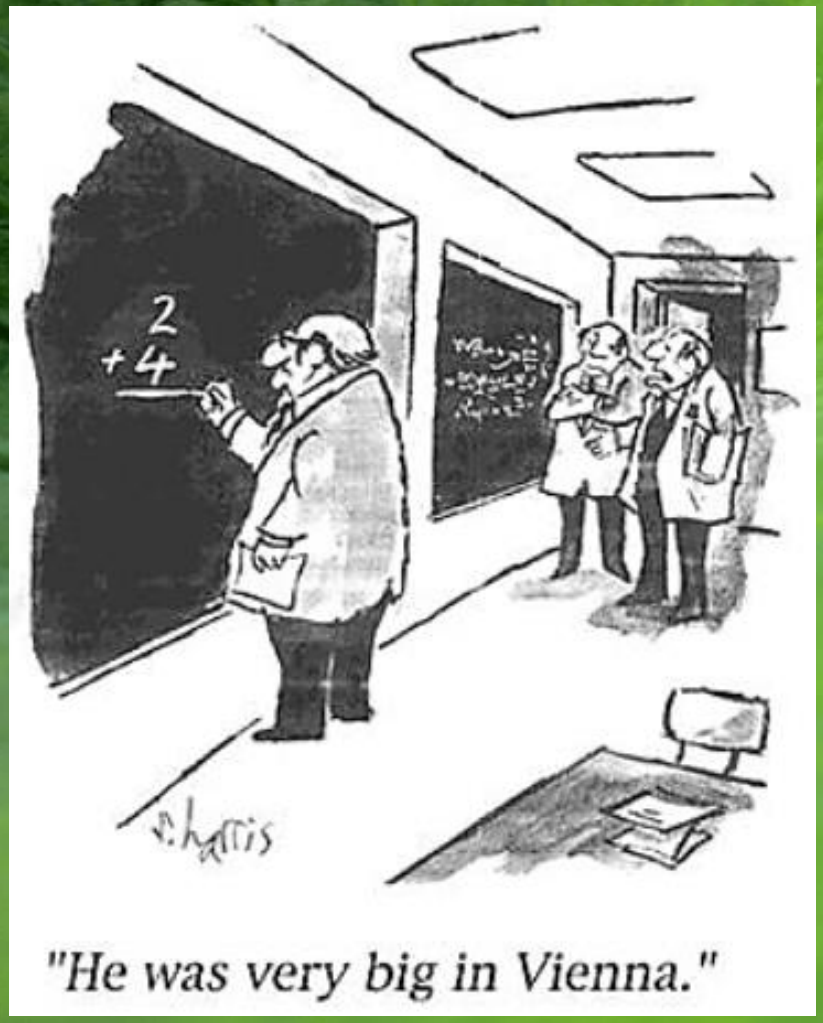
Physics of Condensed Matter I

1100-4INZ`PC



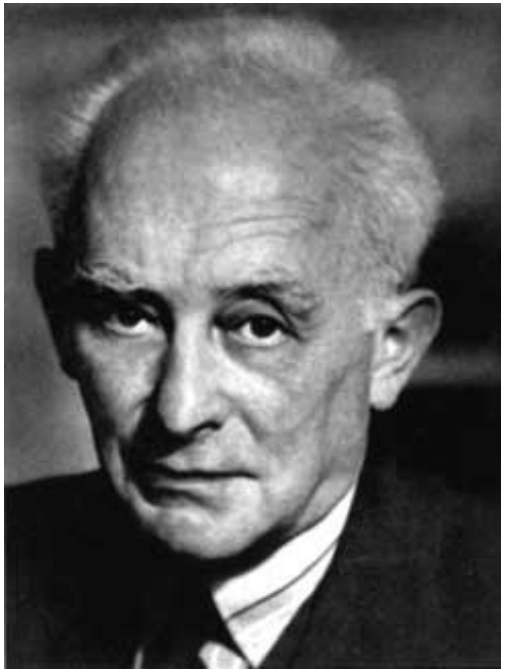
Solid State 1

Faculty of Physics UW

Jacek.Szczytko@fuw.edu.pl

inżynieria nanostruktur

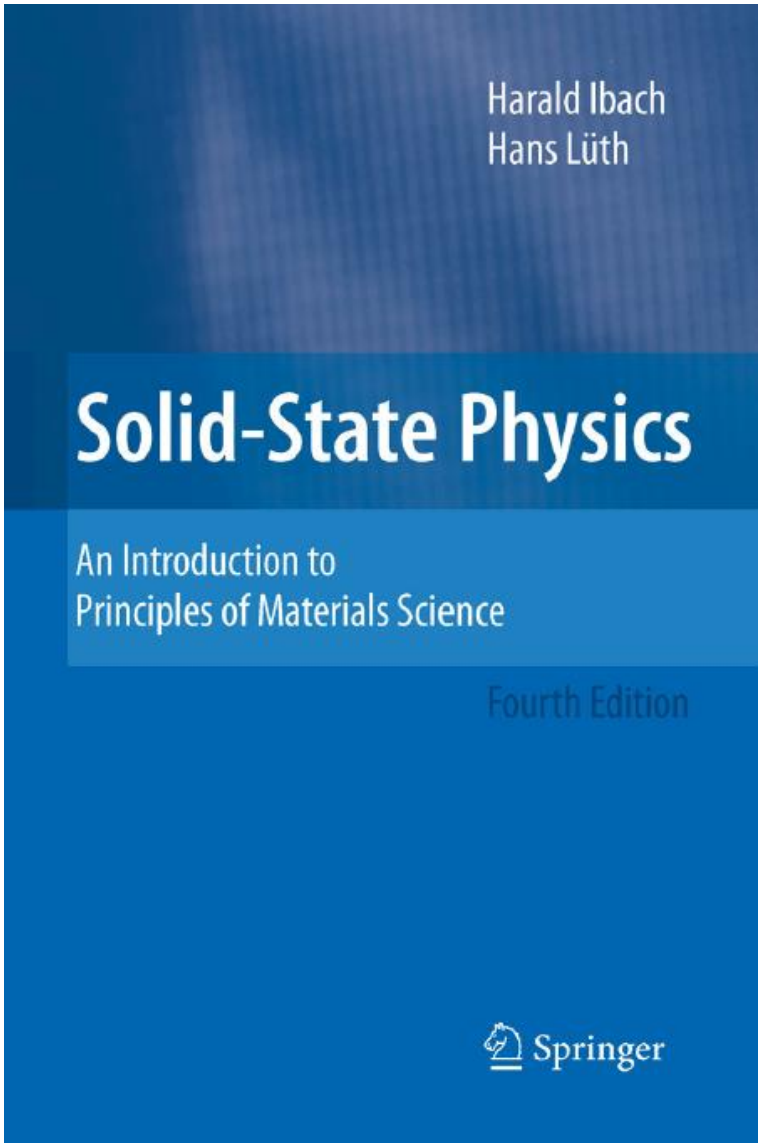
Born Oppenheimer approximation



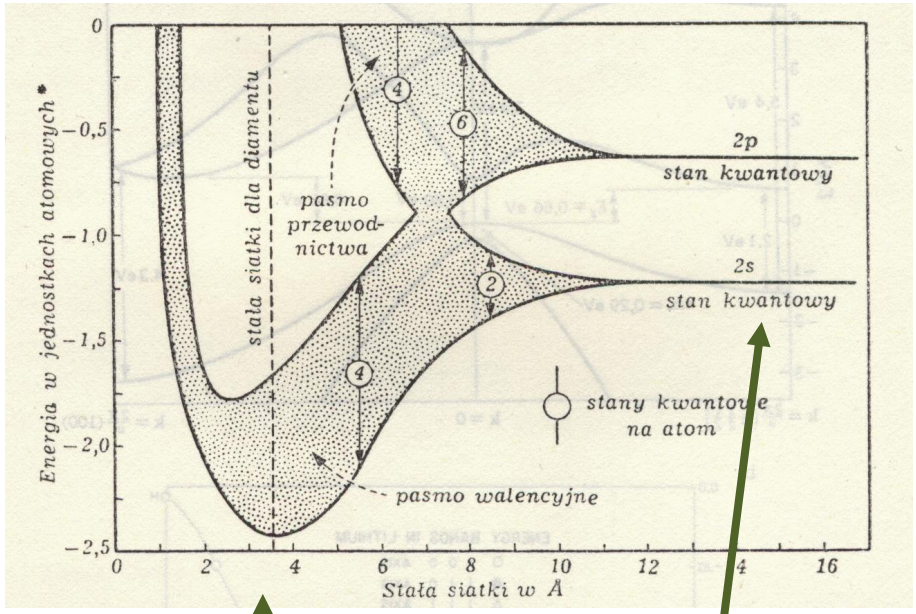
Max Born
(1882-1970)

Jacob R. Oppenheimer
(1904-1967)

Chemical bonding and molecules



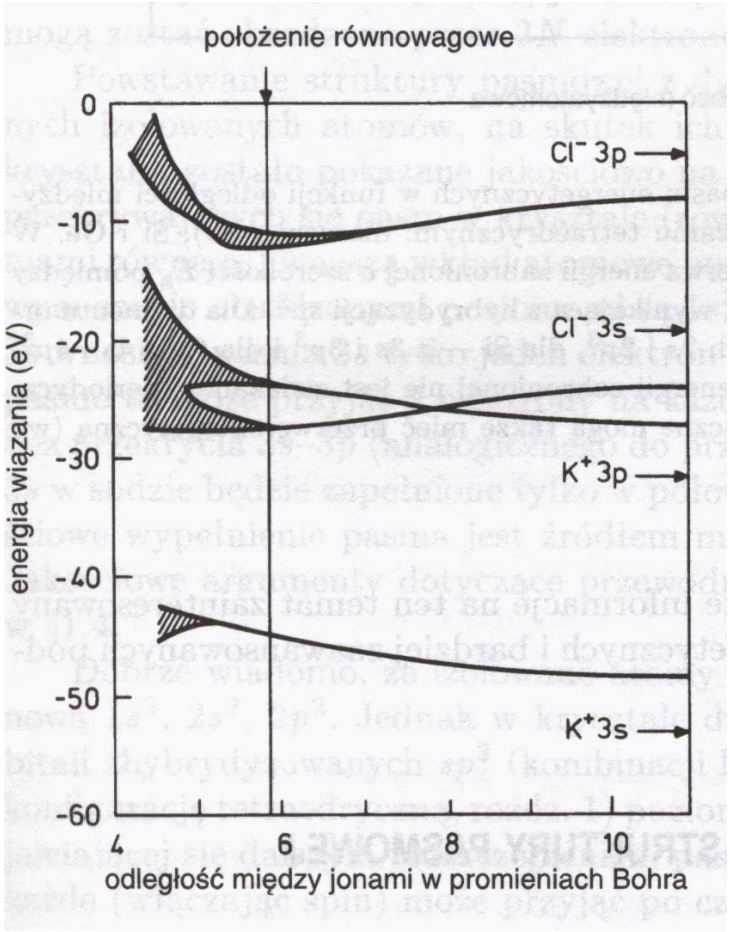
From the molecule to the solid state



J. Ginter

Small distance between atoms
bands (pasma)

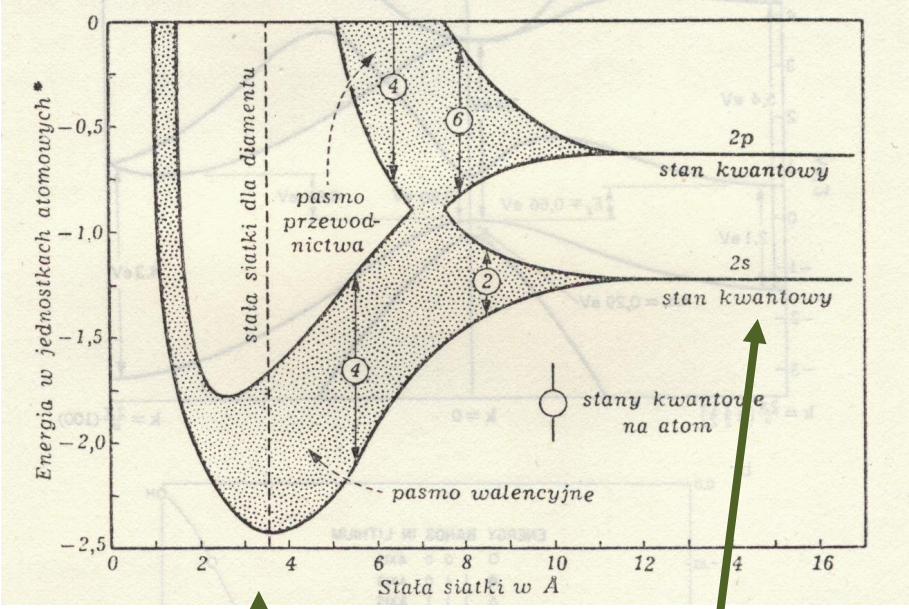
Large distance between atoms
levels (poziomy)



W. Ibach

From the molecule to the solid state

J. Ginter



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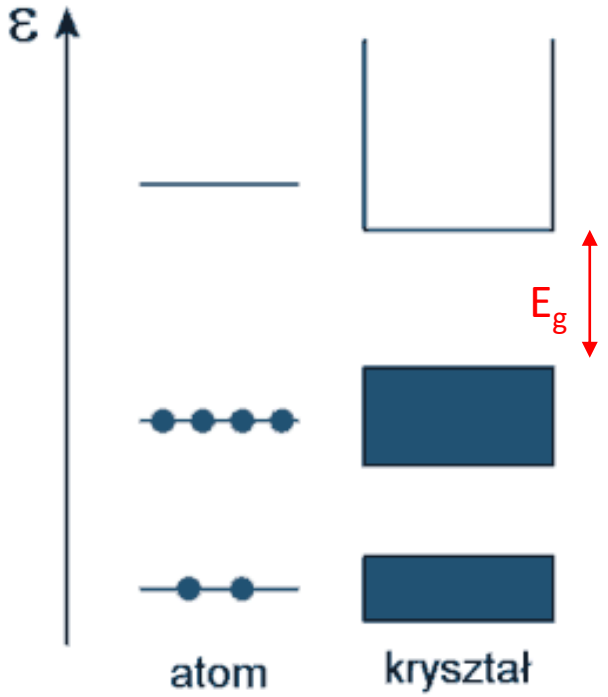
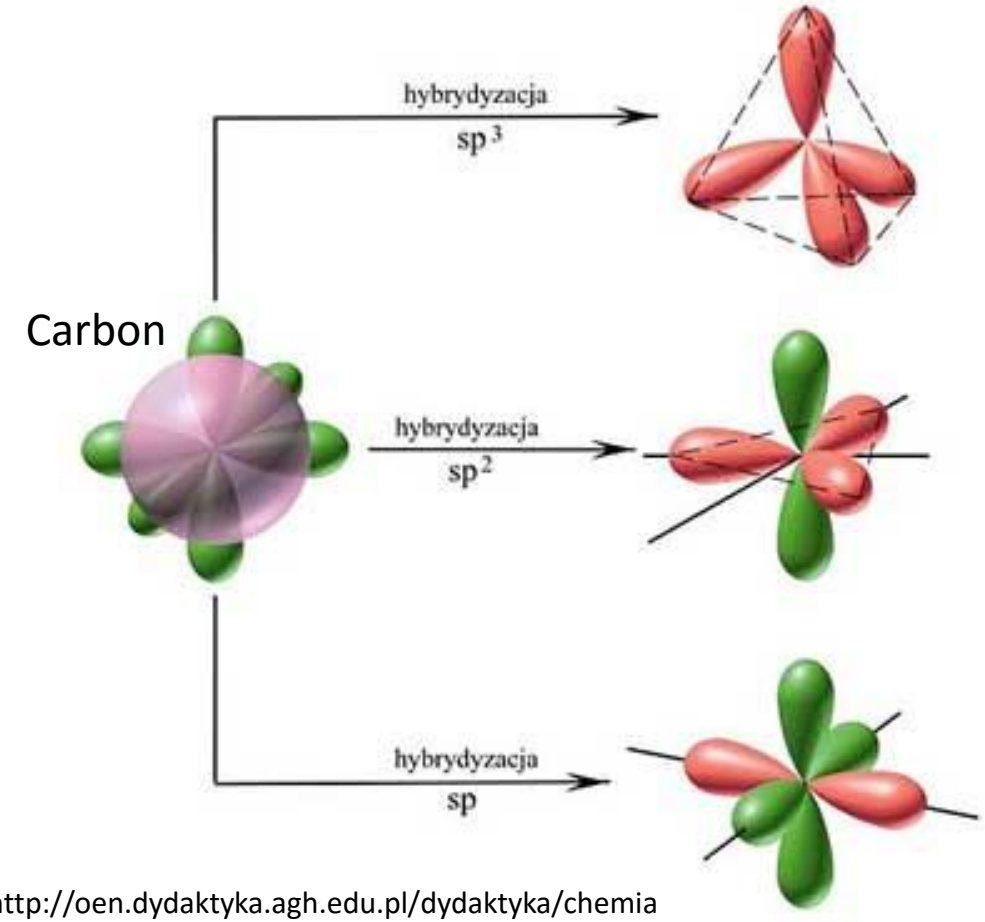


Przerwa energetyczna
Energy **g**ap

Molecules

Hybridization



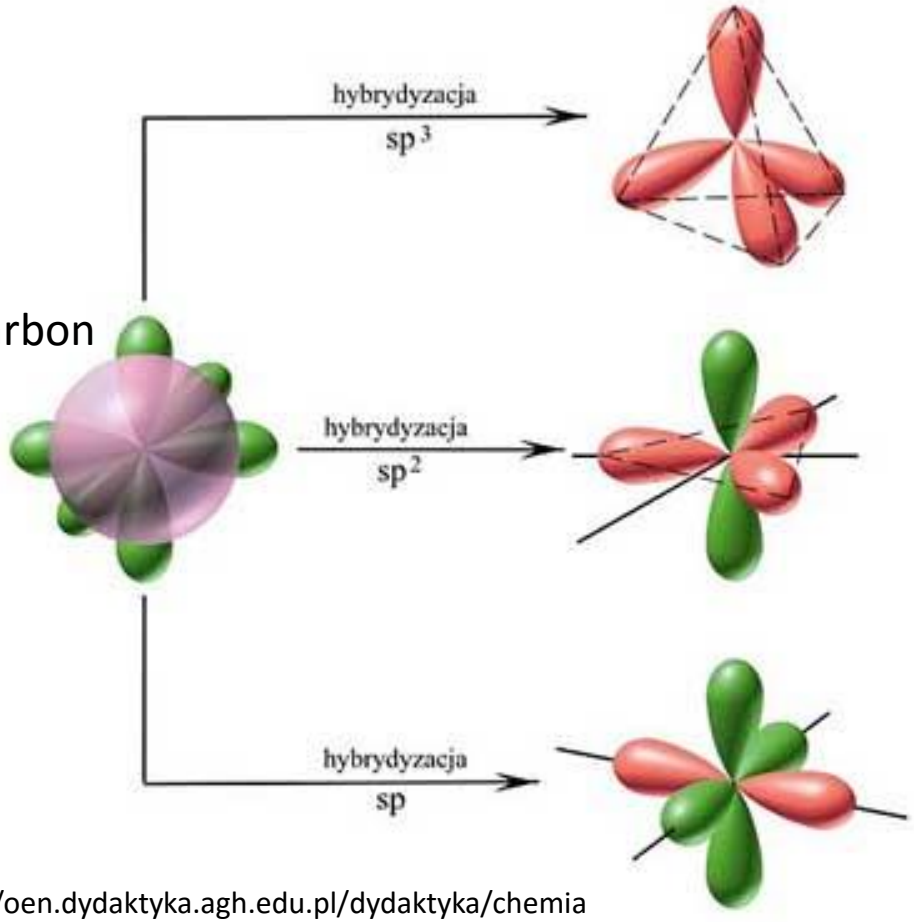
http://oen.dydaktyka.agh.edu.pl/dydaktyka/chemia

Atomic orbitals combined	Hybrid orbitals formed	Bonding electron pairs and lone pairs around central atom	VSEPR geometry
1 *s* orbital & 1 *p* orbital	sp hybrid (2 orbitals)	2	linear
1 *s* orbital & 2 *p* orbitals	sp^2 hybrid (3 orbitals)	3	trigonal planar
1 *s* orbital & 3 *p* orbitals	sp^3 hybrid (4 orbitals)	4	tetrahedral
1 *s* orbital & 3 *p* orbitals & 1 *d* orbital	dsp^3 hybrid (5 orbitals)	5	trigonal bipyramidal
1 *s* orbital & 3 *p* orbitals & 2 *d* orbitals	d^2sp^3 hybrid (6 orbitals)	6	octahedral

http://sparkcharts.sparknotes.com/chemistry/organicchemistry1/section2.php

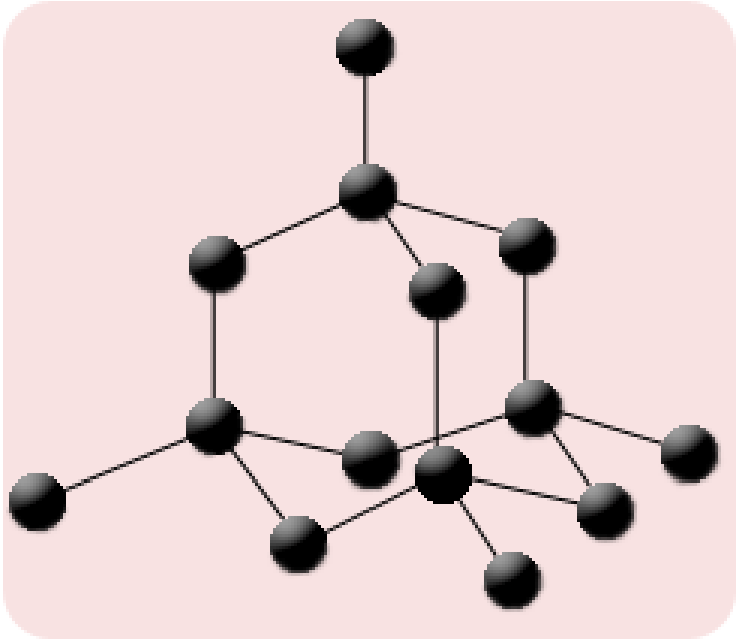
Types of chemical bonds

Hybridization



http://oen.dydaktyka.agh.edu.pl/dydaktyka/chemia

Semiconductors

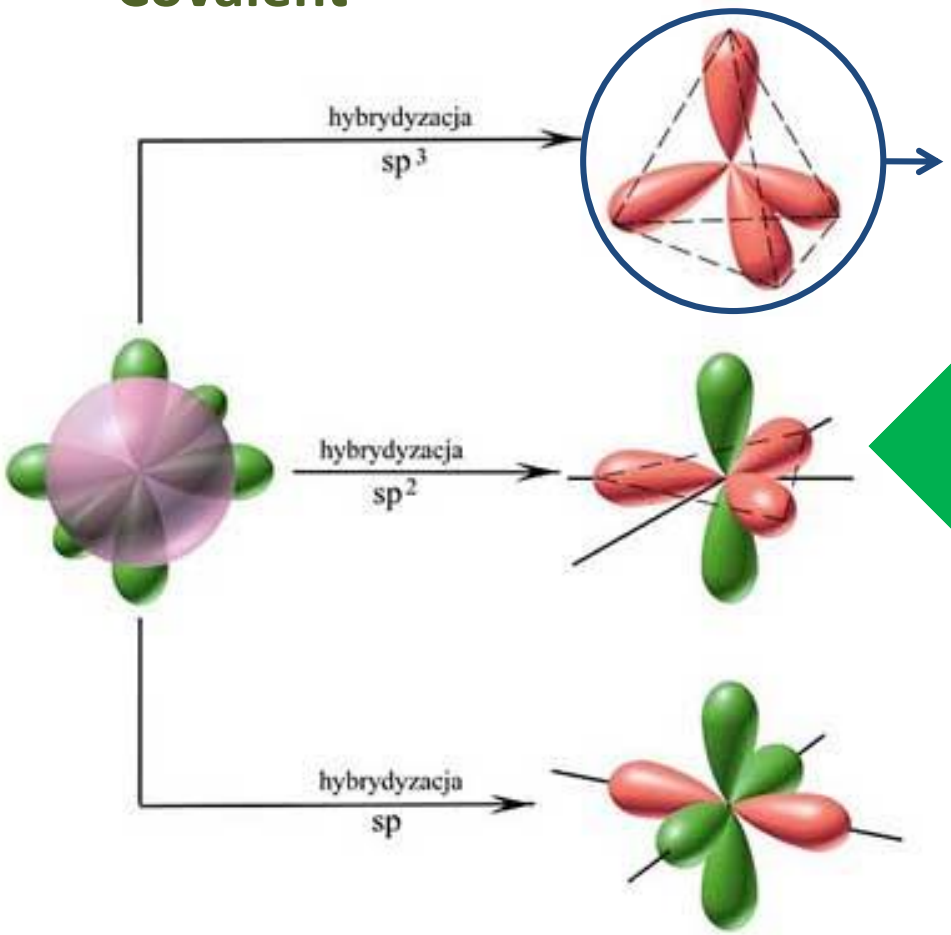


The binding energy per atom:

C (diamond)	7.30 eV
Si	4.64 eV
Ge	3.87 eV

Types of chemical bonds

Covalent



Semiconductors

II	III	IV	V	VI
Be	B	C	N	O
Mg	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In	Sn	Sb	Te

ionicity ionicity

Group IV: diamond, Si, Ge
Group III-V: GaAs, AlAs, InSb, InAs...
Group II-VI: ZnSe, CdTe, ZnO, SdS...

