittle
  - They do not keep electricity in a solid state, but solutions (electrolytes) or molten salts conduct it



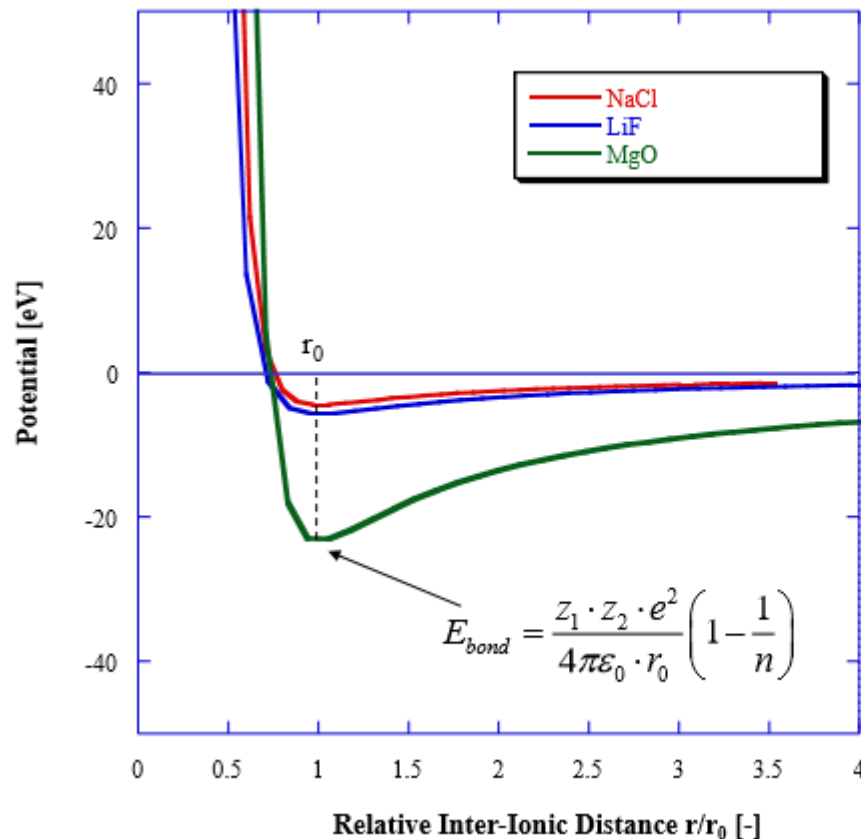


# Prediction of lattice energy

- Two factors determine the lattice energy of ionic compounds.
- Higher charges produce higher lattice energies (2+ and 2- lead to stronger bonds than 1+ and 1-).
- Less energy levels lead to higher lattice energies (LiF has higher lattice energy than NaCl)
- charges are the most important factor



# Comparison of potential dependencies on inter-ionic distances for NaCl, MgO and LiF



- MgO potential well is much deeper than for LiF and NaCl (ca 4x deeper)

- LiF potential well is deeper than for NaCl



- Same crystal structure (Rocksalt)

- Inter-Ionic Equilibrium Distances

- NaCl  $r_0=283$  pm

- LiF  $r_0=209$  pm

- MgO  $r_0=212$  pm

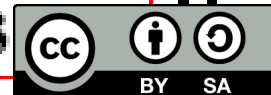
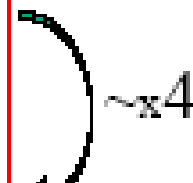
- Valencies are different

# Lattice energy

V kJ/mol:

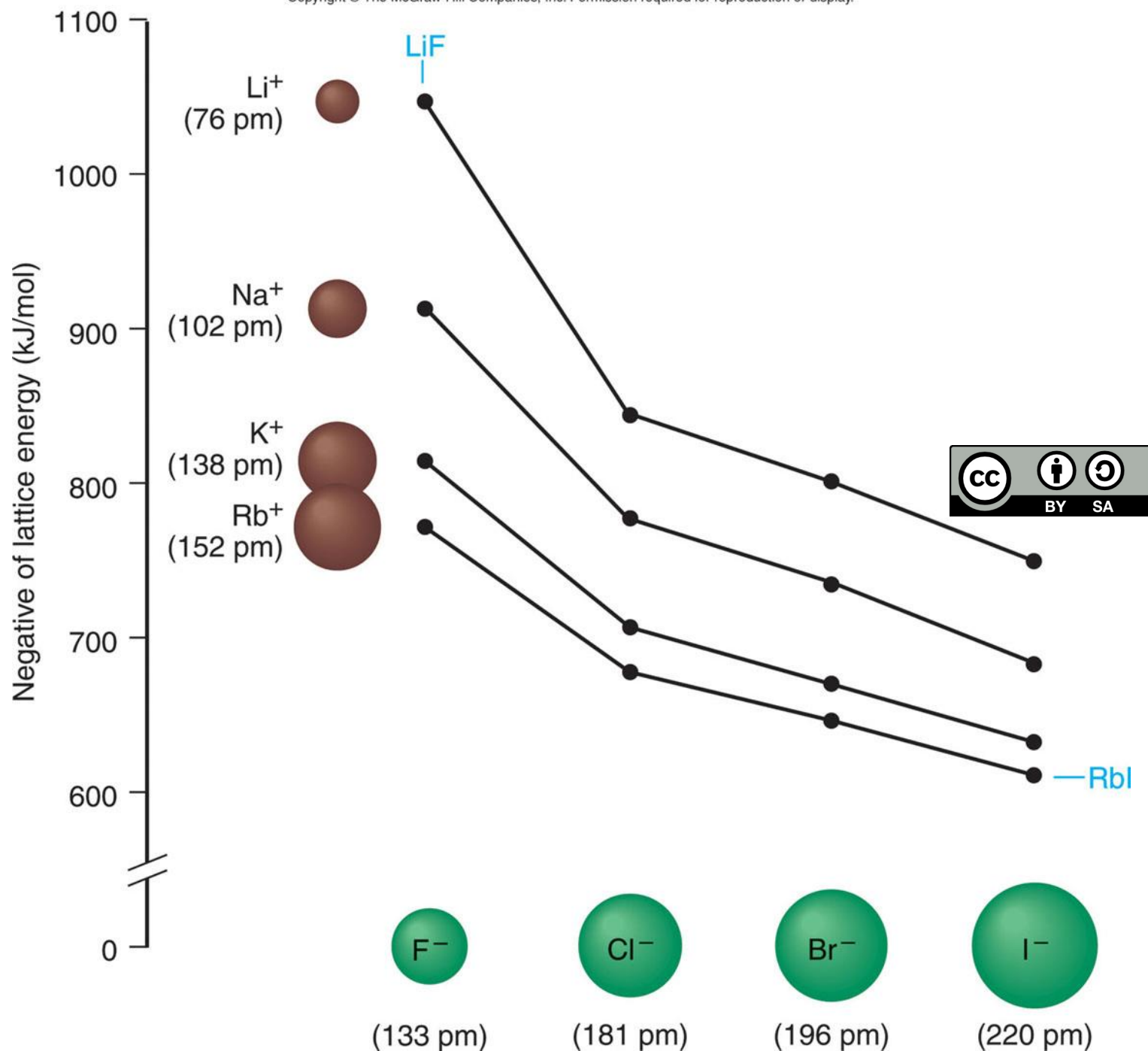


The magnitude of the factor -  $\Delta H_L$  is reduced by an increase in the size of the ions  
( $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ )



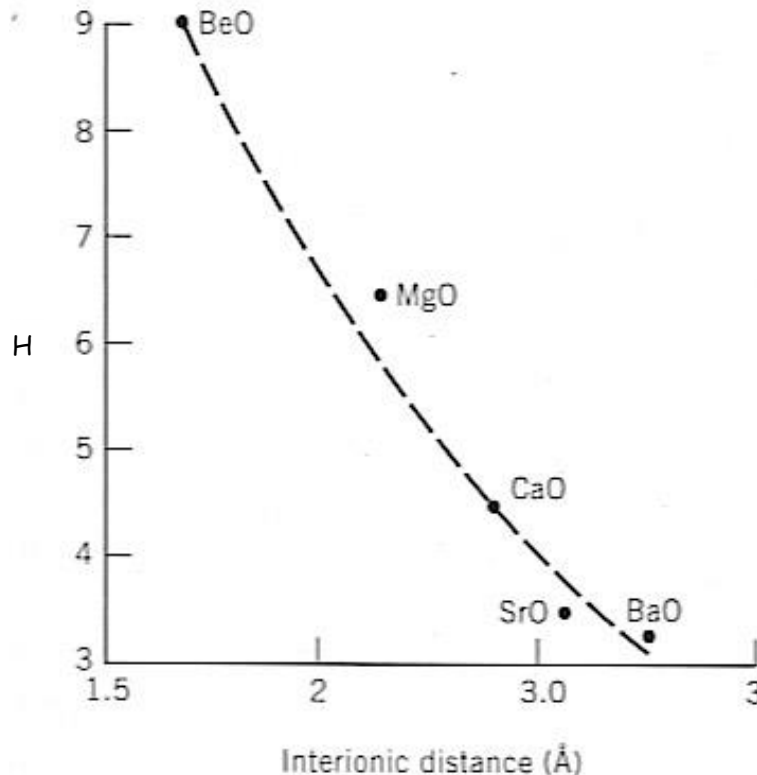
Charge Factor -  $\Delta H_L$  significantly increase with increasing ion charge  
( $\text{Li}^+$ ,  $\text{F}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{O}^{2-}$ )

The strength of the ionic bond is dependent:  
1) at inter-ionic distances  
2) ion charge



# Properties of ionic compounds

## Ion distances and hardness of materials



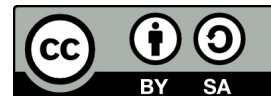
Compound	Interionic distance Å	H Hardness (Mohs)
BeO	1.67	9.0
MgO	2.10	6.5
CaO	2.40	4.5
SrO	2.56	3.5
BaO	2.76	3.3

The increasing hardness is directly proportional to the ionic potential:  
 $\varphi = Z/r$

Hardness increases with decreasing inter-ionic distance at constant cartridge sizes.

