Functional Materials Introduction

Prof. dr. Matjaz Valant

University of Nova Gorica
Slovenia

Kaj se bomo učili (in naučili)

Tuesday 2.4.	Chemical bond, crystal structure	
Tuesday 9.4.	Structural defects Instructions for seminar (doc. Belec)	
Tuesday 16.4.	Diffusion, Synthesis	
Tuesday 23.4.	Synthesis, Phase equilibria	
Tuesday 7.5.	Seminar (doc. Belec)	
Tuesday 14.5.	Student presentations (doc. Belec)	
Tuesday 21.5.	Functional properties I	
Tuesday 28. 5.	Functional properties II	

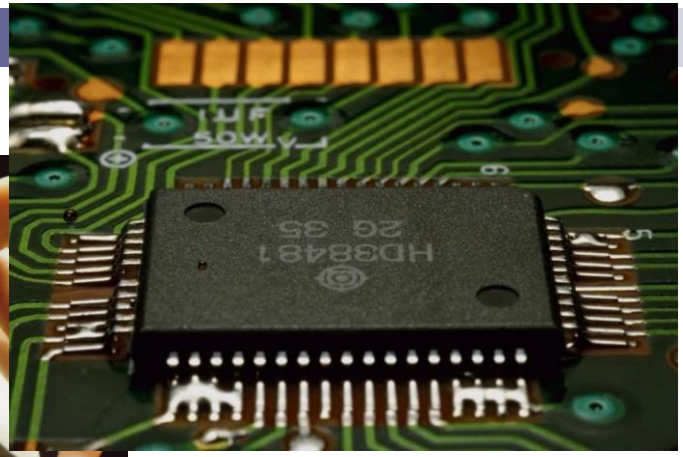
Literature:

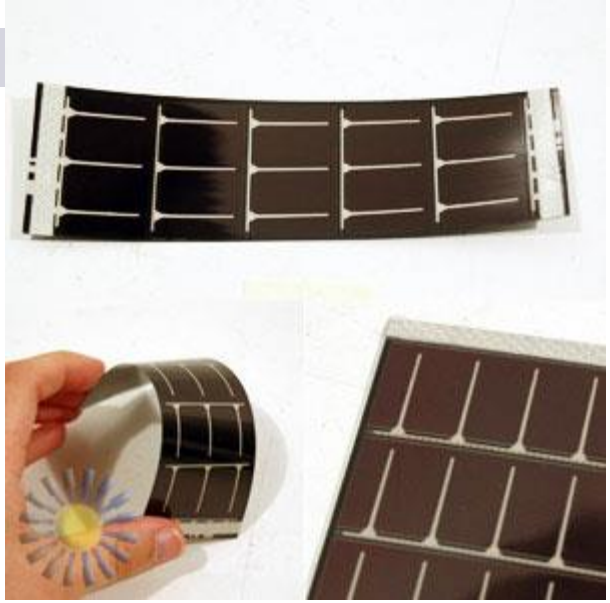
- D. Calister Jr., *Fundamentals of Materials Science and Engineering*
- D. Kolar: *Tehnična keramika 1* in *Tehnična keramika 2*
- S. Pejovnik, M. Gaberšček, *Uvod v znanost o materialih za inženirje*
- W.D. Kingery, H.K. Bowen D.R. Uhlmann, *Introduction to Ceramics*


MOTOROLA


Original Apple II


©GSP






USA
NASA


SMT

Criteria for sustainable materials

- Functionality
- Compatibility
- Reliability
- Durability
- Shaping capability
- Availability
- Economics
- **Environmental sustainability (of products and production)**

Basic groups of materials

Metals and alloys

- Fe and steels
- Al and alloys
- Cu and alloys
- Ti and alloys
- Ni and alloys

Basic groups of materials

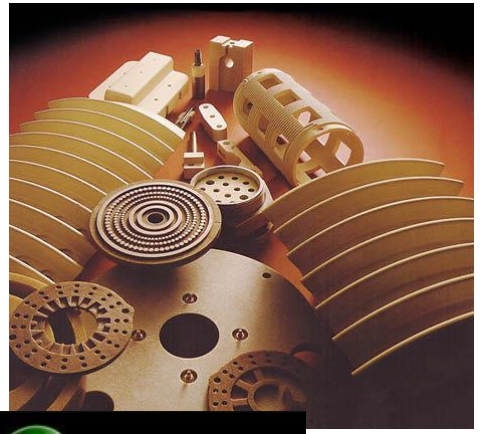
Polymers

- Polyethylene (PE)
- Polymethyl methacrylate (PMMA)
- nylon
- Polystyrene (PS)
- Polyurethane (PU)
- Polyvinyl chloride (PVC)
- acrylonitrile-butadiene-styrene (ABS)

Basic groups of materials

Ceramics, glass

- Corundum (Al_2O_3)
- Porcelain, clay (Al-silicates)
- Carborundum (SiC)
- Silicon nitride (Si_3N_4)
- Perovskite ($BaTiO_3$, PZT)
- Cement, concrete
- Glass

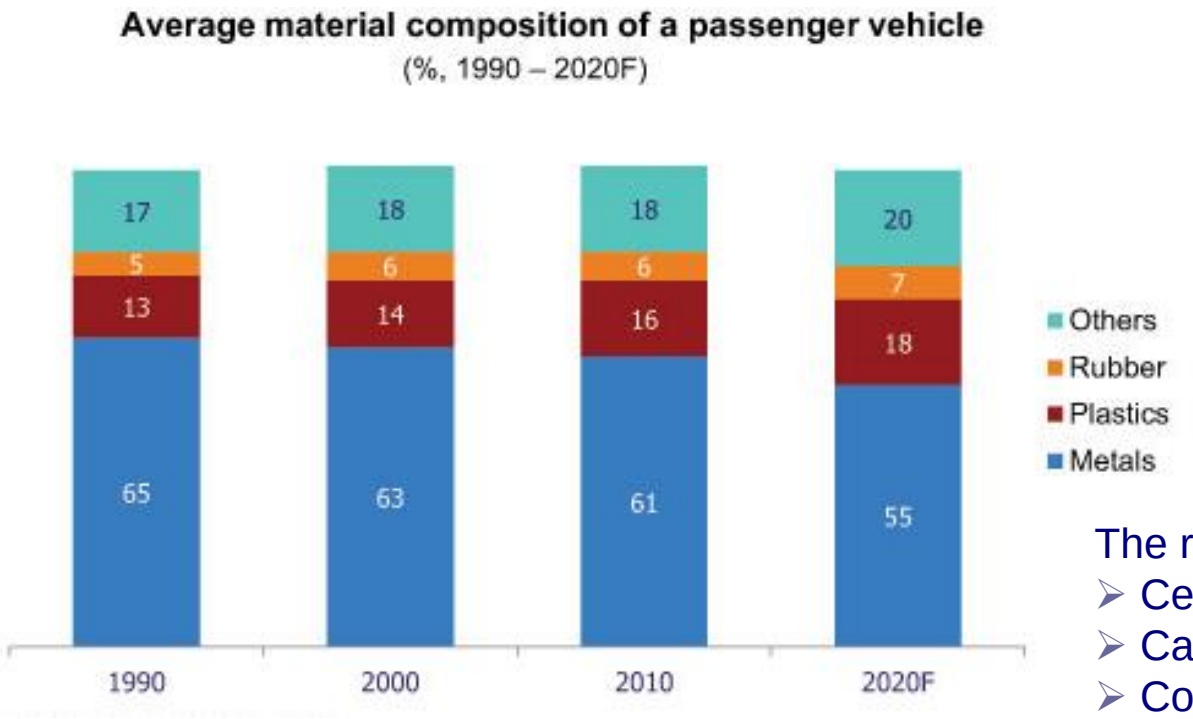


Basic groups of materials

Composites
- wood
- fiberglass
- C-C composites
- glass-ceramics
- cermet (WIDIA)
- polymers with fillers

Materials in industry

Competition among materials in automotive industry



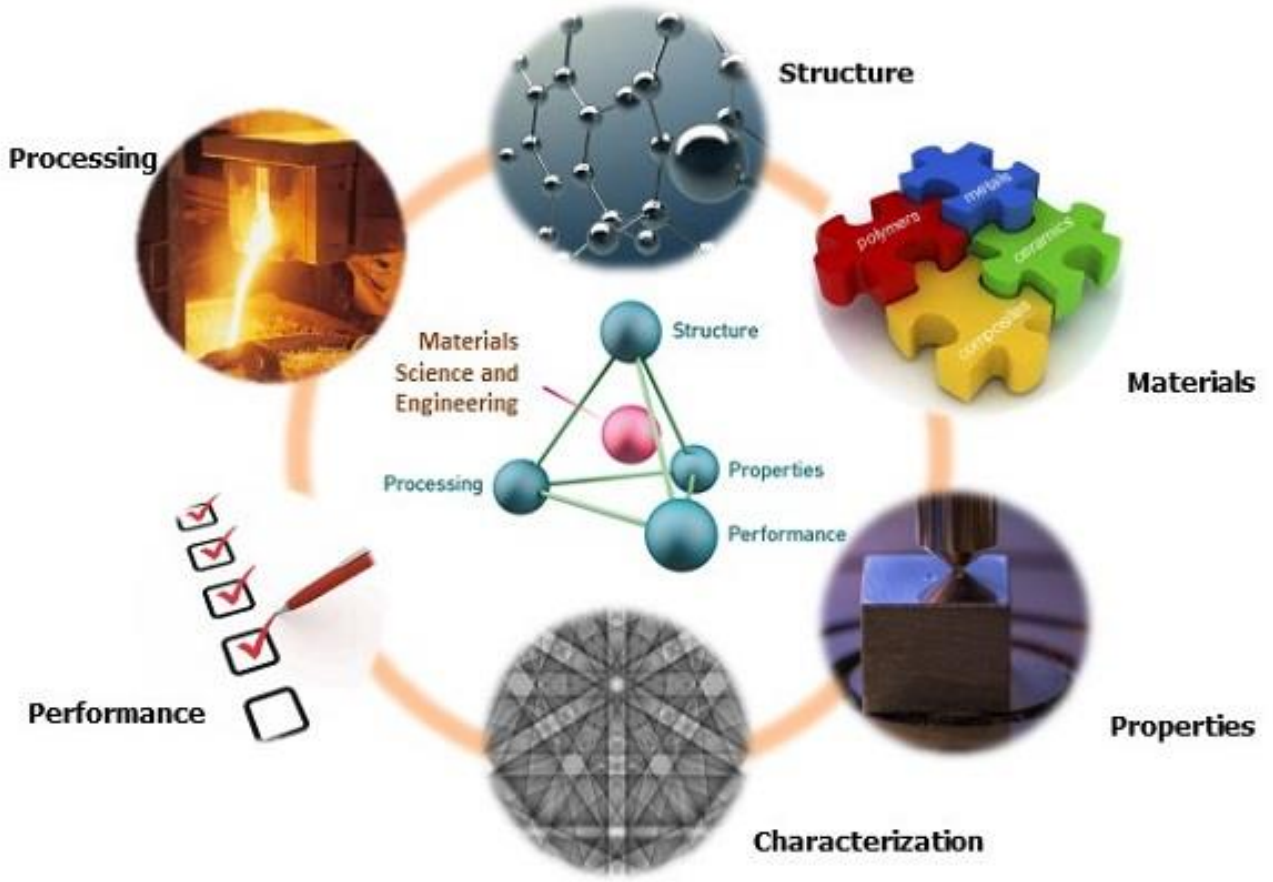
Annual increase in production

Steel	3.4%
Aluminum	8%
Polymers	18%

The rest up to 100%:

- Ceramics
- Carbon
- Composites

Development of functional materials



Functional materials

Chemical bond

Chemical bond

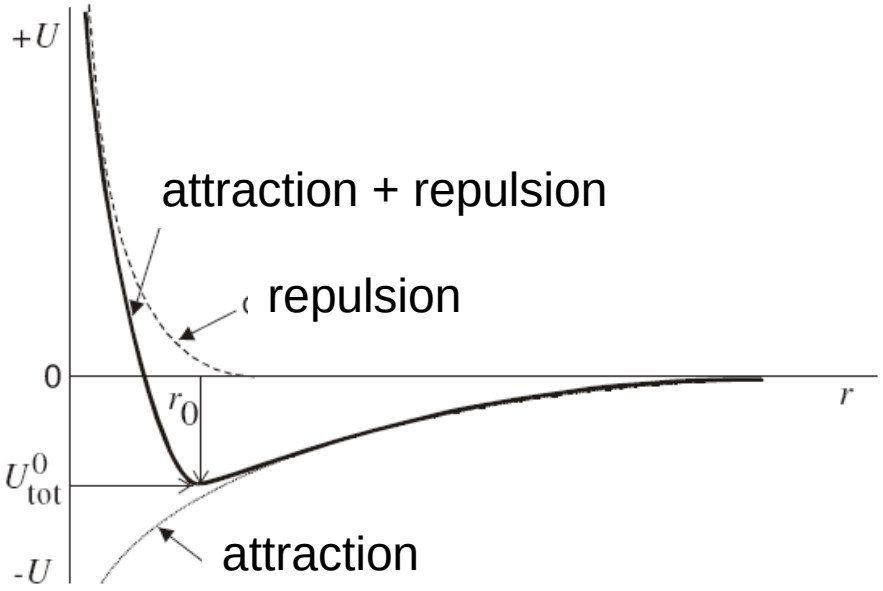
- Primary (strong)
  - Ionic
  - Covalent
  - Metal
- Secondary (weak) – van der Waals bonds
  - Ion-dipole
  - Dipole-dipole (hydrogen bond)
  - Ion-induced dipole
  - Induced dipole – induced dipole (dispersive forces)

Ionic bond between M^+ and X^-

Coulomb (electrostatic) attraction and repulsion act simultaneously

$$U = \frac{z_1 z_2 q^2}{4\pi\varepsilon_0 r} + \frac{b}{r^n}$$

z_1, z_2 … valence
q…electron charge 1.6×10^{-12}C
ε_o..vacuum permittivity
8.85×10^{-12}F/m
b, n…const.
r…distance between ions
U_o…bonding energy



U_o and shape of the potential define majority of material properties

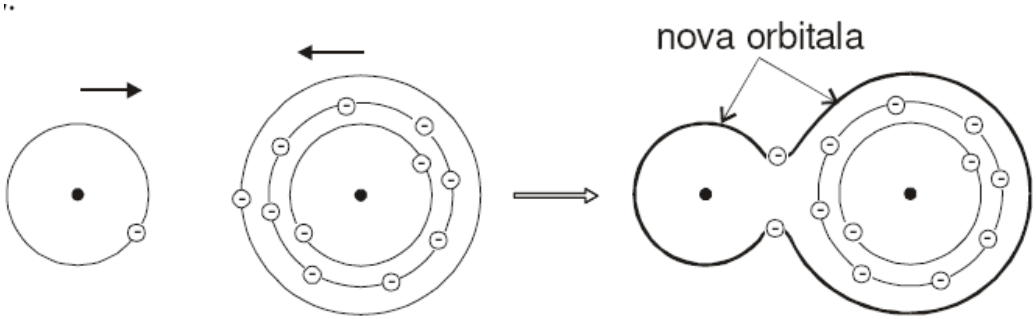
Melting point: low U_0 - gas,
high U_0 - solid

Shallow potential*:* *elastic material, high temp. expension coefficient*

Steep potential: *rigid material, low temp. expension coefficient*

Covalent bond

One ion does not donate electron to another. Valence electrons belong to both ions – formation of **molecular orbitals**



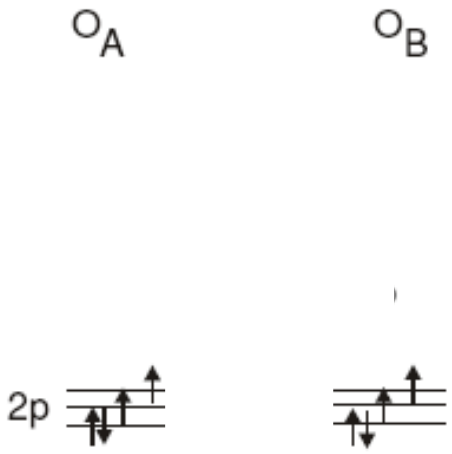
Polymers, diamand, Si, Ge, GaAs, SiC

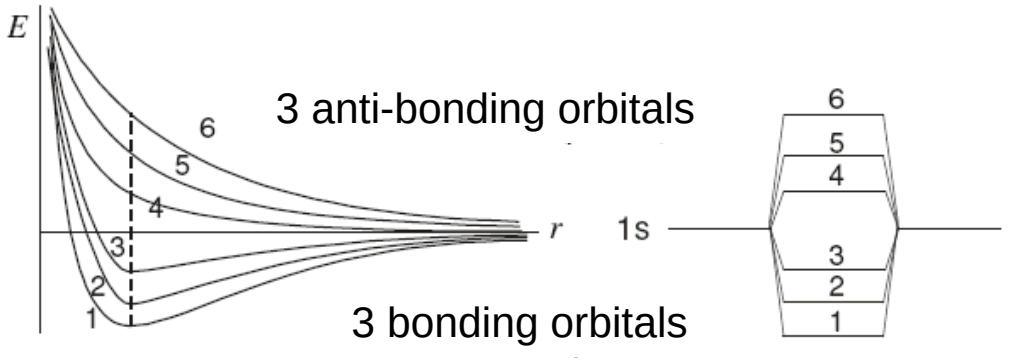
Mainly the covalent bond is stronger then ionic

Tališče diamanta: 3550^{o}C

Tališče NaCl: 801^{o}C

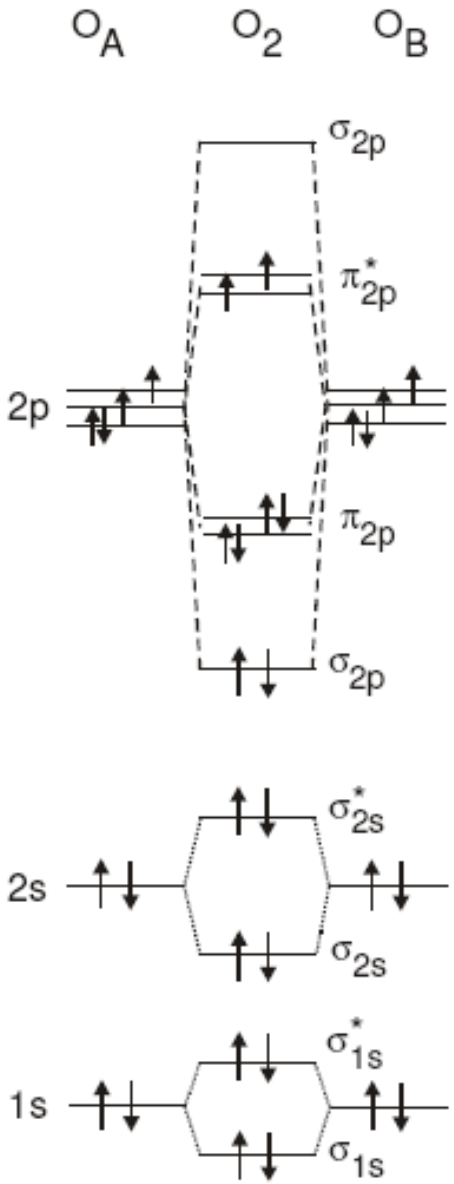
Formation of electron bands

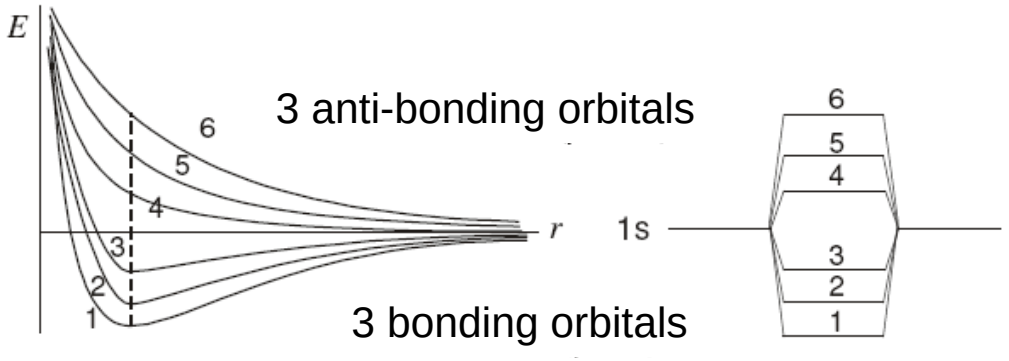




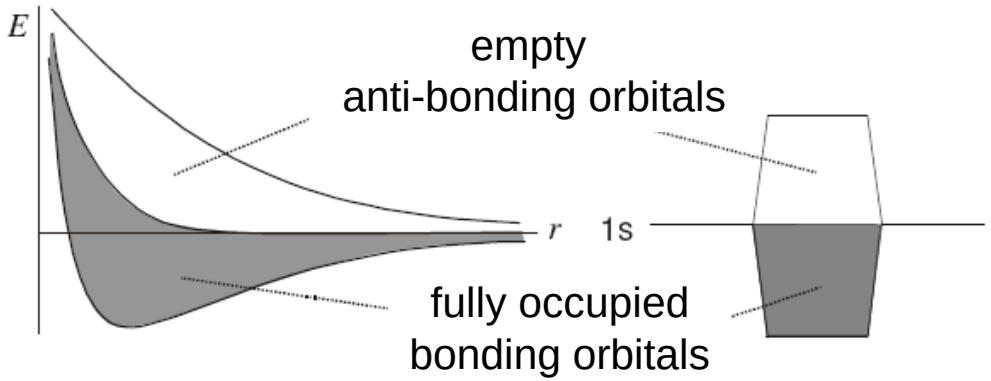
Interaction of 2s orbitals of 6 metal atoms

Formation of electron bands





Interaction of 2s orbitals of 6 metal atoms

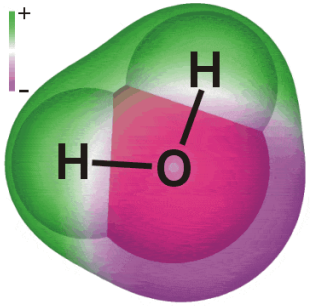


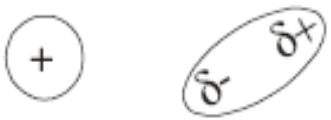
Interaction of 2s orbitals of large number of metal atoms (e.g. one mol) – high densty of orbitals forms electron bands

Secondary (van der Waalsove) bonds

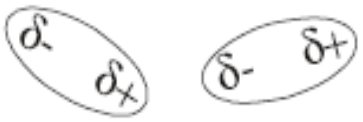
By their nature these bonds are electrostatic. Significantly weaker (10x) than primary bonds (0.1-0.5 eV/atom)

Dipoles are permanent or induced





ion- dipole



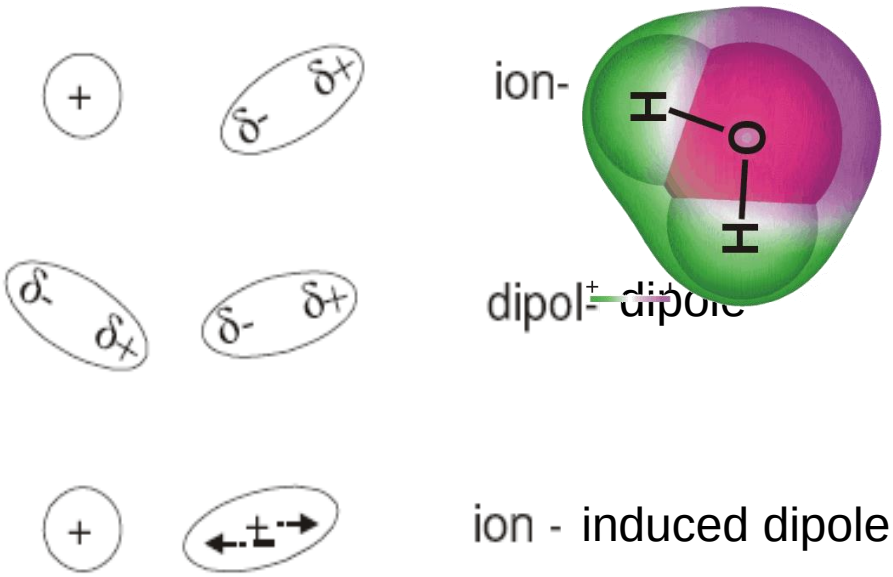
dipol- dipole

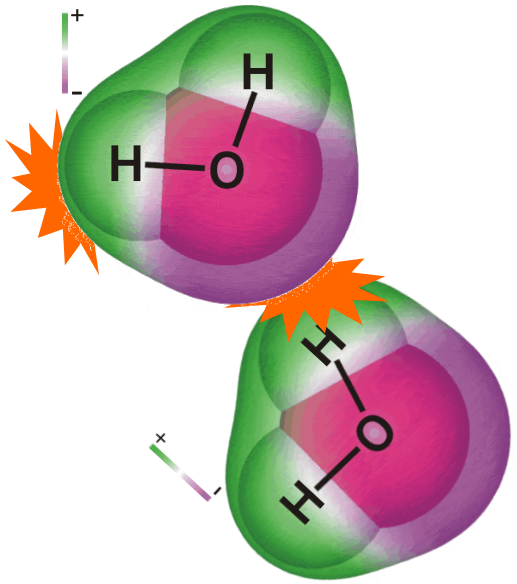
ion - induced dipole

Secondary (van der Waalsove) bonds

By their nature these bonds are electrostatic. Significantly weaker (10x) than primary bonds (0.1-0.5 eV/atom)

