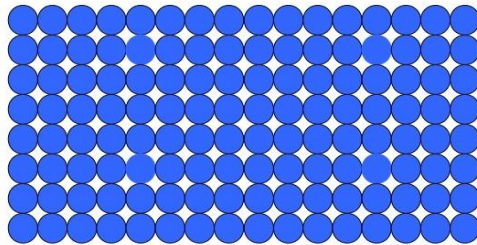


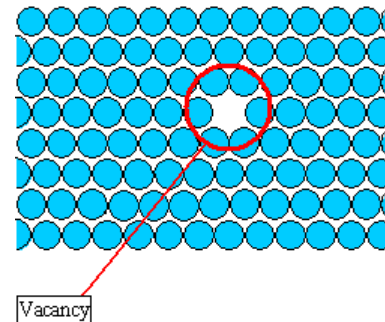
Crystallographic defects

Ideal crystals versus real crystals

- ❑ **Ideal crystal:** a single crystal with perfectly regular lattice, without defects, without impurities
- ❑ 3D infinite structure of perfectly arranged atoms



- ❑ **Real crystals:** show defects or irregularities, that affect their macroscopic characteristics
- ❑ At temperatures other than 0 K, no ideal crystals exist!



Crystal defects

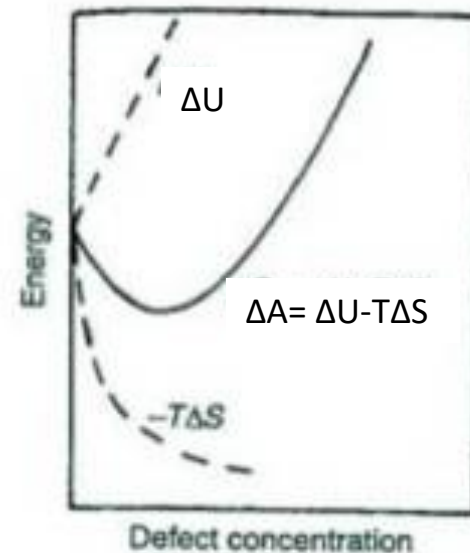
- ❑ the **perfect arrangement** of a crystal gives the **lowest energy**, thus it should be the most **stable structure**
- ❑ however stability is determined by the **free energy**:

$$A = U - TS$$

- ❑ A – Helmholtz free energy
 - U – internal energy (equal to the lattice energy), Joule
 - T – temperature, Kelvin
 - S – entropy, Joule/Kelvin
- ❑ A will be influenced by: *U*, and *TS*.
 - ❑ at ***T=0K***, *S* will be 0, and $A=U$, both will be minimized
 - ❑ in all the other cases, where ***T≠0K***, *S* tends to increase, minimizing *A*, but increasing *U*, thus an equilibrium has to be achieved, where the entropy will be non-zero - **THUS THE CRYSTAL IMPERFECT**

Crystal defects

- ❑ creation of a defect costs energy, but increases the entropy
- ❑ defects will be created, until the free Helmholtz energy will reach its minimum
- ❑ the imperfections of a crystal **STABILIZES** the system



Properties

- ❑ **Crystal defect influence:**
 - ❑ structural properties
 - ❑ electrical properties
 - ❑ chemical properties
 - ❑ scattering properties
 - ❑ thermodynamic properties

Classification

- 0-dimensional defects

 - POINT DEFECTS**

 - vacancy

 - interstitial

 - substitutional

- 1-dimensional defects

 - LINE DEFECTS**

 - edge dislocation

 - screw dislocation

- 2-dimensional defects

 - PLANE DEFECTS**

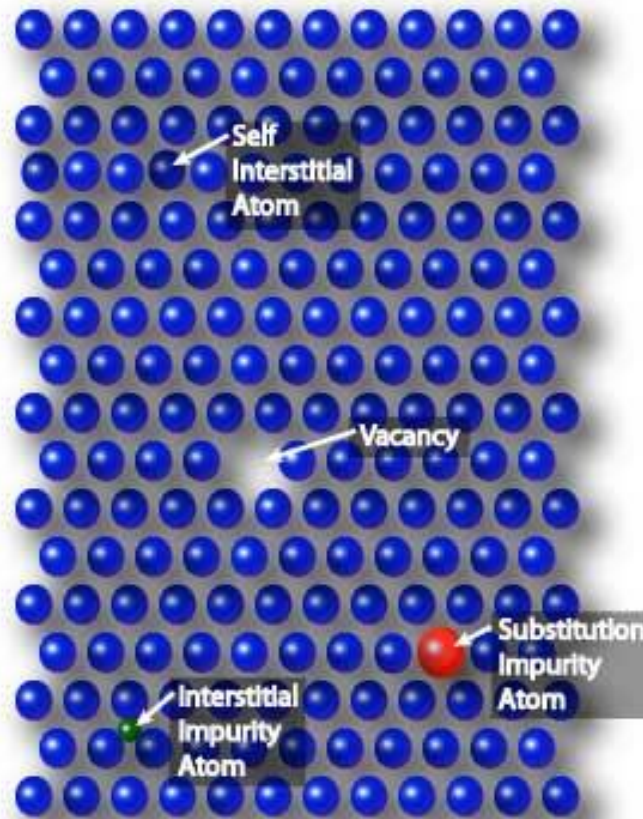
 - grain boundary defects

 - stacking faults

Point defects

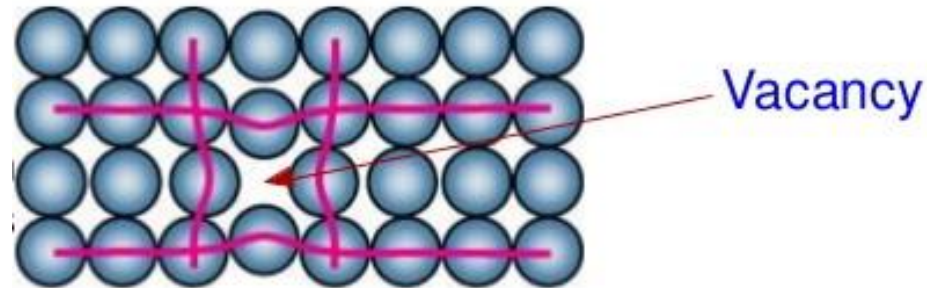
- occur at or around a **single lattice point**
- vibrational energy** of the atoms makes possible the breaking of the bounding, allowing the movement of the atoms. Once the atoms are free, point defects can be formed
- types:**
 - vacancy
 - self-interstitial atoms
 - interstitial impurity atoms
 - substitution impurity atoms

Point defects



Point defects

- Vacancy:** missing of an atom/ion from the lattice point
- properties:**
 - missing atom from a lattice point
 - atoms around the vacancy displaced
 - produced tensile stress
- determined by:**
 - temperature - as the temperature increasing, the number of vacancies is increasing
 - the number of atoms / unit cell
 - the energy that is required for creating a vacancy (specific to the substance)
- effect: DIFFUSION** in crystals, that would not be possible without the existence of vacancies. Ee. grain boundary diffusion under environmental effects, such as stress, pressure etc.