Types of chemical bonds

Carriers:

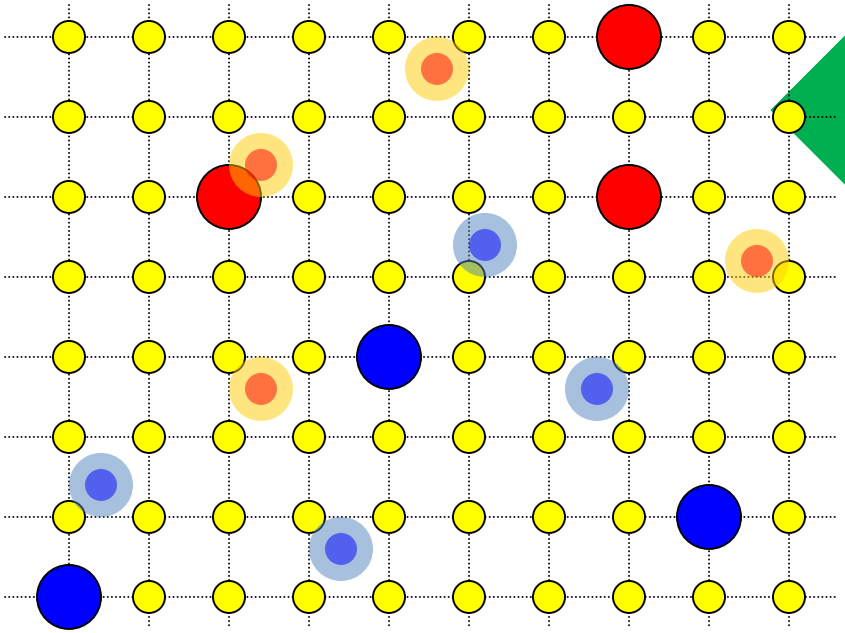
holes +

electrons -

Impurities (domieszki):

Acceptrs (p-type)

Donors (n-type)



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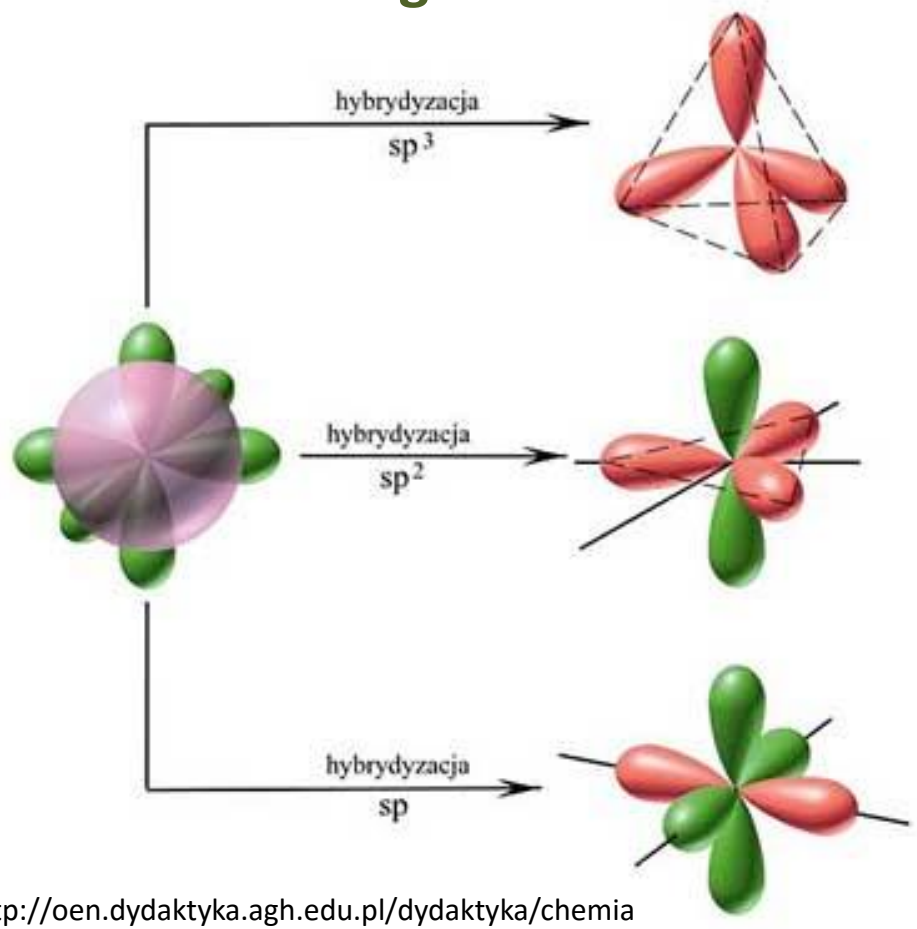
Types of chemical bonds

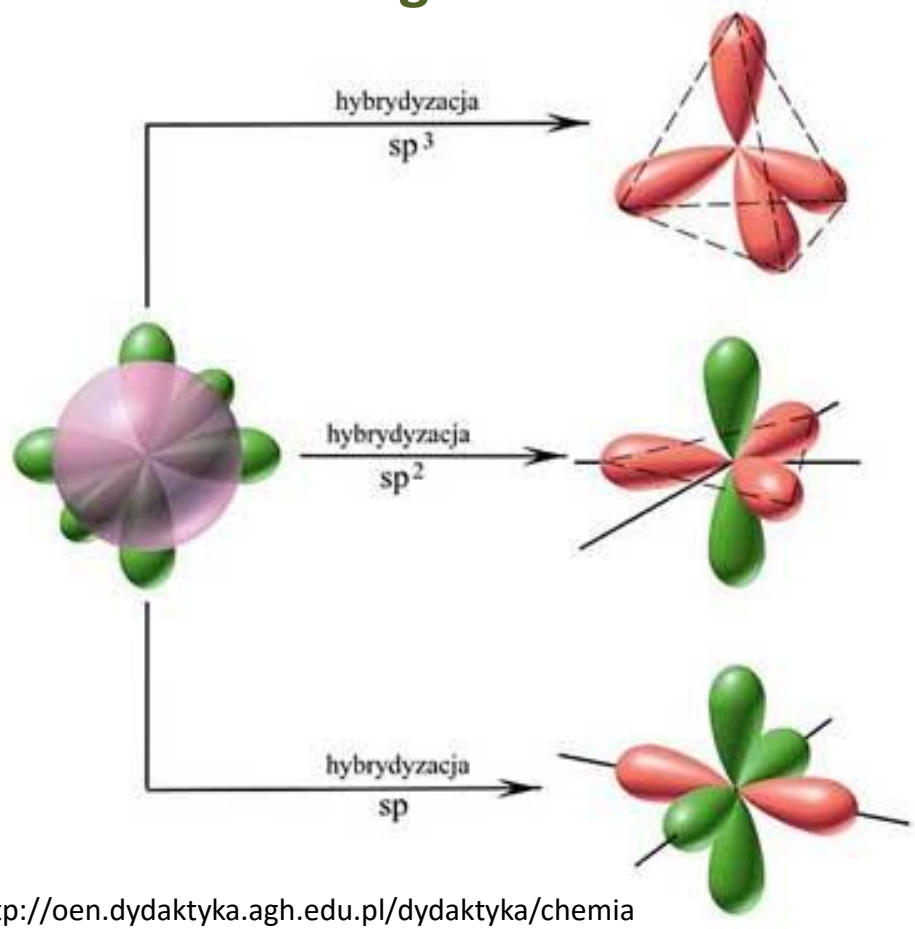
Covalent bonding



http://oen.dydaktyka.agh.edu.pl/dydaktyka/chemia

Types of chemical bonds

Covalent bonding



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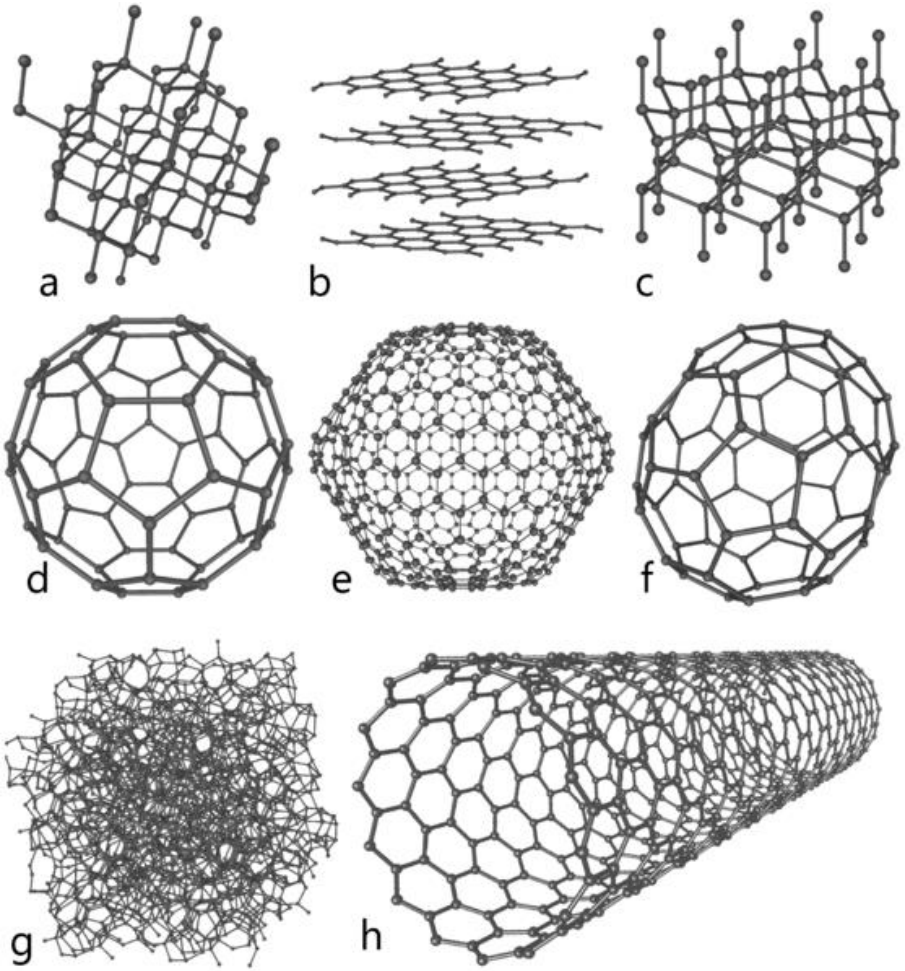
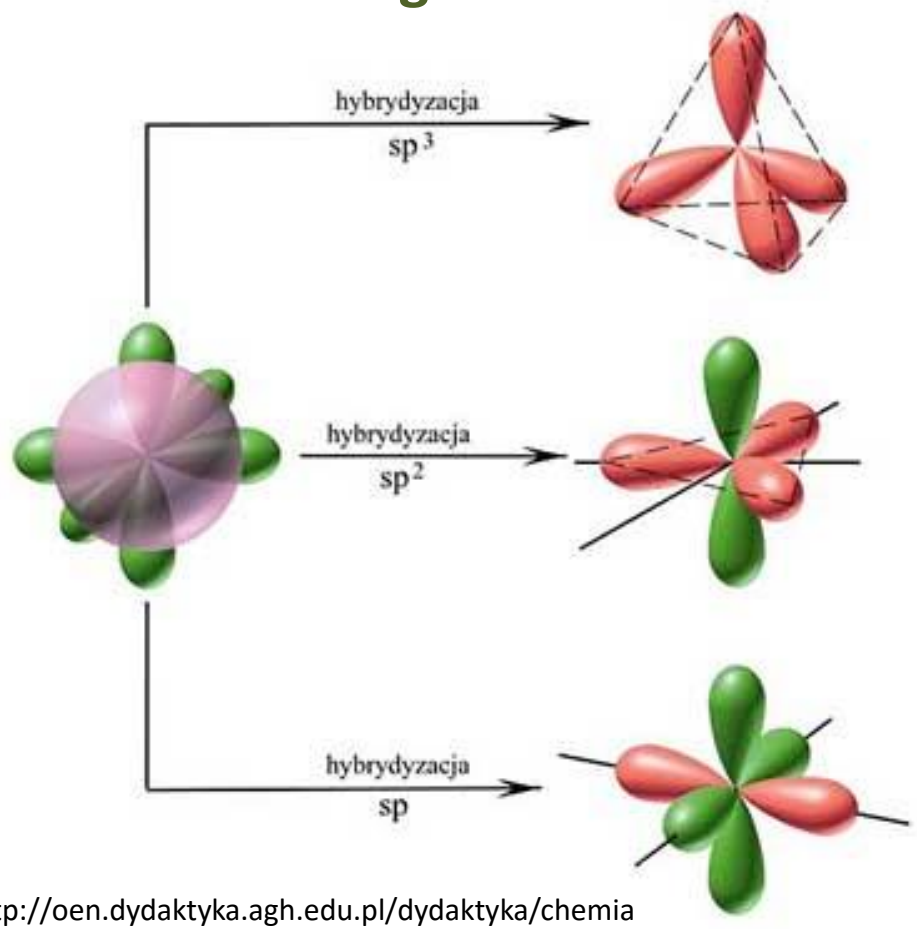


Allotropes of carbon

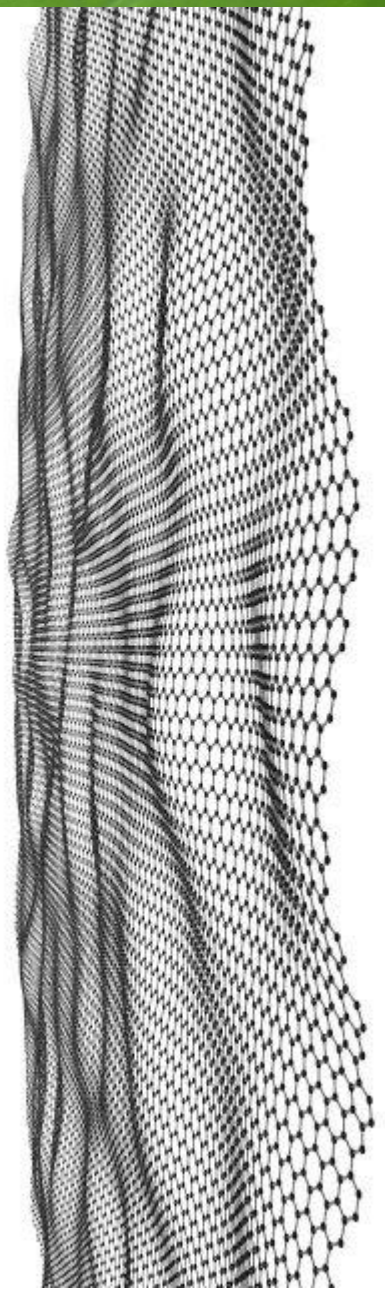
Types of chemical bonds

Covalent bonding



http://oen.dydaktyka.agh.edu.pl/dydaktyka/chemia

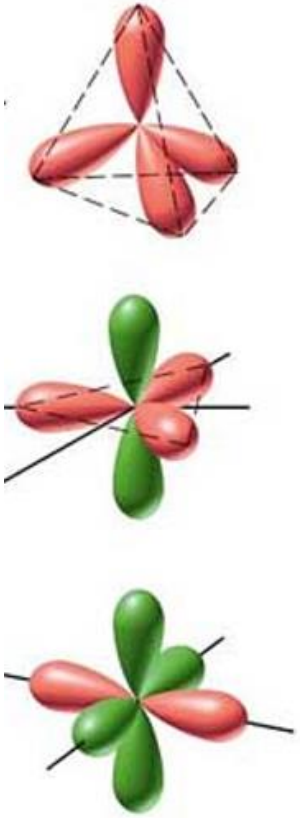
Graphene

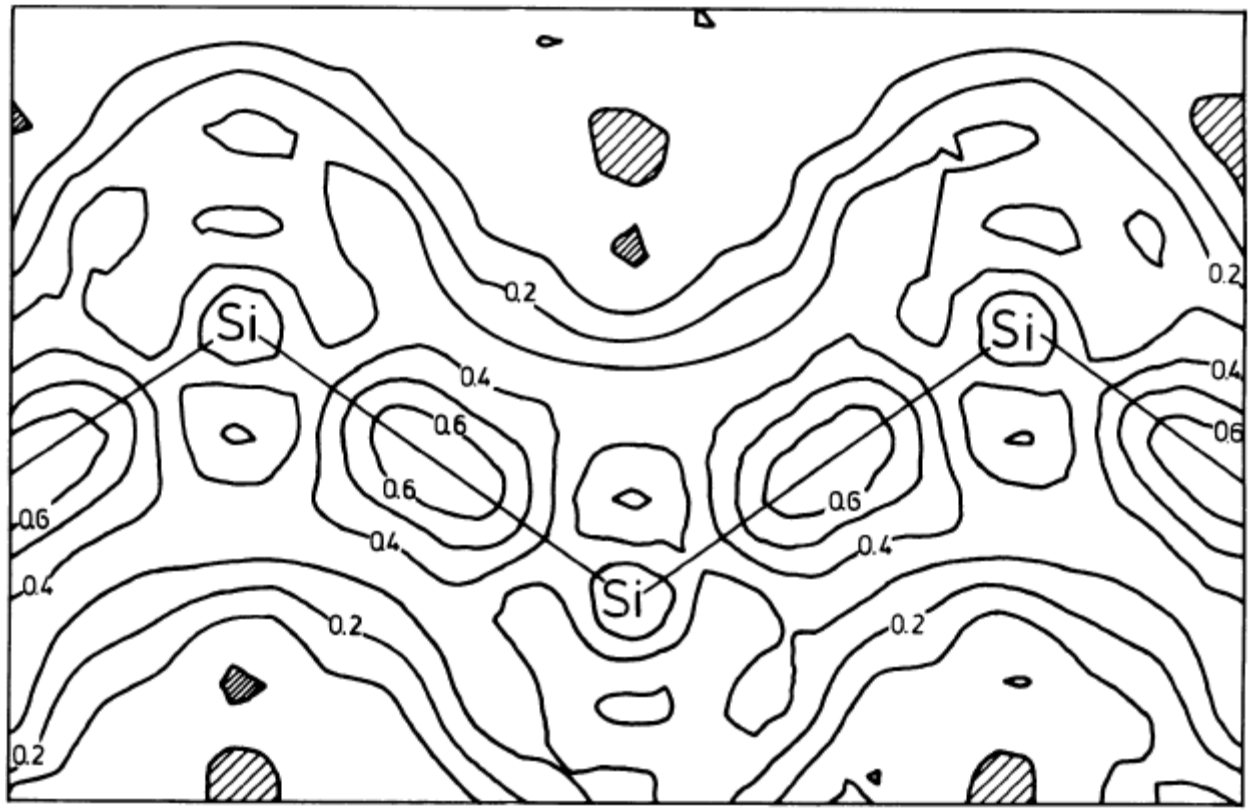


Types of chemical bonds

Covalent bonding (+ polar covalent)

Valence electrons are shared between atoms (non-polar $\Delta\chi < 0{,}4$; polar $0{,}4 < \Delta\chi < 1{,}7$)





http://oen.dydaktyka.agh.edu.pl/dydaktyka/chemia

Ibach. Luth

Types of chemical bonds

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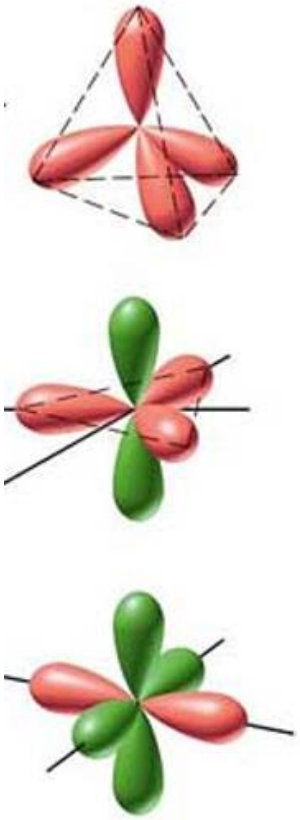
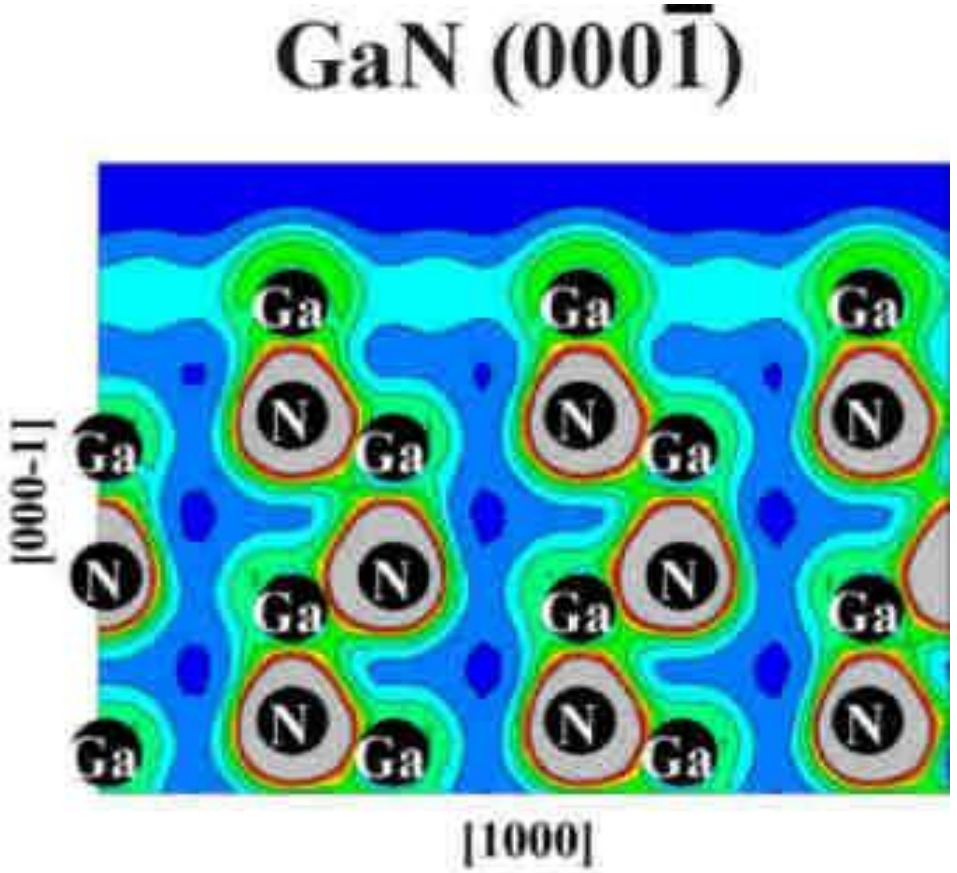




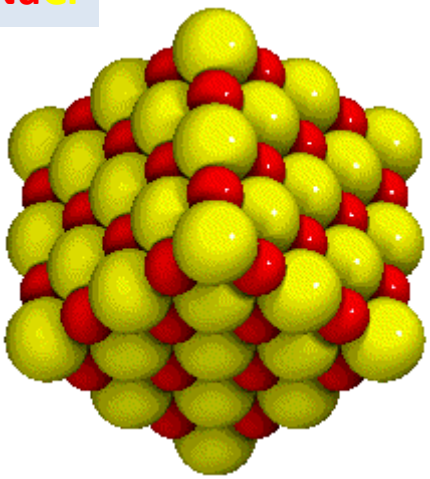
http://oen.dydaktyka.agh.edu.pl/dydaktyka/chemia

Types of chemical bonds

Ionic bonding

Electronegativity (symb. χ) - the tendency of an atom to attract electrons. In the extreme case when the electronegativity of both elements is very different (eg. Li and F), it comes to a full transfer of an electron toward more electronegative atom, which leads to the formation of ionic bond ($\Delta\chi \geq 1{,}7$).