# Chemistry and Physics of Solids – Lecture 9

## Covalent and metallic bond



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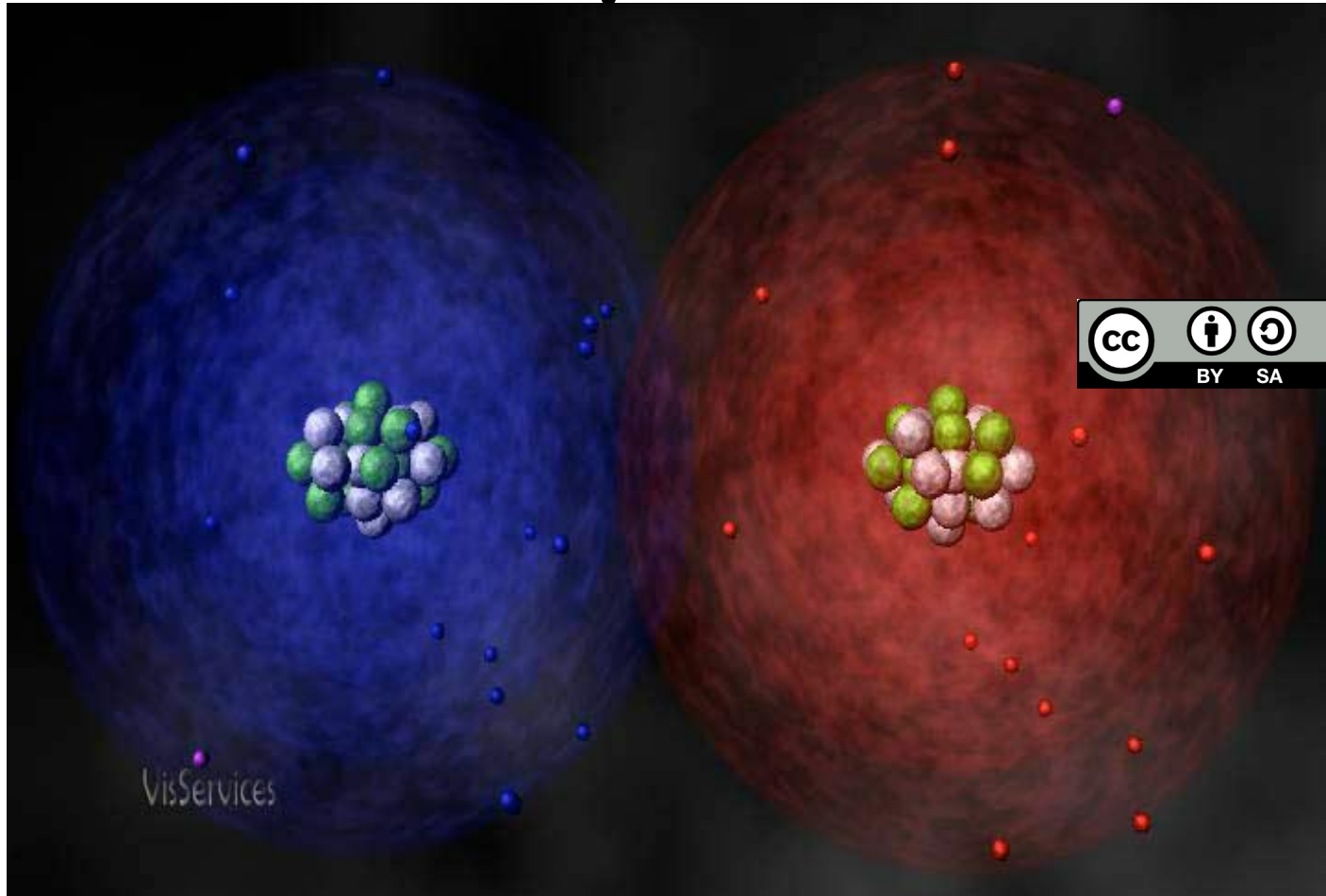


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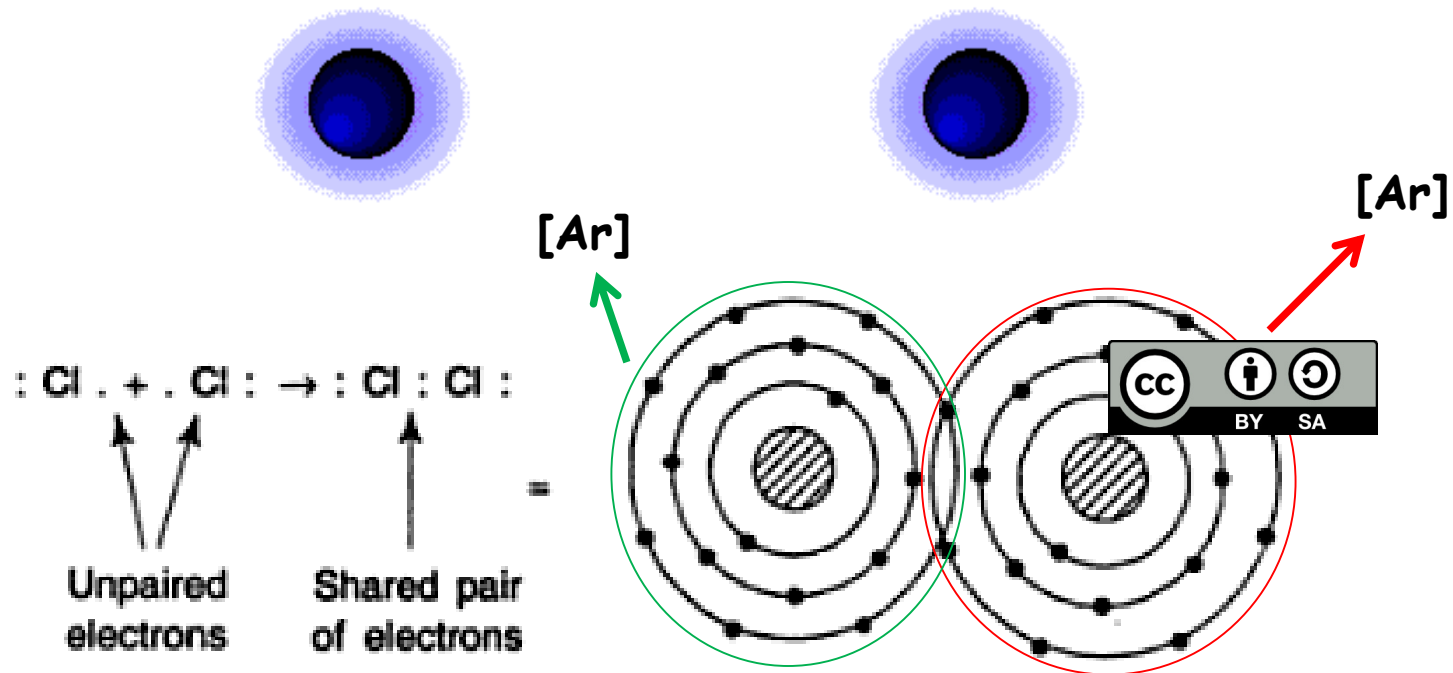
# Covalent bonds in solid compounds



cooperative use of valence electrons

# Covalent bond

Directional properties - prefers only a certain coordination arrangement



Covalent bond between two atoms of chlorine

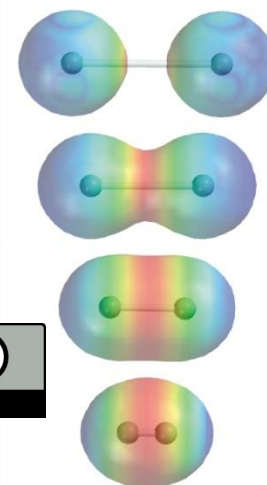
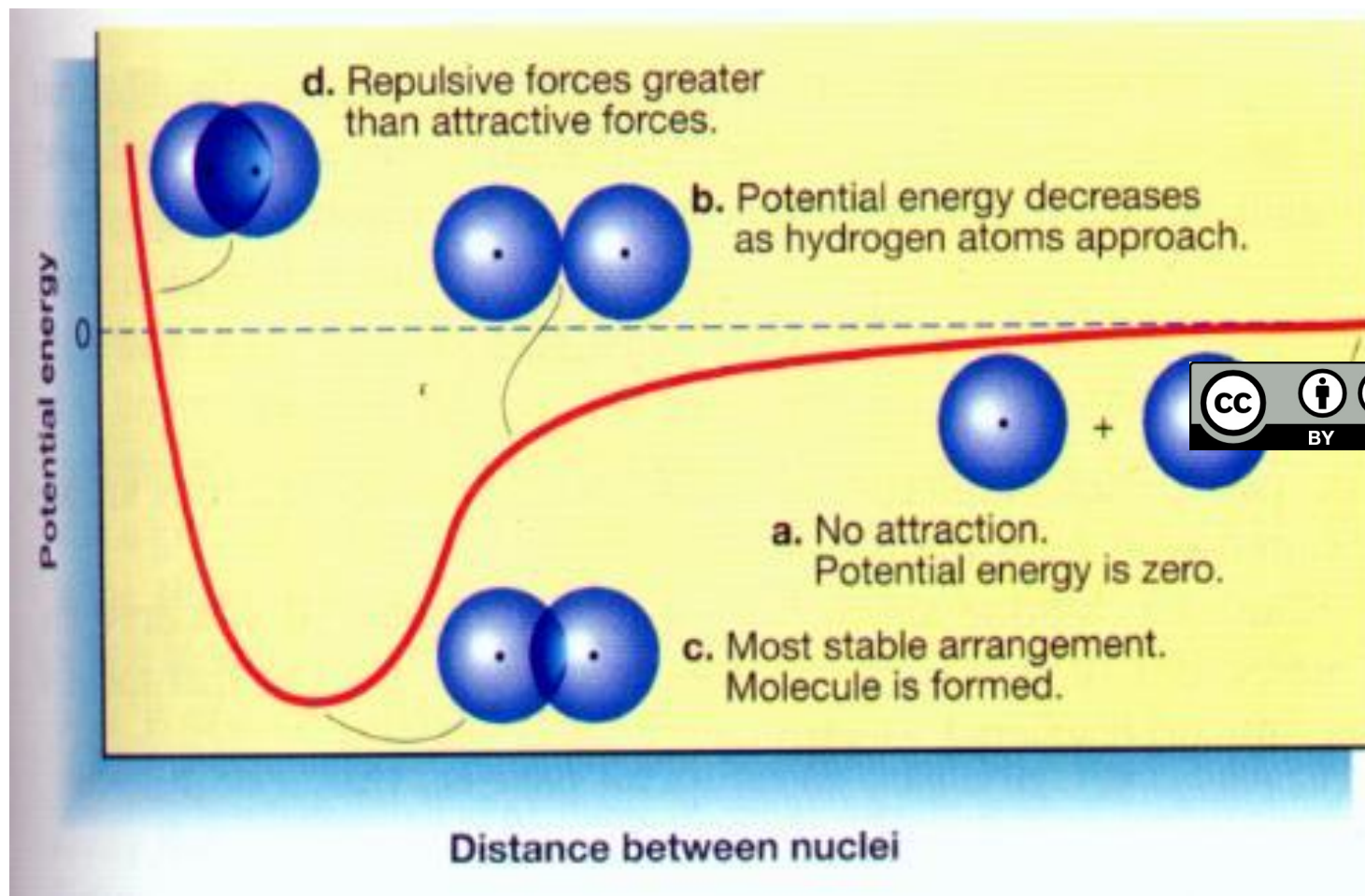
## Examples of covalent bonds:

Non-metallic elemental molecules ( $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{F}_2$ , atd.)