Point defects

- **Equilibrium concentration** of vacancies depends on the **temperature**

$$\frac{N_V}{N} = \exp\left(-\frac{Q_V}{k T}\right)$$

N_V – number of defects

N – number of possible defect sites

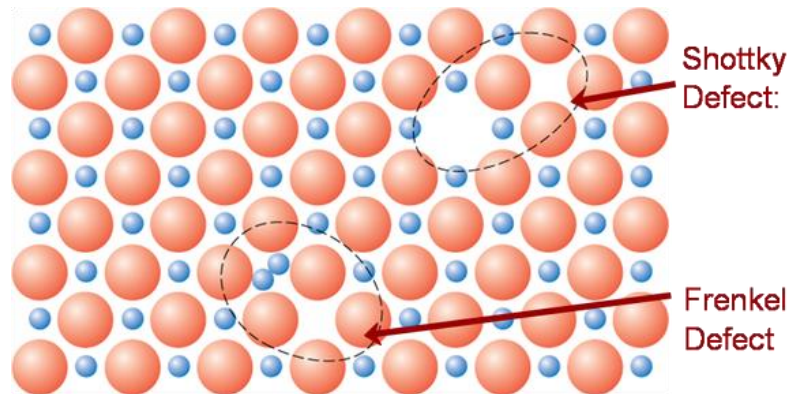
Q_V – activation energy

k – Boltzmann constant ($1.38 \cdot 10^{-23}$ J/K)

T – temperature (K)

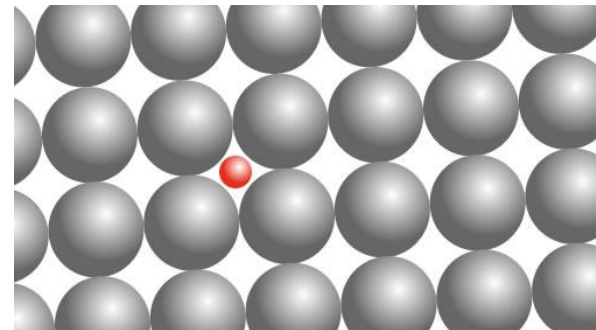
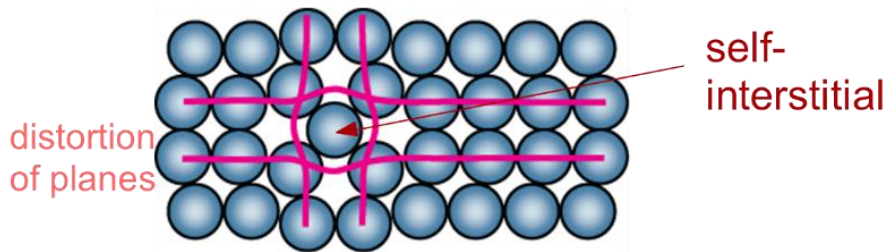
Point defects

- ❑ **Schottky defects**: a vacancy is created by the migration of an atom/ion to the surface of the crystal
- ❑ is dominant in the case of the closest packed structures (migration of **ion pairs** in ionic crystals)
- ❑ depends on **the total number of ion pairs** (mass of the crystal), **temperature, average energy** that is needed for the creation of defect



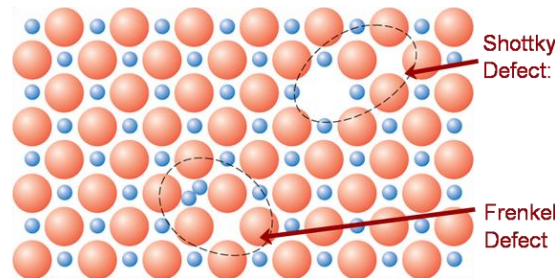
Point defects

- ❑ **Interstitial defects**: when an atom is removed from its "original" place, and occupies a place between lattice points
- ❑ when the atom is the "own" atom, it is called **self-interstitial**
- ❑ when an "outer" atom occupies a place between the lattice points, it is called **impurity interstitial**



Point defects

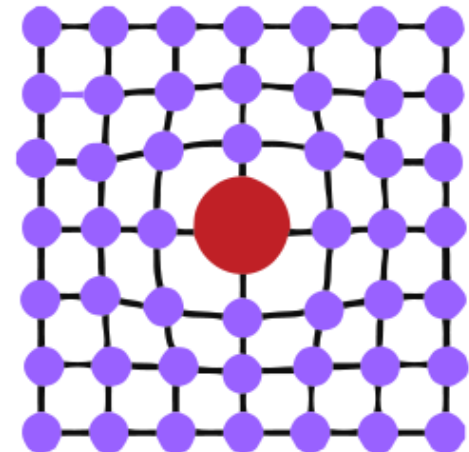
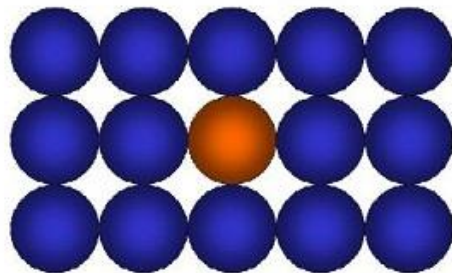
- ❑ **Frenkel defects:** an atom/ion leaves its regular site and occupies a nearby space. Such atoms are **called interstitial atoms**
- ❑ the number of interstitials and vacancies will be equal
- ❑ prevalent in crystals of silver-halid type: AgCl_2 , CaF_2



- ❑ Shottky and Frenkel defects are found together in ionic crystals, helping to maintain the neutrality of the crystal

Point defects

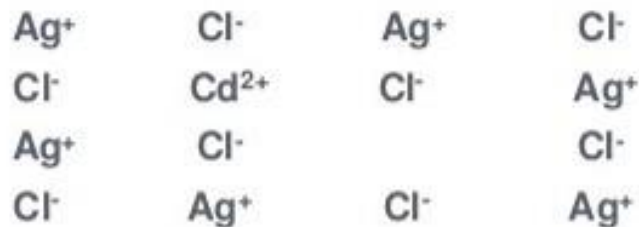
- Substitutional defects:** an impurity atom is incorporated at a regular atomic site
- in case of ionic crystals, the charge balance will be disturbed, that will have the effect of formation of a vacancy or the change of the oxidation state of one of the ions of the lattice
- without or with distortion of the crystal



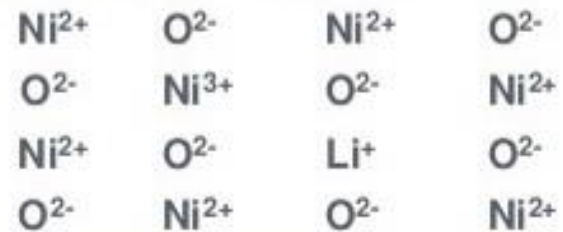
Point defects

□ Substitutional defects

- e.g.: Ag^+ changed with Cd^{2+} in the AgCl lattice will be followed by a vacancy formation, and substitution of Ni^{2+} by Li^+ in the NiO lattice will change the oxidation state of a Ni^{2+} ion to Ni^{3+}



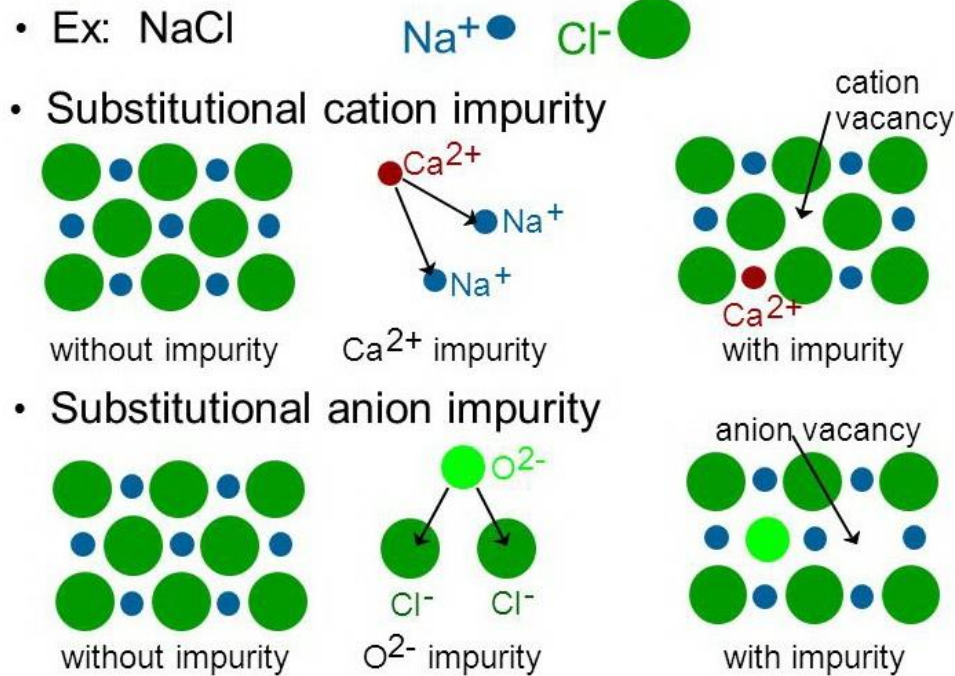
**vacancy produced by
 Cd^{2+} substitution**