NaCl



*Tablica 2.4. V*alues of electronegativity (according Pauling) for several major elements *(for H set 2,1)*

I	II	III	IV	V	VI	VII
Li 1,0	**Be** 1,5	**B** 2,0	**C** 2,5	**N** 3,0	**O** 3,5	**F** 4,0
Na 0,9	**Mg** 1,2	**Al** 1,5	**Si** 1,8	**P** 2,1	**S** 2,5	**Cl** 3,0
K 0,8	**Ca** 1,0	**Ga** 1,6	**Ge** 1,7	**As** 2,0	**Se** 2,4	**Br** 2,8
Rb 0,8			**Sn** 1,7			**J** 2,4

ionicity **ionicity**

Types of chemical bonds

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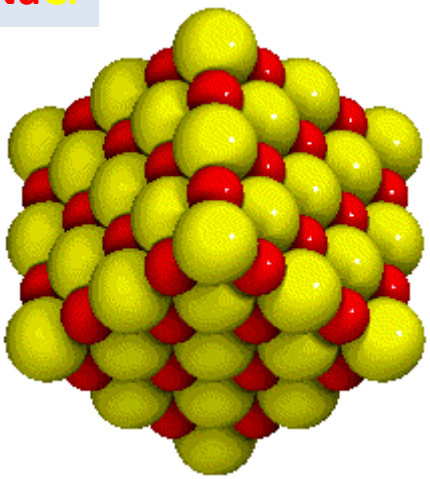

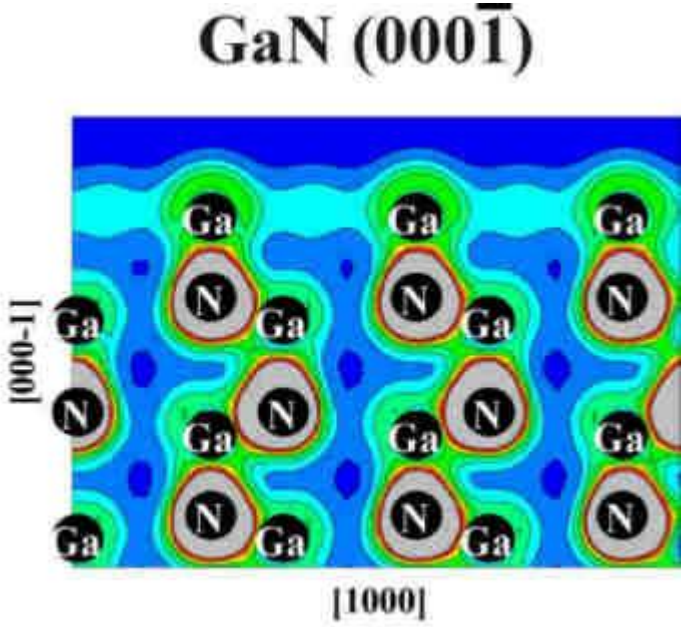

Convention:

Covalent bond	$\Delta\chi \leq 0{,}4$
Polar Covalent	$0{,}4 \leq \Delta\chi \leq 1{,}7$
Ionic Bonds	$\Delta\chi \geq 1{,}7$

Types of chemical bonds

Ionic bonding

Electronegativity (symb. χ) - the tendency of an atom to attract electrons. In the extreme case when the electronegativity of both elements is very different (eg. Li and F), it comes to a full transfer of an electron toward more electronegative atom, which leads to the formation of ionic bond ($\Delta\chi \geq 1{,}7$).

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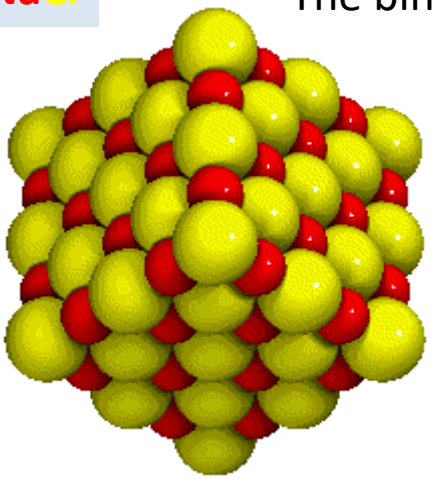
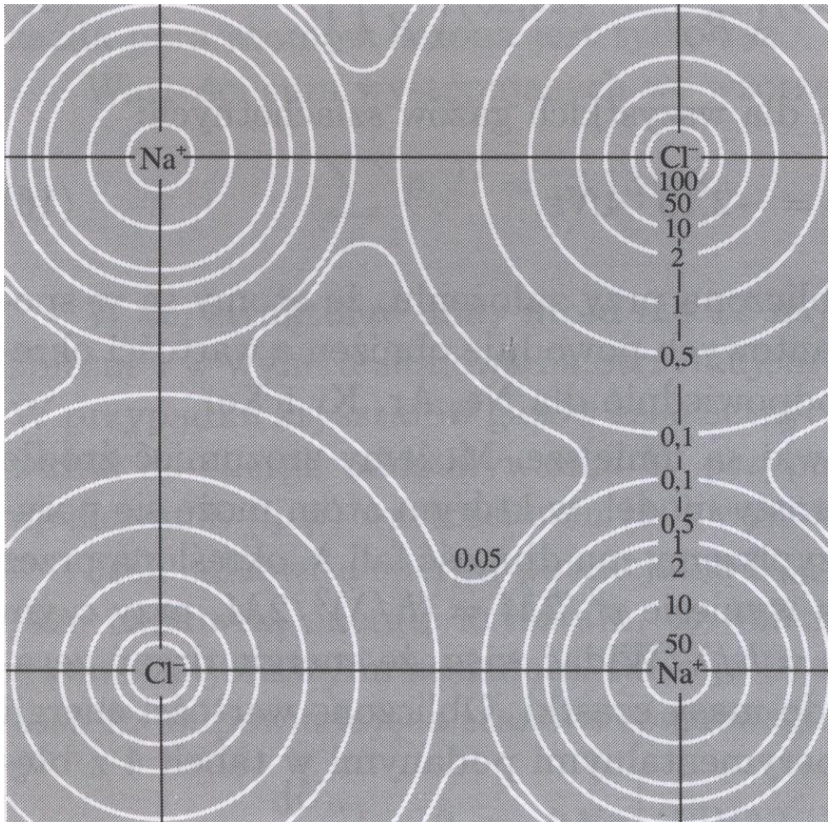


The binding energy per pair of ions :

NaCl	7.95 eV
NaI	7.10 eV
KBr	6.92 eV



Distribution of charge density in the NaCl plane based on X-ray results.

C. Kittel

Types of chemical bonds

Ionic bonding

Electronegativity (symb. χ) - the tendency of an atom to attract electrons. In the extreme case when the electronegativity of both elements is very different (eg. Li and F), it comes to a full transfer of an electron toward more electronegative atom, which leads to the formation of ionic bond ($\Delta\chi \geq 1{,}7$).

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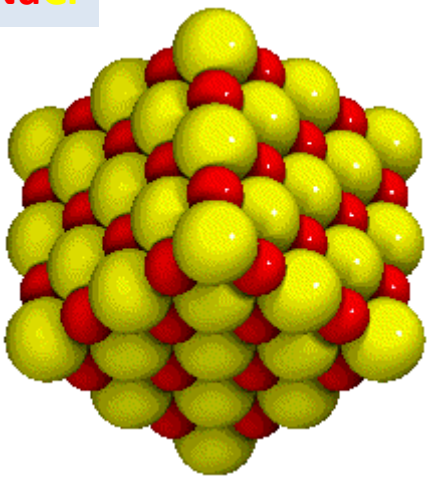


$$V(\vec{r}_{ij}) = \pm\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

Potential energy between two singly charged ions i, j

$$r_{ij} = a\, p_{ij}$$

a: separation of nearest neighbours

p_{ij}: depends on crystal structure

$$V(r) = \sum_{i\neq j} -\frac{e^2}{4\pi\varepsilon_0 a}\frac{\pm 1}{p_{ij}} = -\frac{e^2}{4\pi\varepsilon_0 a}\sum_{i\neq j}\frac{\pm 1}{p_{ij}} = -\frac{e^2}{4\pi\varepsilon_0 a}A$$

The Madelung constant A depends on the structure e.g. $A_{NaCl} = 1.748$

Ibach. Luth

Types of chemical bonds

Covalent bonding (+ polar covalent)

Valence electrons are shared between atoms (non-polar $\Delta\chi < 0{,}4$; polar $0{,}4 < \Delta\chi < 1{,}7$)

Ionic bonding

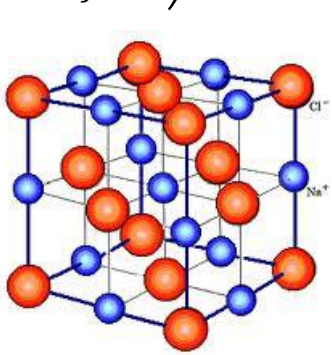
electrons are tranfered between atoms ($\Delta\chi \geq 1{,}7$). An essential contribution to bonds energy of ionic crystals comes from the electrostatic interaction (Madelung energy):

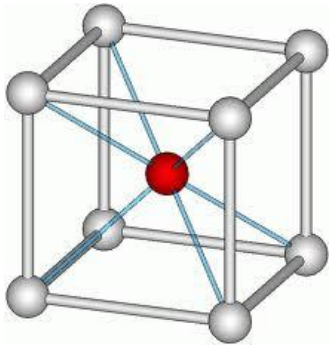
$$U(r) = N\left(-\frac{e^2}{4\pi\varepsilon_0 r}\sum_{i\neq j}\frac{\pm 1}{p_{ij}} + \frac{B}{r^n}\sum_{i\neq j}\frac{1}{p_{ij}^n}\right)$$

r – the distance between atoms

rp_{ij} - the distance between pair of ions i, j

B, n – repulsive potential parameters ($n = 6 - 12$)



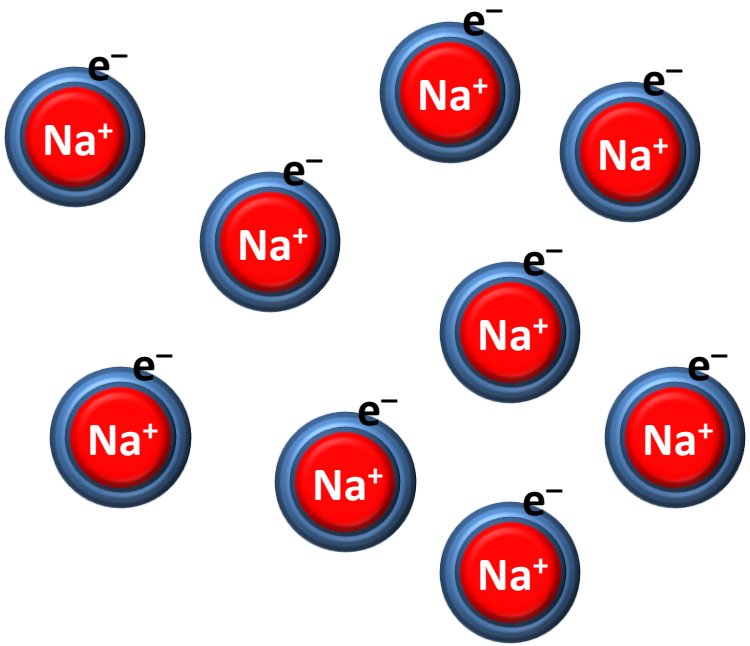


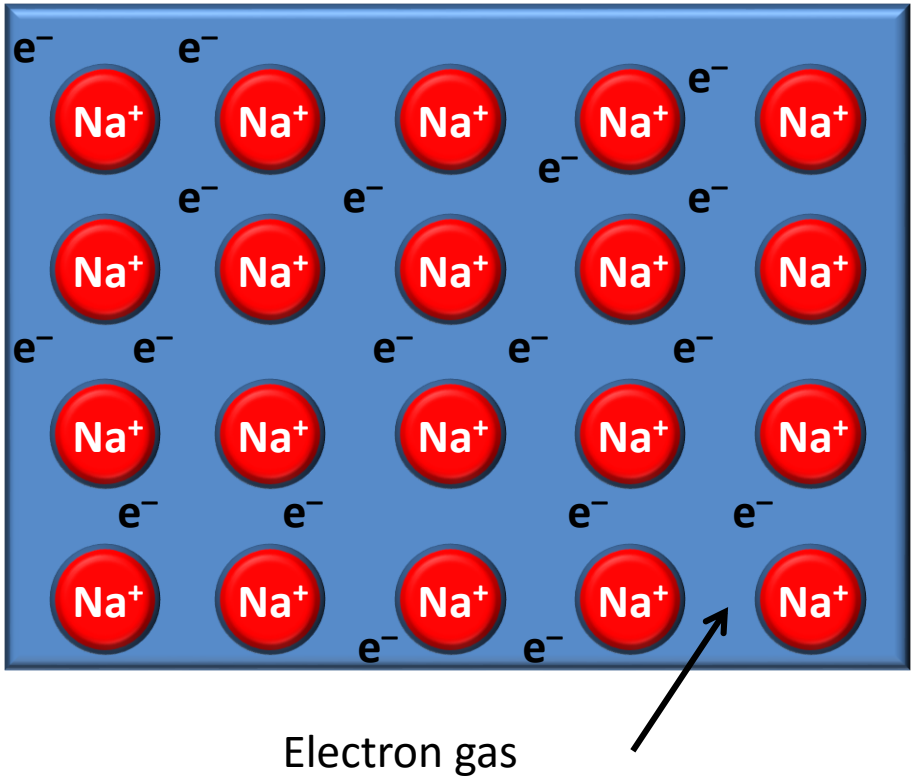
$A = \sum_{i\neq j}\frac{\pm 1}{p_{ij}}$ - the Madelung constant (for NaCl structure $A = 1{,}748$, for CsCl $A = 1{,}763$)

Types of chemical bonds

Metalic bonding

The chemical bond in metals, formed by the electrodynamic interaction between the positively charged atom cores, which are located in nodes of the lattice, and negatively charged **plasma electrons** (**delocalized electrons**, **electron gas**). Similar to a covalent bond, but electrons forming a bond are common to a large number of atoms.





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- In the alkali metals only delocalized electrons of the last shell ns contribute to bonding. In these metals the length of the bonds can be easily changed (high compressibility)
- The metals of further columns of the Periodic Table also deeper shells give an important contribution to bonding (in particular, transition metals and rare earths d and f shells). In these metals the length of the bonds is much harder to change (small compressibility)
- The bonds in metals are usually not very strong, but there are also metals with quite strong bonding - eg. Tungsten (wolfram)

Types of chemical bonds

Metalic bonding

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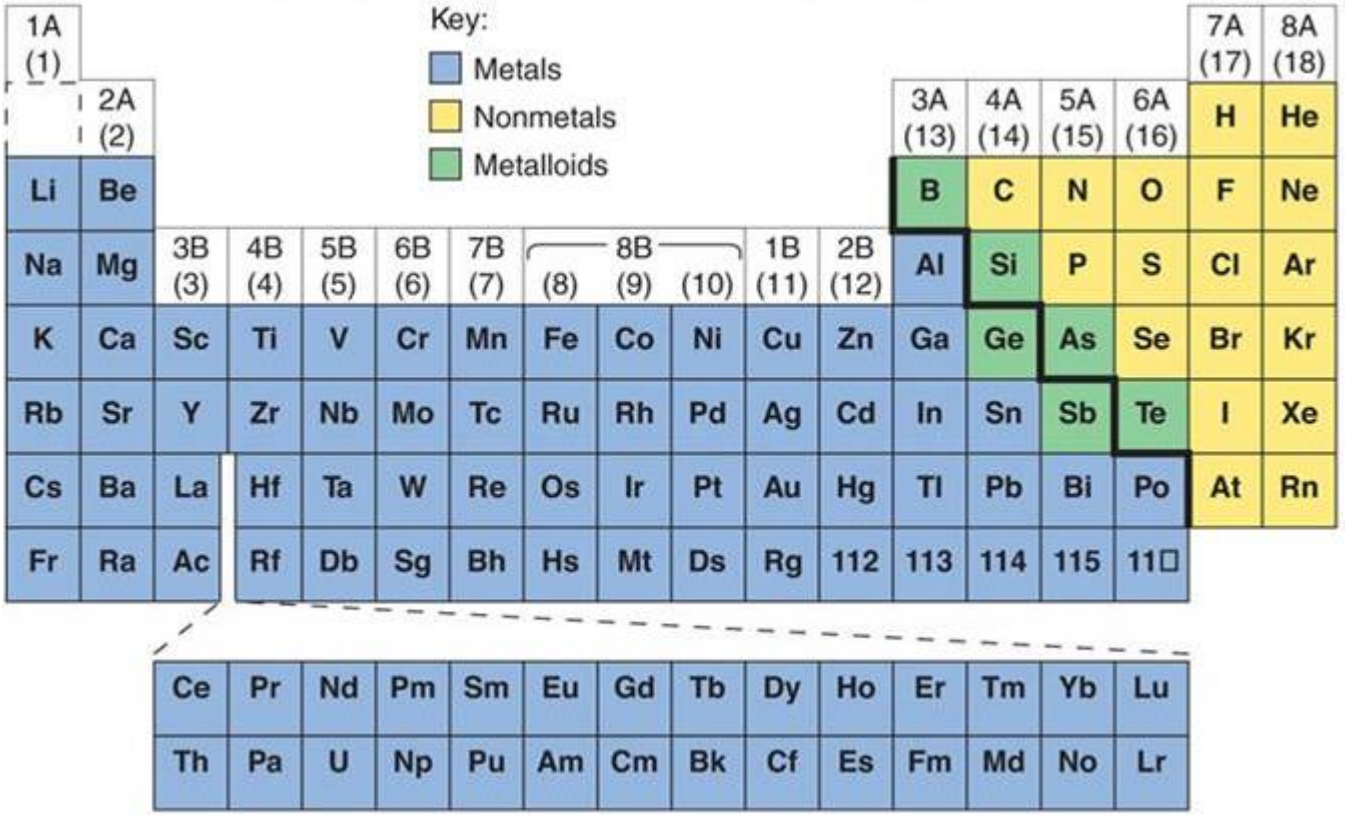
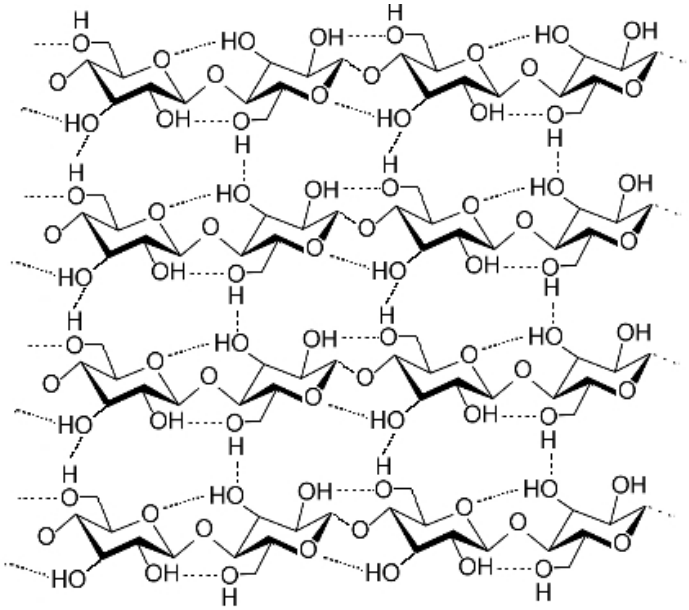