Different atoms ( $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$  a  $\text{HF}$ )

One-element solids (diamond, silicon, germanium)

# Potential energy of the bond H<sub>2</sub>



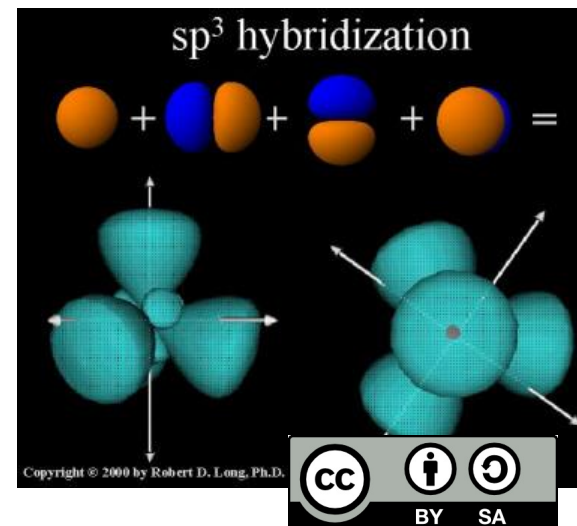
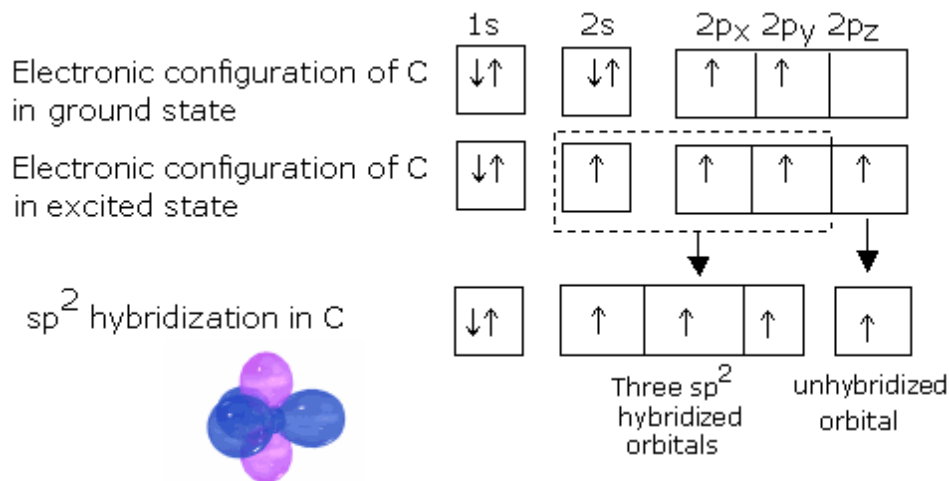
Changing the density of the electrons with mutual approximation

$$V(r) = -\frac{A}{r^m} + \frac{B}{r^n}$$

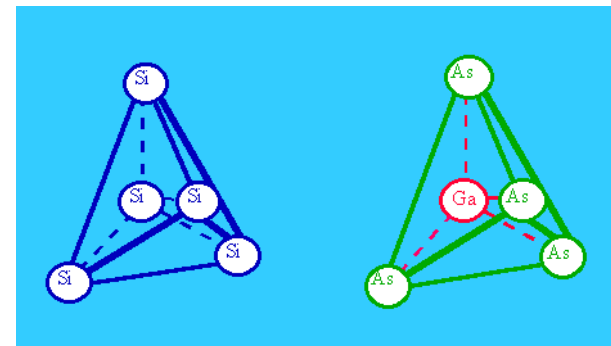
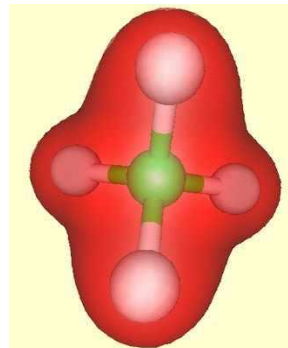
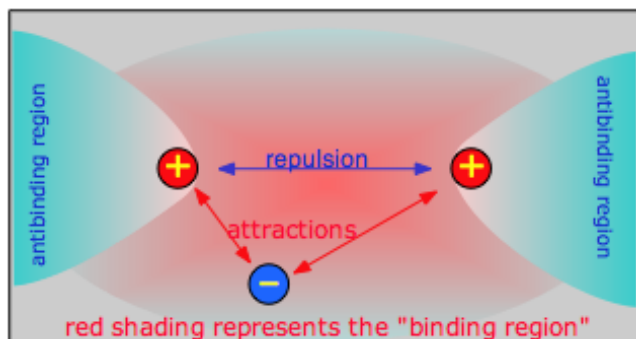
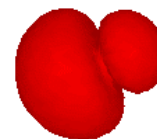
$$m = 4$$

$$n = 6-9$$

# Covalent crystals - $sp^3$ hybridization



Hybrid orbitals are formed from one s and three p orbitals.  
They have the same energy



# Octet rule

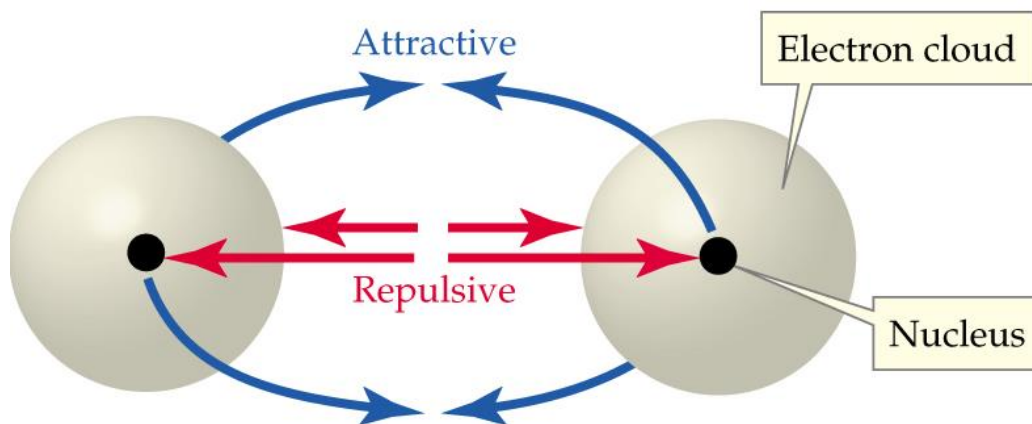
atoms with 8 electrons in the valence sphere are stable  
Atoms are combined to have 8 electrons in the valence sphere.  
They have the same electron configuration as noble gases

**Number of covalent bonds** =  $\{8 - (\text{nb of valence electrons})\}$

Chlorine:  $8 - 7 = 1$  it can bind only one other atom

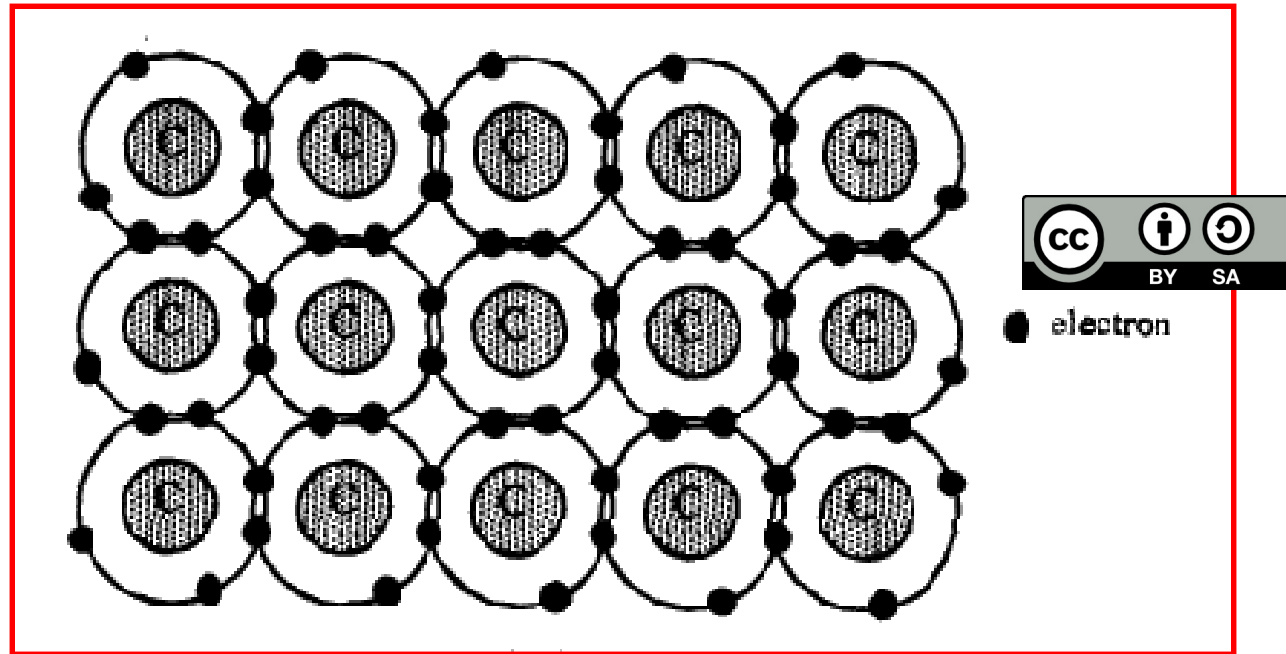
Carbon:  $8 - 4 = 4$  can bind other four atoms

The formation of a covalent bond is associated with the equalization of attractive and repulsive forces between atoms.