Dipoles are permanent or induced





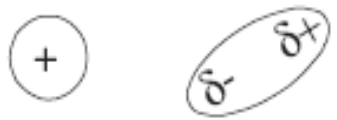
Hydrogen bond between molecules with covalently bound H on O, F, N

One of the strongest secondary bonds

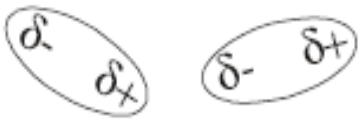
Secondary (van der Waalsove) bonds

By their nature these bonds are electrostatic. Significantly weaker (10x) than primary bonds (0.1-0.5 eV/atom)

Dipoles are permanent or induced

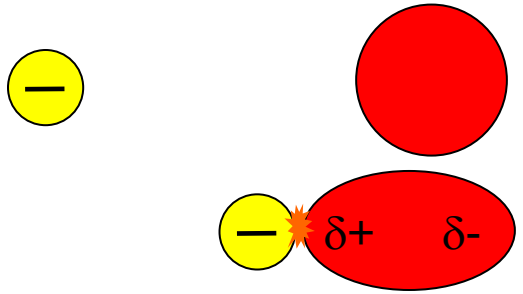


ion- dipole

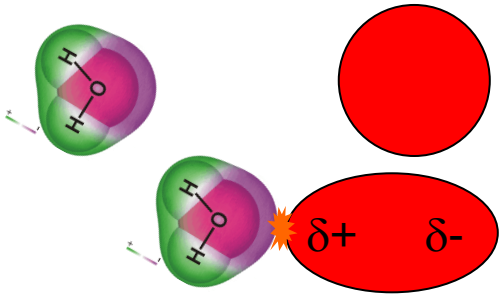


dipol- dipole

ion - induced dipole



Very weak bonds



Bound	Type	Energy kJ/mol	Melting point oC	Boiling point oC
C-C	covalent	346	3550	-
Si-O		452	1710	-
Si-Si		222	1410	2355
Na-F	ionic	477	902	
Na-Cl		408	801	1439
Na-Br		362	757	1393
Na-I		304	660	1300
Mg=O	ionic-double	377	2640	-
Li-Li	metal	105	180	1347
Fe-Fe		268	1535	2750
Cu-Cu		255	1083	2567
Ne-Ne	dispersion	2.1	-249	-246
Ar-Ar		7.7	-189	-186
HO...H	H- bond	~25	0	100

Functional materials

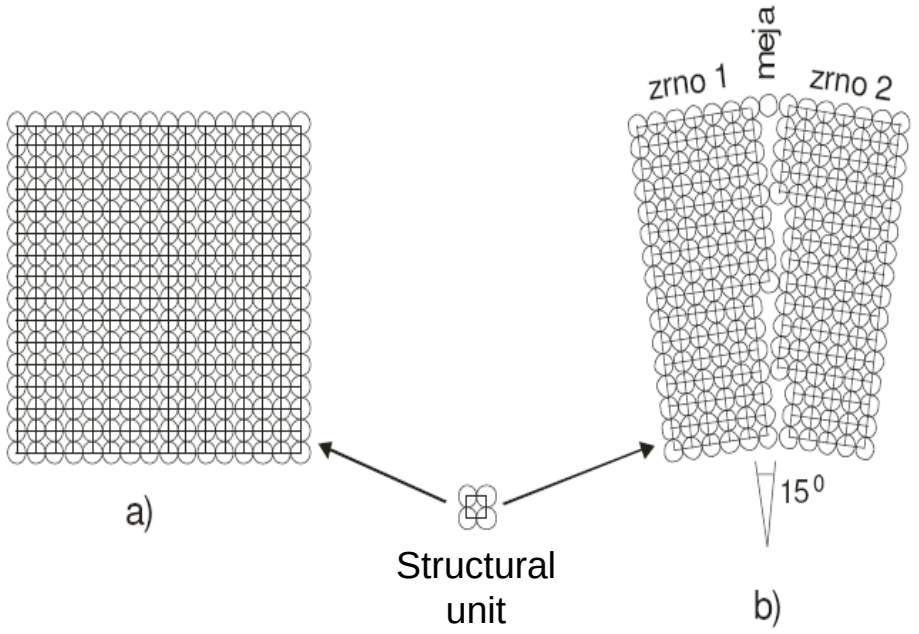
Structural defects

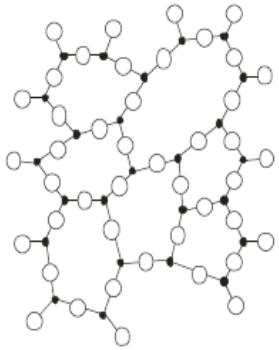
Basic types of structural ordering

•*Single crystals*
Long-range order, complete translation symmetry

•*Polycrystalline material*
Long-range order in constrain domains – **grains**,
Orientational mismatch between the grains – **grain boundaries**

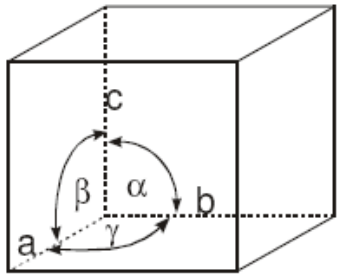
•*Amorphous material*
Supercooled liquids, no longe-range order, possible short-range order





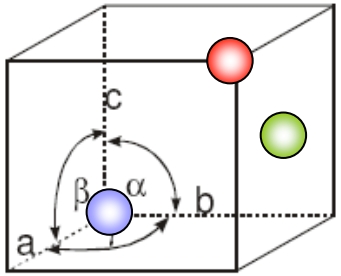
Basic concepts of crystallography

Translational movement of the unit cell fills the whole space - the unit cell must have the shape of a parallelepiped



a, b, c … unit cell parameters (edges)
α, β, γ … unit cell angles

The position of the item inside the unit cell is described by point coordinates - point coordinates are relative - written as the proportion of the edge of the unit cell

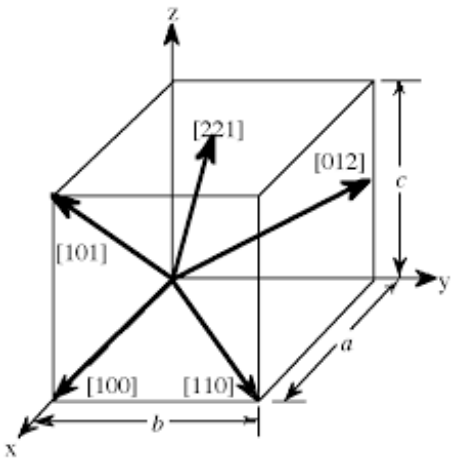


(0,0,0)

(½,1,½)

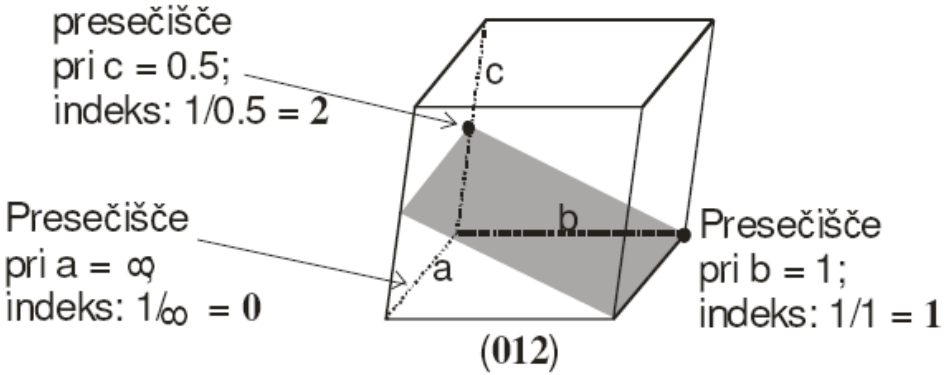
(1,1,1)

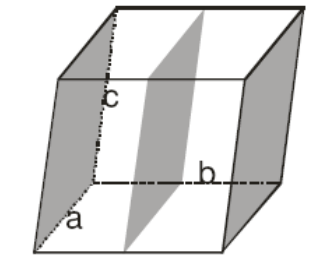
Crystallographic directions: We define them as vectors with a starting point in point (0,0,0) and a certain grid position, which is written with a set of three integers in square brackets

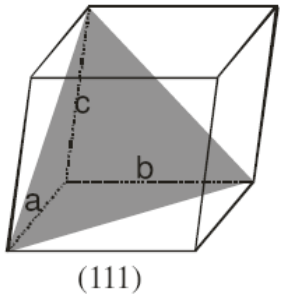


(x,y,z) = (1/a, 1/b, 1/c)

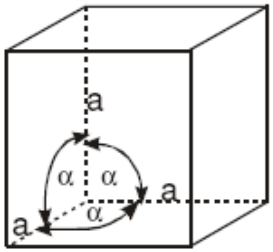
Crystallographic planes: Crystallographic planes are defined by the intersection with the edges of the unit cell. We write them in the form of Miller indices in parentheses



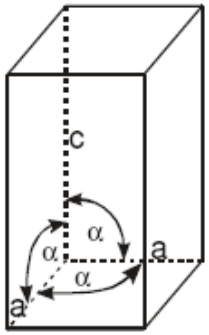




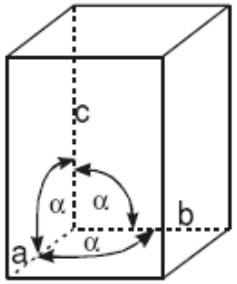
Crystal systems - syngonia



kubična: a = b= c, $\alpha = \beta = \gamma = 90^o$



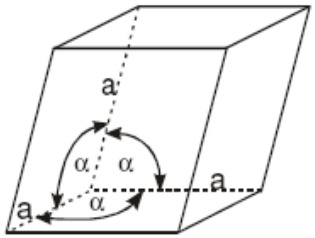
tetragonalna: a = b≠ c, $\alpha = \beta = \gamma = 90^o$



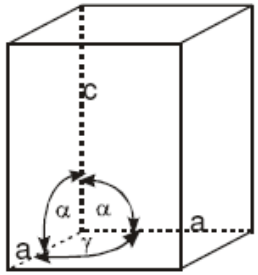
ortorombska: a ≠ b≠ c, $\alpha = \beta = \gamma = 90^o$

Lower symmetry

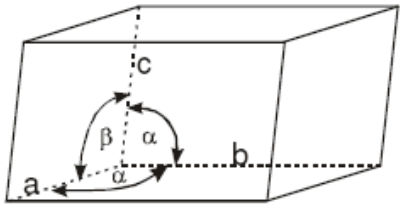
Kristalni sistemi - singonije



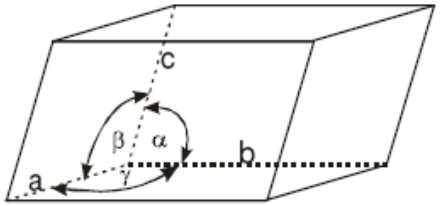
romboedrična: $a = b = c$, $\alpha = \beta = \gamma \neq 90^o$



heksagonalna: $a = b \neq c$, $\alpha = \beta = 90^o$, $\gamma = 120^o$



monoklinska: $a \neq b \neq c$, $\alpha = \gamma = 90^o \neq \beta$



triklinska: $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^o$

Lower symmetry

Close packed Structures

Most of metals with the same kind of atoms (Pb, Fe, Ni...) crystallize in one of the three unit cells:

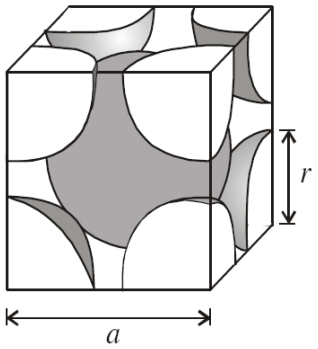
- body centered cubic (bcc)
- face centered cubic (fcc – closed packed)
- hexagonal close packed (hcp)

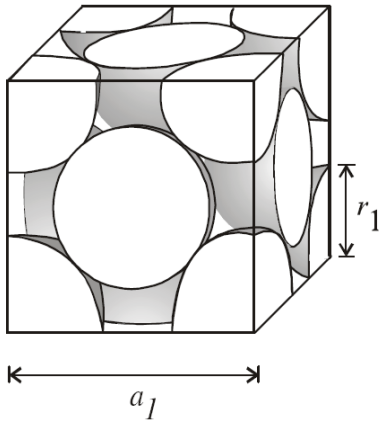
$$d = a\sqrt{3} = 4r$$

$$V_{osn.celica} = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3$$

$$V_{atomov} = 2\frac{4\pi r^3}{3}$$

$$x = \frac{V_{atomov}}{V_{osn.celice}} = \frac{3\pi\sqrt{3}}{24} = 0{,}6802$$





x=0,7405

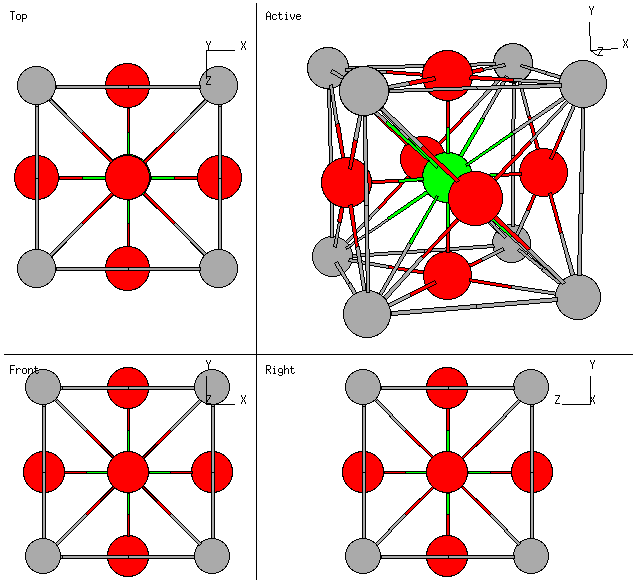
Calculation of theoretical density

$$\rho = \frac{\textit{mass of atoms in unit cell}}{\textit{unit cell volume}}$$

$BaTiO_3$

Ba…137,33 g/mol
Ti… 47,90 g/mol
O…16,00 g/mol

ρ=6.035 g/cm^3



Unit cell volume
a=b=3,99Å = 3,99·10^{-10} m
c=4,03Å = 4,03 ·10^{-10} m

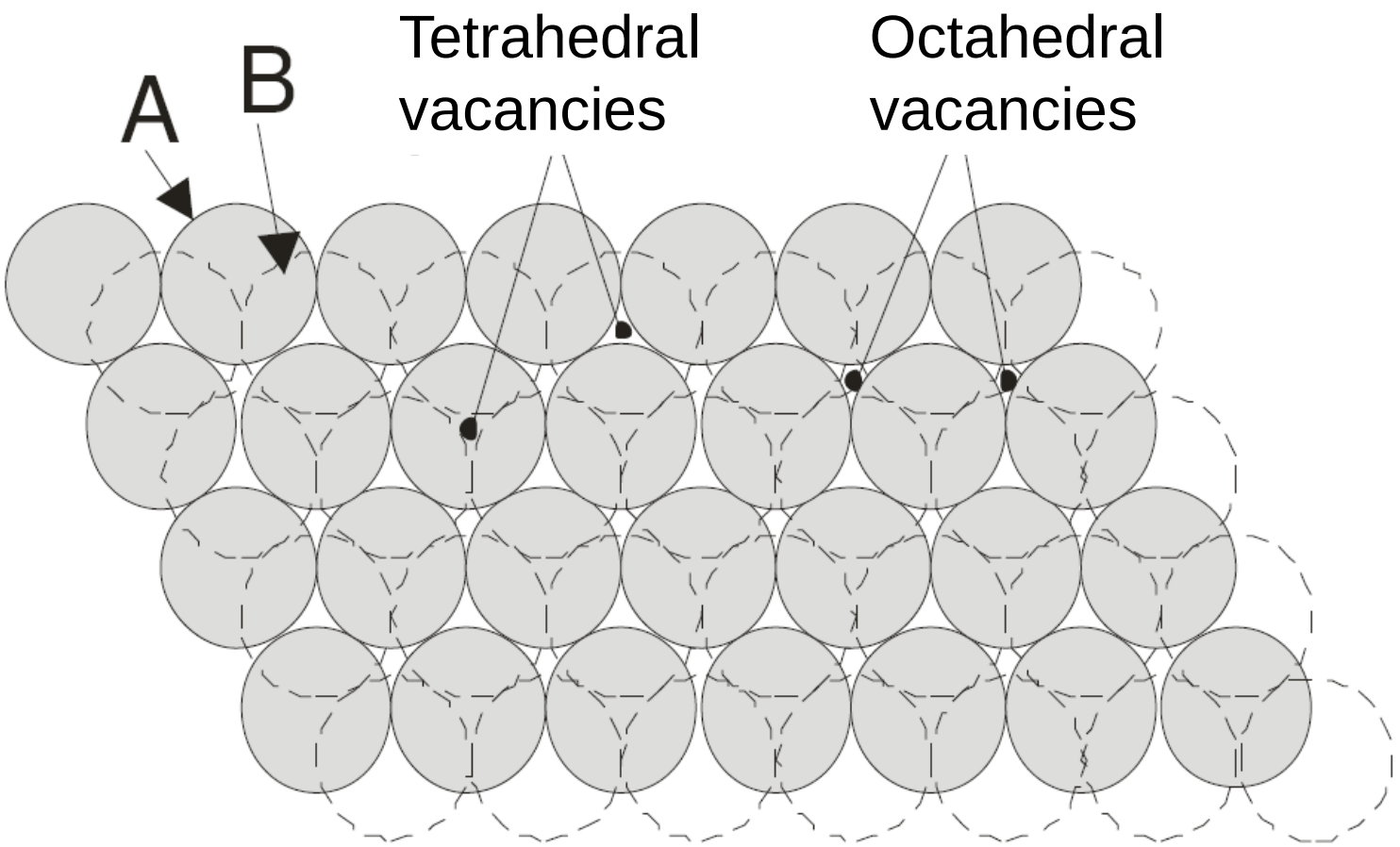
Volume = 64,158 ·10^{-30} m^3

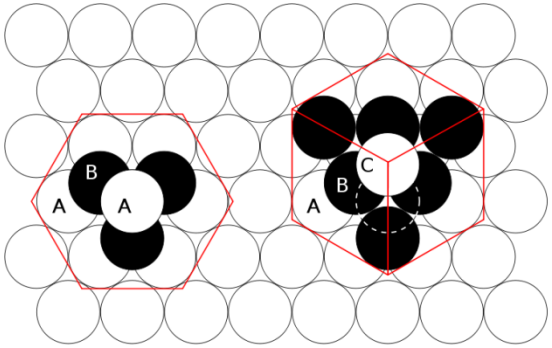
6 x 1/2 oxygen ions=	3O
8 x 1/8 Ba ions =	1Ba
1 x 1 Ti ion =	1Ti

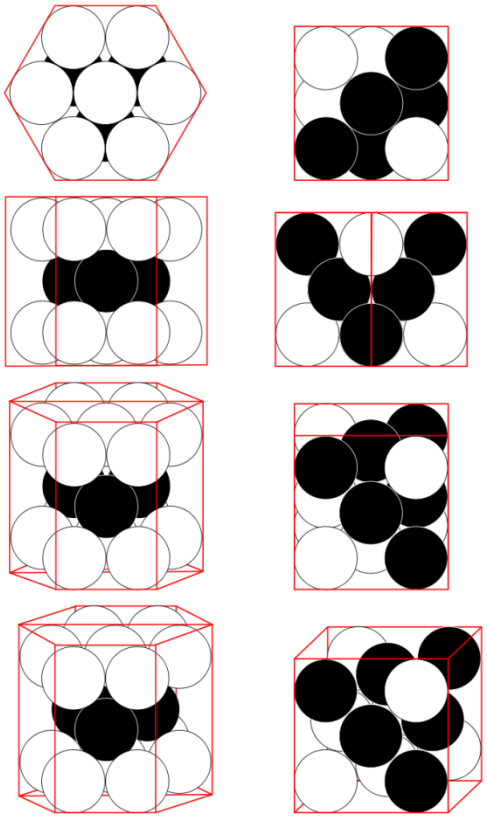
Mass of all ions m_i= 233,23g / N_A

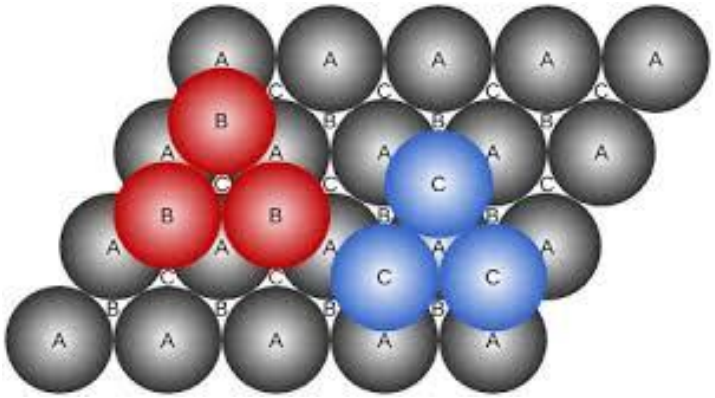
$\rho = m_i/(N_A V_{osn.c.})$
ρ=233,23 g / (6.023· 64,158 ·10^{-7} m^3)
ρ=6035604 g/m^3
ρ=6,035 g/cm^3

Close packed structures









Two simple regular lattices that achieve the highest density of atom packing.

- **cubic close packed** - also called Face-centered cubic (**FCC**)
- **hexagonal close-packed** (**HCP**),

FCC and HCP have the same space filling factor

Complex crystal structures

Oxides, nitrides, carbides, chalcogenides, intermetallic compounds

They are composed of different species (ions or atoms), which makes the crystal structures more complex

Three major factors that determine the type of a crystal structure:

- **Electronegativity:** parameter that tells how strong the species attract the electron. Larger the difference in electronegativity between the species, more ionic the bond will be.
- **Charge**

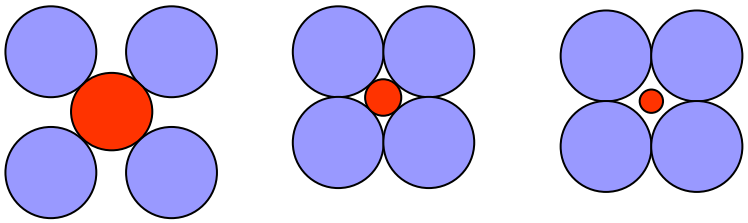
  Electroneutrality condition determines the stoichiometry of the unit cell and also the charge distribution (ion position) within the cell.