**valence defect produced
by Li^+ substitution**

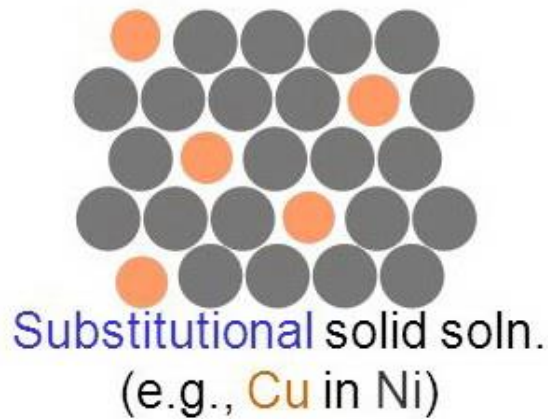
Imperfections in ionic type crystals

□ charge balance must be maintained

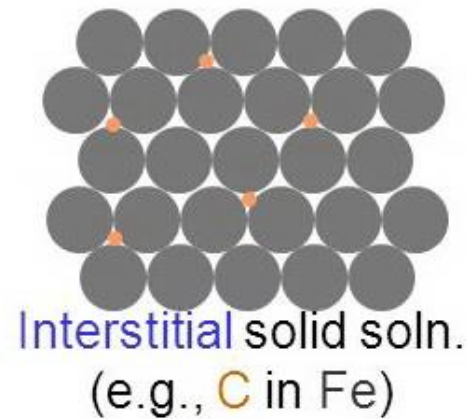


Point defects in metals

- A – host atom, B – impurity
- **1 type**: solid solution of B in A

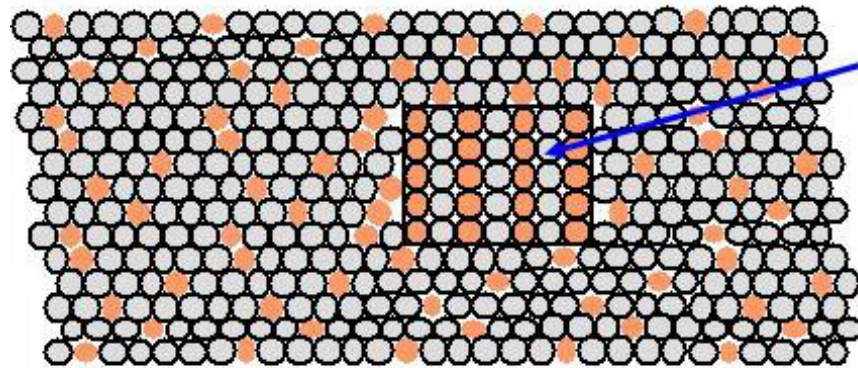


OR



Point defects in metals

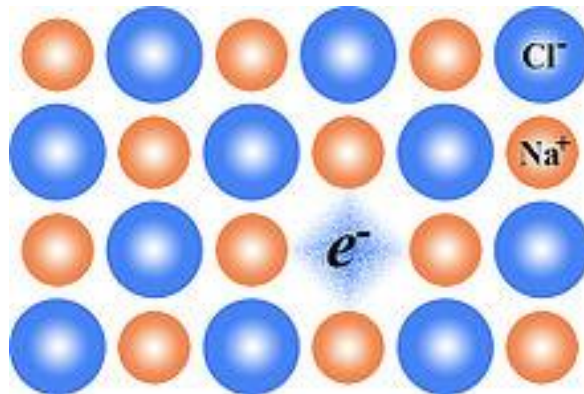
- A – host atom, B – impurity
- **2 type:** solid solution of B in A, plus second phase material is formed (usually for a larger amount of B)



Second phase particle
-- different **composition**
-- often different structure

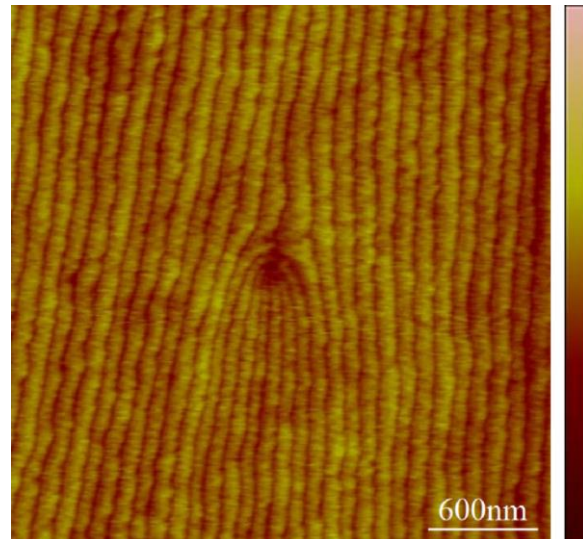
Colour centres

- ❑ an **anionic vacancy** is filled up with one or more **unpaired** electrons
- ❑ typical to **metallic-oxides** and **ionic crystals** (NaCl)
- ❑ electrons in such vacancy tend to absorb visible light – colours the crystal



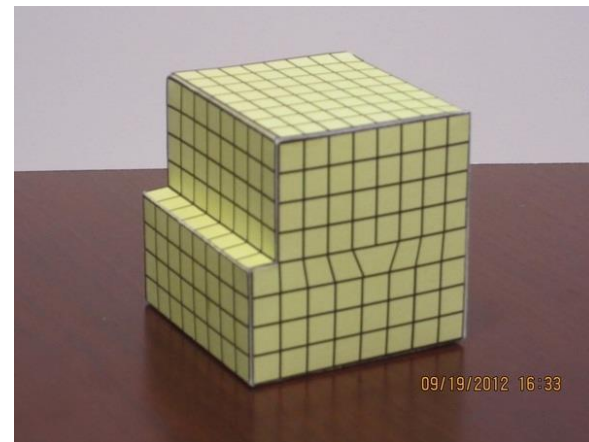
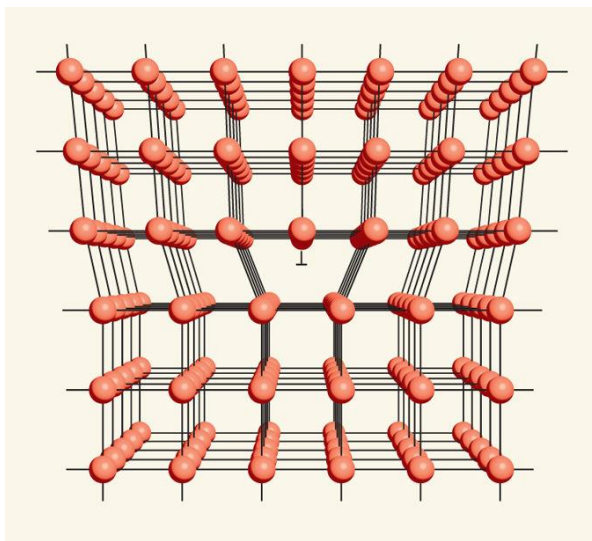
Line defects