# Covalent crystals

They usually do not have free electrons.  
Crystals are insulators (often semiconductors)

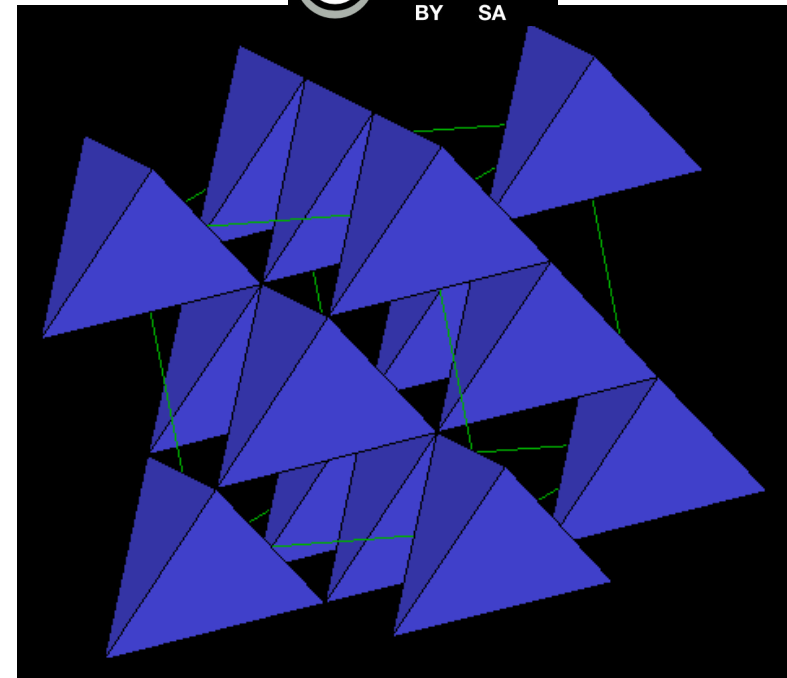
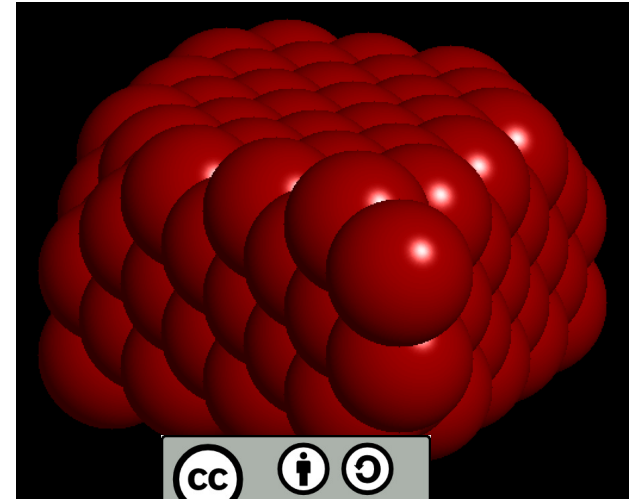
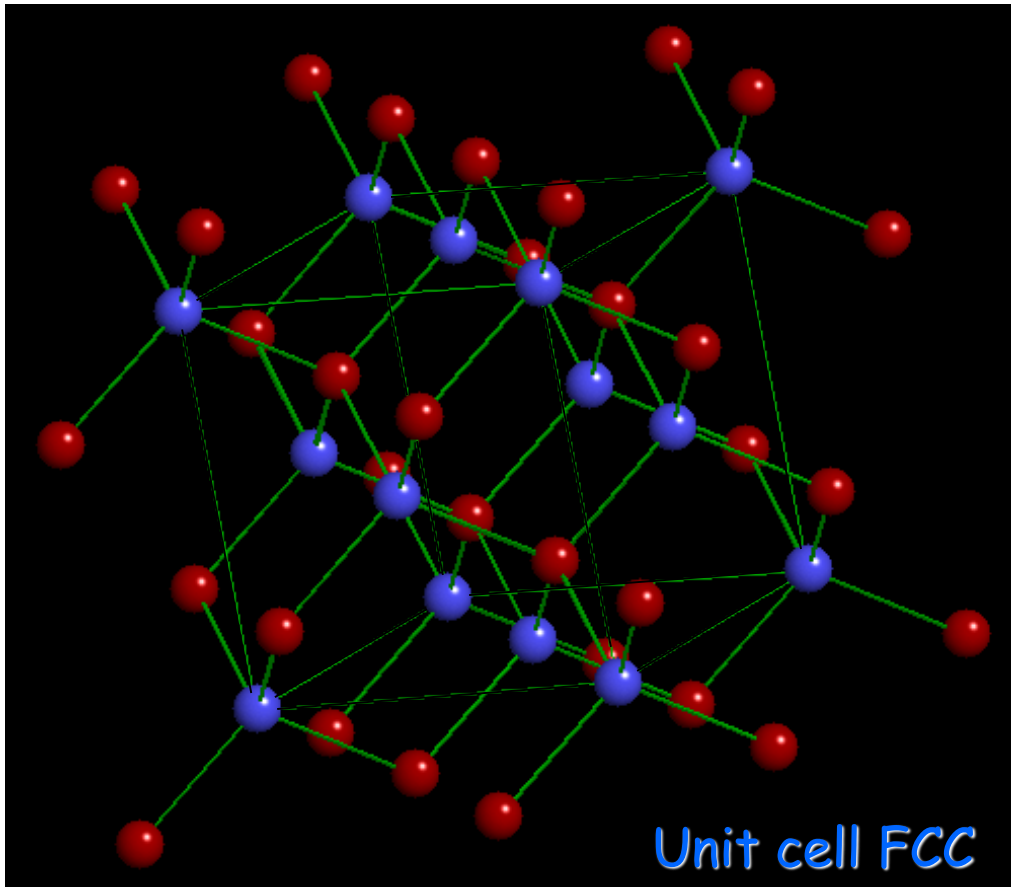


Examples: diamond, silicon, graphite (in plane), SiC, germanium



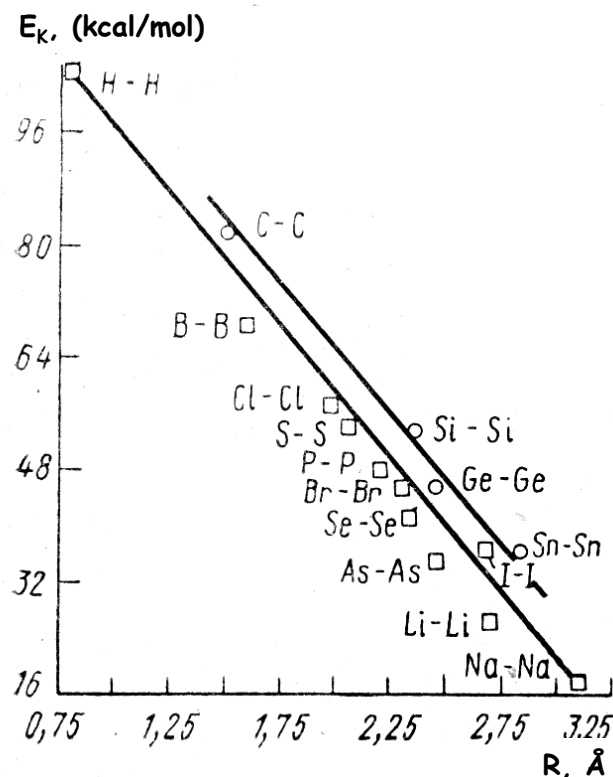
# Structure of diamond

Carbon is in coordination IV





# Covalent bond - directional valence theory



Dependence of energies of single covalent bonds on interatomic distances



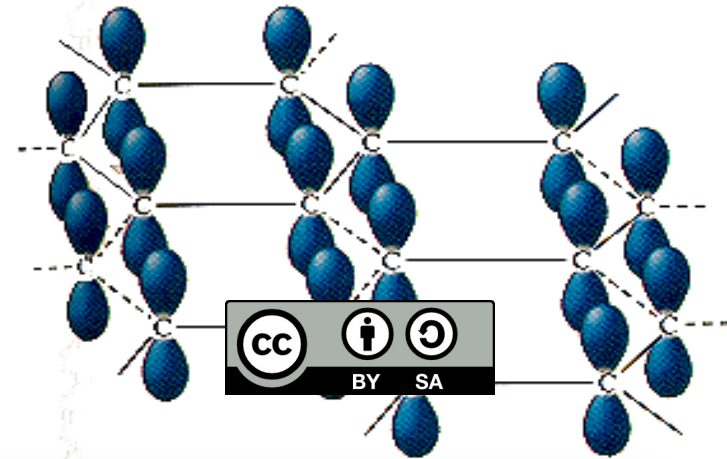
$$E(\text{kcal}) = -38R(\text{\AA}) + 143$$

For elements of the IV. group  
(C, Si, Ge, Sn):

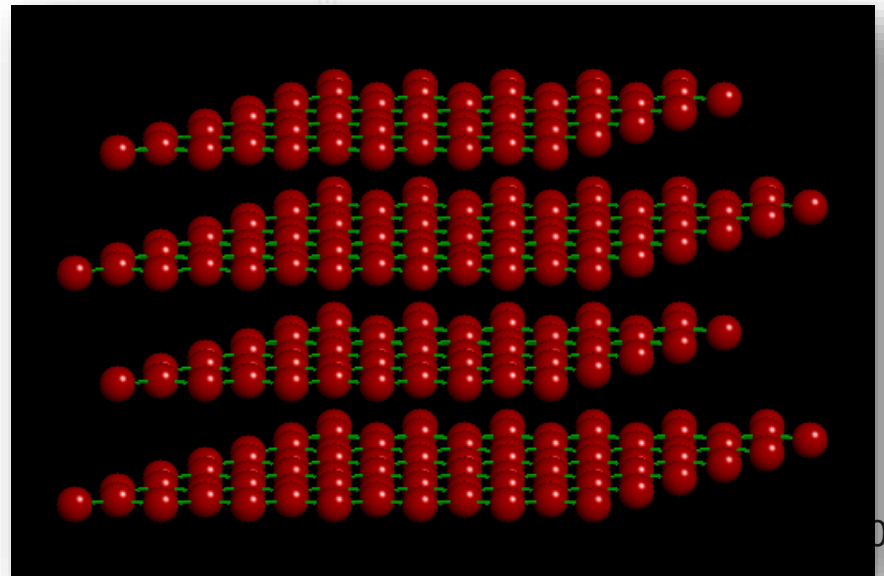
$$E(\text{kcal}) = -38R(\text{\AA}) + 143$$

# The graphite structure is different

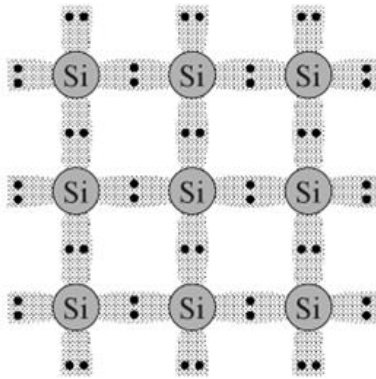
- Each carbon is connected with another three.  
Hybridization  $sp^2$ .
- Molecule is planar  $120^\circ$   
with connected hexagonal rings.
- $\pi$  bonds are above and below the plane.



... but graphite has a higher cohesive energy than a diamond!



# Crystal structure of covalent compounds



Covalent bonds in Si.  
Each Si atom contributes one of its four valence electrons to a common bond with another Si. Atoms are identical, and electrons are most likely located halfway between them.