- **Ionic radius**

  Determines the coordination number, cell geometry and ion position

Coordination number (CN) is a number of closest neighbors

CN=4

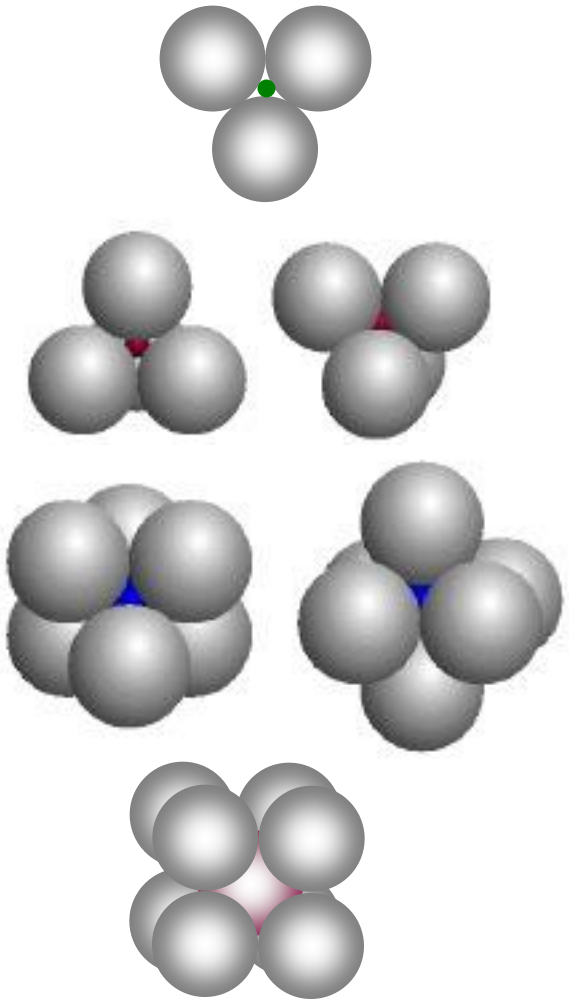


less stable stable least stable

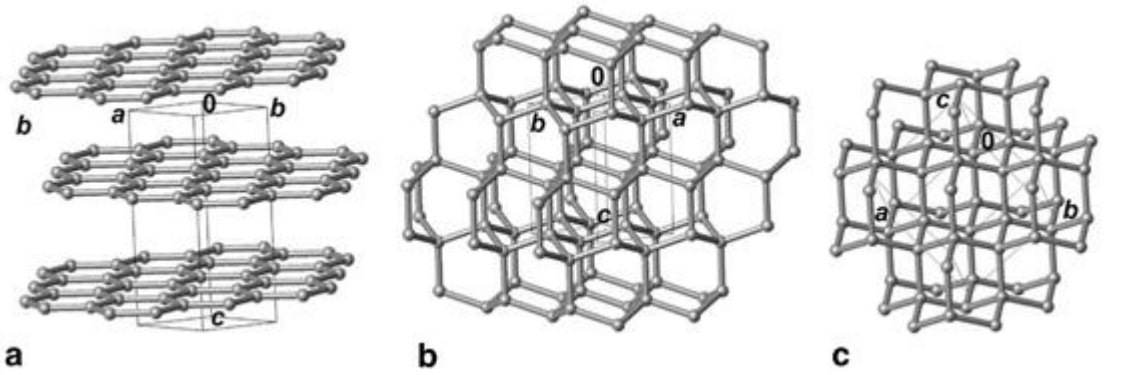
Radius of an ideal interstitial ion with CN=4

$$r_{ideal} = \frac{\sqrt{2}-1}{2} = 0{,}207$$

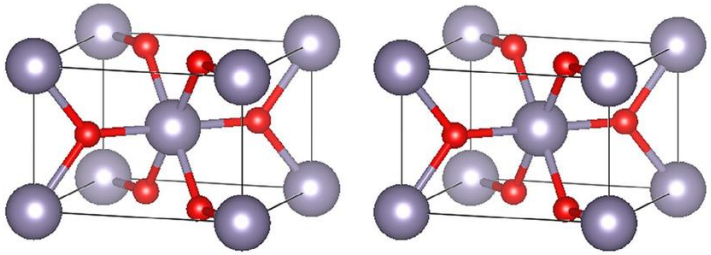
CN	r_a/r_b
2	<0.155
3	0.155-0.255
4	0.255-0.414
6	0.414-0.732
8	0.732-1.0



Some common structural types

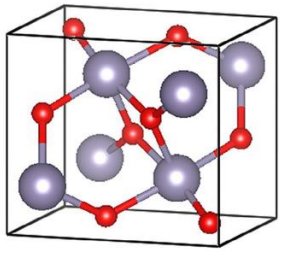


graphite **a**,
hexagonal diamond (lonsdalite) **b**
cubic diamond **c**,

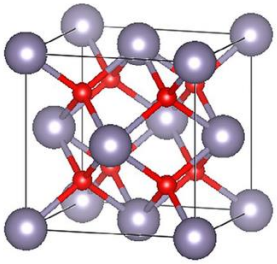


a) *Rutile -type*

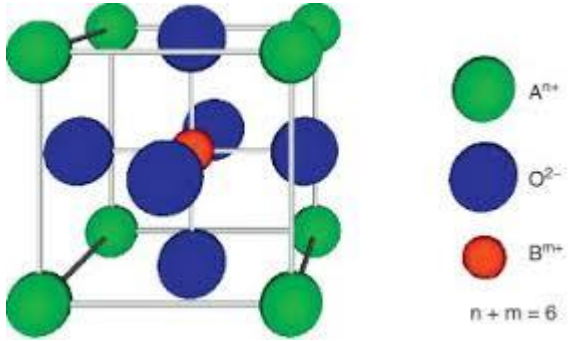
b) *$CaCl_2$ -type*



c) *α-PbO_2 -type*



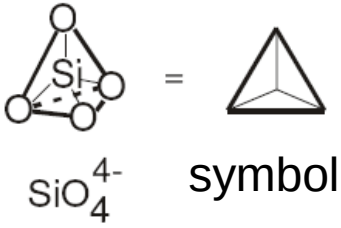
d) *Fluorite -type*



Silicates

$r(Si^{4+}) / r(O^{2-}) = 0.039nm / 0.132nm = 0.295$

Si^{4+} is tetrahedrally coordinated. The tetrahedron is the basic structural element of silicates Tetrahedrons can connect over corners or edges.

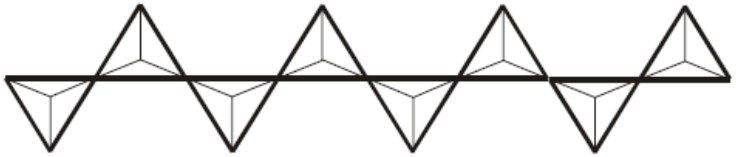


disilicate

$Si_2O_7^{6-}$

olivine and forsterite

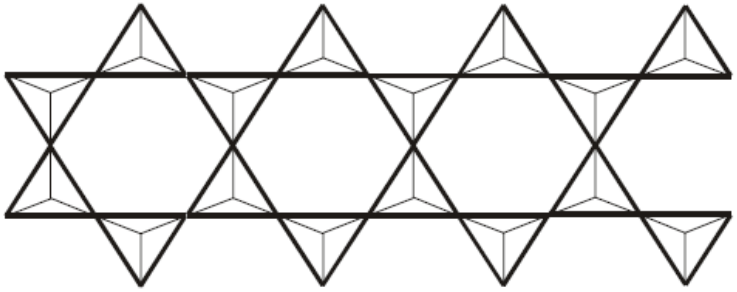
chain



$(Si_2O_6^{4-})_n$

pyroxenes

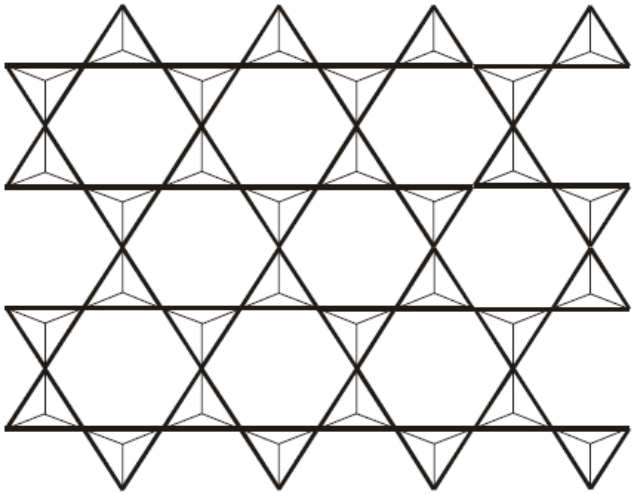
double chain



$(Si_4O_{11}^{6-})_n$

amphiboles

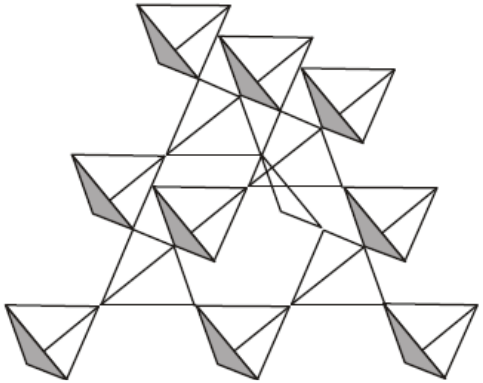
plastovit silikat



$(Si_2O_5^{2-})_n$

- clays - kaolin
- talc
- muscovite

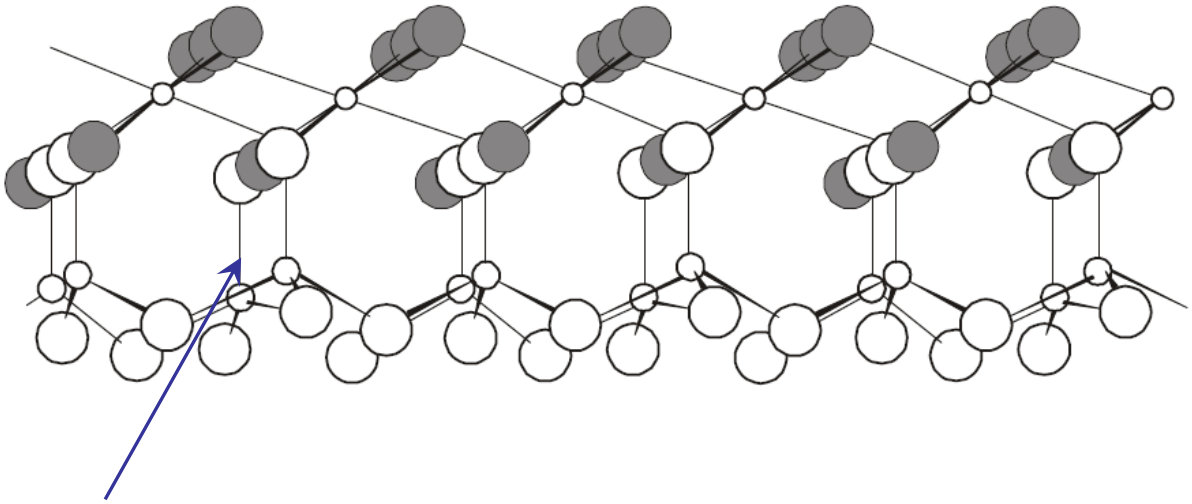
tridimenzionalni silikat



$(SiO_2)_n$

- feldspares
- SiO_2 polymorphs (quartz, tridymite, cristobalite)

Kaolinite clays



OH^-

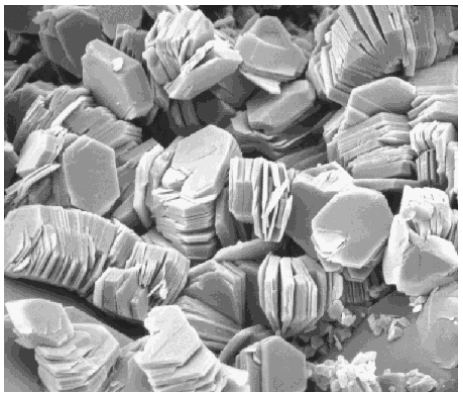
Al^{3+}

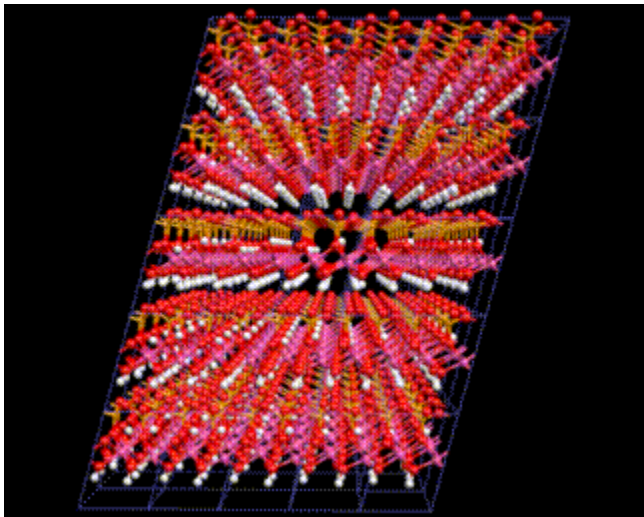
O^{2-}, 2 OH^-

Si^{4+}

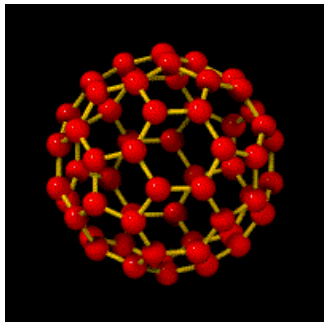
O^{2-}

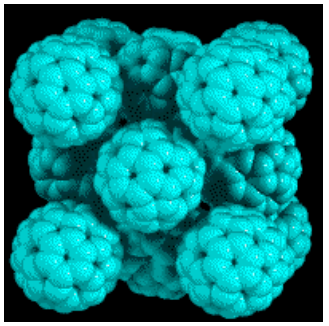
Hydrogen bond – the reason for plasticity of the clays