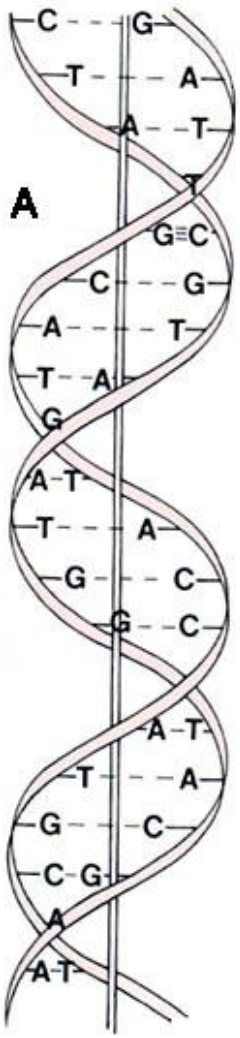
Types of chemical bonds

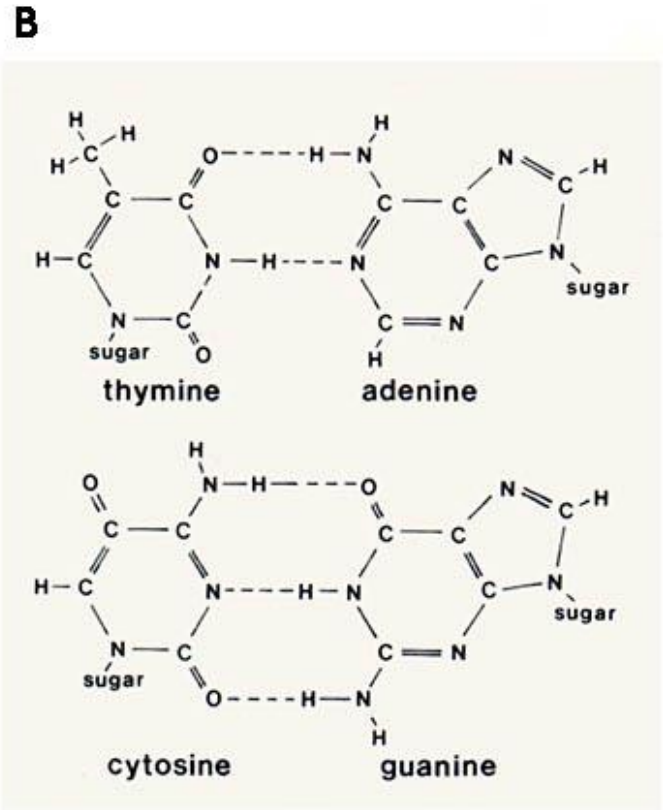
Hydrogen bonding

Hydrogen is shared between atoms

Celulose







C

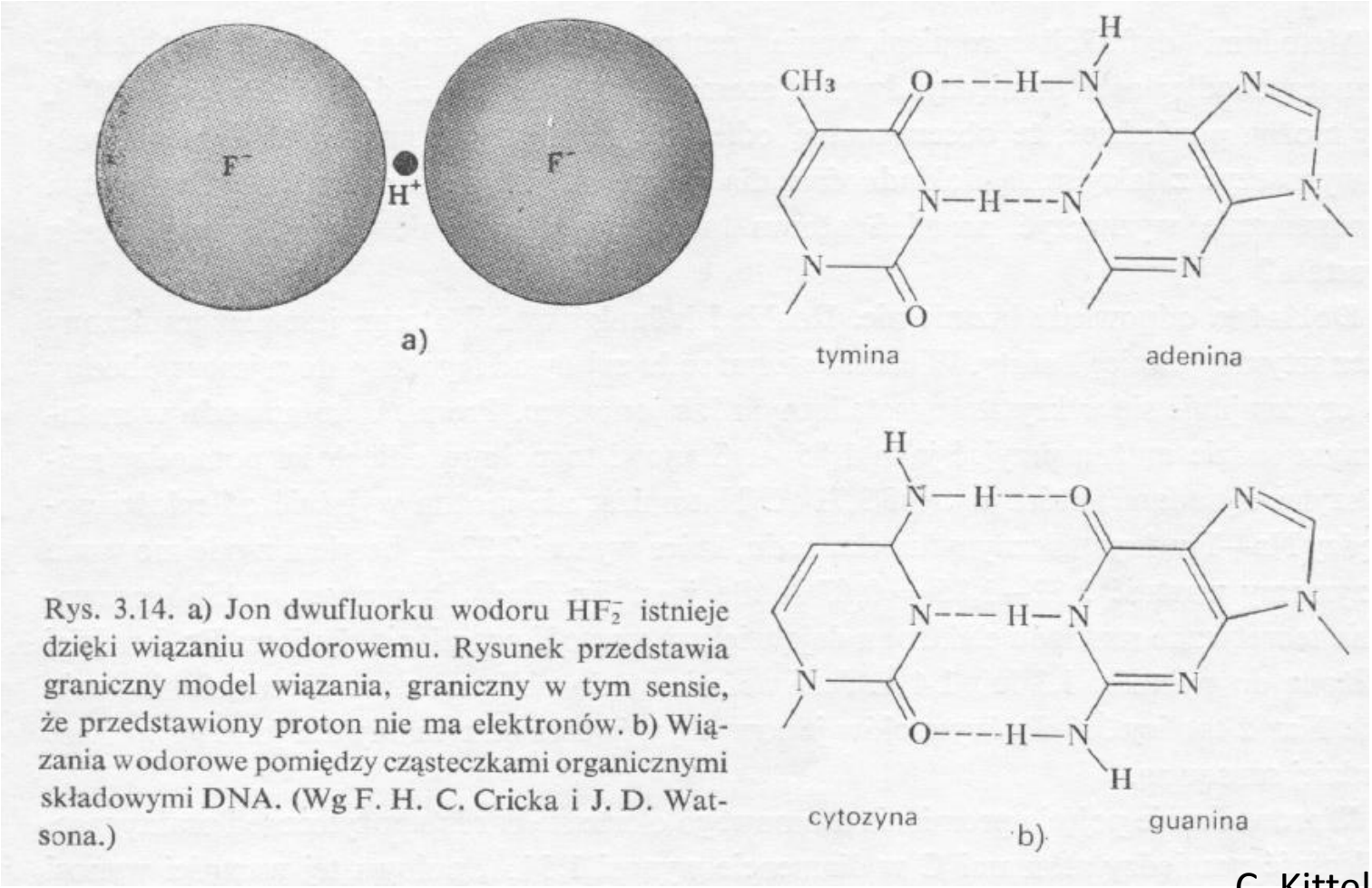
T---A
C---G
G---C
A---T
A---T
T---A
C---G

Wiązania

Hydrogen bonding

Hydrogen is shared between atoms

HF_2^-



Rys. 3.14. a) Jon dwufluorku wodoru HF_2^- istnieje dzięki wiązaniu wodorowemu. Rysunek przedstawia graniczny model wiązania, graniczny w tym sensie, że przedstawiony proton nie ma elektronów. b) Wiązania wodorowe pomiędzy cząsteczkami organicznymi składowymi DNA. (Wg F. H. C. Cricka i J. D. Watsona.)

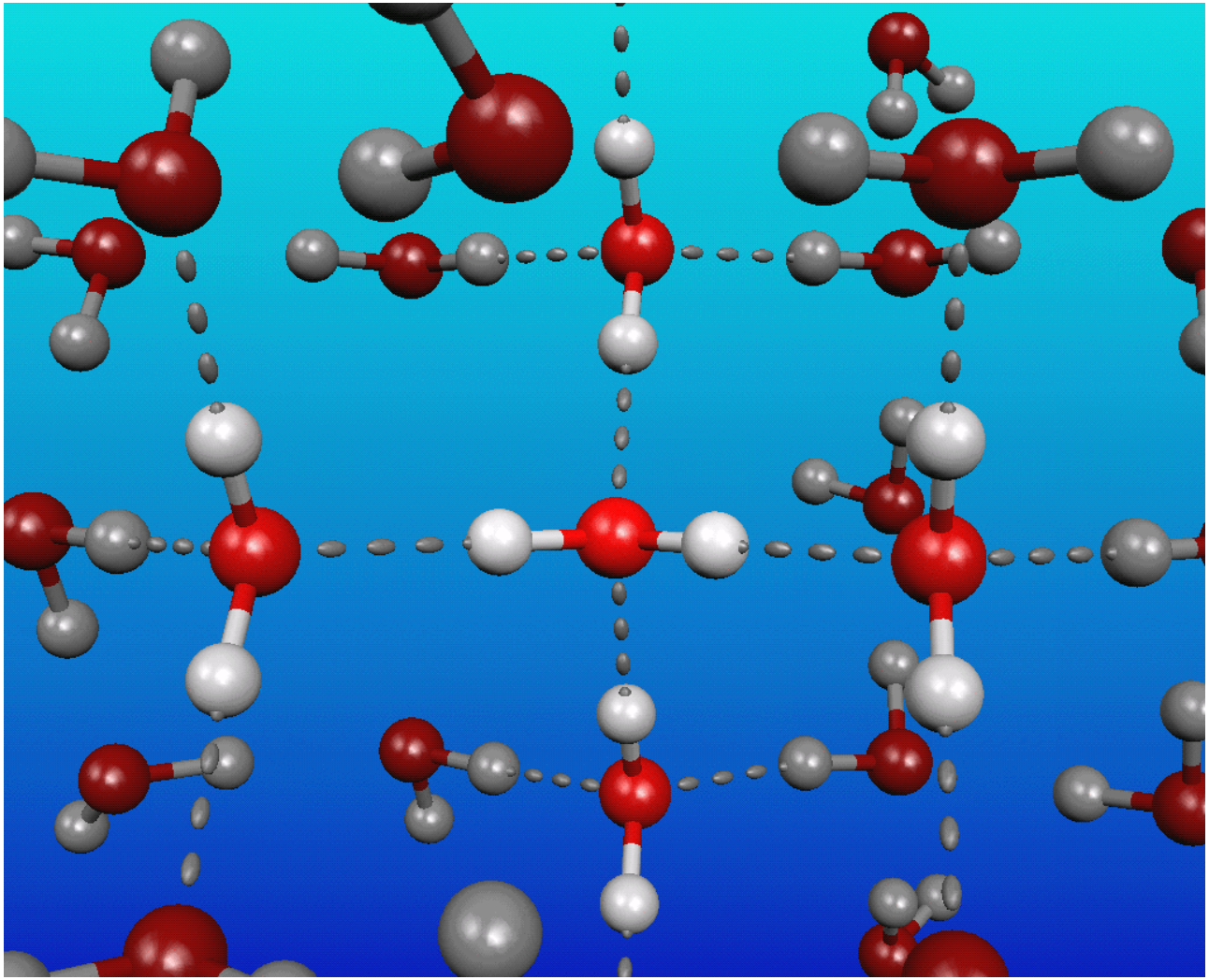
C. Kittel

Types of chemical bonds

Hydrogen bonding

Hydrogen is shared between atoms

(H_20)

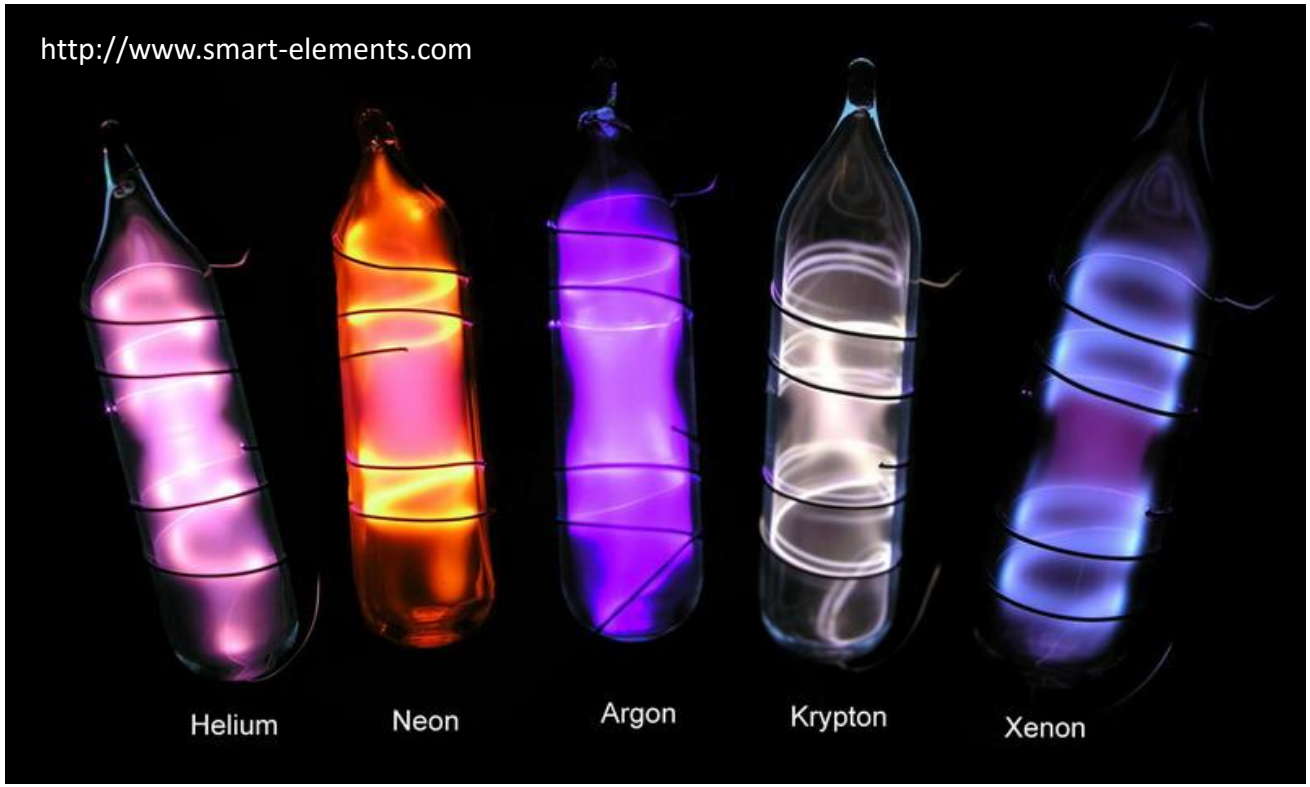


http://www.mbi-berlin.de/en/research/projects/2-04/highlights/water_librational_mode.gif

Types of chemical bonds

Van der Waals bonds

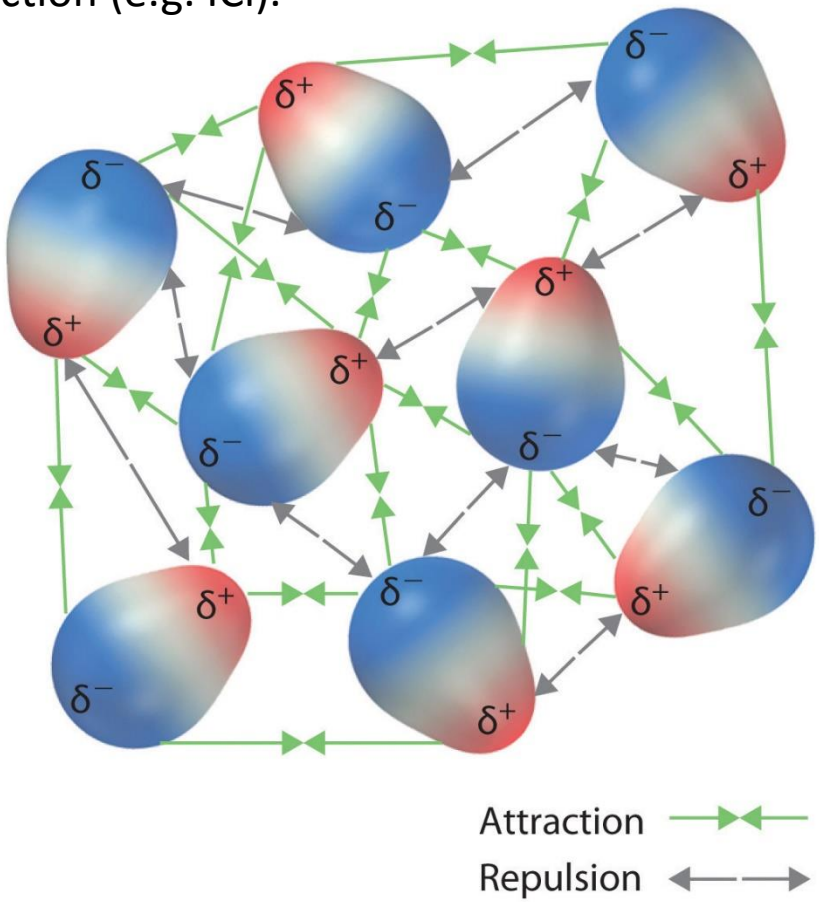
Ne, Ar, Kr, Xe – interaction of induced dipole moments.



Types of chemical bonds

Dipole bonding (also *intermolecular interaction*)

attractive forces between the positive end of one polar molecule and the negative end of another polar molecule - intermolecular interaction (e.g. ICl).



https://saylordotorg.github.io/text_general-chemistry-principles-patterns-and-applications-v1.0/s15-02-intermolecular-forces.html

Types of chemical bonds

Van der Waals bonds (also *intermolecular interaction*)

- interaction between permanent dipoles (Keesom interaction)
- interaction between permanent and induced dipoles (Debye interaction)
- London interaction – London dispersion forces (interaction between induced dipoles)
- Lennard-Jones potential

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The potential energy of N atoms $\quad U_{tot}(r) = 2N\varepsilon\left[\sum_{i\neq j}\left(\frac{\sigma}{p_{ij}r}\right)^{12} - \sum_{i\neq j}\left(\frac{\sigma}{p_{ij}r}\right)^{6}\right]$

Van der Waals bonds

Ne, Ar, Kr, Xe – interaction of induced dipole moments.

Responsible for the possibility of condensation and solidification of noble gases (London ineraction)

Types of chemical bonds

Covalent bond	Ionic bond	Metallic bond
• Directional bond (hybrydization) • Isolators or semiconductors (charge between atoms) • Many of the covalent compounds dissolved in non-polar solvents, and are insoluble in water	• non-directional bond • Isolators (charge in ions) • Many of the ionic compounds dissolved in a polar solvent (water) and not soluble in non-polar	• non-directional bond, delocalised electrons • The more electrons, the stronger the bond • Conductors (free charge) • Metals crystallize preferentially in closed packed structures (fcc, hcp, bcc) • Plastic (metal ions can easily move under the influence of an external force)

Types of chemical bonds

Covalent bond	Ionic bond	Metallic bond
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Bonding Type	Substance	Bonding Energy kJ/mol (kcal/mol)	Bonding Energy eV/Atom, Ion, Molecule	Melting Temperature (°C)
Ionic	NaCl	640 (153)	3.3	801
	MgO	1000 (239)	5.2	2800
Covalent	Si	450 (108)	4.7	1410
	C (diamond)	713 (170)	7.4	>3550
Metallic	Hg	68 (16)	0.7	−39
	Al	324 (77)	3.4	660
	Fe	406 (97)	4.2	1538
	W	849 (203)	8.8	3410
van der Waals	Ar	7.7 (1.8)	0.08	−189
	Cl_2	31 (7.4)	0.32	−101
Hydrogen	NH_3	35 (8.4)	0.36	−78
	H_2O	51 (12.2)	0.52	0

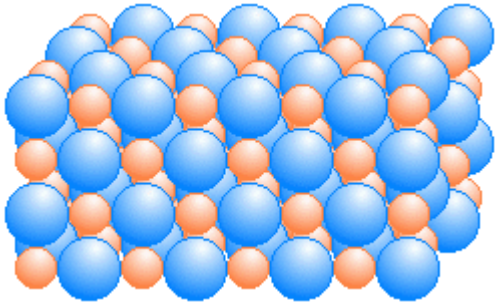
Crystal structure

Crystals

$$\vec{T} = n_1\vec{t}_1 + n_2\vec{t}_2 + n_3\vec{t}_3$$

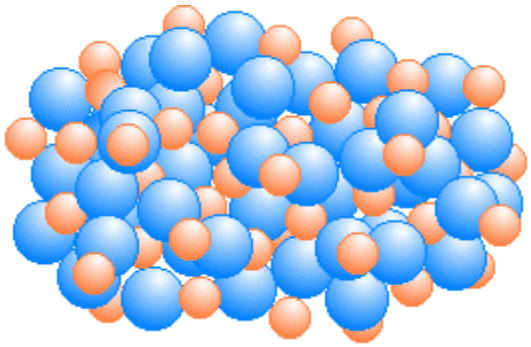
primitive translation vectors

$$V(\vec{r}) = V(\vec{r} + \vec{T})$$



Kryształ

Lattice is a regular and periodic arrangement of points in space (*lattice sites* or *lattice points*).
It is a mathematical abstraction; the crystal structure there is only when the base is uniquely assigned to each network node



Ciało amorficzne

Crystal structure

Crystals

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primitive translation vectors

Crystal structure

Crystals

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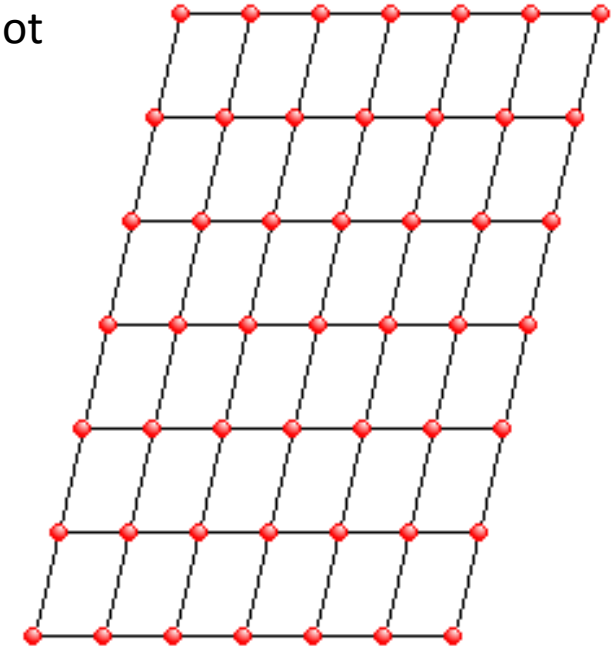
primitive translation vectors

Primitive translation vectors are not selected unambiguously!