- a discontinuity (dislocation) in the regular structure of the crystal in 1D is called **line defect**
- it produces a **boundary** between two sides
- AFM image of a dislocation line in hexagonal SiC
- types:**
 - edge dislocation
 - screw dislocation



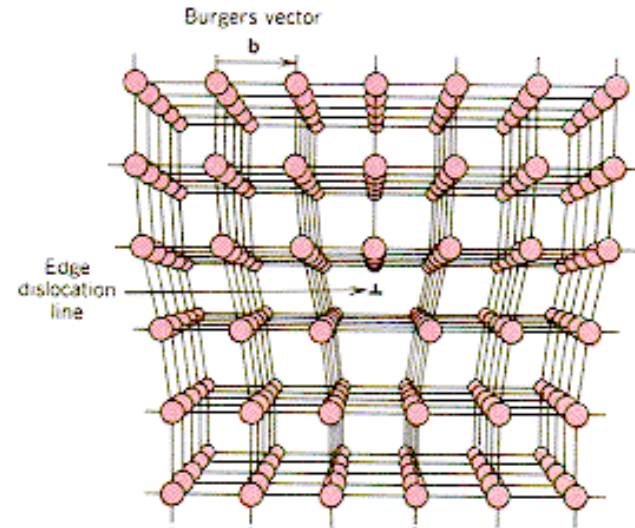
Line defects

- ❑ **Edge dislocation:** insertion (or removal) of an extra half plane among the lattice planes
- ❑ ionic and covalent crystals can present edge dislocations

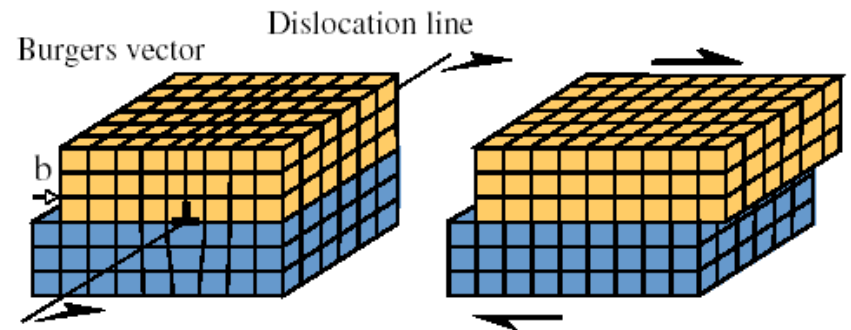
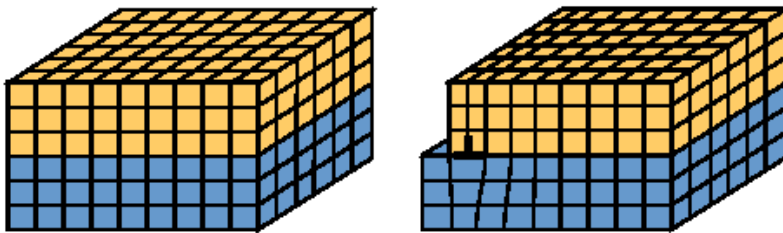


Line defects

- ❑ edge dislocation
- ❑ **Burgers vector:** perpendicular to the dislocation line
- ❑ **Movement of an edge dislocation**

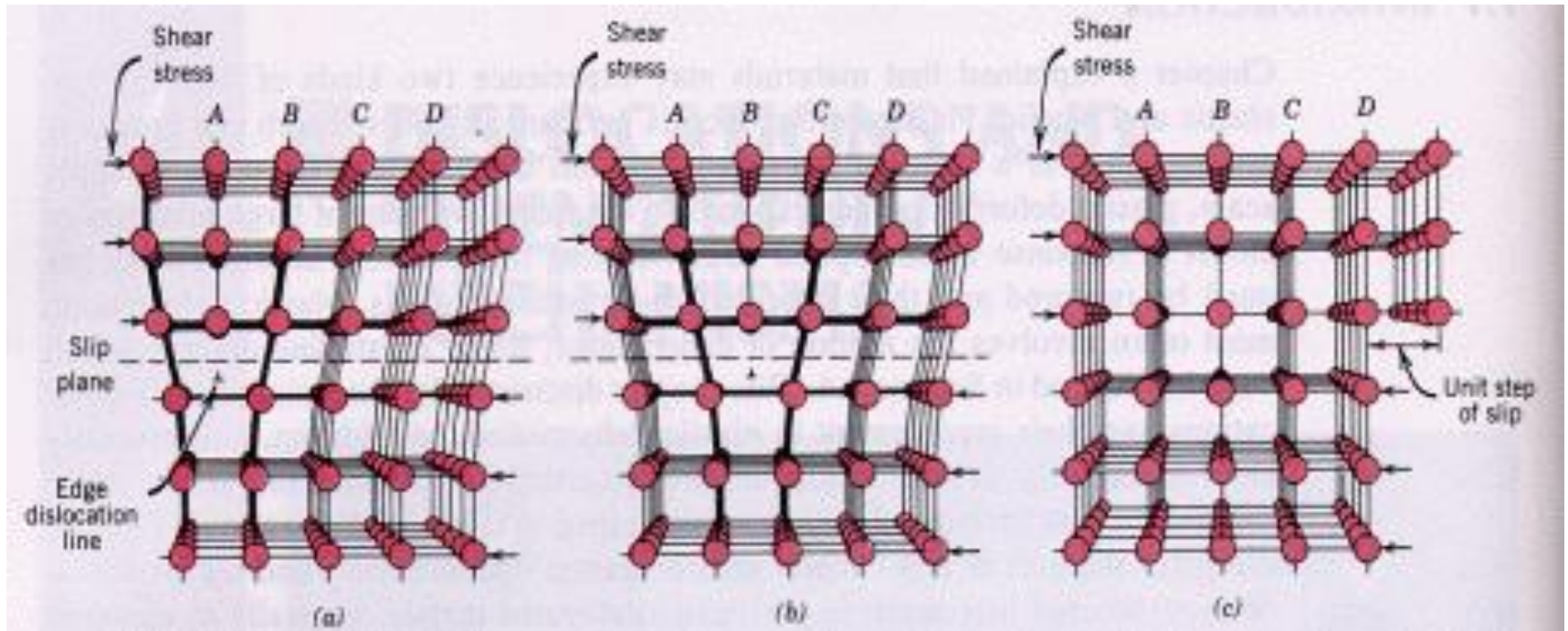


Intracrystalline slip: Edge dislocation



Line defects

- **Movement** of an edge dislocation: effect of shear stress



Line defects

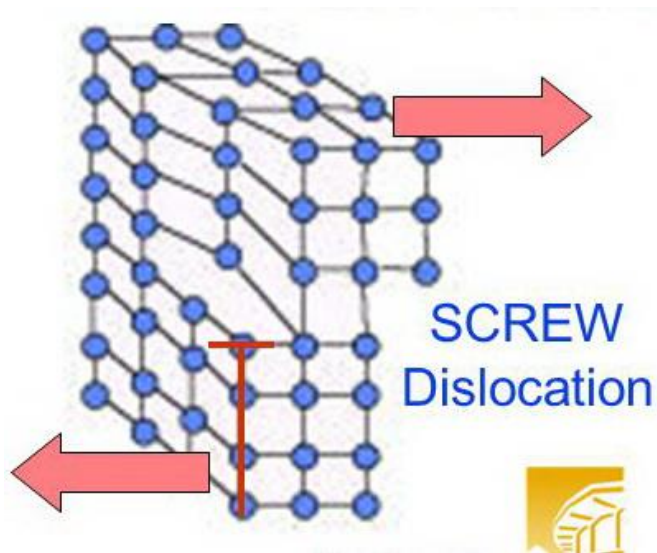
Dislocation density = total dislocation length/unit volume