II	III	IV	V	VI
	5 <b>B</b> 2.0	6 <b>C</b> 2.5	7 <b>N</b> 3.0	8 <b>O</b> 3.5
	13 <b>Al</b> 1.5	14 <b>Si</b> 1.8	15 <b>P</b> 2.1	16 <b>S</b> 2.5
30 <b>Zn</b> 1.6	31 <b>Ga</b> 1.6	32 <b>Ge</b> 1.8	33 <b>As</b> 2.0	34 <b>Se</b> 2.4
48 <b>Cd</b> 1.7	49 <b>In</b> 1.7	50 <b>Sn</b> 1.8	51 <b>Sb</b> 1.9	52 <b>Te</b> 2.1
80 <b>Hg</b> 1.9	81 <b>Tl</b> 1.8	82 <b>Pb</b> 1.8	83 <b>Bi</b> 1.9	84 <b>Po</b> 2.0
$s^2$	$s^2p^1$	$s^2p^2$	$s^2p^3$	$s^2p^4$

compounds III-V and II-VI are arranged symmetrically around the group IV

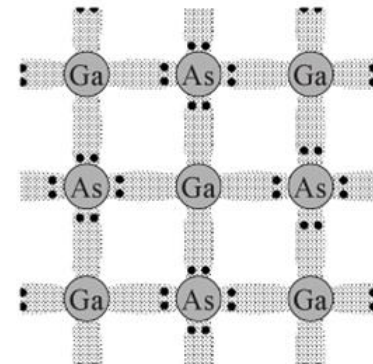
and usually crystallize in the structures of sphalerite or wurtzite



GaAs:

Ga  $4s^24p^1 \rightarrow Ga^- 4 \times sp^3$

As  $4s^24p^3 \rightarrow As^+ 4 \times sp^3$

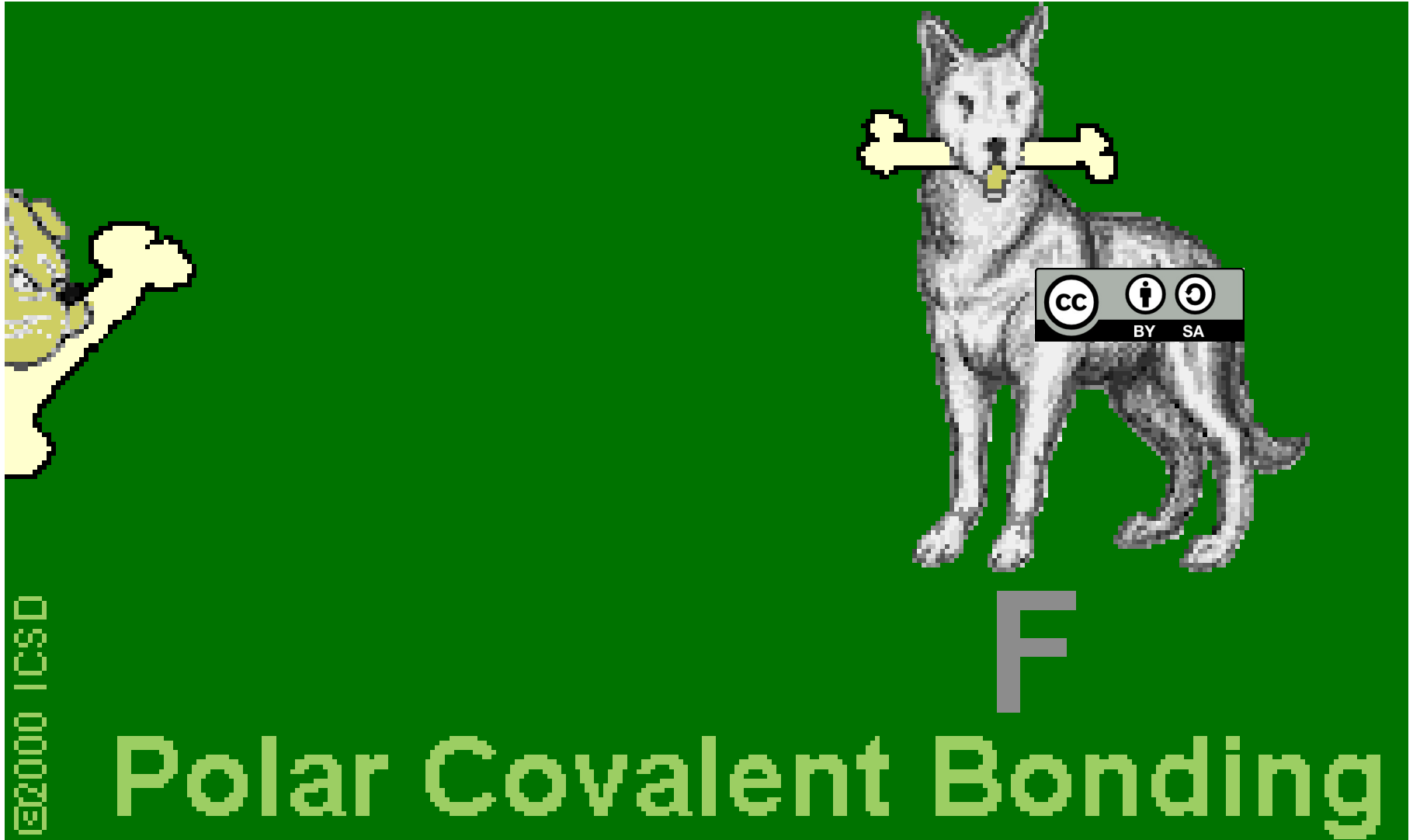


Polar bond in III-V intermetallic compounds.

One bond arises from the sharing of two electrons from the As atom

Ga contributes by an empty orbital. Atoms are not the same, and the electrons are shifted towards the larger core.

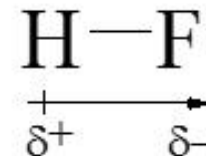
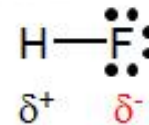
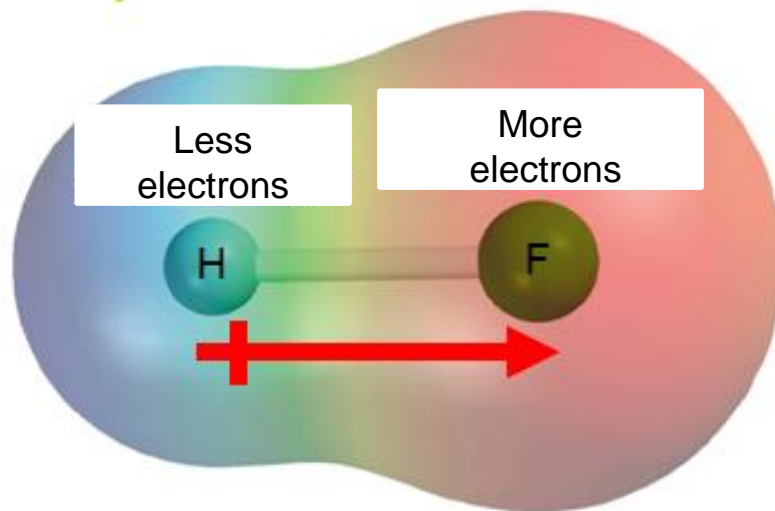
# Polar covalent bonds



# Mixed bonds

## ionic to covalent

- Covalent or ionic bonds are simple extreme cases.
- Most molecules share electrons "unequally" due to differences in electronegativity and electron affinities
- The polar molecule generates a dipole momentum.

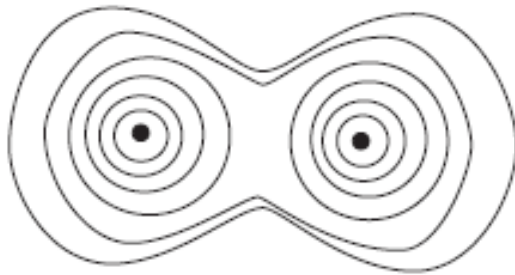


# Solids with mixed bonds

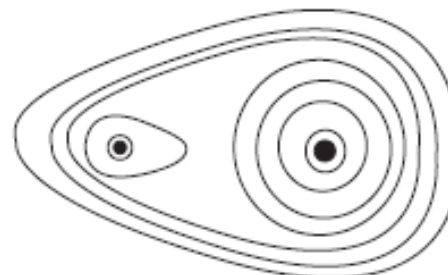
If the atoms of the elements forming the covalent solid are different

For example, Zn and Se in ZnSe - the electrons are located closer to one of the atoms (with higher electron affinity)

the covalent bond contains the ionic component



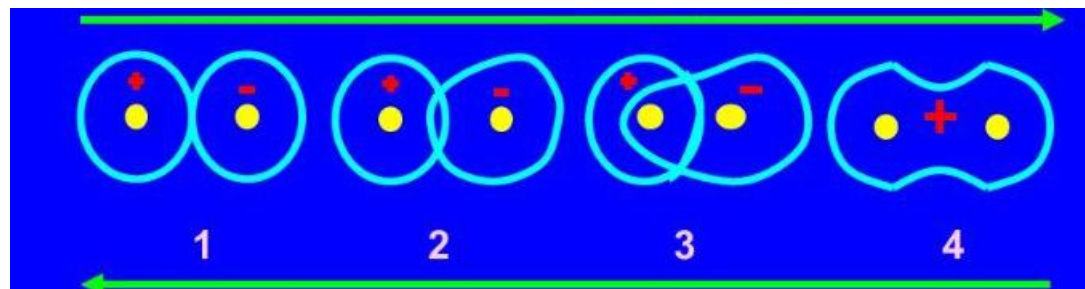
covalent



Ionic to covalent



Increasing the mutual deformation of ions



Increasing the bonding polarity

# Ionic to covalent character of compounds

An empirical relationship to derive the ionic character of a molecule bond :

$$\% \text{ of ionic character } f(\text{AB}) \text{ ter} = \left( 1 - e^{-\frac{1}{4}(x_A - x_B)^2} \right) 100$$

Table 6.2 Percent Ionic Character of a Single Chemical Bond with Oxygen

Difference in electronegativity	Ionic character, %	Difference in electronegativity	Ionic character, %
0.1	0.5	1.7	51
0.2	1	1.8	55
0.3	2	1.9	59
0.4	4	2.0	63
0.5	6	2.1	67
0.6	9	2.2	70
0.7	12	2.3	74
0.8	15	2.4	76
0.9	19	2.5	79
1.0	22	2.6	82
1.1	26	2.7	84
1.2	30	2.8	86
1.3	34	2.9	88
1.4	39	3.0	89
1.5	43	3.1	91
1.6	47	3.2	92

Electronegativity:

Ga - 1.8, As - 2.2

Zn - 1.6



% of ionic character GaAs 4%

% of ionic character ZnS 15%



# Solids with covalent bonding


The melting temperature of isoelectronic compounds, depending on their polarity

30	31	32	33	34
Zn	Ga	Ge	As	Se
1.6	1.6	1.8	2.0	2.4

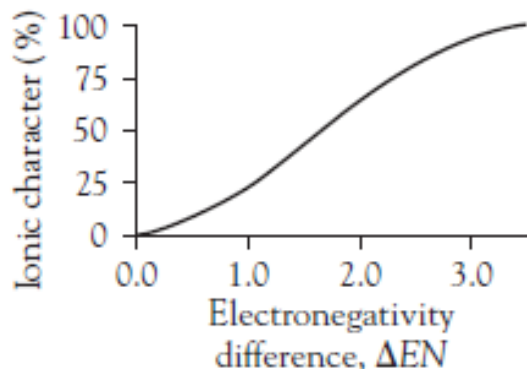


group	compound	percent ionic	$T_m(^{\circ}\text{C})$
IV	Ge	0%	937
III-V	GaAs	4%	1238
II-VI	ZnSe	15%	1517