Crystal structure

Crystals

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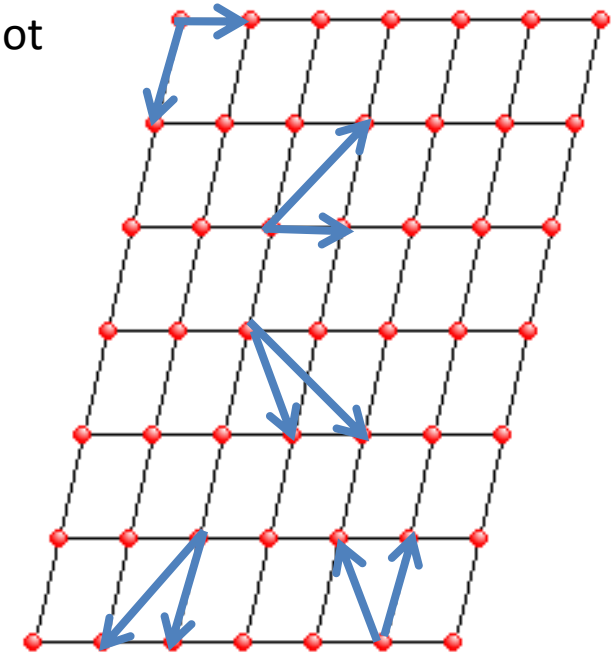

Crystal structure

Crystals

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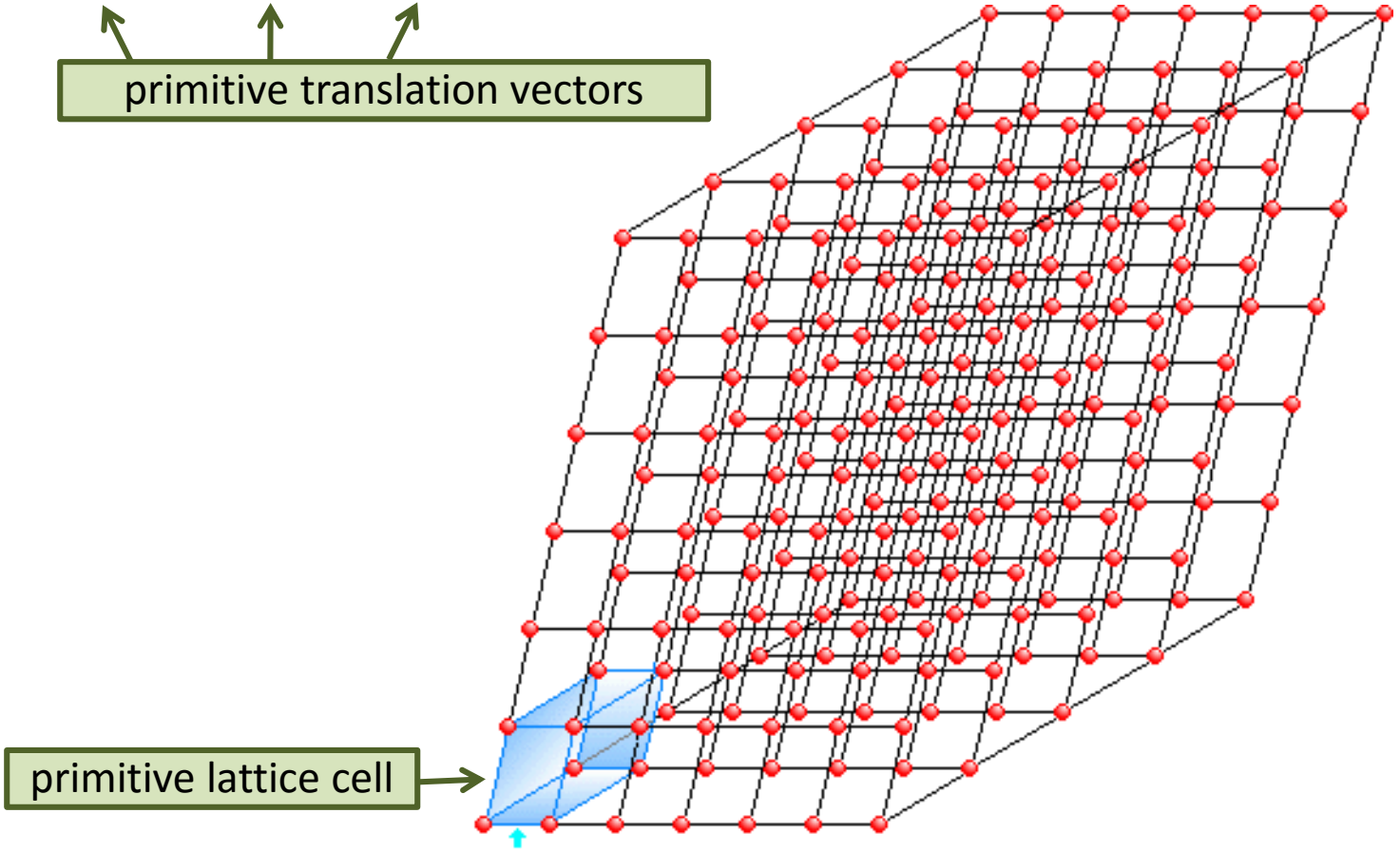
primitive translation vectors



Crystal structure

Crystals

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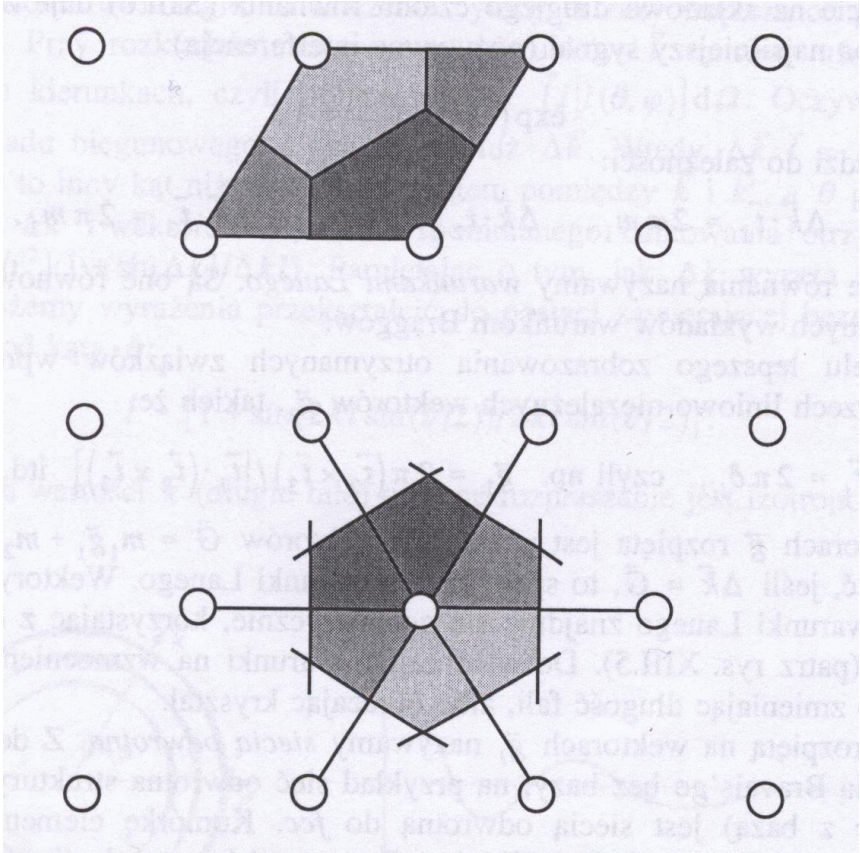
primitive translation vectors

Wigner-Seitz primitive cell



C. Kittel

Crystal structure

Crystals

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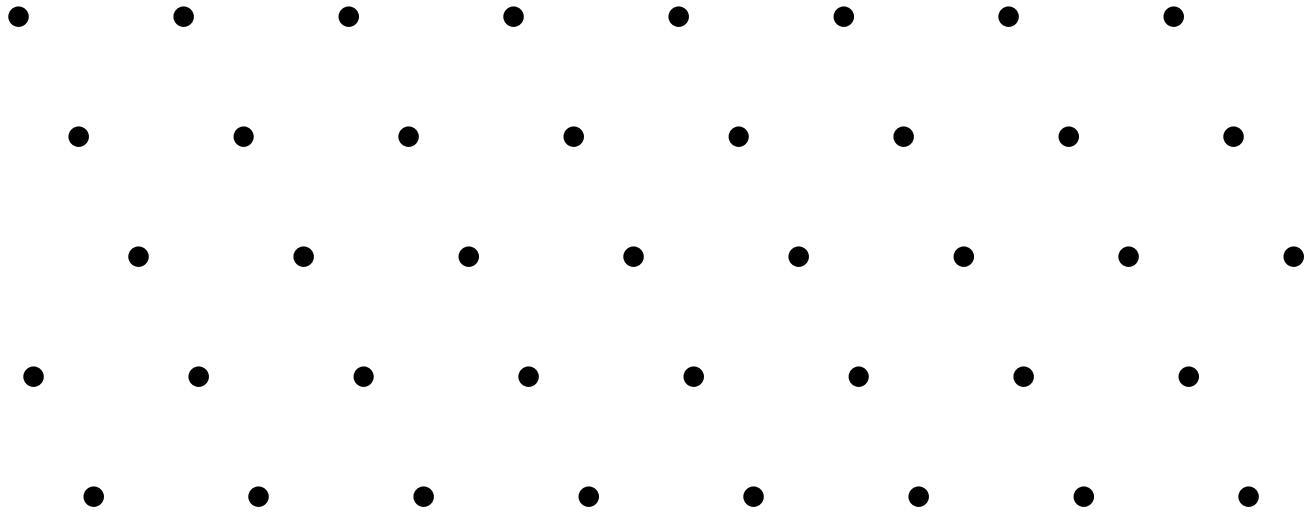
primitive translation vectors



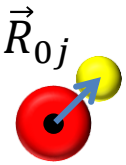
The basis (*baza*) may be a single atom, ion, a set of atoms, eg. proteins 10^5, positioned around each and every lattice point.

Crystal structure

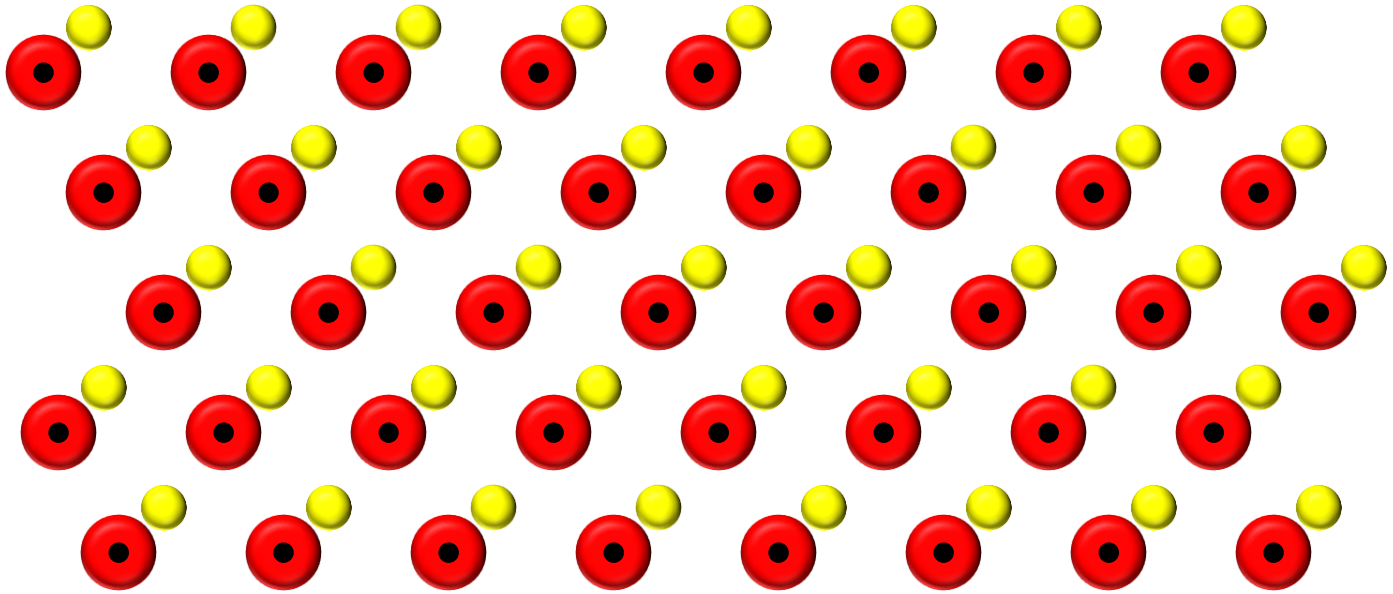
Crystals

$$\vec{T} = n_1\vec{t}_1 + n_2\vec{t}_2 + n_3\vec{t}_3$$

primitive translation vectors



$$\vec{R}_{nj} = \vec{R}_{0j} + \vec{T}$$



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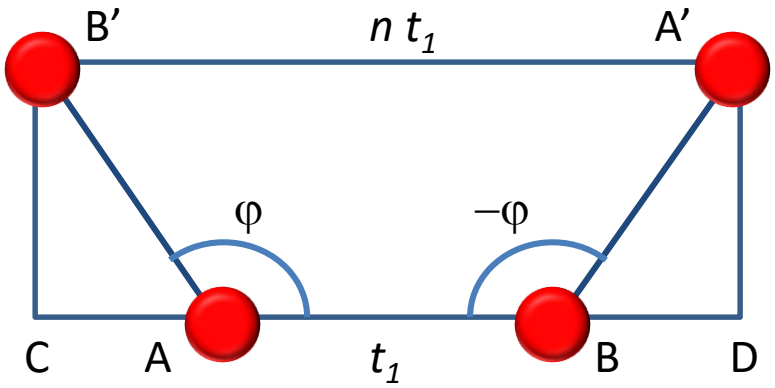
Crystal structure

Crystals



$$B'A' = CD = nt_1 = t_1(1 - 2\cos\varphi)$$

$$\cos\varphi = \frac{1}{2}(1 - n)$$

n	$\cos\varphi$	φ	Obrót
−1	1	0°	ε
0	1/2	60°	C_6
+1	0	90°	C_4
+2	−1/2	120°	C_3
+3	−1	180°	C_2

Crystal structure

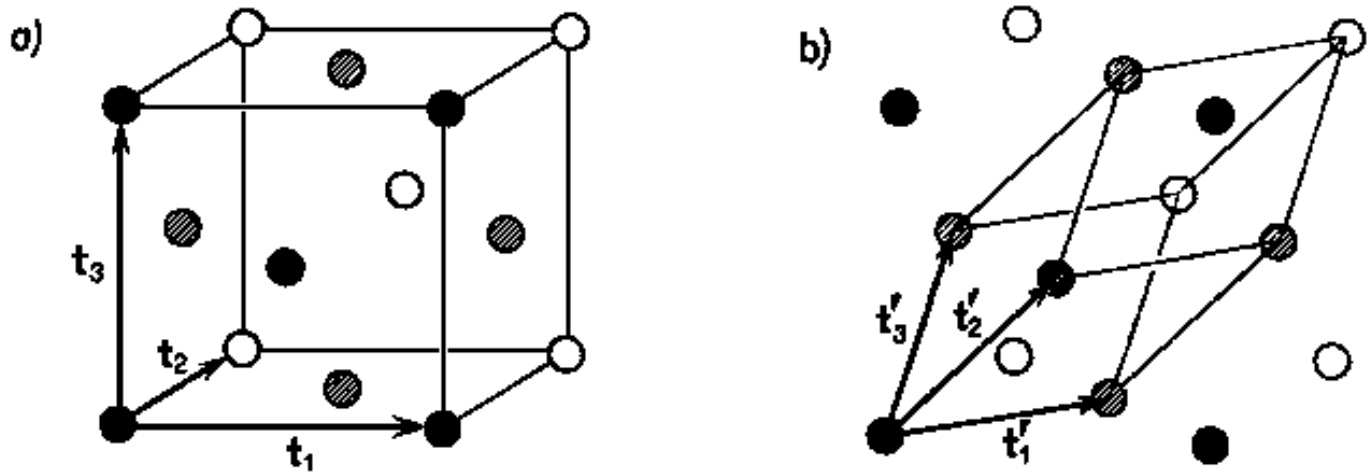
Crystals

$$\vec{T} = n_1\vec{t}_1 + n_2\vec{t}_2 + n_3\vec{t}_3$$

primitive translation vectors

High symmetry cell

Primitive cell



Dwa sposoby wyboru komórki elementarnej w sieci kubicznej centrowanej na ścianach: a) komórka o wysokiej symetrii, b) komórka prosta

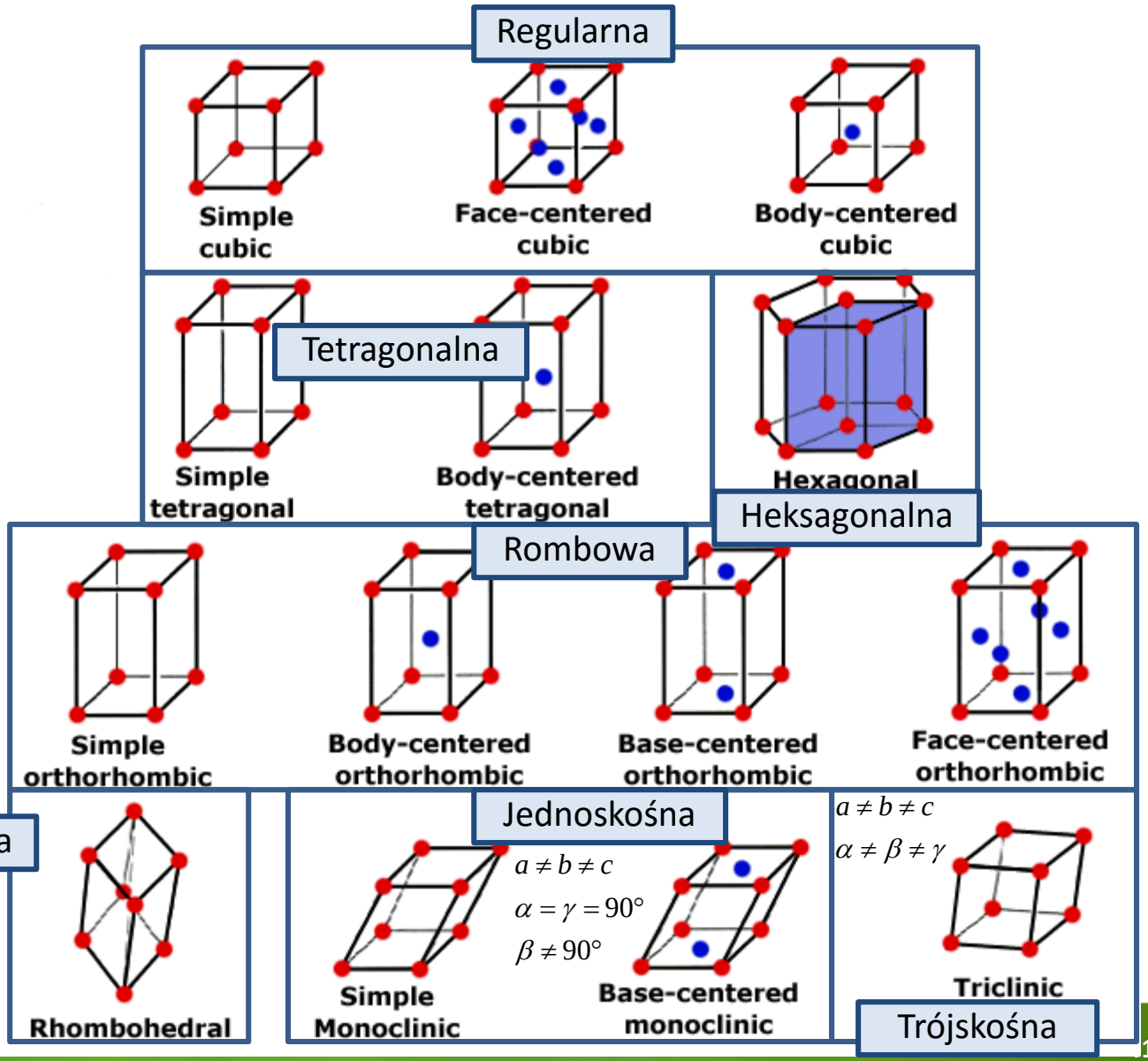
Crystal structure

Bravais lattice

In three-dimensional space, there are 14 **Bravais lattices**.

They form 7 lattice systems

Auguste Bravais
1811-1863



Crystal structure

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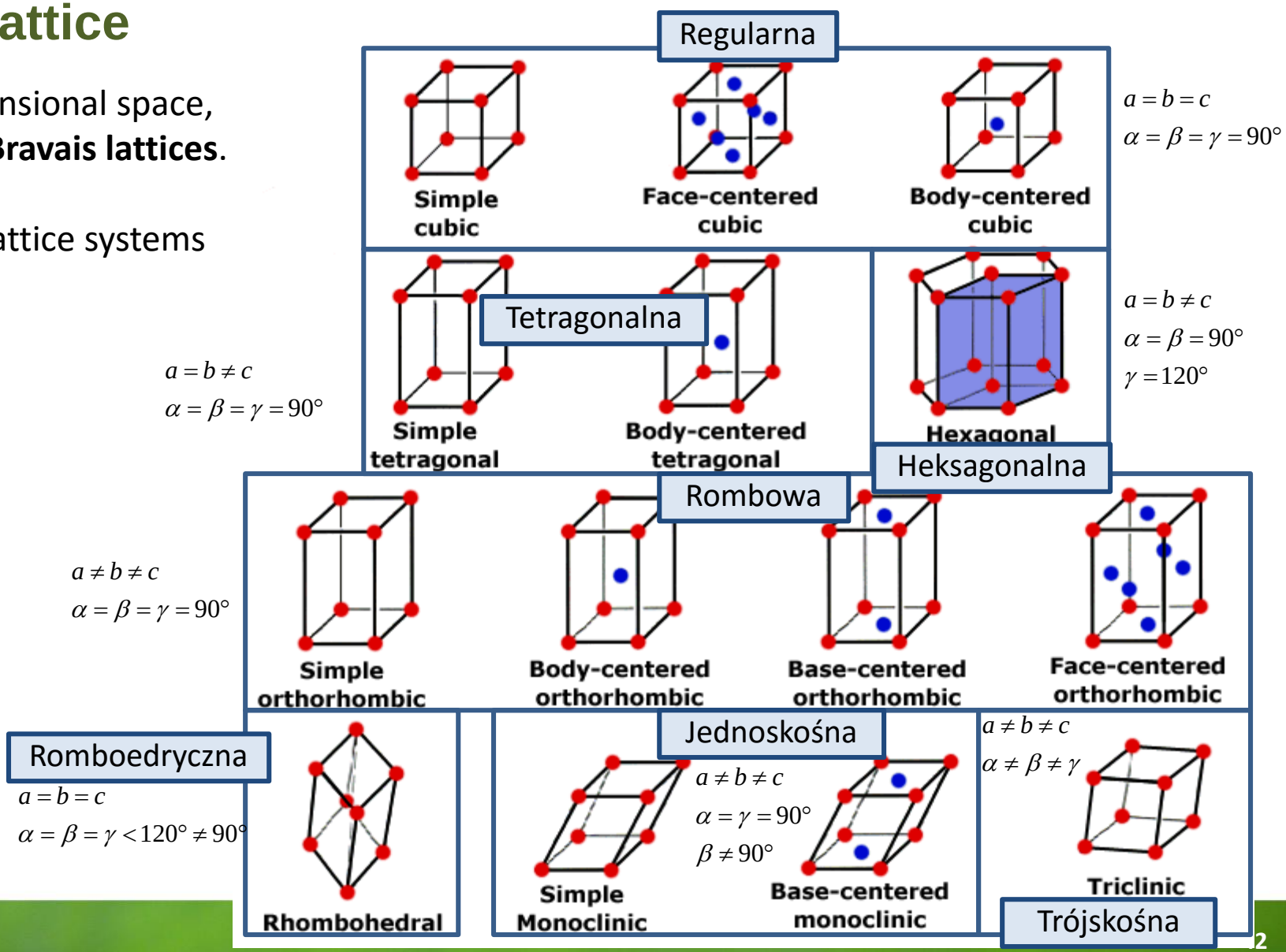