Carbon





Most common modifications of carbon

- Soot (amorphous carbon) – pigment, vulcanisation, printing
- Graphite

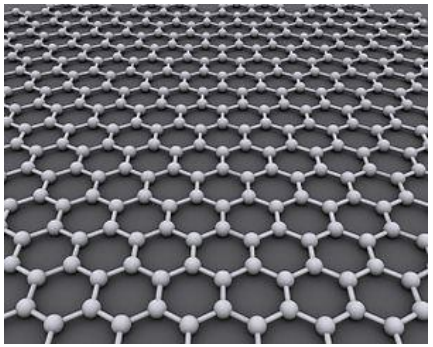
  moderator v nuclear technology, electrographite, sealing, thermal isolator
- Diamond

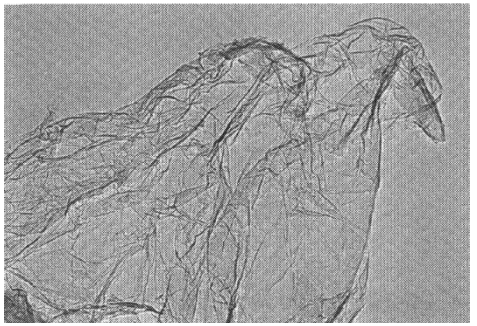
  abrasive, cutting tools, spintronic material
- Fulerenes (e.g. C_{60})

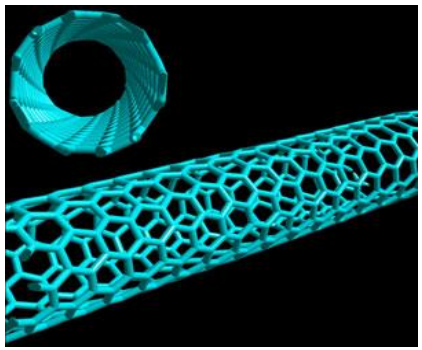
  lubricant, drug delivery
- Graphene

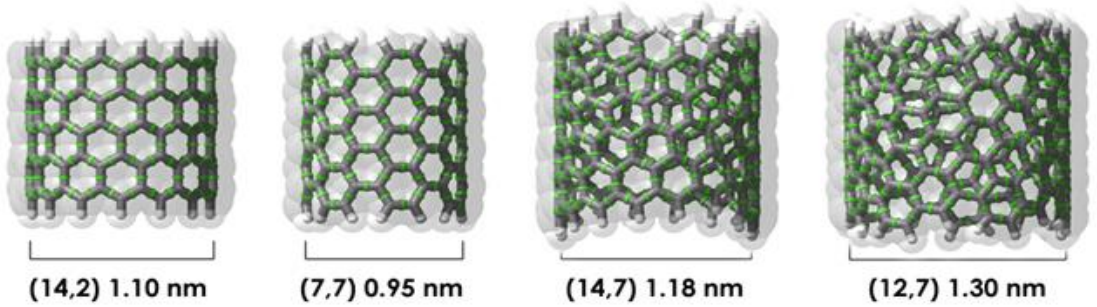
  electronics
- Carbon nanotubes

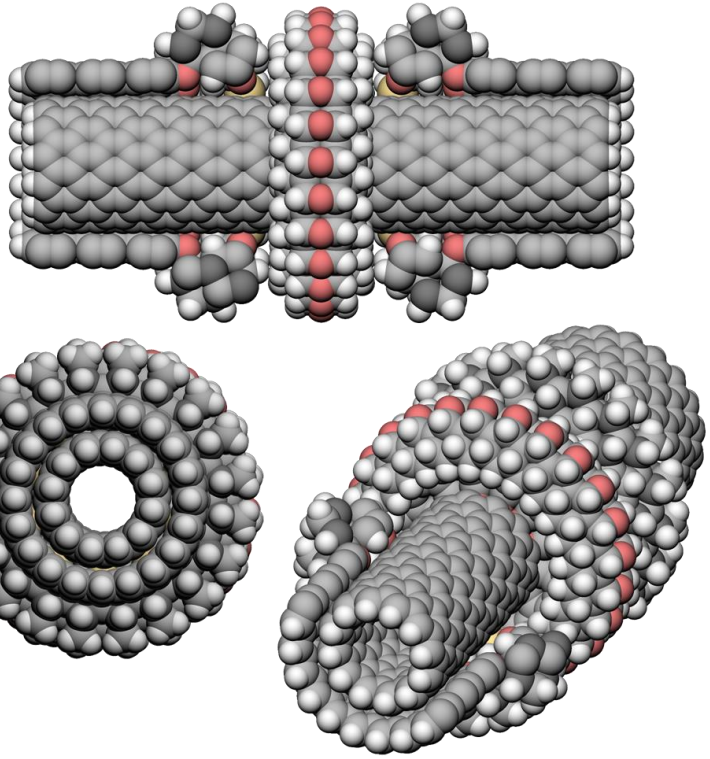
  structural reinforcement,
  clinical aplications

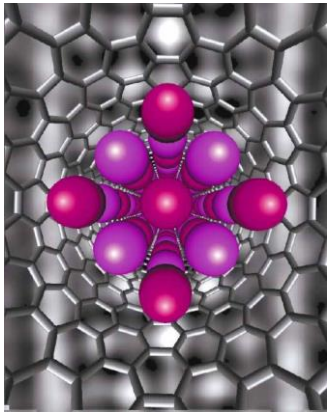


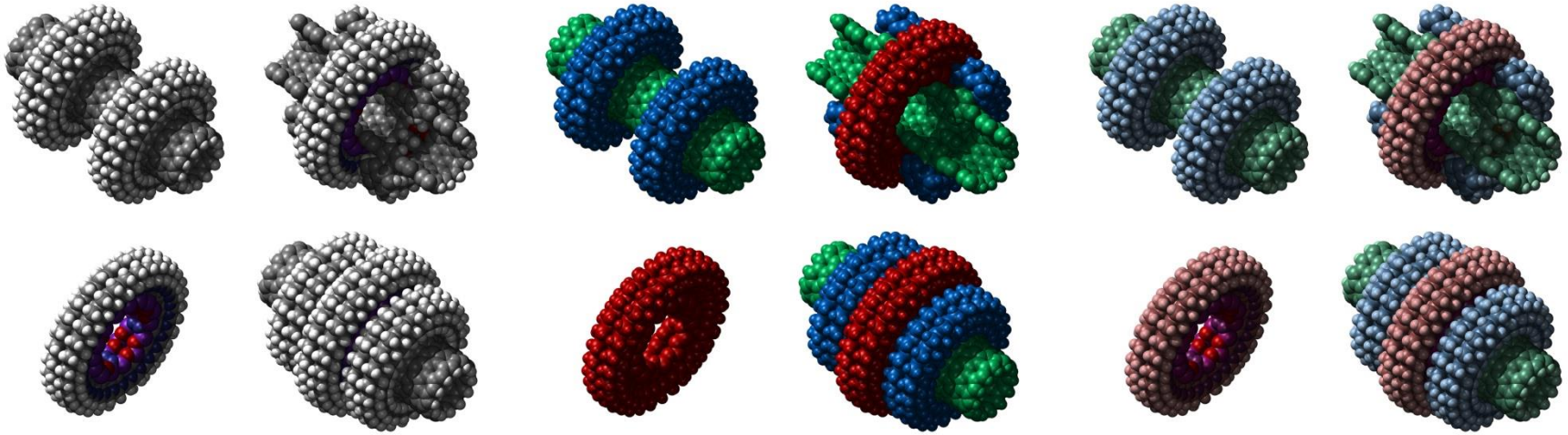












Structural defects

People are like crystals. It is the defects in them that make them interesting. Sir F. Charles Frank

Perfection has one grave defect : it is apt to be dull

W. Somerset Maugham

Because of the defects, materials possess special new properties

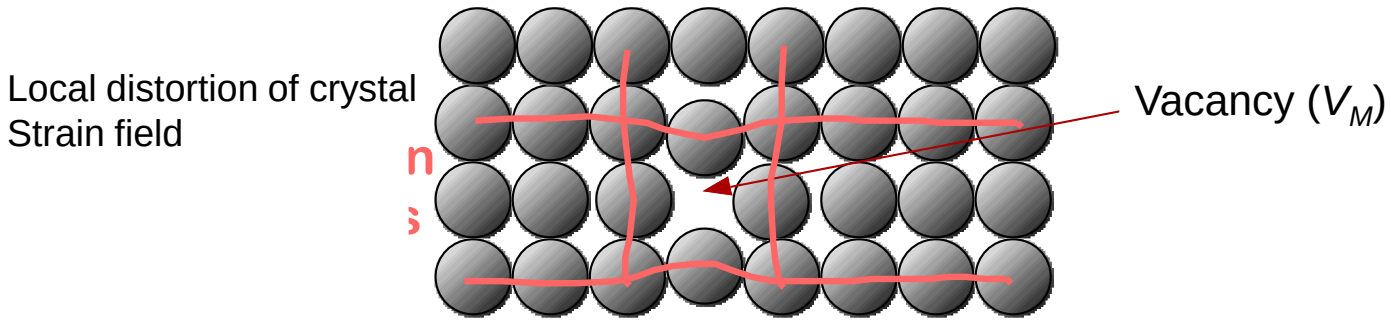
The new properties can be technoogicaly useful or damaging

- Point defects (vacancies and interstitial atoms)
  - Intrinsic – not involving other kind of atoms
  - Extrinsic – due to presence of other atoms
- Multidimensional defects
  - Line defects (dislocations)
  - Planar defects (grain boundaries, stacking faults, slip planes)

Point defects - intrinsic

Vacancies

- Atom is removed – vacancy in a regular crystal structure
- according to Kroger-Vink notation, a symbol for the vacancy on the M atom site is $\boldsymbol{V_M}$
- All crystals have vacancies – vacancies are thermodynamic necessity. A "perfect" crystal is impossible to grow/produce



Charged vacancies: for ionic crystals – conservation of charge, mass and crystal sites

M^+ removed: $MX \rightarrow V_M' + X_X + M^+$ electron localized on V

$MX \rightarrow V_M + e' + X_X + M^+$ delocalized electron

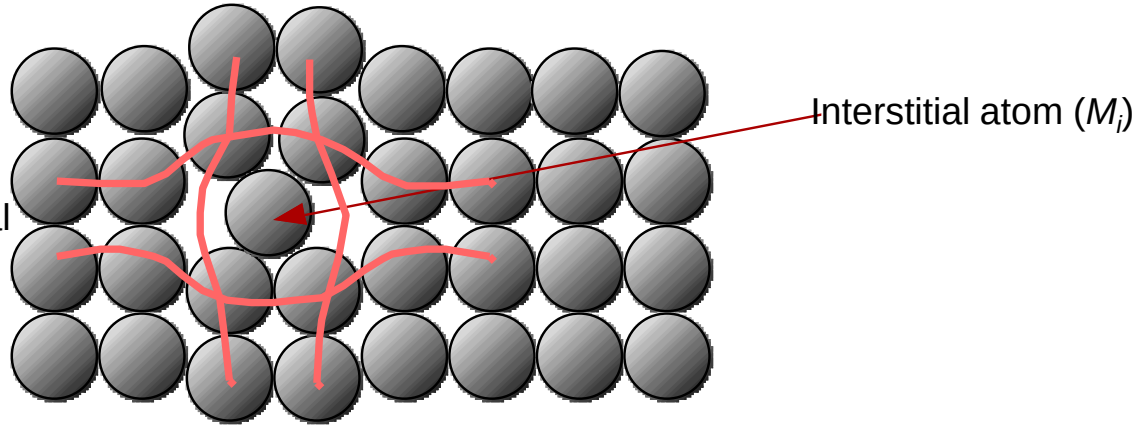
X^- removed: $MX \rightarrow V_X^{\bullet} + M_M + X^-$ electron hole localize on V

$MX \rightarrow V_X + h^{\bullet} + M_M + X^-$ delocalized electron hole

Point defect - intrinsic

Interstitial atoms (atoms of the parent crystal)