# Effective ion charges

Compound	Effective charge	Compound	Effective charge
NaCl	+0,87	SiO <sub>2</sub>	+1,97 -0,99
NaBr	+0,83	Al <sub>2</sub> O <sub>3</sub>	 +1,77 -1,02
NaJ	+0,75		
MgCl <sub>2</sub>	+1,5	Al <sub>2</sub> S <sub>3</sub>	+1,26 -1,00
AlN	+1,32		

# Sorting bonds based on differences in electronegativity



Approximate relationship between electronegativity differences and ionic character of bonds

## difference

0 to 0.4

$\geq 2$

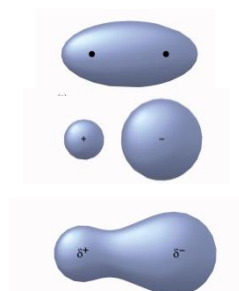
$0.5 < \Delta < 2$

## Bond type

covalent

ionic

Polar to covalent



Increasing electronegativity differences

covalent

Polar to covalent

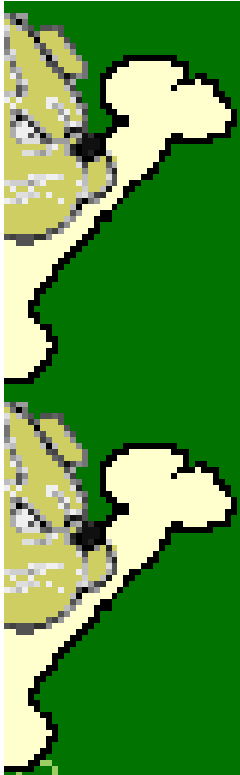
ionic

Sharing of  $e^-$

Partial transfer of  $e^-$

$e^-$  transfer

# Metal Bond: Obedient dogs with many bones around.



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# Metallic Bonding

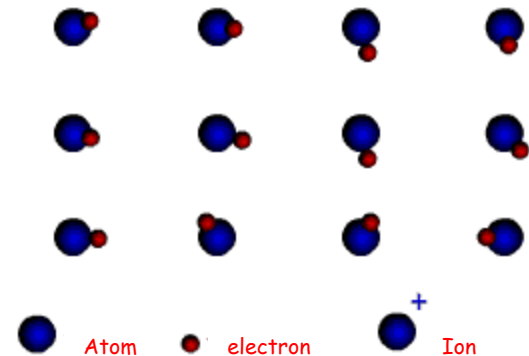
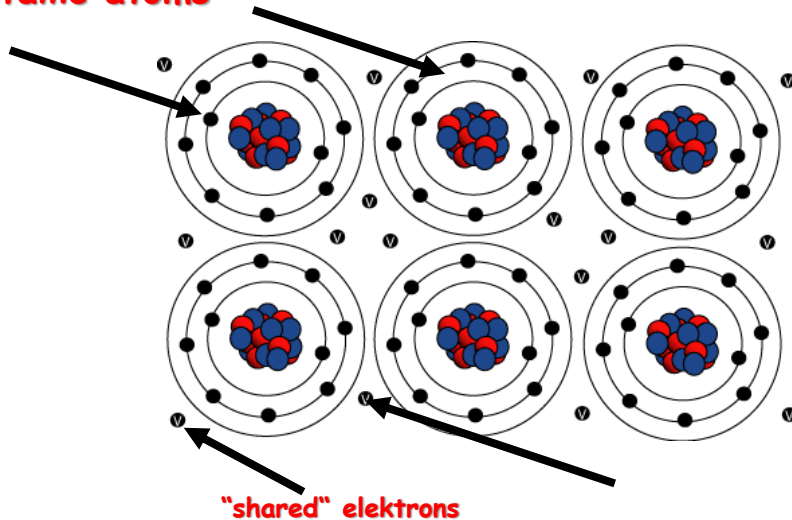
# Metallic bond

- Metals can be considered as stacks of stationary ions, which are surrounded by electrons 'sea'.
- The concept is based on a bounded covalent bond, where electrons are shared by all crystal ions
  - Metallic bond is not directional



Scheme of metal bond formation

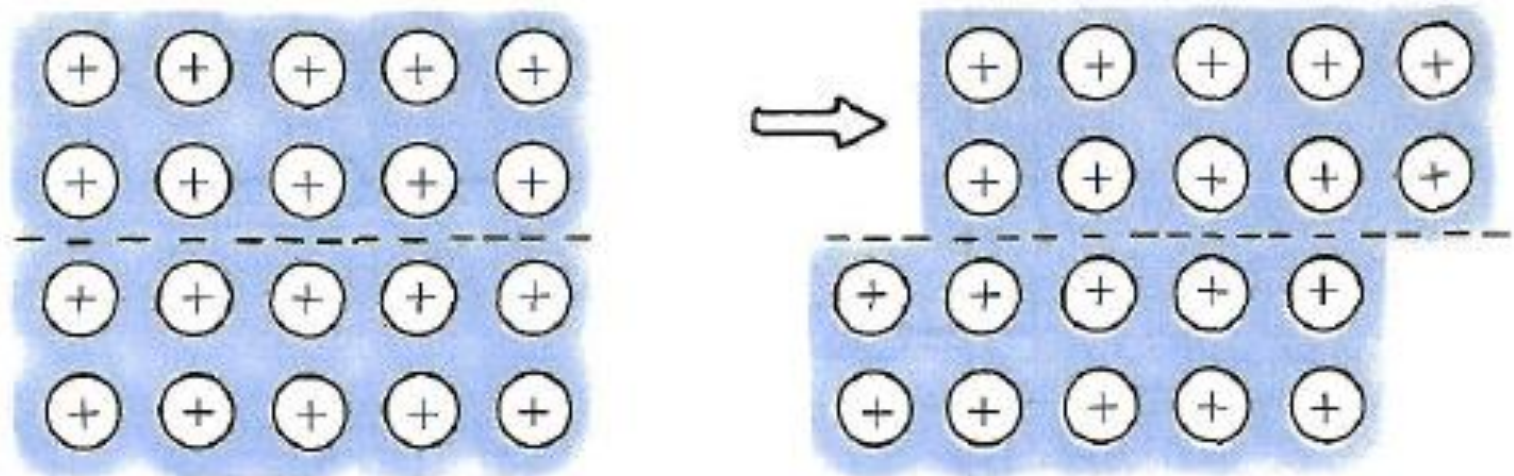
Metallic atoms



# Solids with metallic bonds

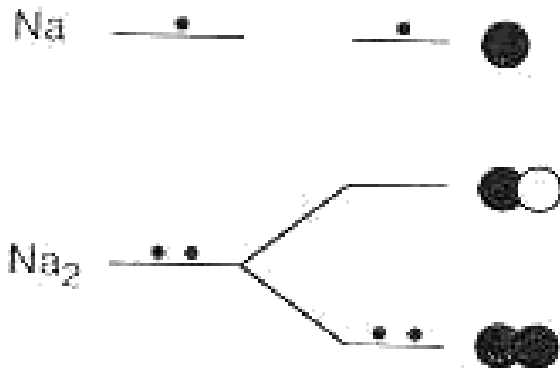
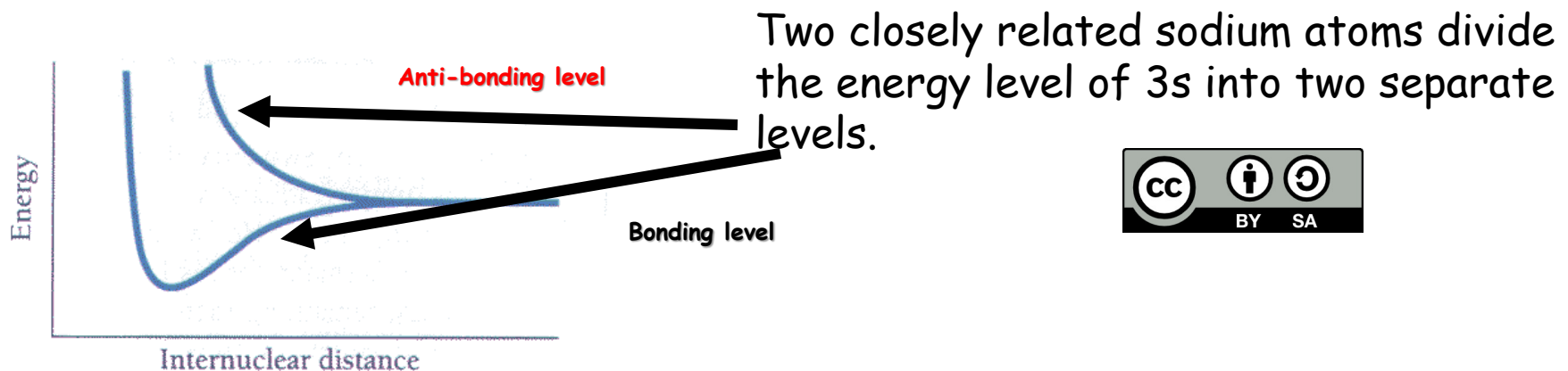
*If the number of valence electrons per atom is lower than  $KC$ , then a metal bond is formed*

Metal bonds are non-directional; same in all directions.  
The resulting structures are therefore tightly arranged with a maximum coordinate number of 12 (hexagonal or cubic) or 8



# Electronic band structure of solids

What happens in crystalline solids when approaching atoms are so close that valence electrons form one system?

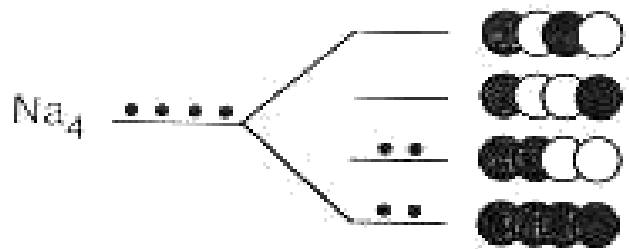


The energy reduction is associated with the transition of both electrons with antiparallel spins to a lower energy level.