Crystal structure

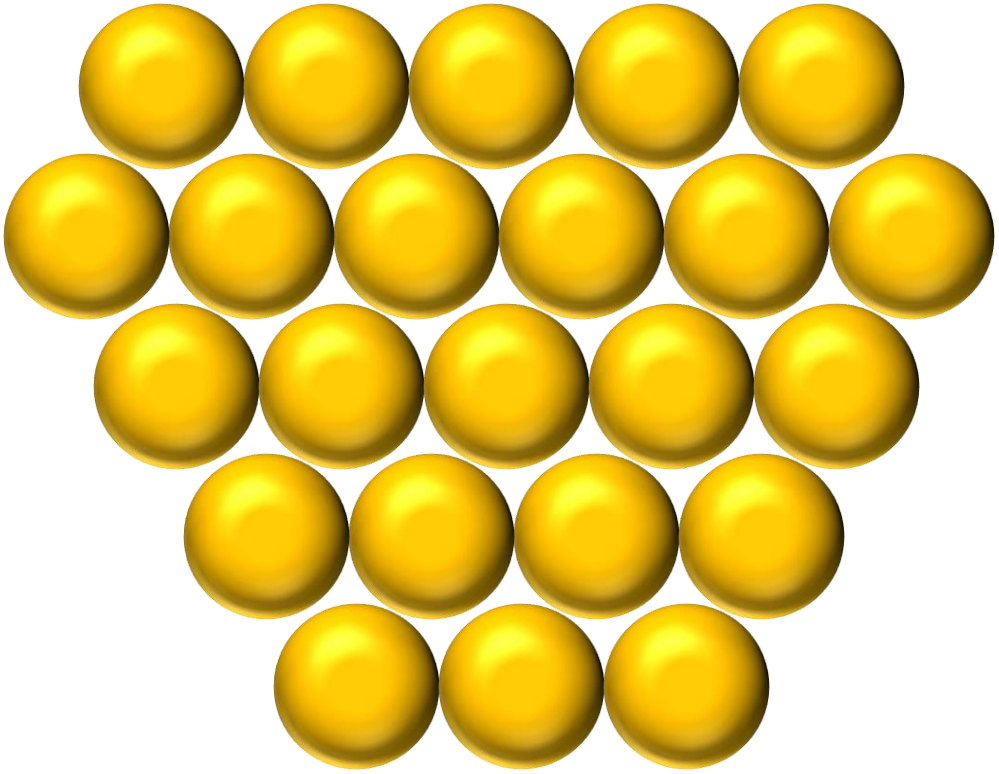
Bravais lattice

Crystal structure

Bravais lattice

Example: close packed structure

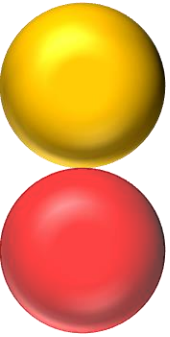
1 layer **A**



Crystal structure

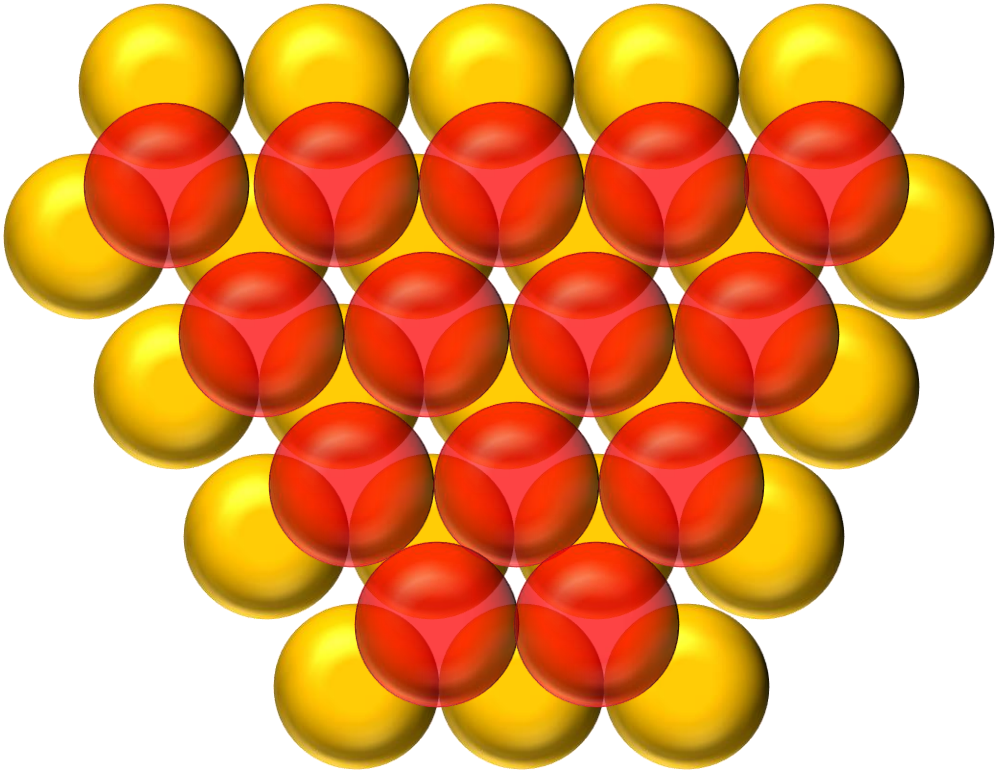
Bravais lattice

Example: close packed structure



1 layer **A**

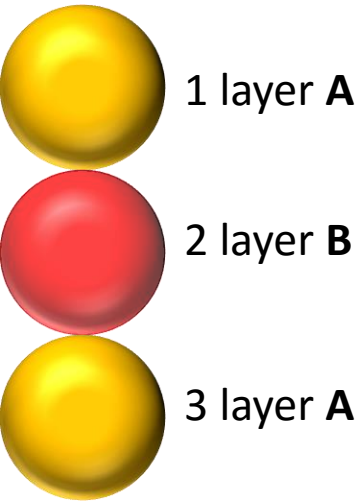
2 layer **B**



Crystal structure

Bravais lattice

Example: close packed structure



1 layer **A**

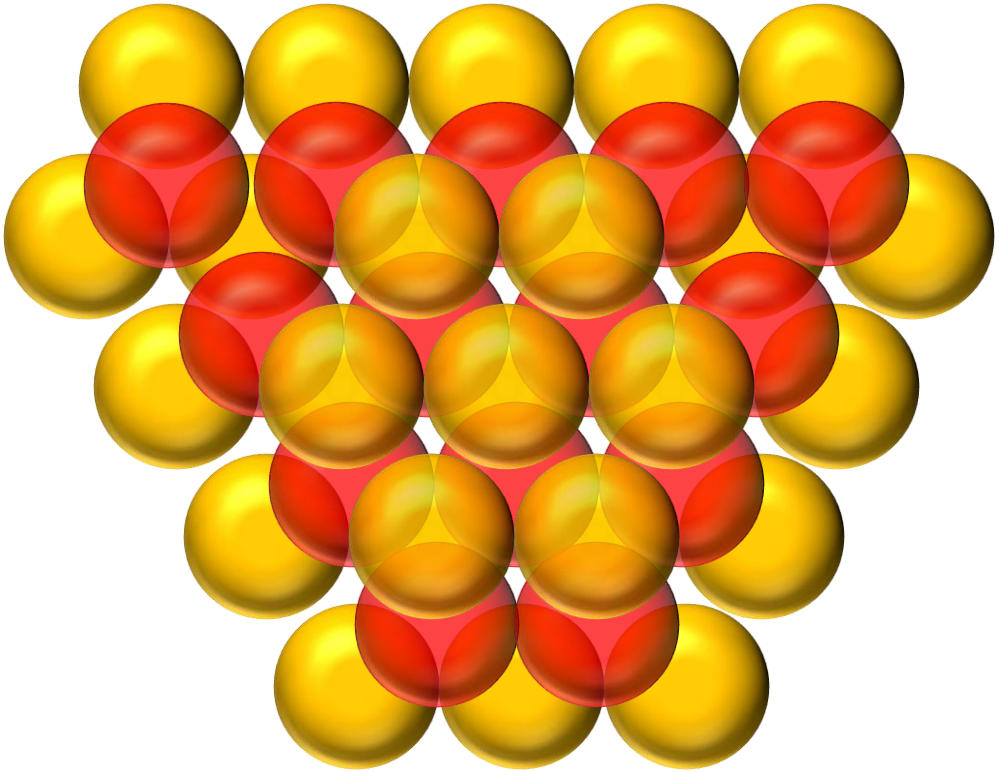
2 layer **B**

3 layer **A**

B

A

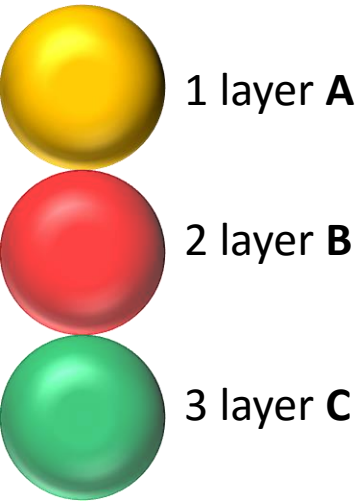
B



Crystal structure

Bravais lattice

Example: close packed structure



1 layer **A**

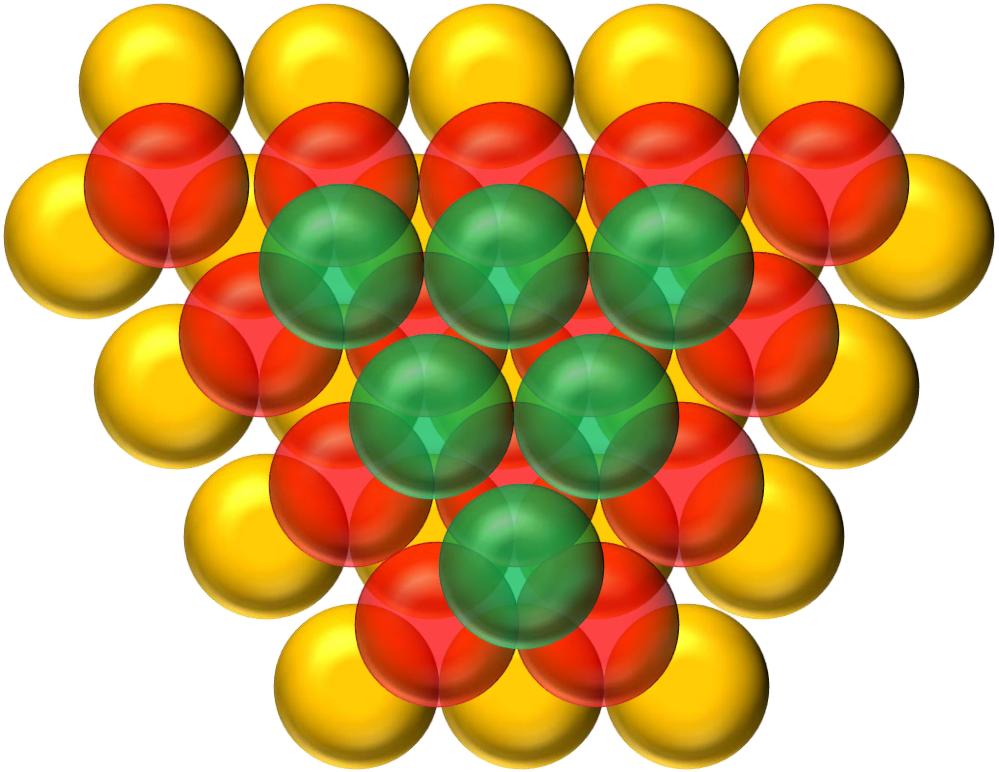
2 layer **B**

3 layer **C**

A

B

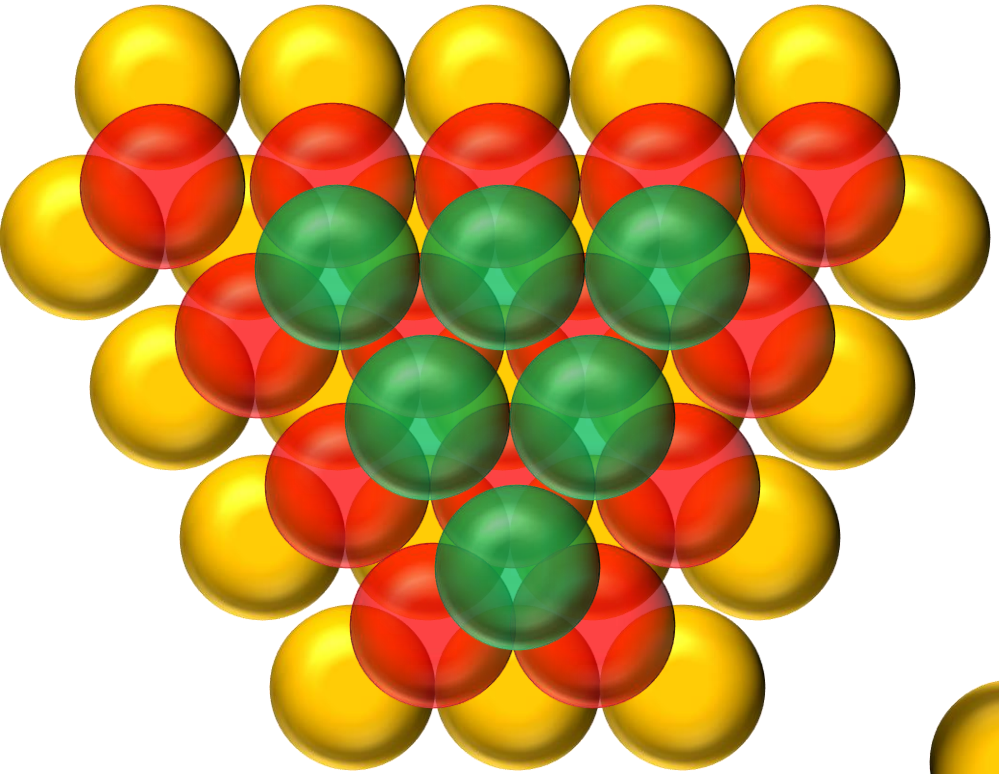
C



Crystal structure

Bravais lattice

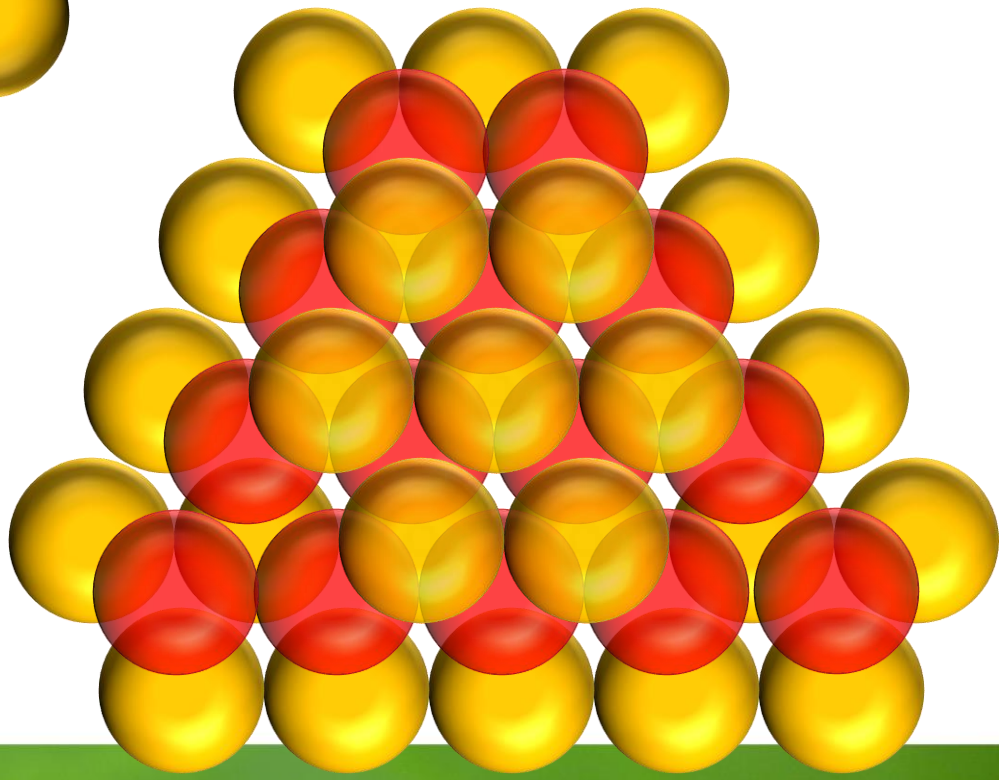
Example: close packed structure



fcc lattice

hexagonal close-packed (HCP)

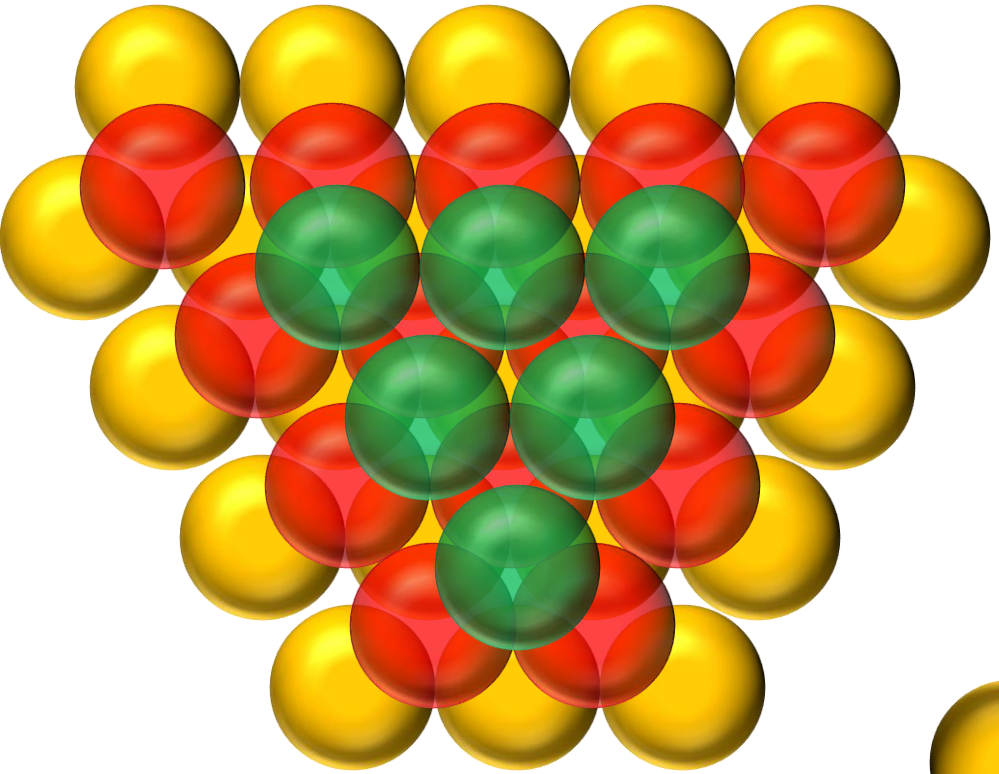
Hexagonal lattice with basis



Crystal structure

Bravais lattice

Example: close packed structure



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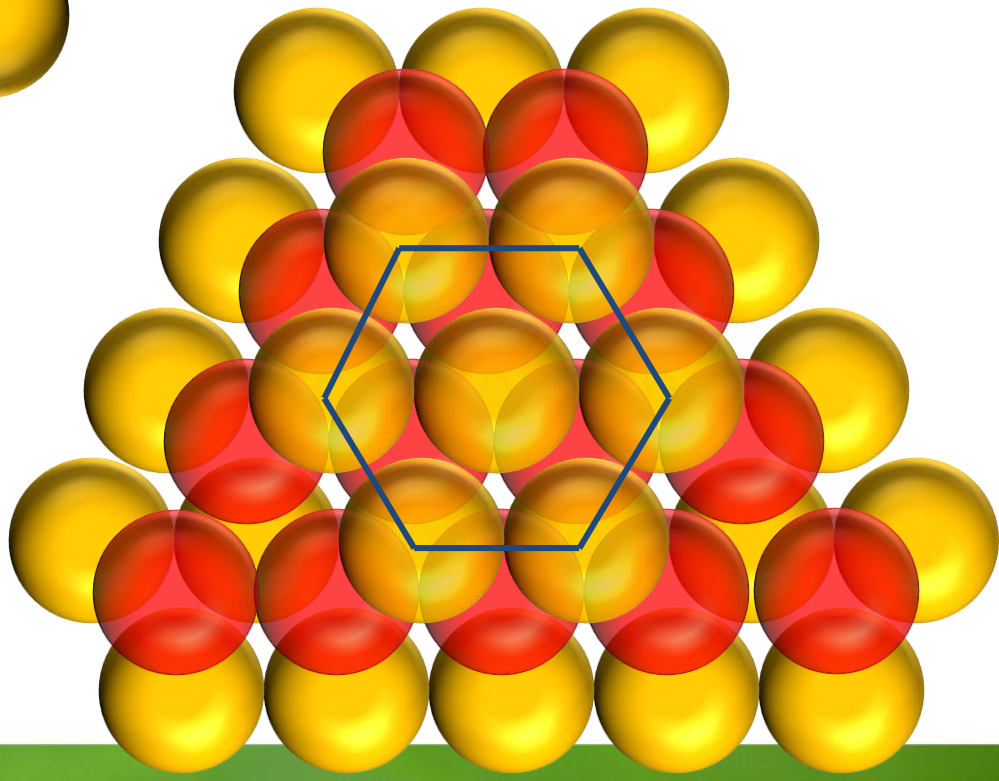

Crystal structure

Bravais lattice

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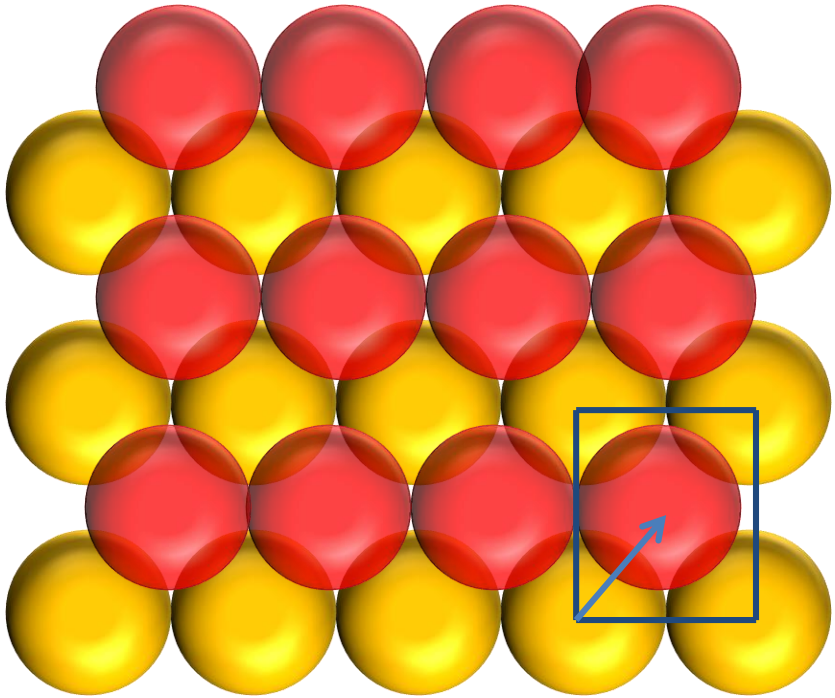