Processes that increase the dislocation density:

- cold rolling
- cold forging
 - large amount of dislocations are forming

Line defects

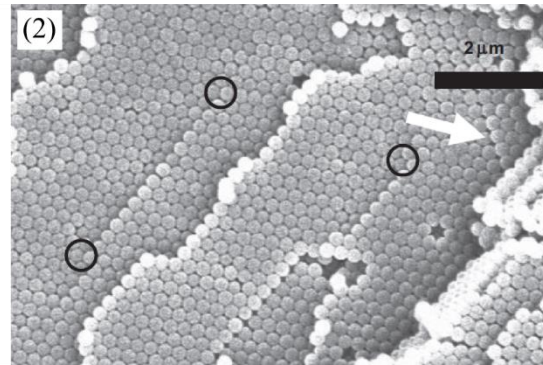
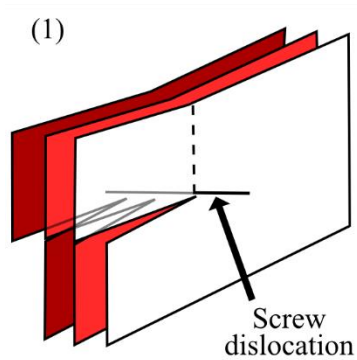
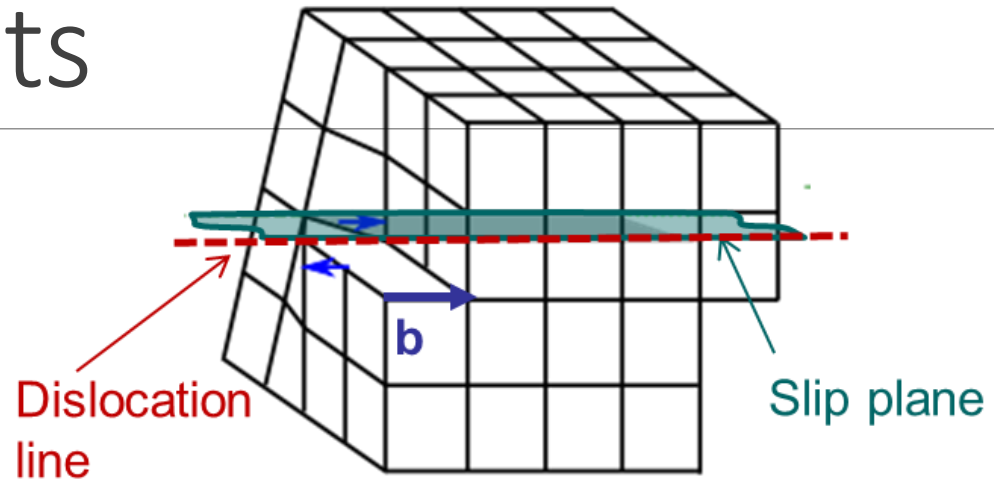
- ❑ **Screw dislocation:** transformation of successive atomic planes due to **shear stress**
- ❑ the crystal "is cut", then the cut part is sheared



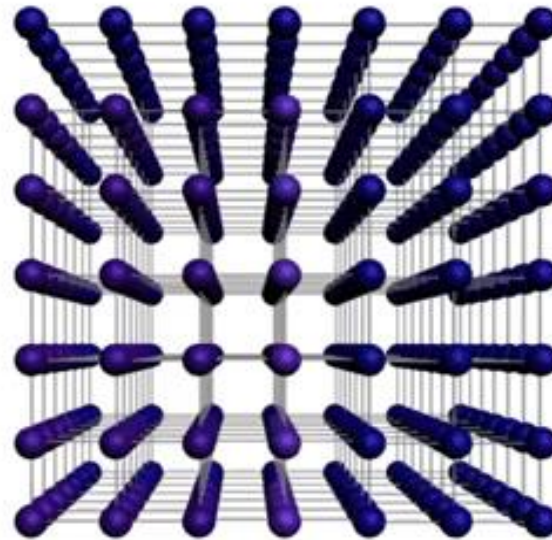
Line defects

- ❑ **Screw dislocation**

- ❑ Burgers vector is parallel to the dislocation line



Screw dislocation



SCREW DISLOCATION

Effects of line defects

- ❑ they are the basis for **plastic deformations**
- ❑ as soon a **shear stress** is applied on a crystal and critical value is achieved, dislocations start moving
- ❑ many dislocations are necessary to **cause macroscopic deformation**
- ❑ as soon the dislocation reached the surface, the crystal is **freed from stress** caused by the dislocation
- ❑ **strength of the materials** are related to dislocations and defects in the crystal

Planar (surface) defects

- ❑ **two dimensional defects**

- ❑ they are introduced in the crystal during mechanical and thermal treatments

- ❑ **types:**

- ❑ grain boundary

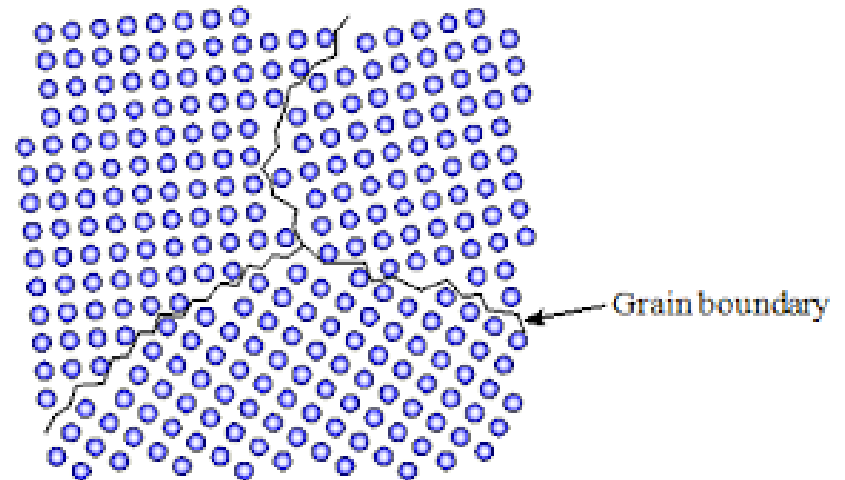
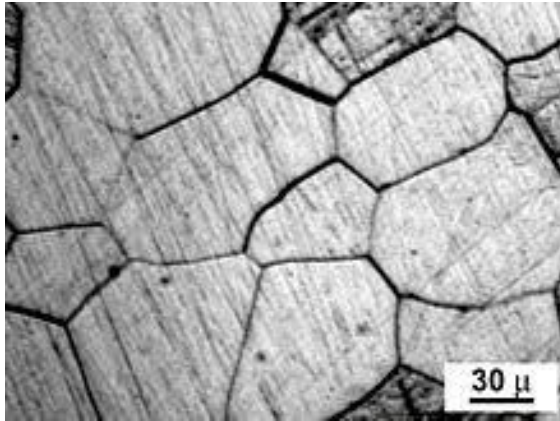
- ❑ tilt boundary