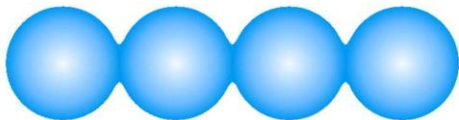
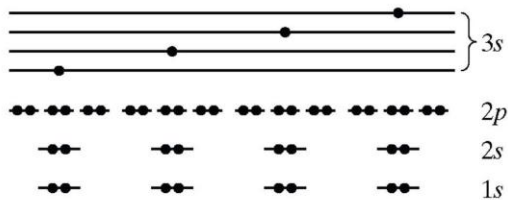


# Electronic band structure of solids

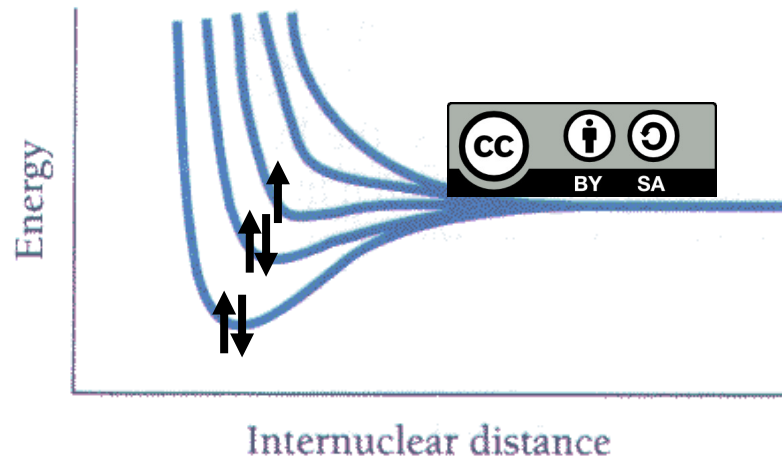
What happens in crystalline solids when approaching atoms are so close that valence electrons form one system?



4 atoms of sodium split the 3s energy level into four separate levels.



Hypothetical  $\text{Na}_4$  molecule

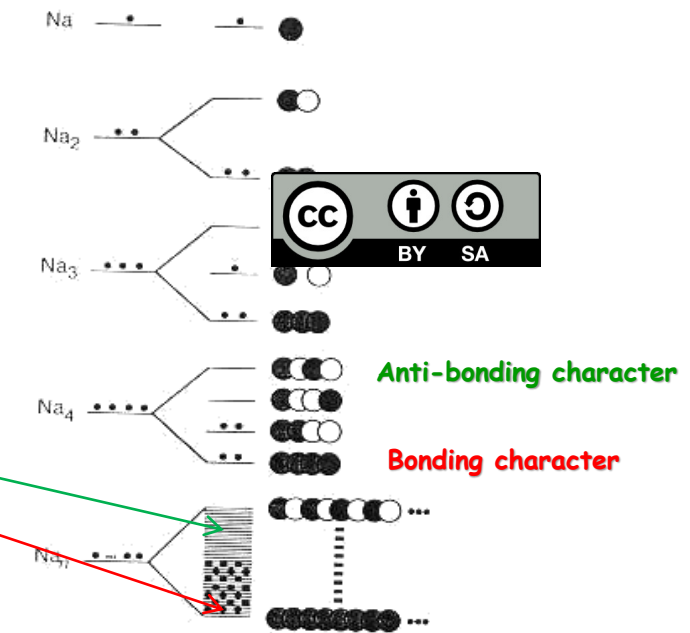


The five atoms of sodium in contact split the 3s energy level into five separate levels.

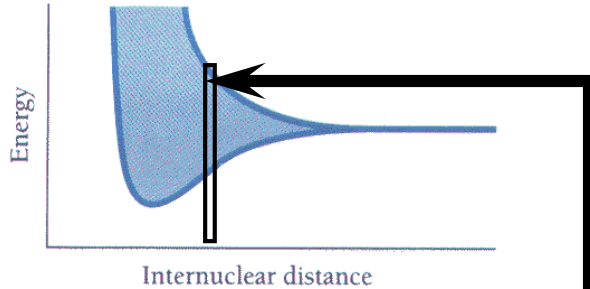
# Electronic band structure of solids

What happens in crystalline solids when approaching atoms are so close that valence electrons form one system?

- In solids, the distance between individual energy levels is negligible so that the levels fuse into the bands.
- A band that is occupied by valence electrons is called a valence band.
- A partially filled or low-lying empty band of energy levels is called a conductive band.



# Electronic band structure of Na

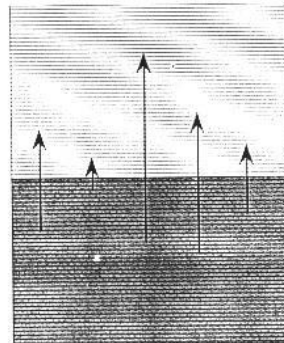
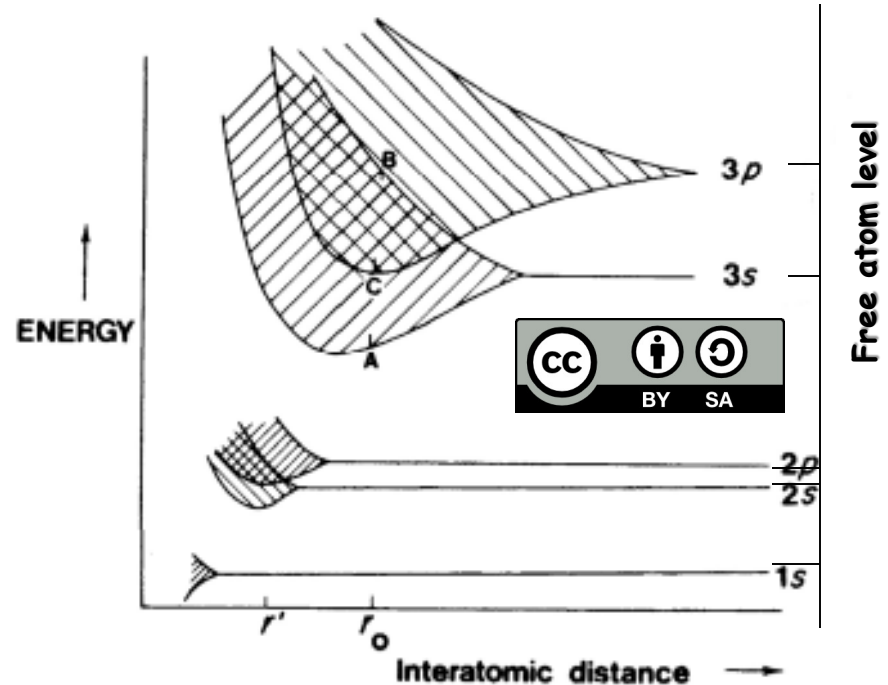


By contacting  $N$  atoms of sodium (large number), the 3s energy level is split into  $N$  separate energy levels.

$N$  atoms occupied the 3s belt. The electrons occupy the lowest possible levels.

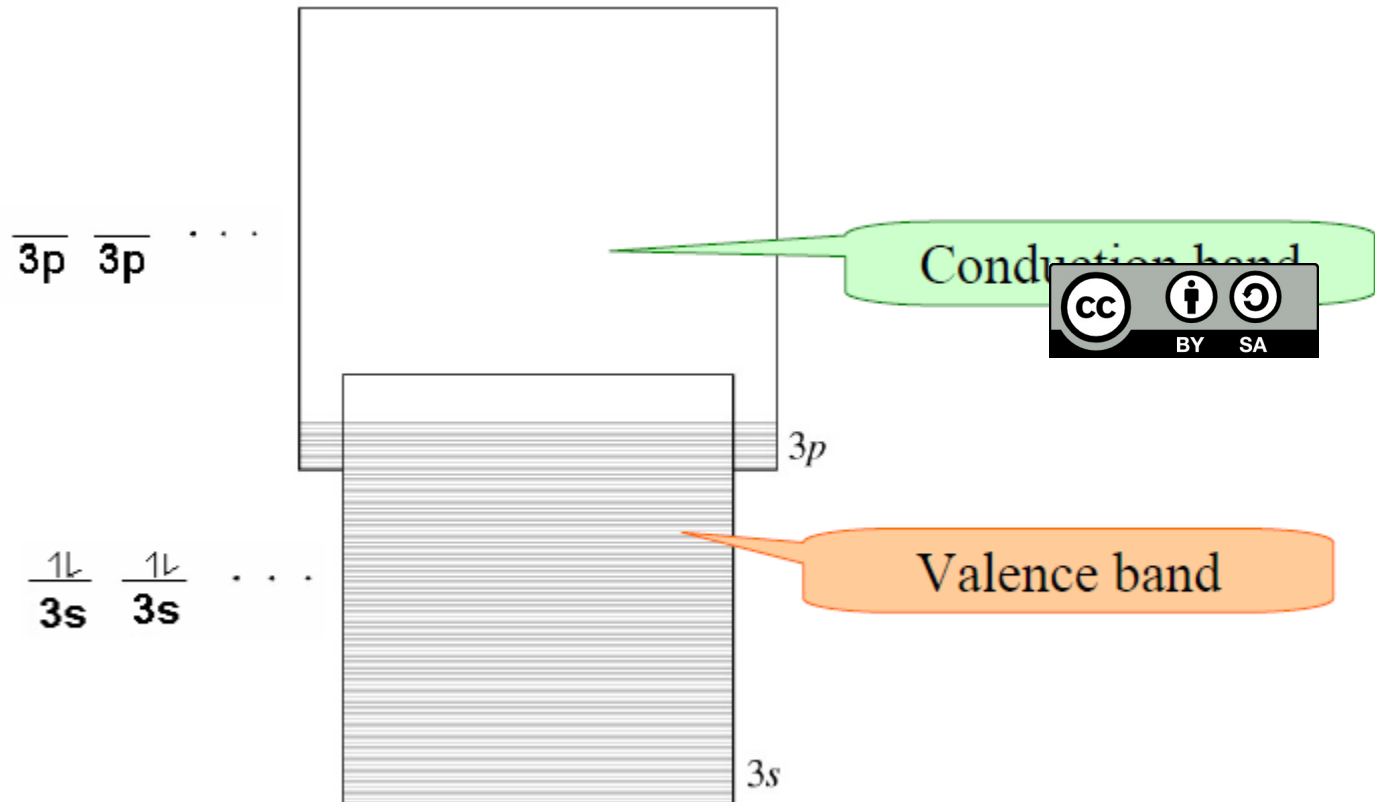
The colored area is **allowed band** of not filled levels. In the chosen phenomenon between atoms, these are allowed states of energy.

Belt theory explains very well the shine and lead colors of metals.