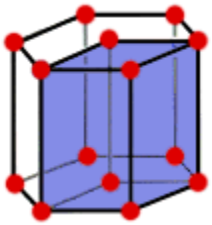

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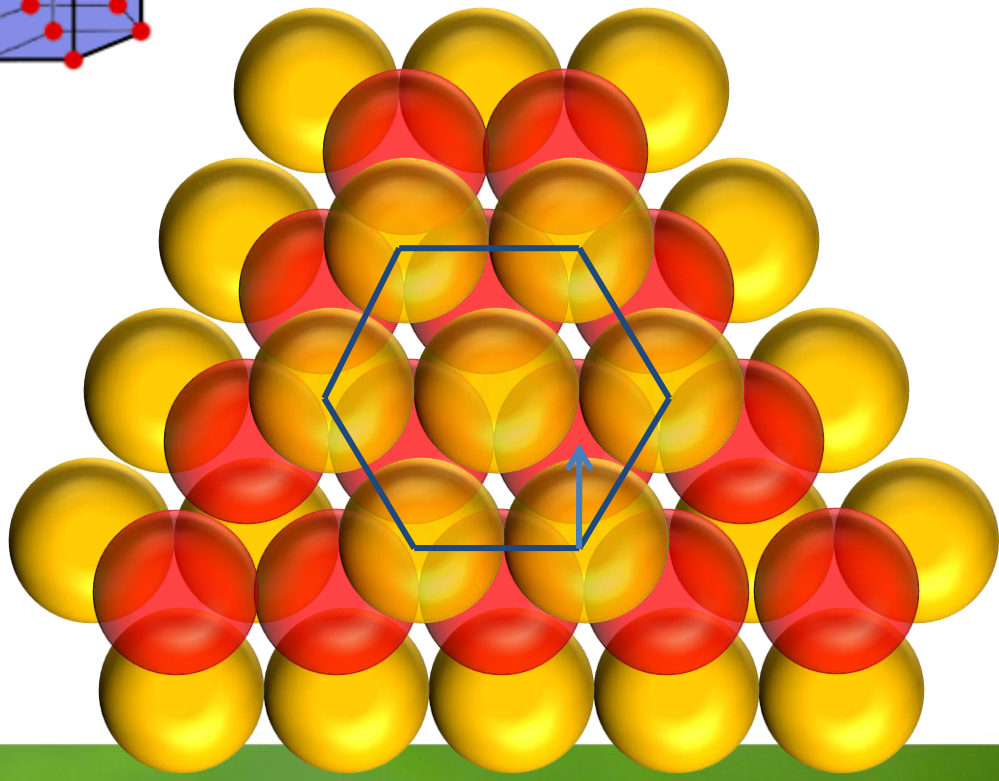
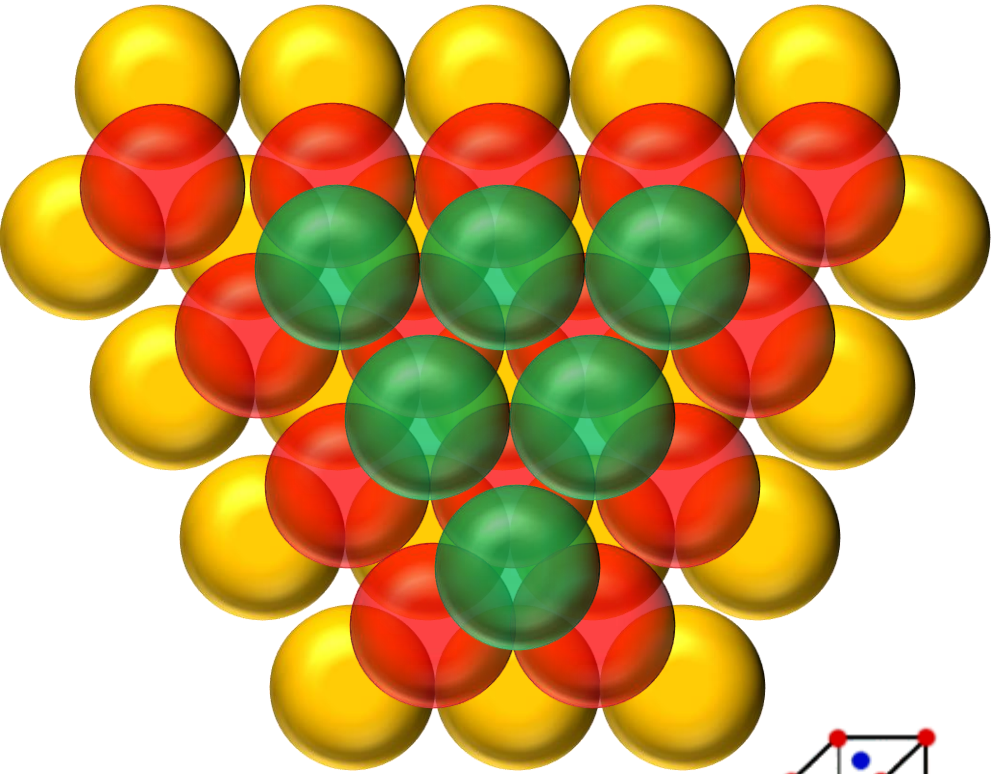


Crystal structure

Bravais lattice

Example: close packed structure



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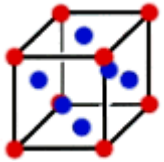
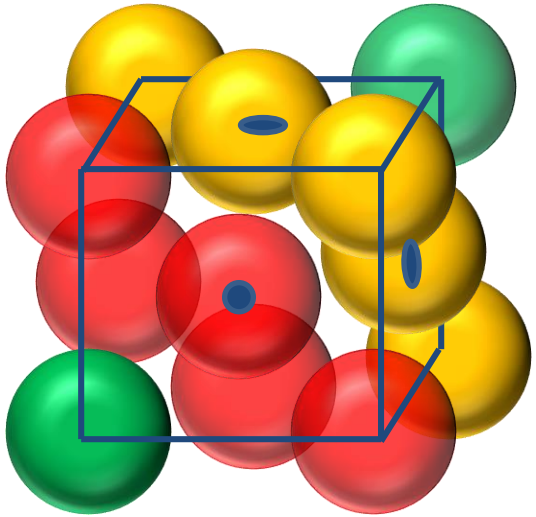
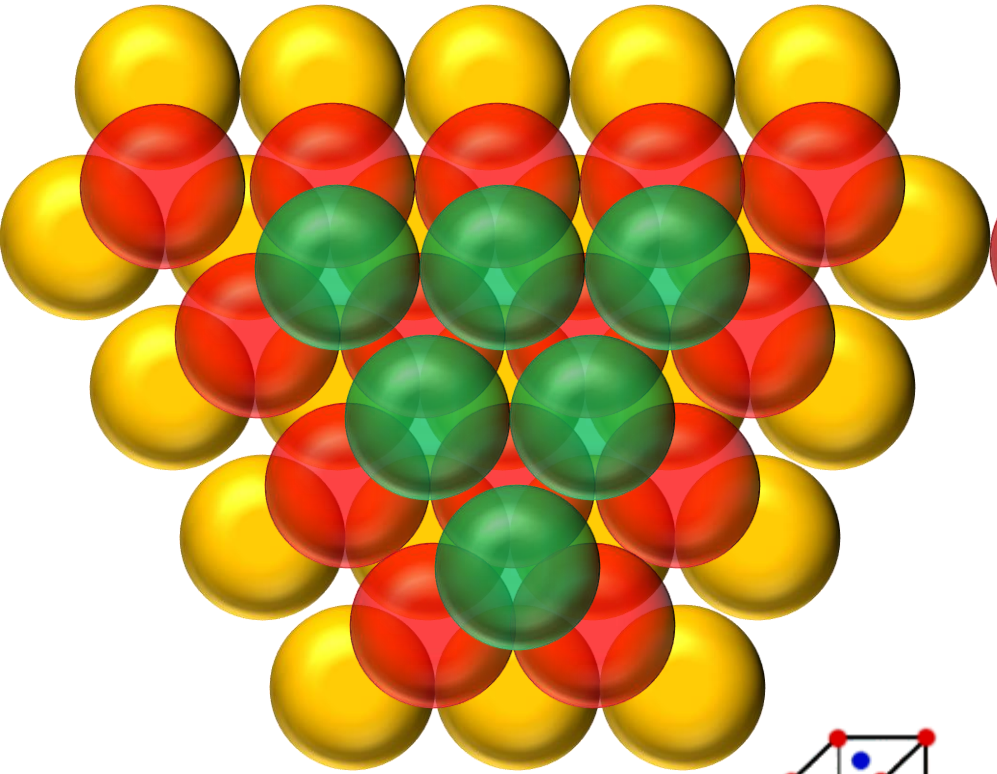




Crystal structure

Bravais lattice

Example: close packed structure



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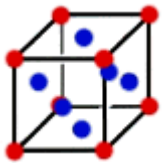

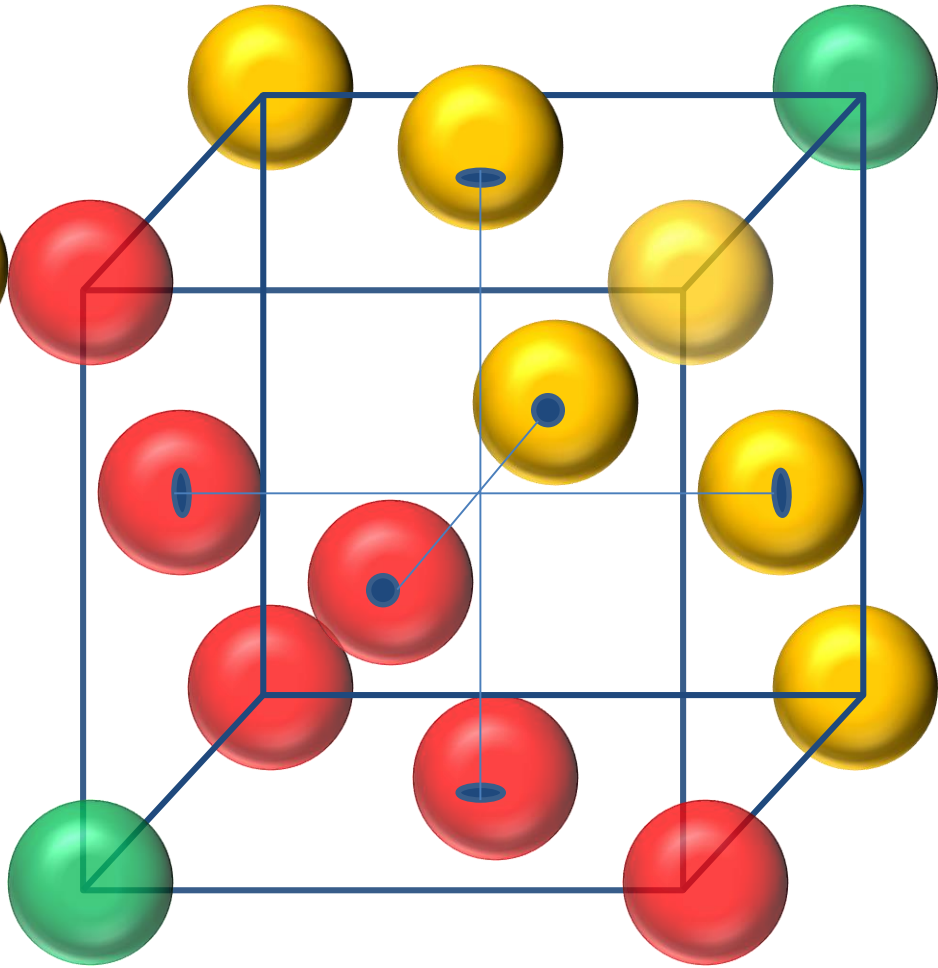

Crystal structure

Bravais lattice

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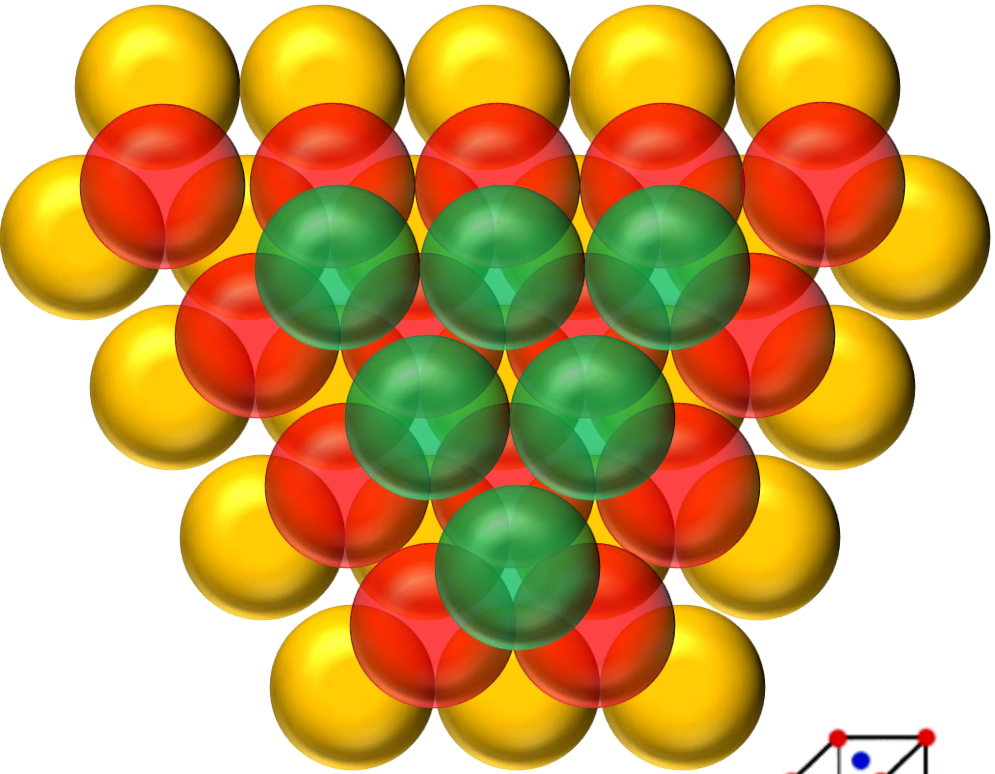

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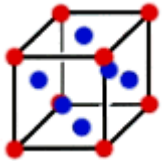
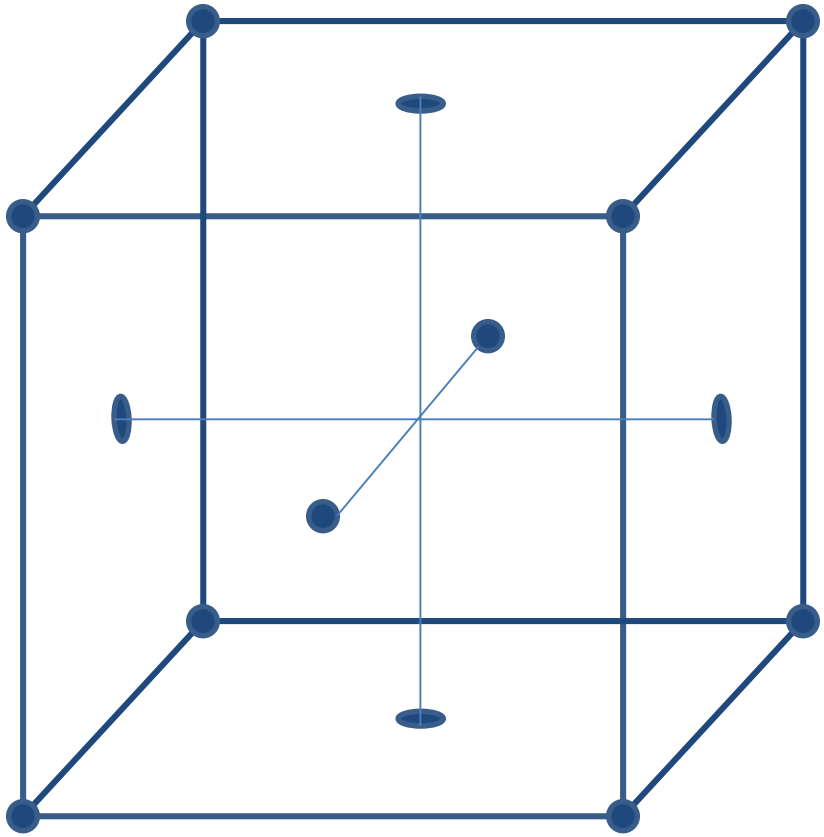




Crystal structure

Lattice points

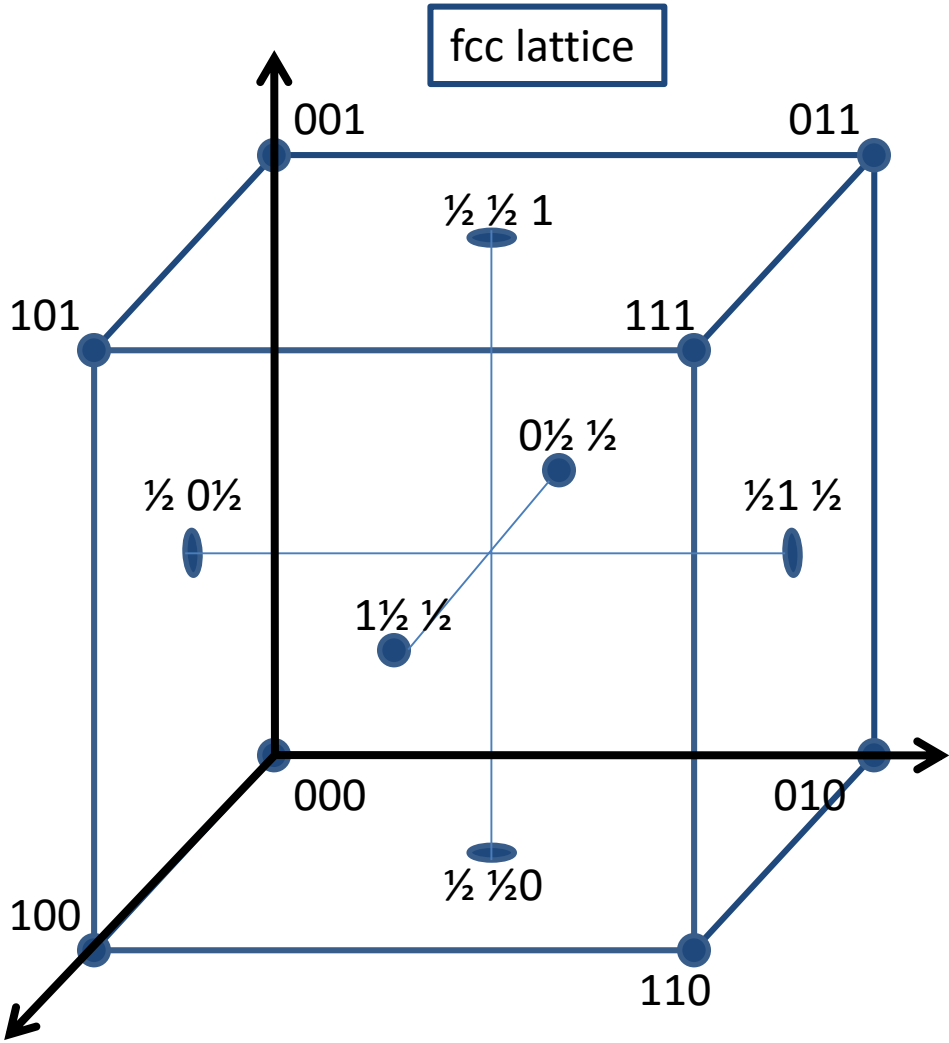
$$\vec{T} = n_1\vec{t}_1 + n_2\vec{t}_2 + n_3\vec{t}_3$$

primitive translation vectors

Translation vectors of lattice

$$[n_1\vec{a}_1, n_2\vec{a}_2, n_3\vec{a}_3]$$

Coordinates of a cell



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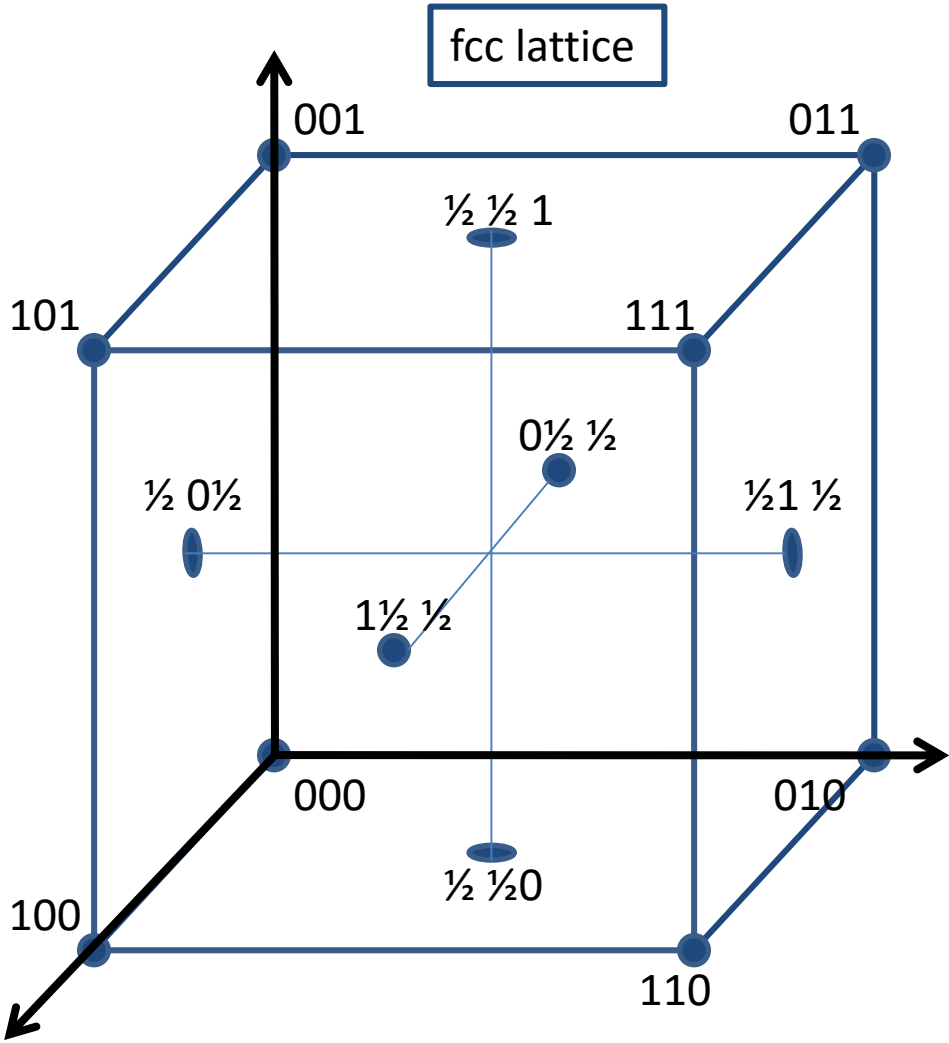
Coordinates of a cell

$$n_1, n_2, n_3$$



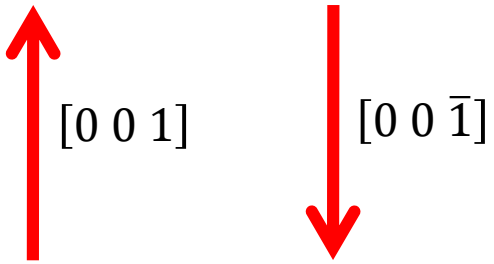
Crystal structure

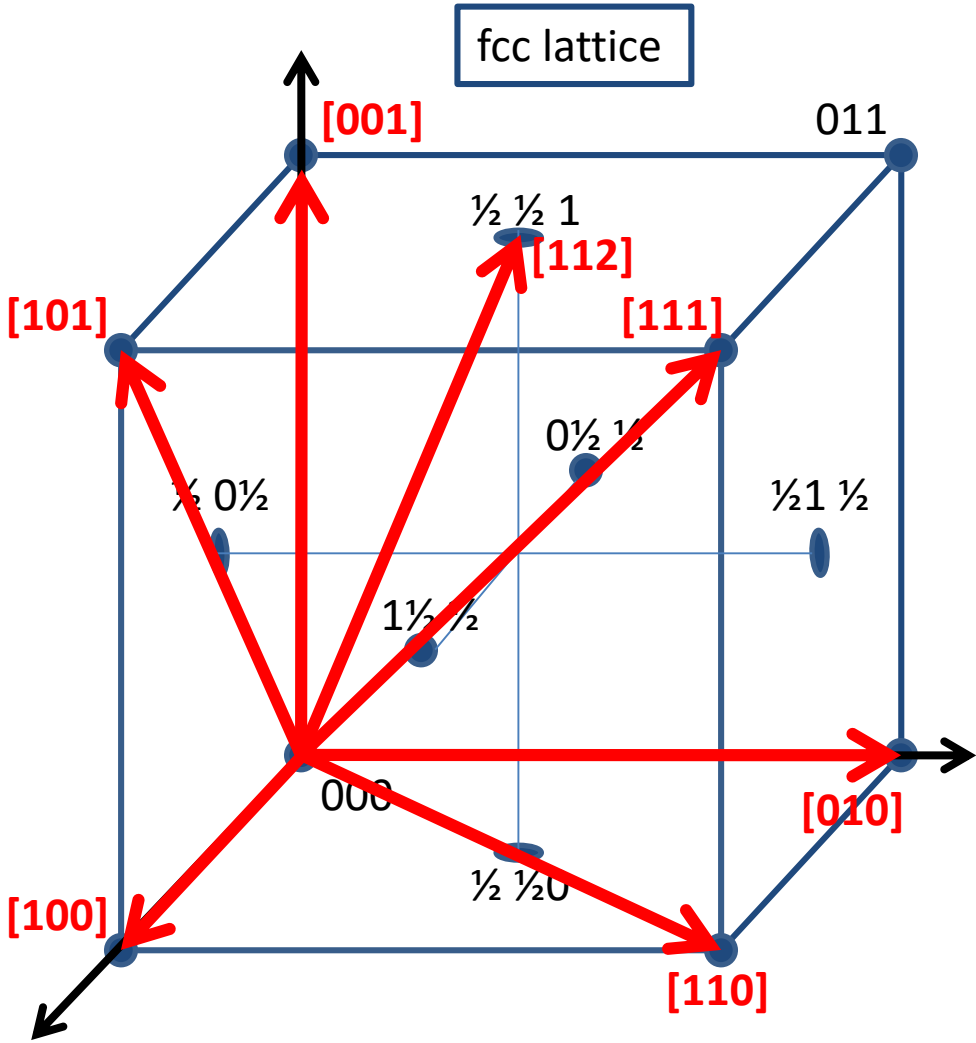
Lattice directions

The set of any of integers relatively prime (coprime, *względnie pierwsze*) which are to each other as the projections of a vector parallel to the direction of crystal axes..