- ❑ twin boundary

- ❑ stacking faults

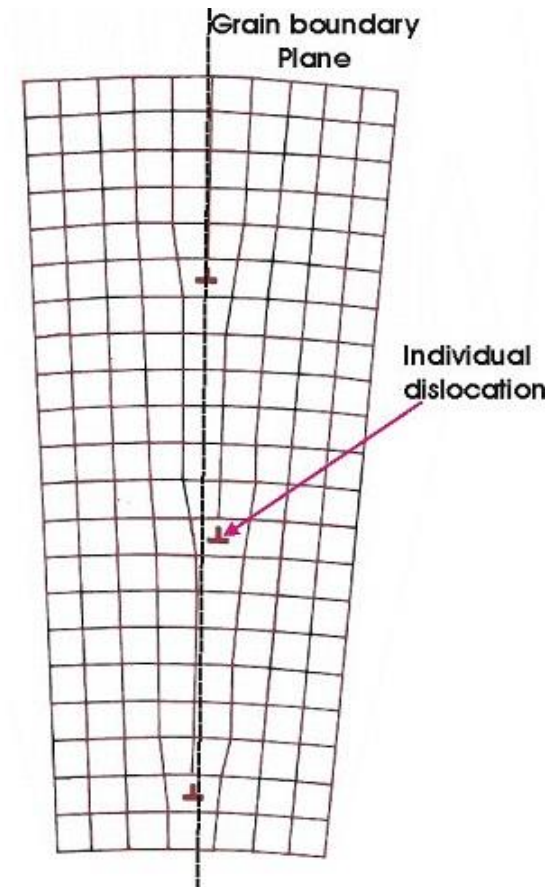
Planar (surface) defects

- ❑ **Grain boundary:** general planar defect, separates grains with different crystallographic orientation inside a polycrystalline material
- ❑ polycrystallites are the results of uneven growth of the crystals



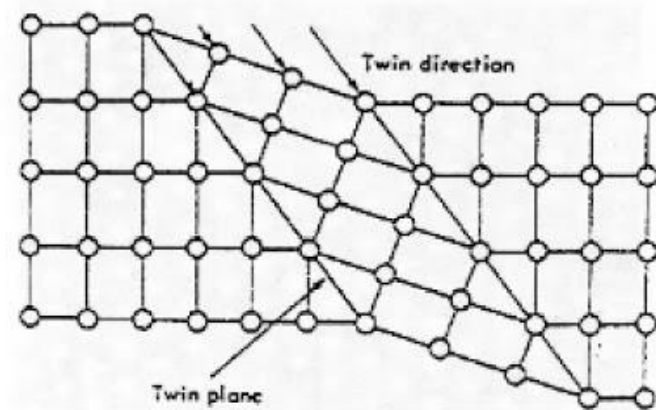
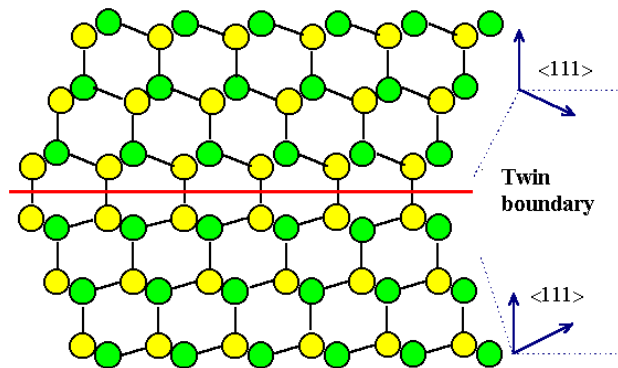
Planar (surface) defects

- ❑ **Tilt boundaries:** there is an angle between two crystallites, but the distortion is not so drastic
- ❑ Called also **low angle boundary**
- ❑ It can be described as a set of parallel edge dislocations



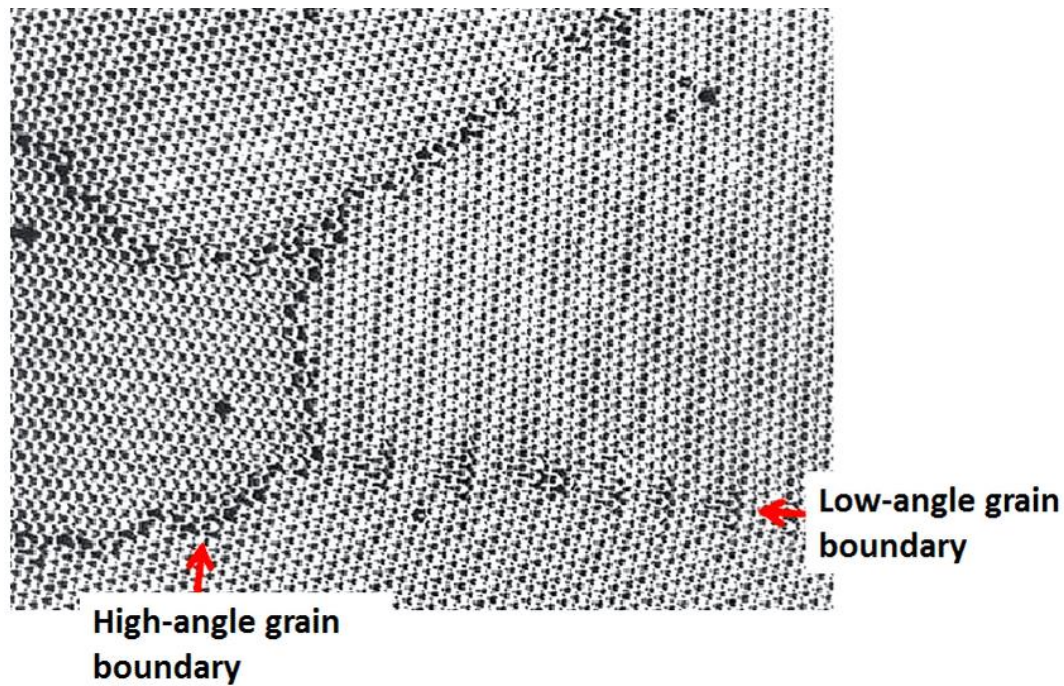
Planar (surface) defects

- ❑ **Twin boundaries:** the atomic arrangement on one side of the boundary is the mirror of the arrangement of the other side
- ❑ the whole volume is called a twin
- ❑ the plane is called: twinning plane



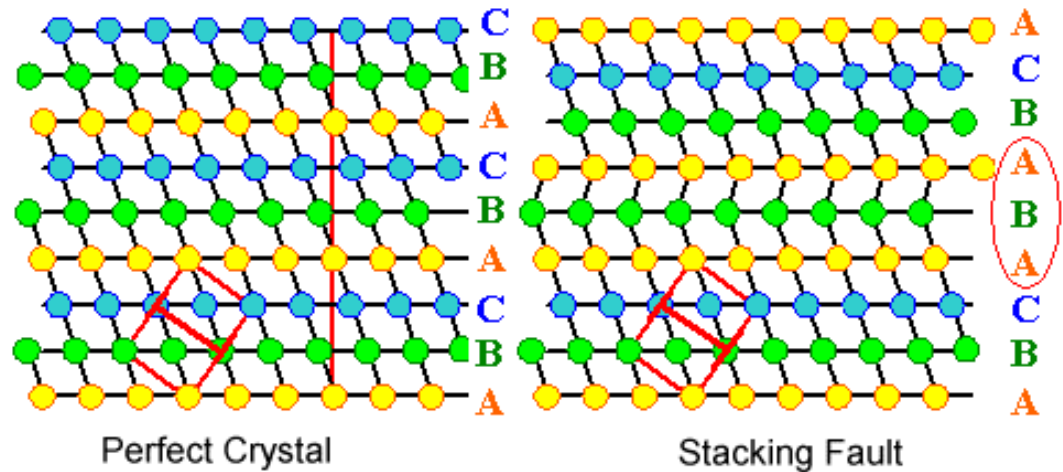
Planar (surface) defects

- High and low angle boundaries



Plane (surface) defects

- ❑ **Stacking faults:** appear in closed packed structures (but not only), especially in **fcc and in close packed hexagonal** structures. It is a disorder of the layers
- ❑ They occur as an effect of crystal growing and they are dislocation of dislocations
- ❑ the CBA order will be disturbed