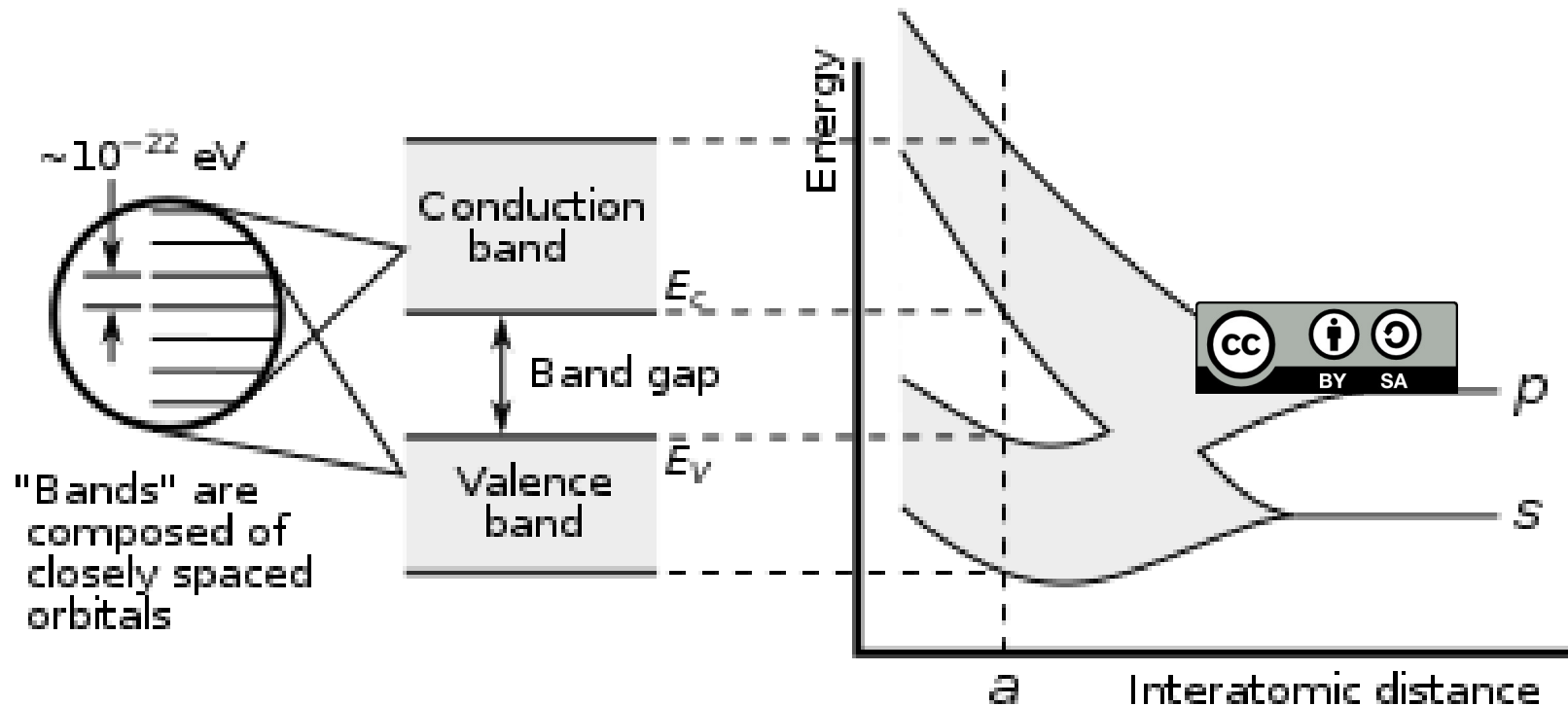


Na ( $1s^2 2s^2 2p^6 3s^1$ ):  
3s and 3p the bands overlap  
the inter-atomic distance  $r_0$ , the valence electron is not limited to 3s with the band

# Overlap of bands in Mg

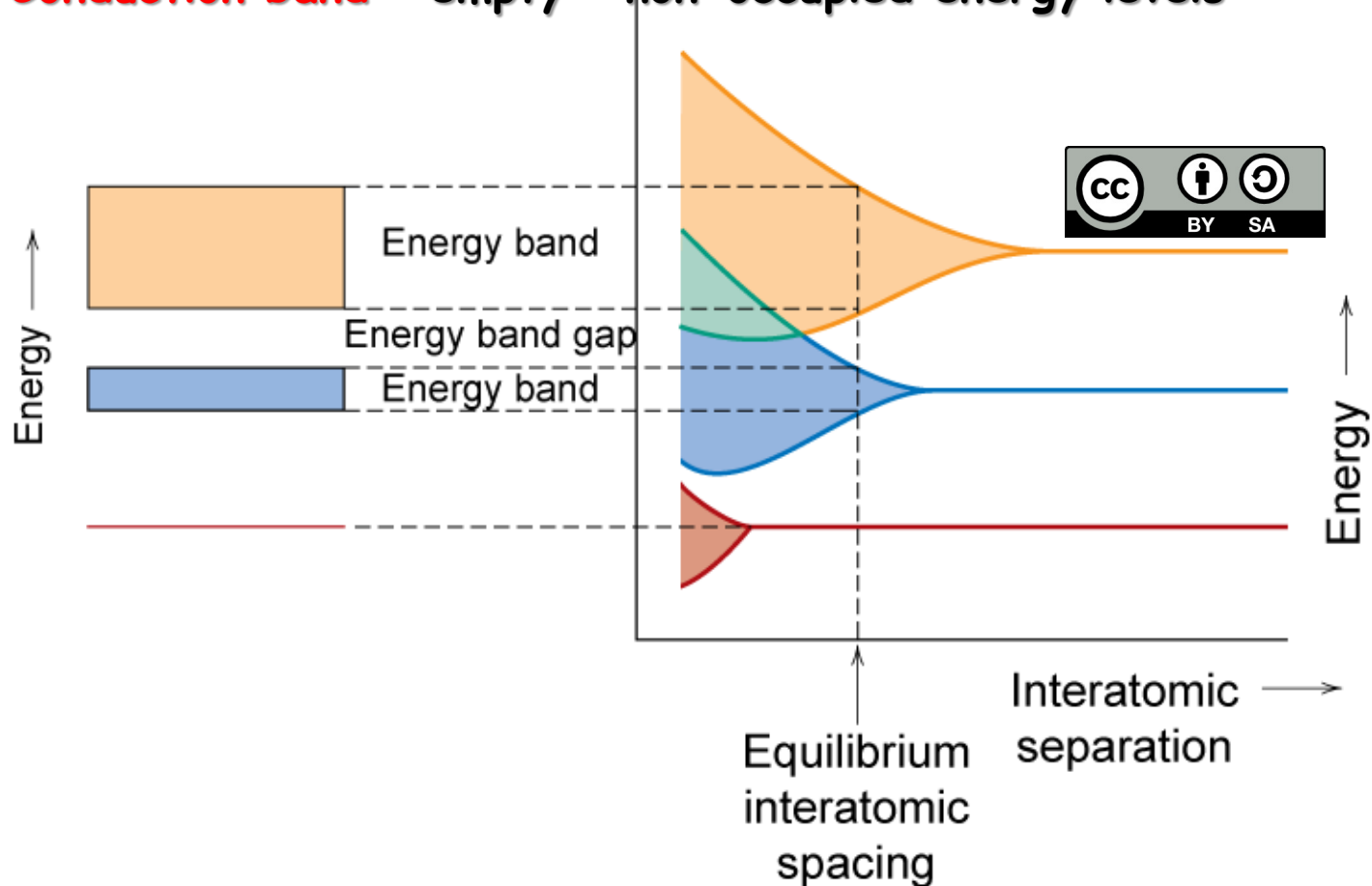


# Band structure of diamond

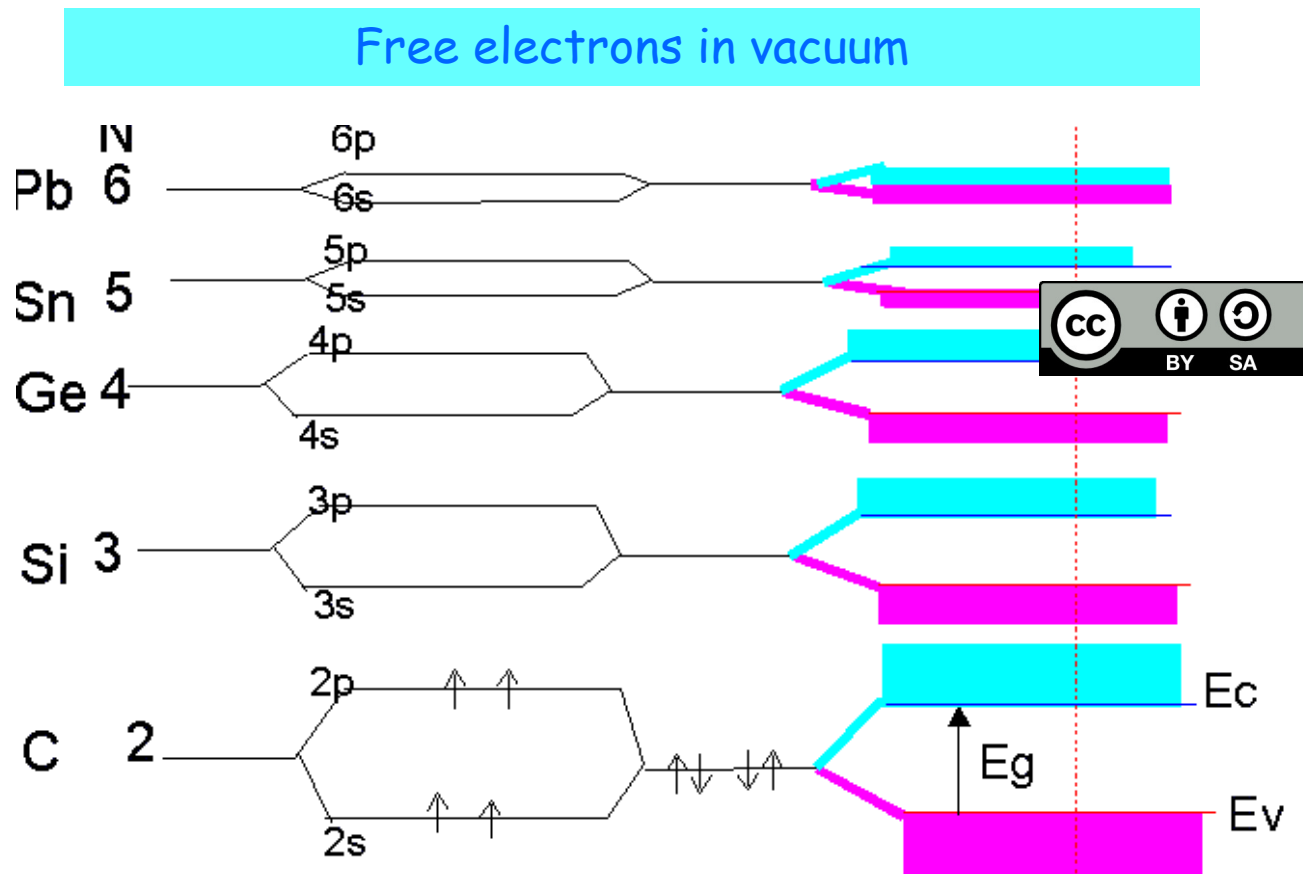


# Band structure of solids

- **valence** band - filled - highest occupied energy levels
- **Conduction band** - empty - non-occupied energy levels



# Schematic diagram of the formation of zones of semiconductors 14 of the periodic system of elements





# Band theory of solids

## Electrical behavior