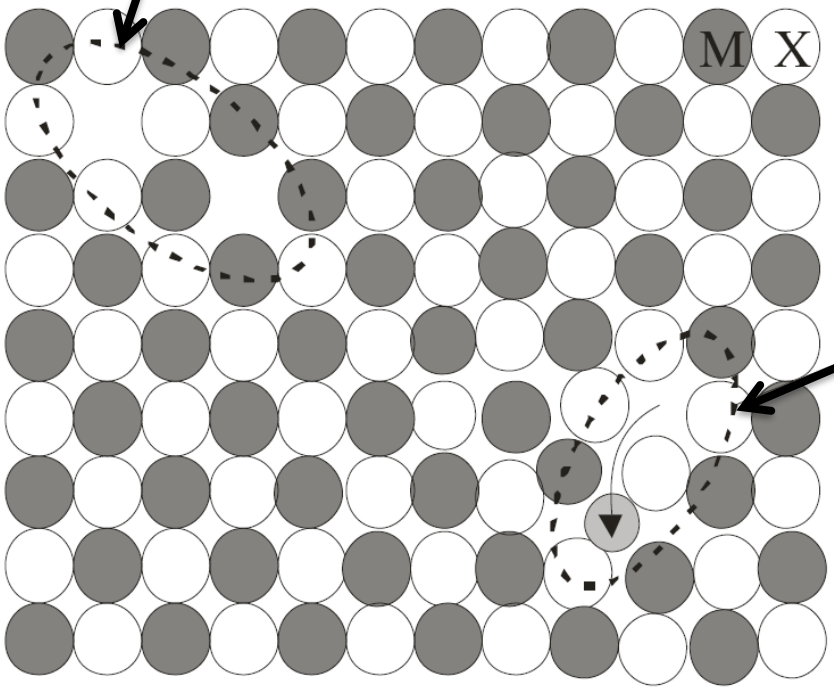
- Interstitial atom is located on what used to be originally unoccupied crystal site (interstitia - vacant space in a regular crystal structure)
- According to Kroger-Vink notation the symbol for the interstitial atom M is M_i
- Interstitial atom induces large local strain fields in the crystal because the atom is much larger than the interstitia



Point defect - intrinsic

Combined defects are often more energy favourable (cancelling of the strain or charge neutralization)

Schottk pair: $MX \rightarrow V_X + V_M + M^+ + X^-$



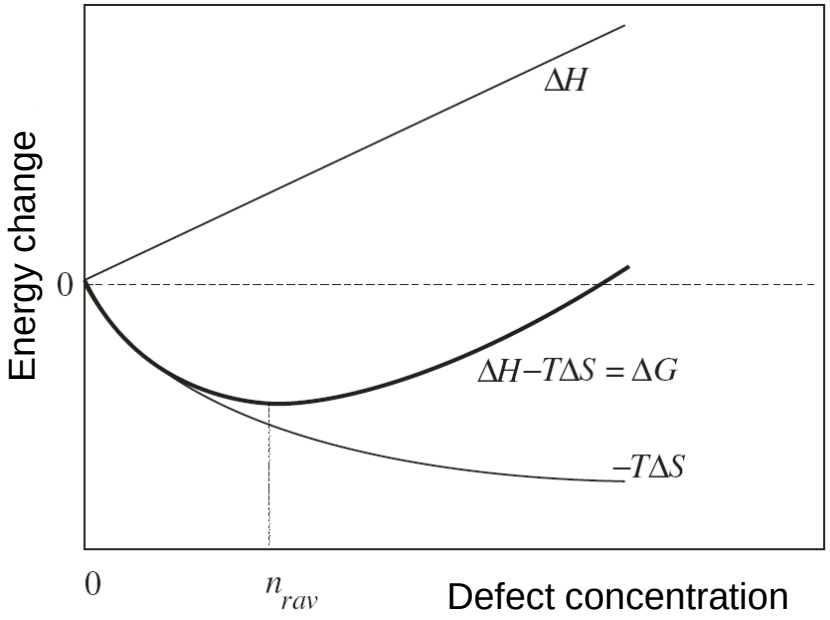
Frenkelov pair: $M_M \rightarrow M_i + V_M$

Concentration of intrinsic defects

- Free energy for defect formation: $\Delta G = \Delta H - T\,\Delta S$
  - $\Delta H > 0$ (enthalpy of the system increases)
  - But $\Delta S > 0$ (defect $\Rightarrow$ disorder $\Rightarrow$ entropy increases)
  - $\Delta G = \Delta H - T\,\Delta S$ **< 0**

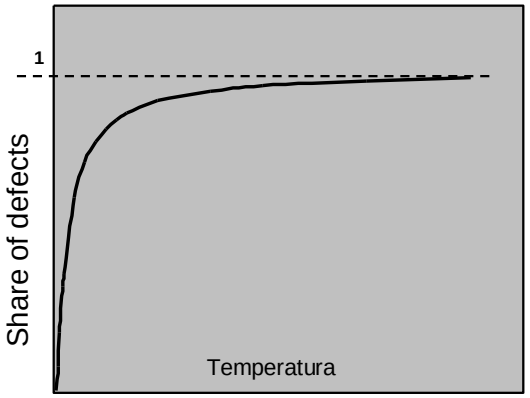
Free energy for defect formation is negative – the process is favorable (entropic effect)

At any temperature higher than 0K the crystals are not perfect. They involve (at least) thermodynamic concentration of defects 0K. The concentration is **temperature dependent**



Concentration of intrinsic defects

$$\frac{n}{N} = e^{\frac{-\Delta H_f}{kT}}$$ *Boltzmann distribution law*



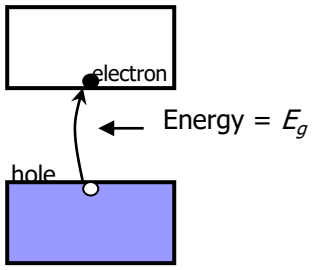
n = number of defects,
N = number of crystallographic sites
ΔH_f = enthalpy for defect formation
k = Boltzmann constant ($1.38 \cdot 10^{-23}$ J/K)

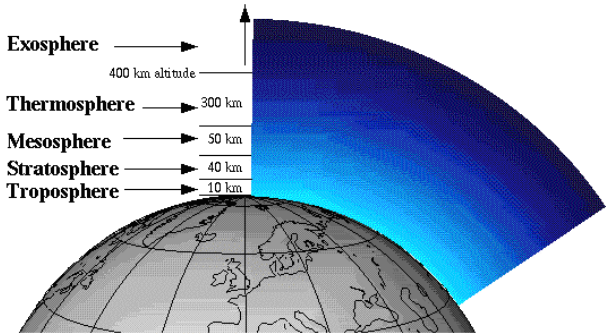
Other examples:

Elektronic excitation $P_e = e^{\frac{-E_g}{2kT}}$

– Density of atmosphere

$$n(h) = n(O)e^{\frac{-mgh}{kT}}$$





Concentration of intrinsic defects

Vacancies in metals

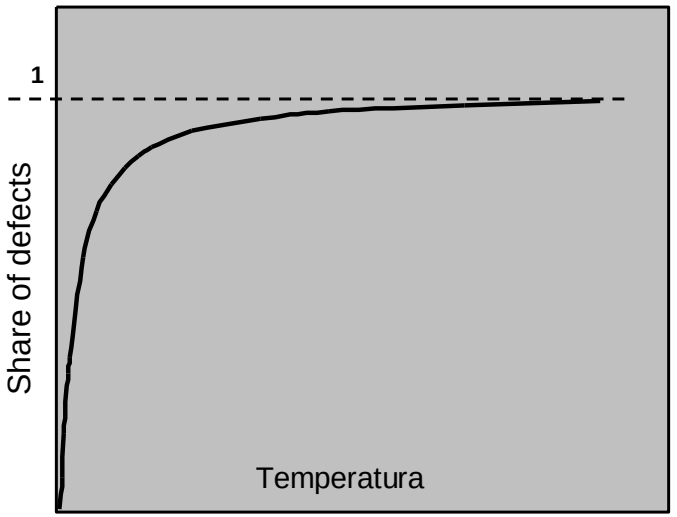
$$\frac{n}{N} = e^{\frac{-\Delta H_f}{kT}}$$

$\Delta H_{f(v)} \approx 1$ eV

T = 300 K	$n_v / N \approx 10^{-18}$	under detection limit
T = 1200 K	$n_v / N \approx 10^{-5}$	measurable

Higher $T \Rightarrow$ more defects

Lower $\Delta H_f \Rightarrow$ more defects



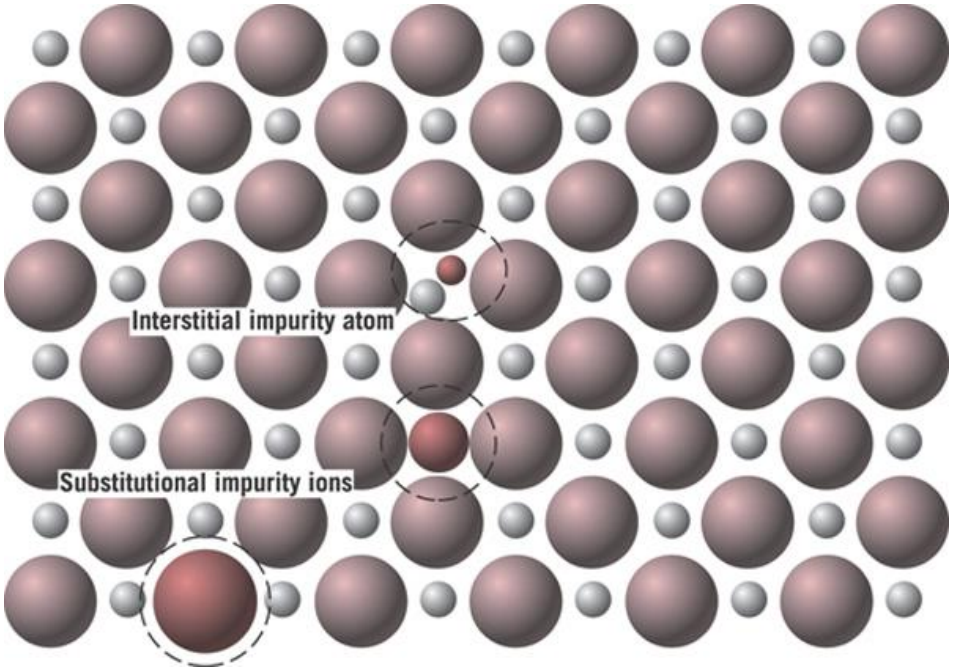
Vacancies: often the vacancy formation energy is slightly lower than binding energy (typical values for metals are around 1eV and covalent materials 4eV (Si) – 7eV (diamant)

Point defects- extrinsic

They appear due to presence of other kind of atoms (impurities or dopants)

There is no perfectly pure material. Impurities are always present. Materials with purity 99.9999% will have 10^{22} - 10^{23} impurity atoms per m^3.

Extrinsic point defects can be interstitial or substitutional



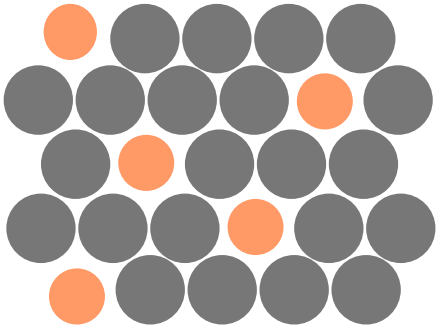
Solid solutions

Introduction of dopants into the crystal lattice causes formation of first **a solid solution** and then **a secondary phase**

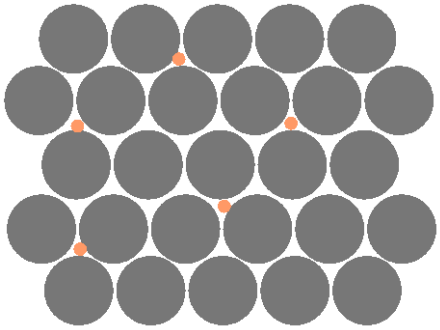
The processes depend on properties of the dopant (size and charge), its concentration and temperature.

At low concentrations the solid solution is formed. The dopant atoms are randomly distributed. Electroneutrality must be conserved.