Diffusion in solids

- moving of the defects in a crystal will result in **diffusion of vacancies, ions, planes, lines** inside the crystal
- it is a **thermally activated transport of the matter**
- it is responsible for several **important processes**, like the solid state reactions
- examples:**
 - addition of C to Fe to produce **Steel**
 - addition of Cu to Ni to make **thermocouple wires**
 - addition of Cr to Fe for **increasing the corrosion resistance**
 - introduction of grain boundaries to **strengthen materials**

Solid construction materials

Solid construction materials

Natural stones (aggregates)

Inorganic binders

Gypsum

Cement

Mortar

Concrete

Ceramics

Glass

Artificial rocks

Metals

Plastics

Wood

Bitumen and asphalt

Insulator materials

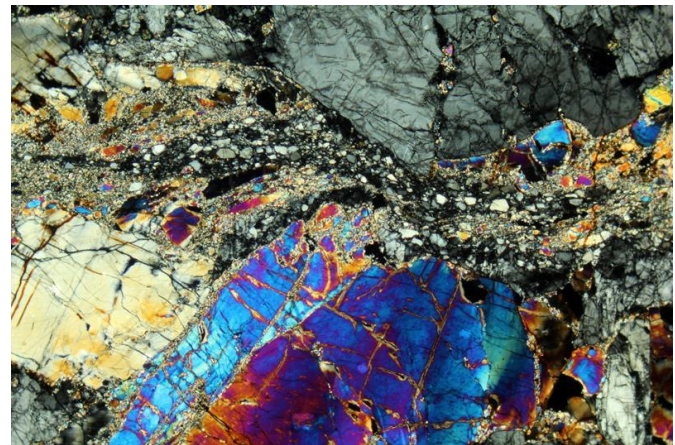
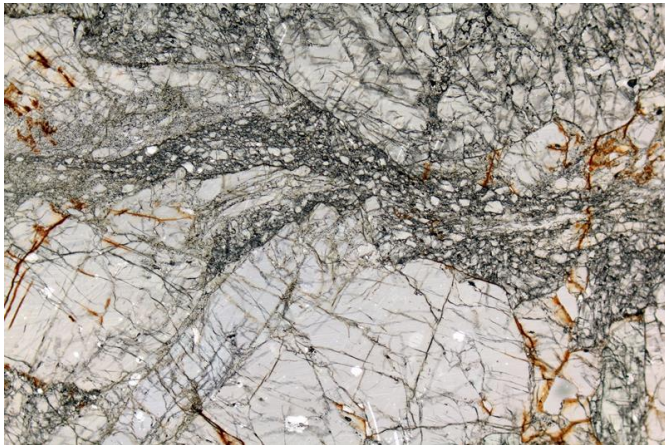
Pigments, paints

Natural stones (rocks)

Natural aggregates of one or more **minerals** (chemical compounds)

Formed of **homogeneous solid grains** held together with **chemical bonds**

Mylonitic Dunite (7mm view field, optical microscope)



Natural stones (rocks)

Formation of rocks:

- sedimentation
- crystallization from melt or magma
- metamorphic rocks (subjected to different processes)

Geologically classified **according to chemical composition, texture, grain size, permeability**

Main constituent of the natural mineral rocks is: silica SiO_2 – 74% of the Earth crust

Natural stones

Sandstone

- may have any color due to impurities

- composed of quartz or feldspar

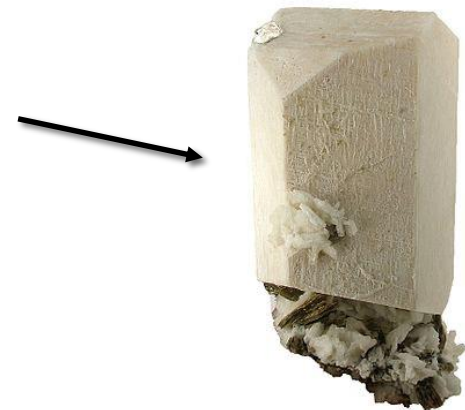
Quartz (SiO_2)

- trigonal or hexagonal

Feldspar

(KAlSi_3O_8 – $\text{NaAlSi}_3\text{O}_8$ – $\text{CaAl}_2\text{Si}_2\text{O}_8$)

- triclinic or monoclinic



Natural stones

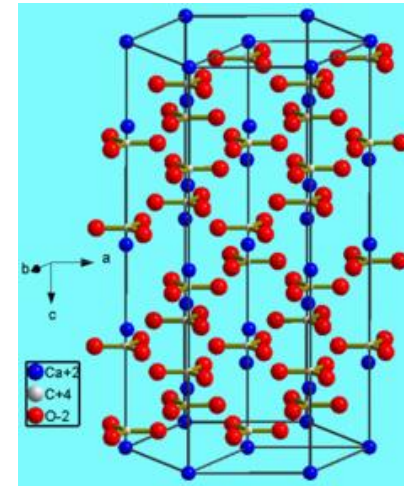
Limestone



Limestone: sedimentary rock, composed of **calcite**, **aragonite** and **dolomite**

Calcite: CaCO_3

- unit cell: trigonal
- colorless, white etc
- granular
- hardness: 3 (Mohs)
- brittle
- soluble in dilute acids

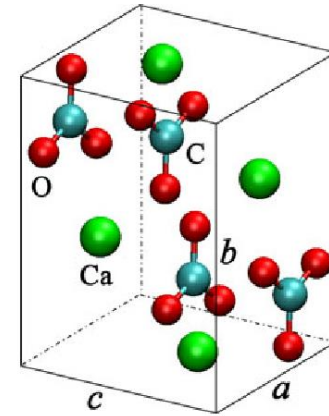


Natural stones - limestone

Limestone

Aragonite: CaCO_3

- unit cell: orthorhombic
- colorless, white etc
- hardness: 3.5-4 (Mohs)
- soluble in dilute acids
- brittle

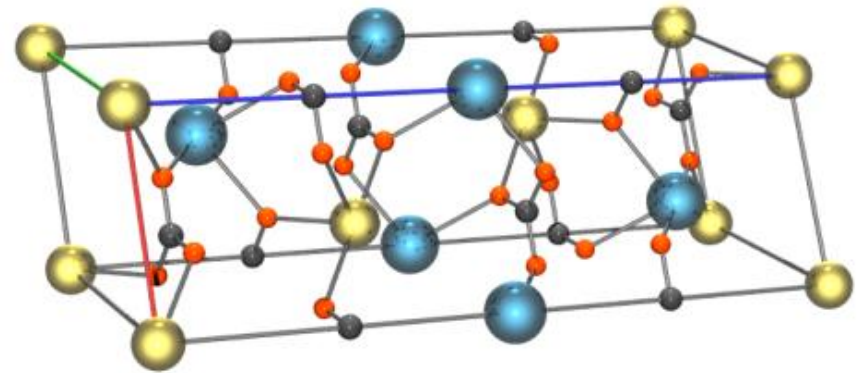


Natural stones - limestone

Limestone

Dolomite: $\text{CaMg}(\text{CO}_3)_2$

- unit cell: trigonal
- white, grey etc
- hardness: 3.5-4 (Mohs)
- less soluble in dilute acids
- brittle



Glass



GLASS INDUSTRY

Glass

Definition: those amorphous materials that undergo **glass-transition** are called glasses