$[u\ \bar{v}\ w]$

Negative values denoted by the bar over the number





Crystal structure

Planes in the crystal

A family of lattice planes are written (hkl), and denote the family of planes that intercepts the three points:

$$\frac{\vec{a}_1}{h}, \frac{\vec{a}_2}{k}, \frac{\vec{a}_3}{l}$$

If one of the indices is zero, it means that the planes do not intersect that axis (1/0 = infinity)

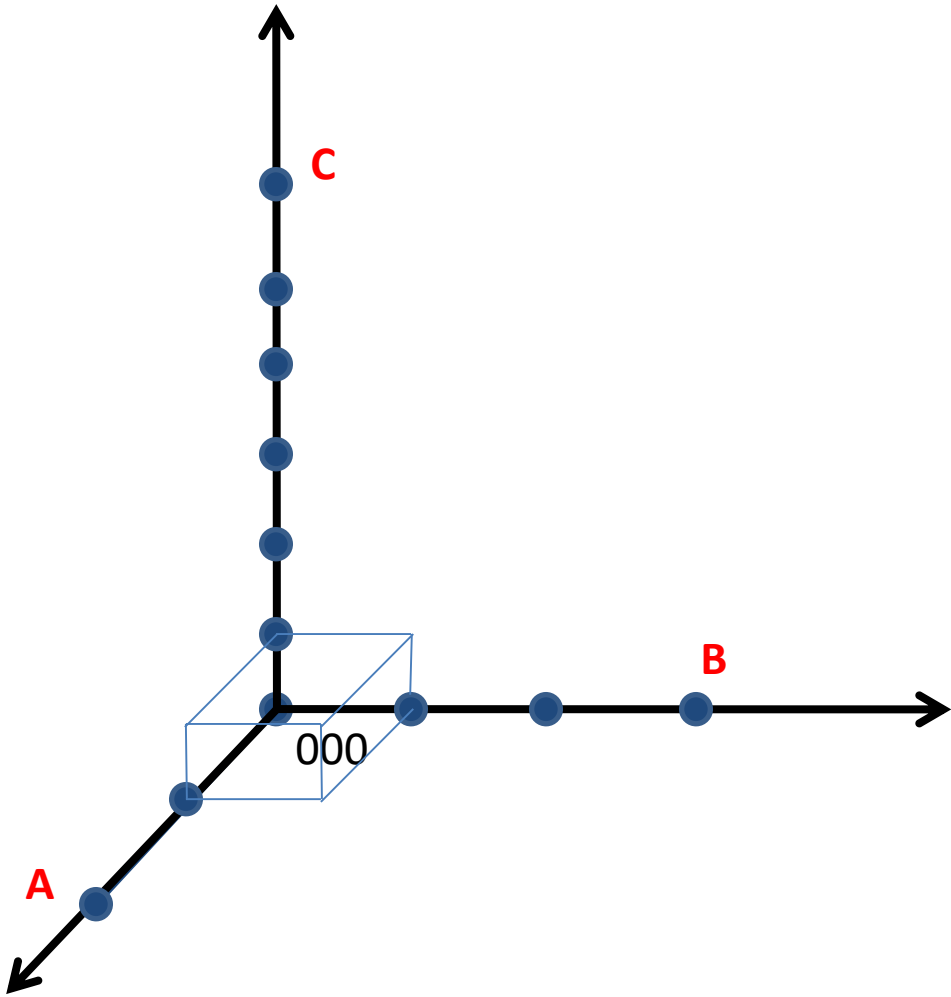
Also: the family of planes orthogonal to:

$$h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3$$

Where $\vec{g}_1$, $\vec{g}_2$, $\vec{g}_3$ are reciprocal lattice vectors

E.g.: A=2, B=3, C=6, plane $(3,2,1)$

(hkl) plane
$\{hkl\}$ set of planes
$[hkl]$ diections
$\langle hkl \rangle$ set of directions



Crystal structure

Planes in the crystal

A family of lattice planes are written (hkl), and denote the family of planes that intercepts the three points:

$$\frac{\vec{a}_1}{h}, \frac{\vec{a}_2}{k}, \frac{\vec{a}_3}{l}$$

If one of the indices is zero, it means that the planes do not intersect that axis (1/0 = infinity)

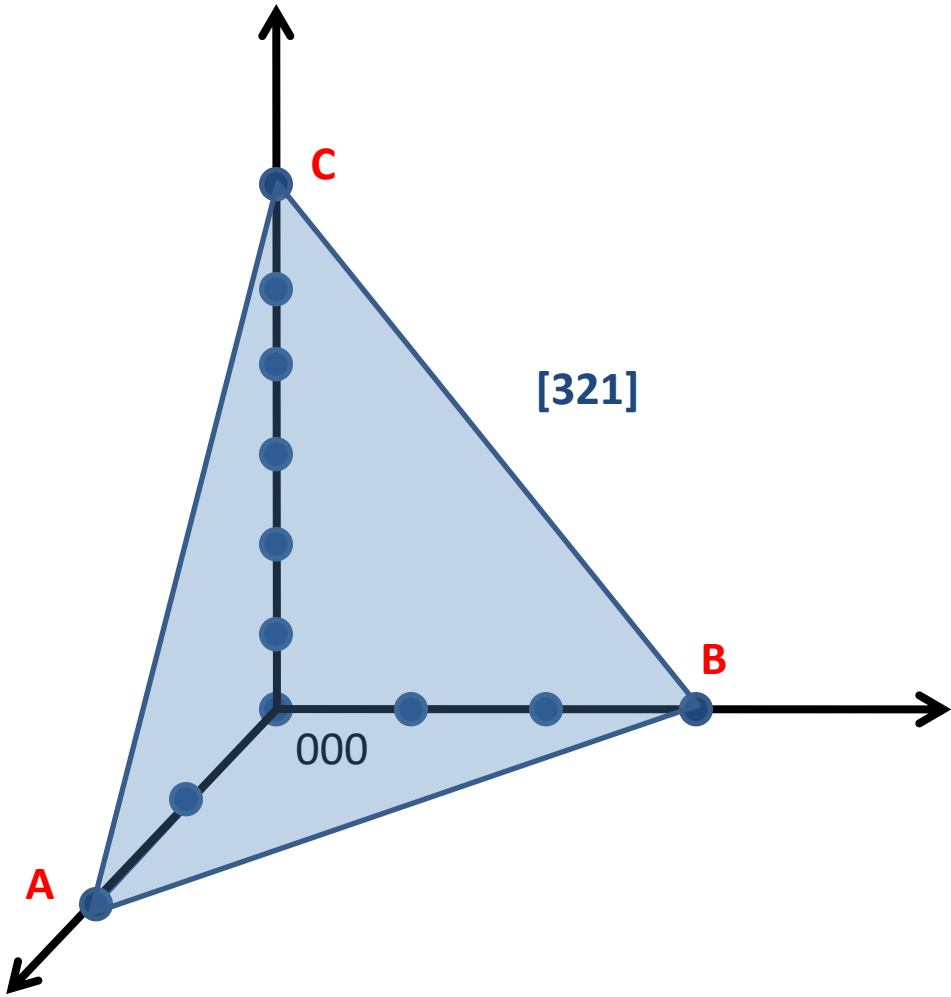
Also: the family of planes orthogonal to:

$$h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3$$

Where $\vec{g}_1$, $\vec{g}_2$, $\vec{g}_3$ are reciprocal lattice vectors

E.g.: A=2, B=3, C=6, plane $(3,2,1)$

(hkl) plane
$\{hkl\}$ set of planes
$[hkl]$ diections
$\langle hkl \rangle$ set of directions



Crystal structure

Planes in the crystal

A family of lattice planes are wr
denote the family of planes tha
three points: $\frac{\vec{a}_1}{h}, \frac{\vec{a}_2}{k}, \frac{\vec{a}_3}{l}$

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planes do not intersect that axi

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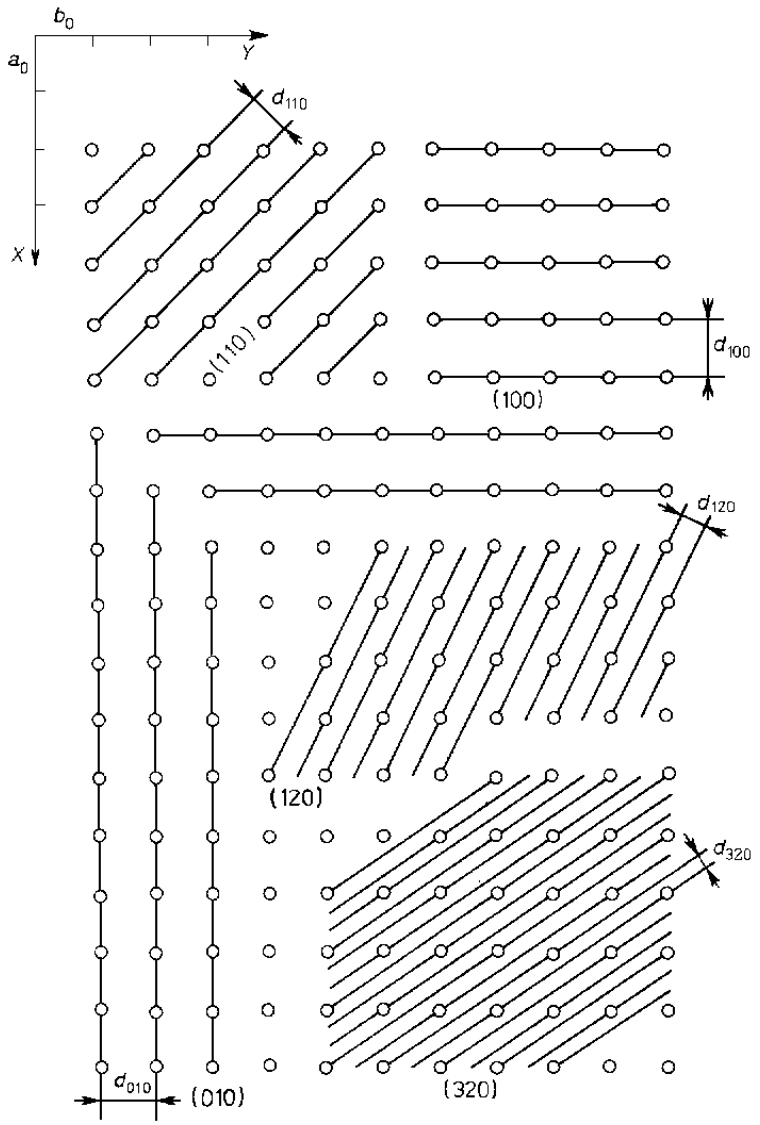
$h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3$
Where $\vec{g}_1$, $\vec{g}_2$, $\vec{g}_3$ are reciprocal

E.g.: A=2, B=3, C=6, plane (3,2

(hkl) plane
$\{hkl\}$ set of planes
$[hkl]$ diections
$\langle hkl \rangle$ set of directions



Rys. 1.27. Kilka rodzin płaszczyzn $(hk0)$ i ich odległości międzypłaszczyznowe d_{hk0} w rzucie na płaszczyznę (001) prostokątnej sieci przestrzennej

Crystal structure

Planes in the crystal

A family of lattice planes are written (hkl), and denote the family of planes that intercepts the three points:

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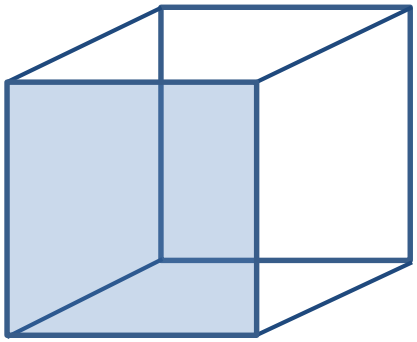
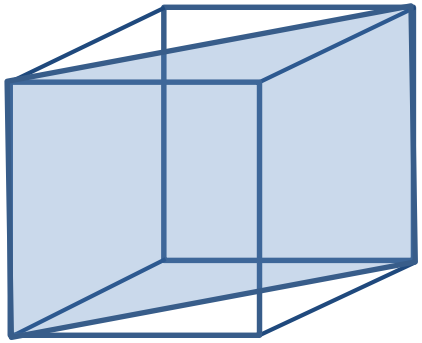
If one of the indices is zero, it means that the planes do not intersect that axis (1/0 = infinity)

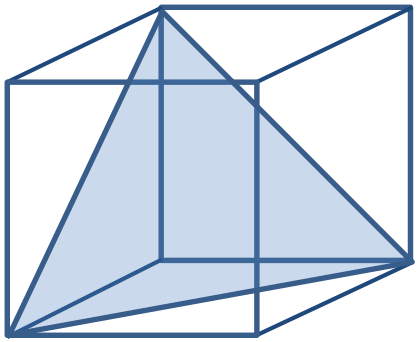
(100)



(110)



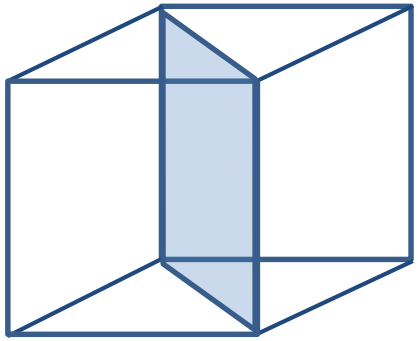
(111)



Crystal structure

Planes in the crystal

($\bar{1}10$)



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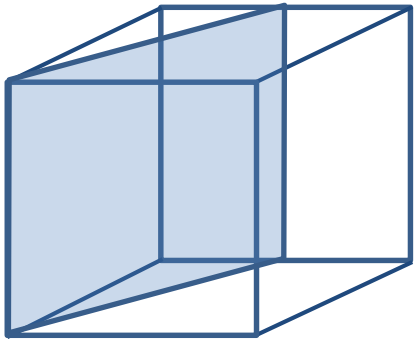

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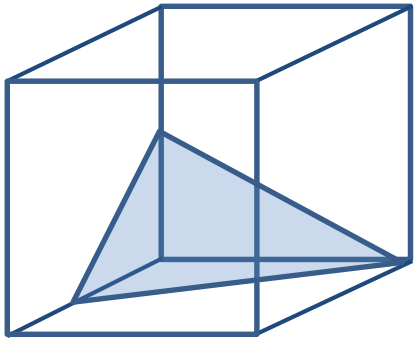

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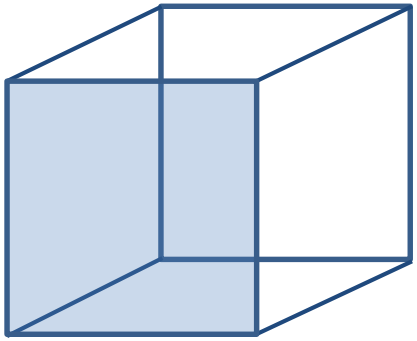

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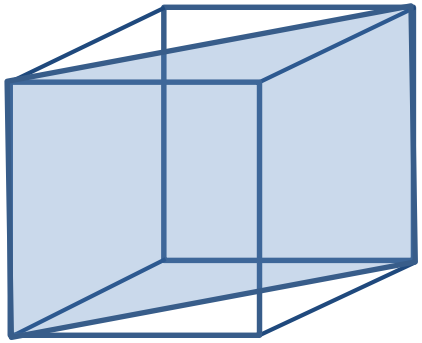

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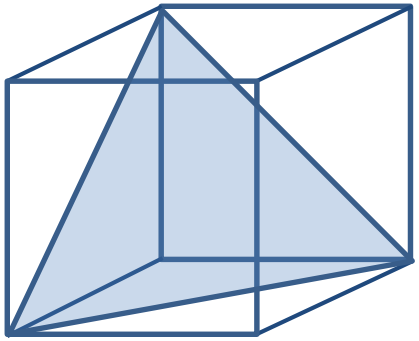
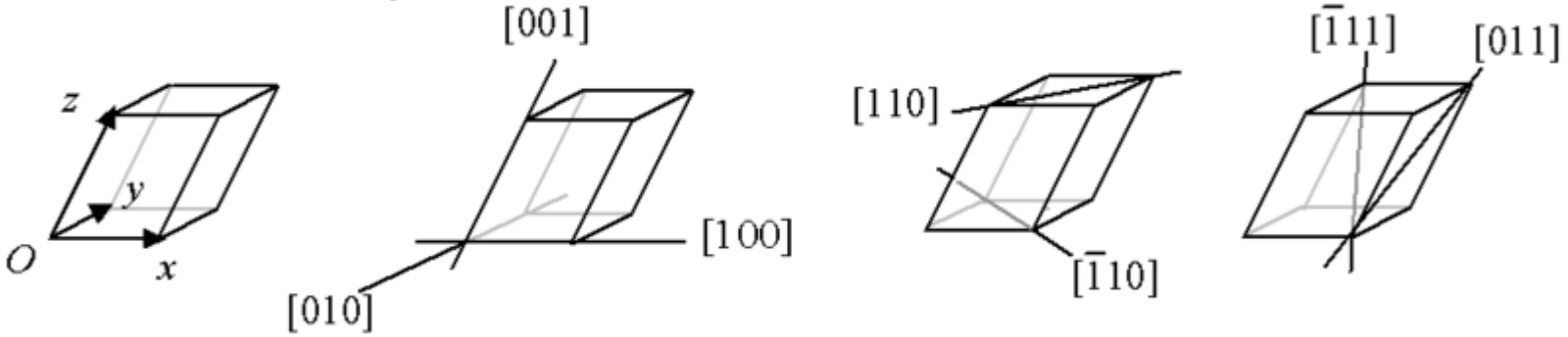
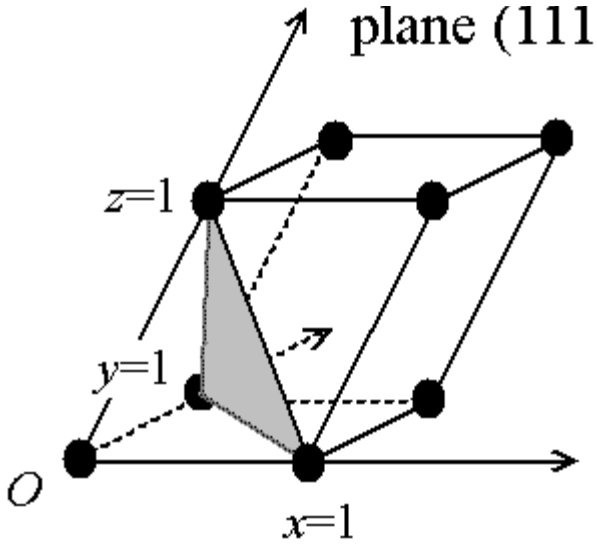
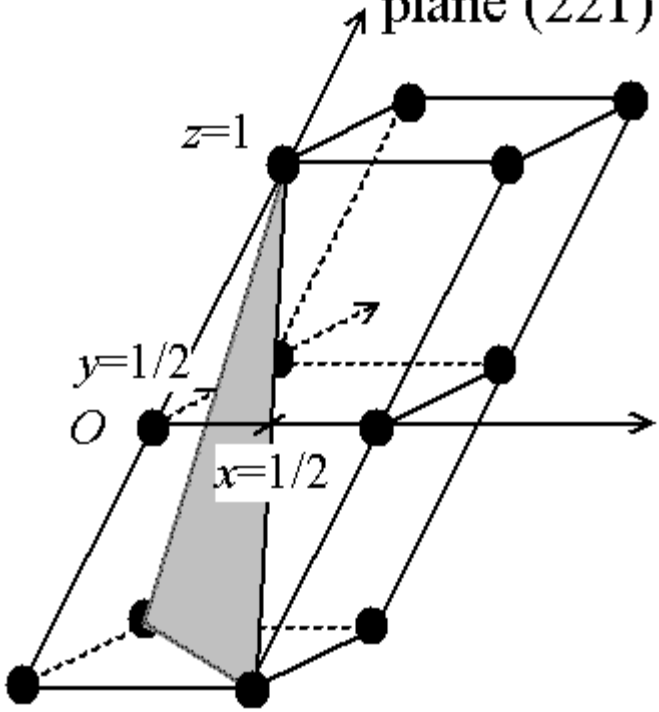


Crystal structure

Planes in the crystal







http://pl.wikipedia.org/wiki/Wskaźniki_Millera

Planes in the crystal

The crystalline structure is studied by means of the diffraction of photons, neutrons, electrons or other light particles