Two types of the solid solutions:



Substitutional



Interstitial

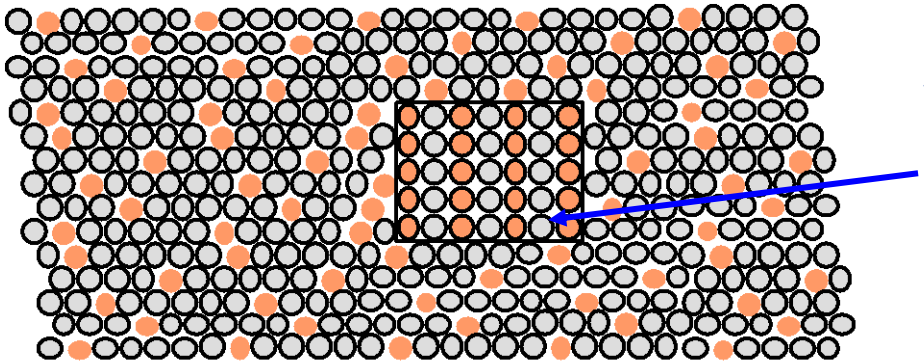
Solid solutions

Properties of solid solutions

- Crystal structure of the parent phase is conserved (no change in space group)
- No secondary phase
- Composition of the solid solution is homogeneous (the dopants are randomy distributed)
- Unit cell volume is changed (Vegard's law)

Vegard's law: Unit cell volume is changing linearly with the dopant concentration

When the solid solubility limit is exceeded, the atoms start to form a new crystal phase
The grains/domains of **a secondary phase** are formed



Secondary phase

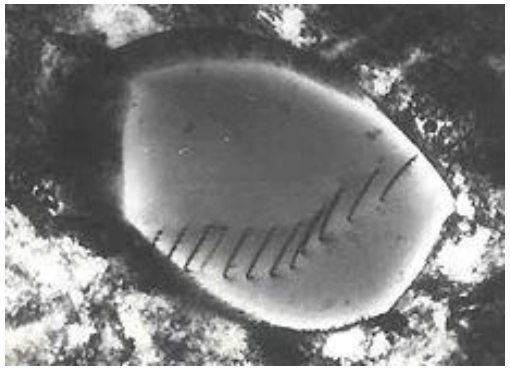
- different stoichiometry
- different crystal structure

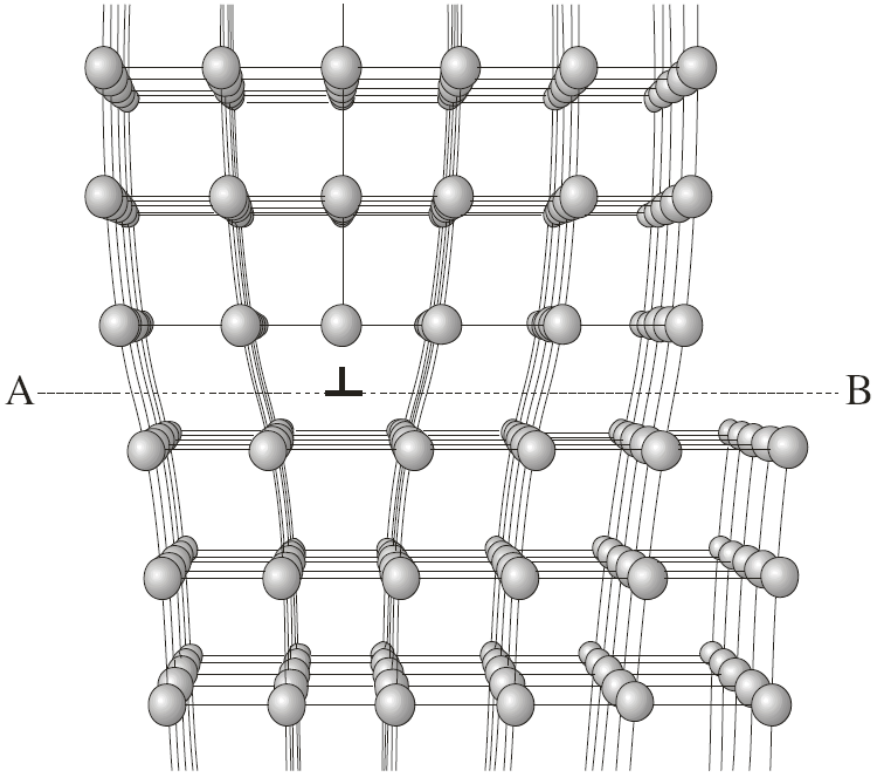
Line defects – Edge dislocation

Extra plane inserted into te crystal lattice

Distortion of lattice and large strain fields

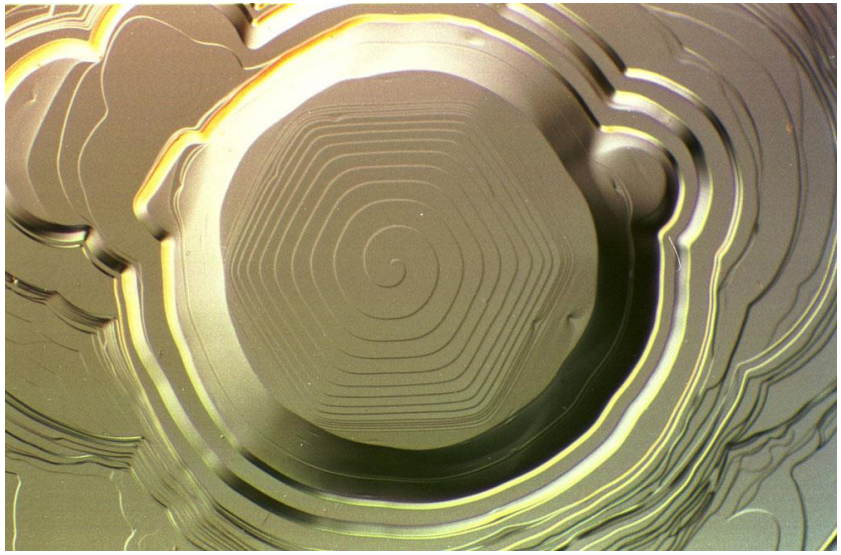
Strong influence on mechanical properties (strengthening of steel)

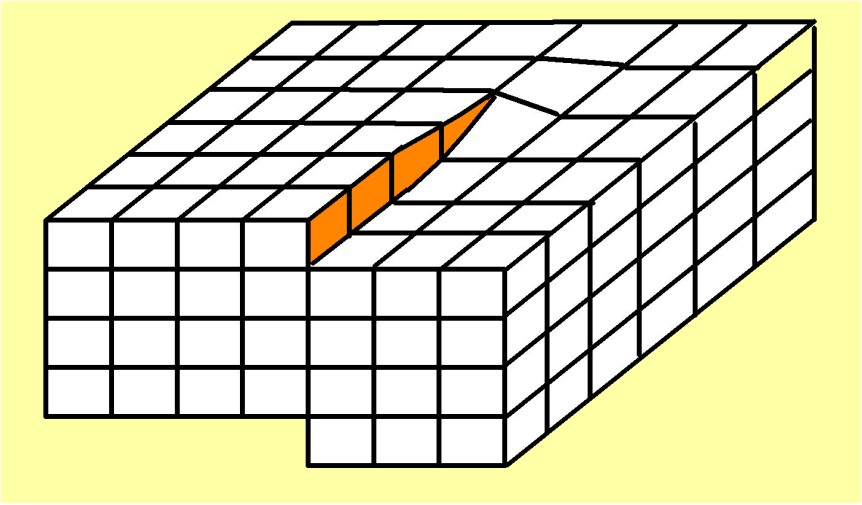




Line defects – Screw dislocation

No extra crystal plane – the defect occurs because of partial shift of crystal planes napaka

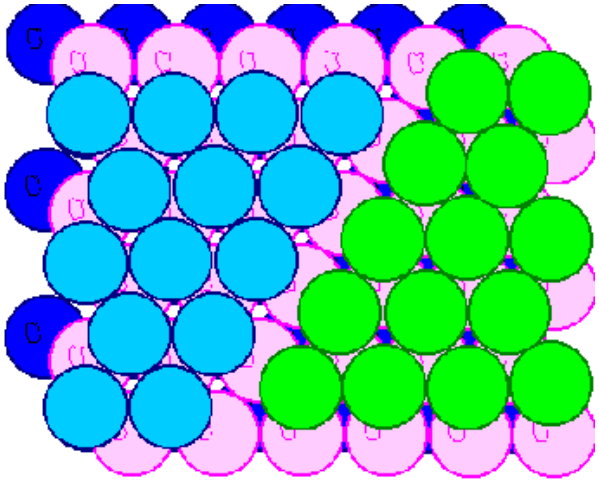




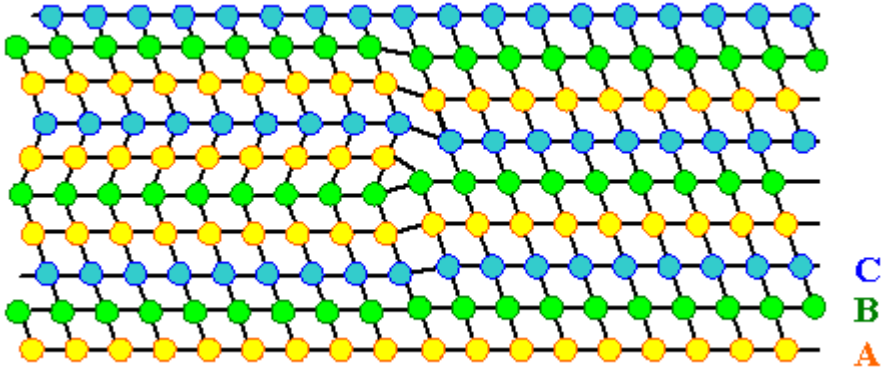
Planar defects – Stacking fault

regular hcp sequence - ABABABA
regular ccp sequence - ABCABCA.

Stacking fault happens with the stacking mistake of the atom planes
e.g. ABCBCABCABC (missing A) or ABCABACABC (extra A)

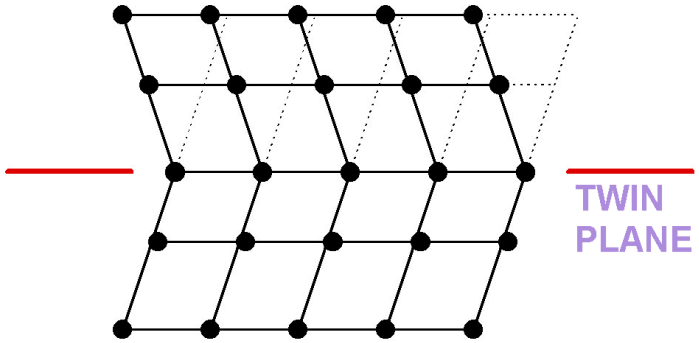


Stacking fault associated with a dislocation



Planar defects – Twinning

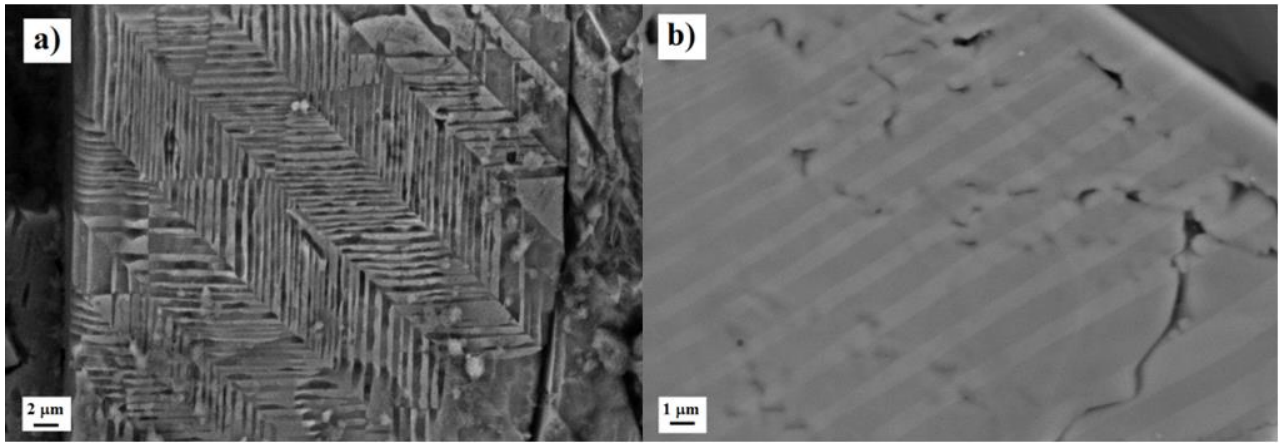
Crystals often grow with a defect where a part of the crystal is a mirror image of another part



In the close packed structures twinning occurs due to stacking fault.

ABCAB<u>C</u>BACBA

where C is the twin plane



The most investigated twinning systems are **ferroelectric domains** where the domain boudaries represent twin planes