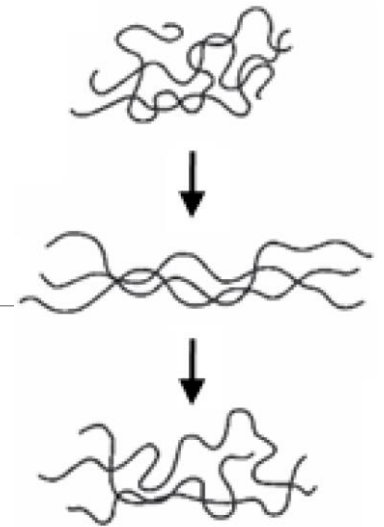
Glass-liquid transition

Reversible process between glassy-rubbery state, according to the temperature change

Glass transition temperature is lower than the melting point

Construction glasses:

- soda-lime silicate glass (flat glasses, etc.)
- borosilicate glass (firing resistant glass)



Glass



Constituents of **soda-lime silicate glass**:

- silica matrix: melted at 1600°C, **rapid cooling**: amorphous silica glass
- **additives**:
 - soda (Na_2O) in the form of soda ash (Na_2CO_3) **lowers the melting point by about 500°C** but leaves the glass soluble in water
 - lime (CaO) in the form of limestone, calcium carbonate (Ca_2CO_3) **makes the glass insoluble** and widens its working range.
 - dolomite, which adds some magnesium oxide (MgO), and a number of other metal oxides in small quantities **to control the melting point, working range and colour**
- broken glass (CULLET) improve the heat transfer

Glass



In construction technology the most used ones are the **soda-lime silicate glasses**

- 75% silicon dioxide (SiO_2)
- sodium oxide (Na_2O)
- sodium carbonate (Na_2CO_3)
- lime (CaO)
- several minor additives

transparent to visible light

non-soluble, resistant to chemical attack

Borosilicate glasses:

70% silica

10% boric oxide

8% sodium oxide

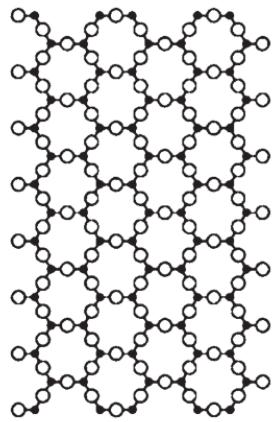
8% potassium oxide

1% calcium oxide.



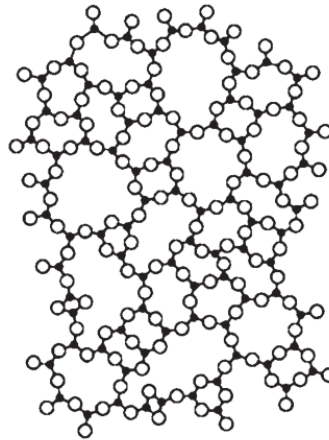
Glass

a. crystalline silica



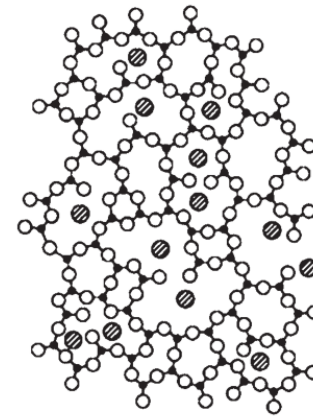
a

b. silica glass



b

c. soda glass

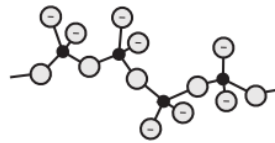


c

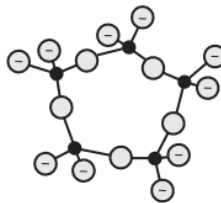
○ Oxygen atom
● Silicon atom
◐ Sodium atom



(a) Silica tetrahedron, SiO_4^{4-}



(b) Silica chain



(c) Silica ring

Glass

Coatings can be applied

- **low emissivity glass** (increases the insulation)
- deposition of fluorinated tin oxide (sprayed)
- sputtering: **silver layer** with stabilizing coating
- these coatings modify the emissivity of the glass, while remain transparent to the visible light
- disadvantage: focusing effect, lock of the radio frequency

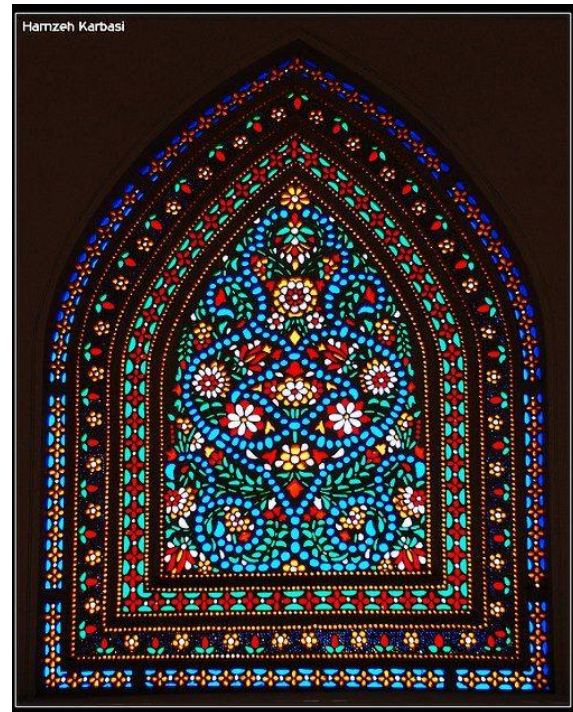


Shandong Jingcheng Glass Technology Co.,Ltd.

Glass

Colouring:

- addition of colouring ions
- colouring inclusions: bone ash, SnO_2 , As, Sb
- precipitation of nanometer sized colloids (gold, selenium)
- dichroic dyes (organic)



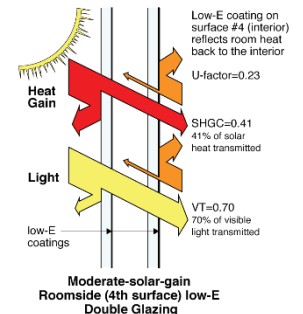
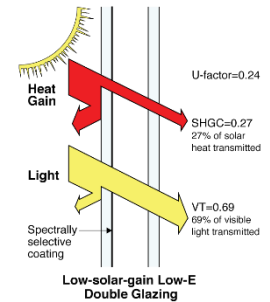
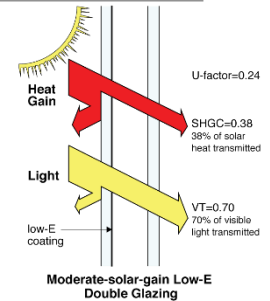
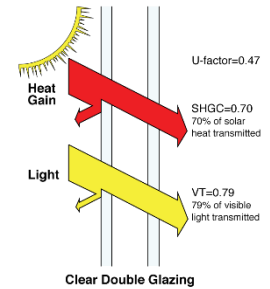
Glass

- **solar-control glass:** solar energy: 47% visible light, 50% short IR radiation, 3% UV. For cold climate: low-e glasses are the solution, but for hot climates the coatings are designed such that they reflect the IR back into the environment
- **self cleaning glass:**
 - liquid applied coatings, made the glass hydrofobic
 - super hydrophylic strategy: TiO_2 coating: lowering the surface tension, the water wets the surface totally, and the titanium dioxide can act as a catalyst under UV light, breaking the organic dirt's bonding



Glass

- **solar-control glass:** solar energy: 47% visible light, 50% short IR radiation, 3% UV. For cold climate: low-e glasses are the solution, but for hot climates the coatings are designed such that they reflect the IR back into the environment
- **self cleaning glass:**
 - liquid applied coatings, made the glass hydrofobic
 - super hydrophilic strategy: TiO_2 coating: lowering the surface tension, the water wets the surface totally, and the titanium dioxide can act as a catalyst under UV light, breaking the organic dirt's bonding



Float glass process

