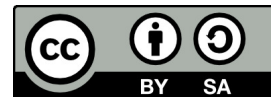


Chemistry and Physics of Solids – Lecture 10

Solid state reactions



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Solid state reactions

1. Solid compound $\rightarrow$ gas
(reaction, decomposition)

2. Solid compound + gas $\rightarrow$ solid compound



solid compound + liquid $\rightarrow$ solid compound
Solid compound $\rightarrow$ liquid (melt)

3. Solid compound $\rightarrow$ solid compound

4. Intercalation

Solid state reactions

Heterogeneous reactions:

1. Topochemical reactions: reactions occurring at the phase boundary
2. Diffusion kinetics: Reactions occur through the diffusion of the reactant by the solid reaction product (porous or non-porous) or through their mixture with the starting material

(1) solid compound $\rightarrow$ solid compound + gas

solid compound + gas $\rightarrow$ solid compound



(1) decomposition: $A(s) \rightarrow B(s) + C(g)$



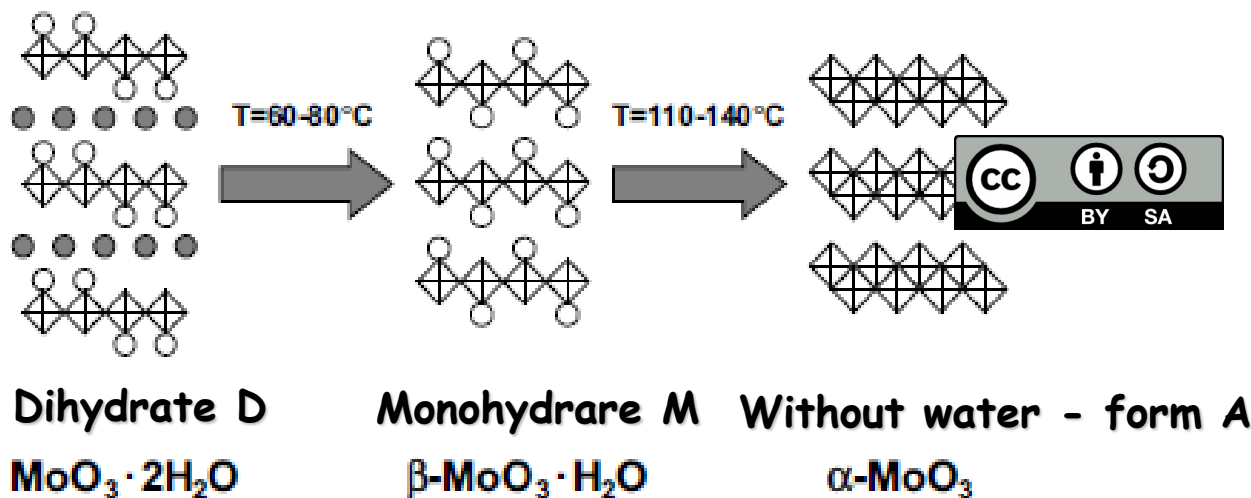
(2) Addition: $A(s) + B(g) \rightarrow C(s)$



Topochemical reaction

- The topochemical reaction - the atomic arrangement of the crystals remains mostly unaffected
 - Reactions may occur within materials without separation of the new phase.
 - The minimum reorder.
- It is possible to synthesize metastable phases ("mild" conditions - "soft" chemistry procedures).

Dehydration $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$

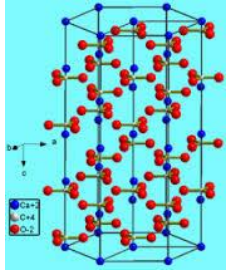


Processing at medium temperatures MoO_3 (type ReO_3)

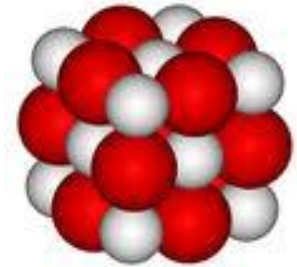
At higher temperatures a phase with mixed valence occurs:



Decomposition reactions



Typical example:



Incongruent dissociation evaporation



Congruent dissociation evaporation



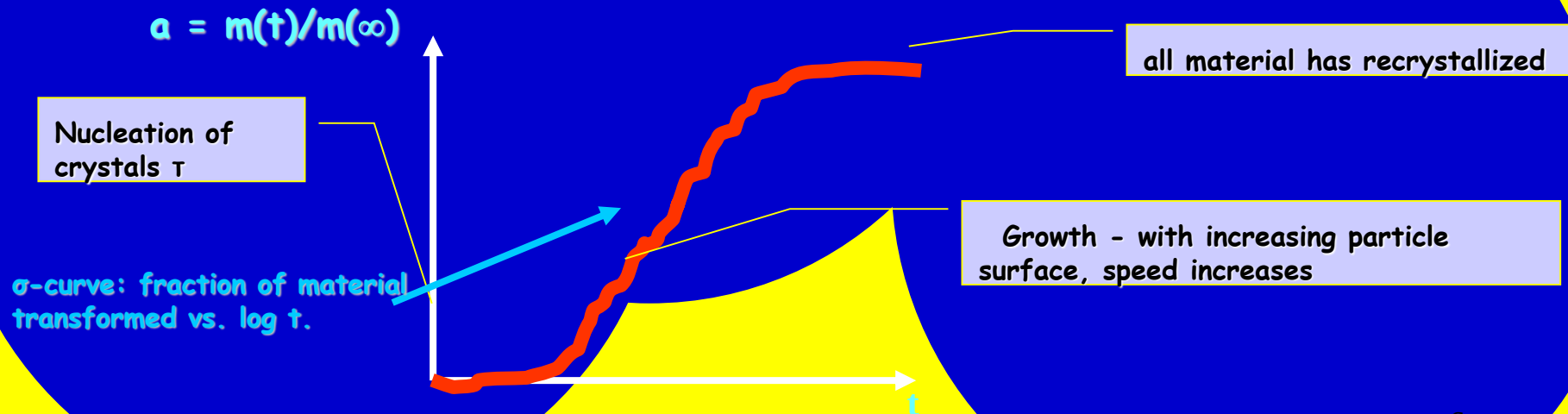
The solid $R(s)$ is sublimed to the components. Component A is re-deposited

Transformation solid -> solid

Nucleation and growth of one solid within another is described by Avrami kinetics - random and isolated nucleation with 1-D, 2-D or 3-D growth

a = complete transformation fraction, k = velocity constant, τ = incubation nucleation time, n = exponent dependent on growth dimensionality

$$a = m(t)/m(\infty) = 1 - \exp(-kt)$$

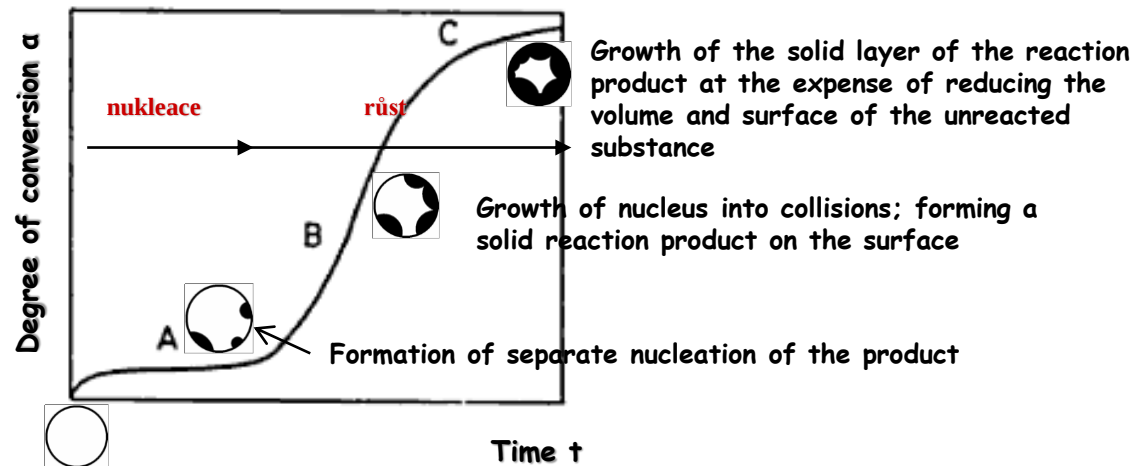


Kinetics of decomposition reactions - decomposition of one phase (nucleation-based reaction)



Reactions involving nucleation can be described by Avrami
(or Avrami-Erofee) equation:

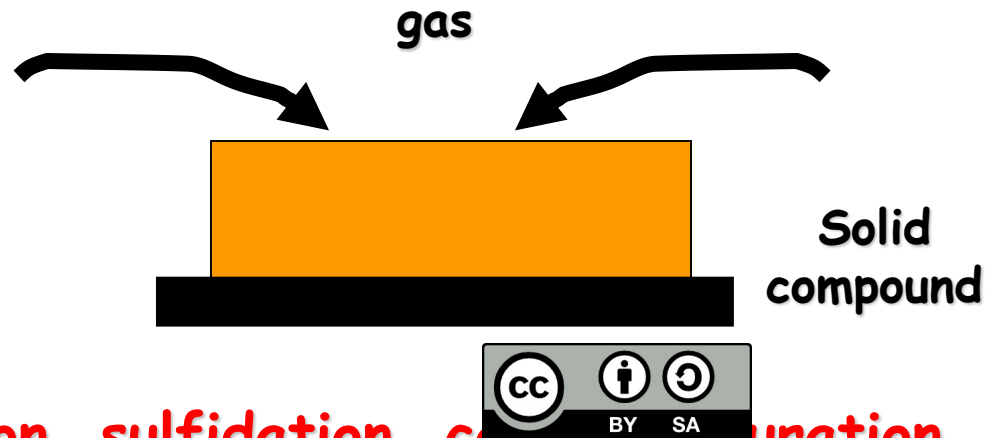
$$\alpha = 1 - \exp(-kt^n)$$



Dependence α -reaction time of isothermal decomposition of solids.
A induction period, B acceleration period; C period of deceleration
(attenuation)

2) Solid-gas reaction (addition)

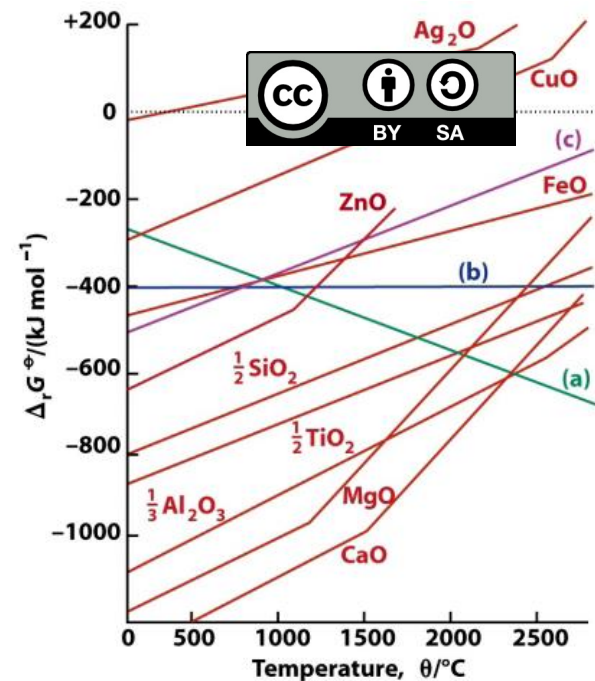
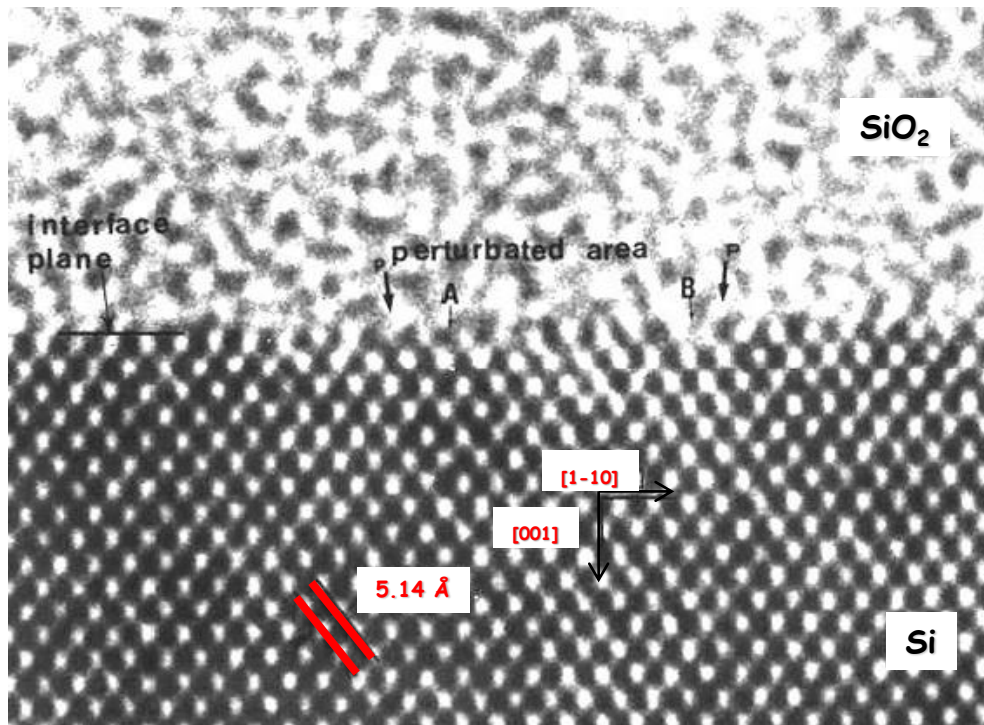
Diffusion kinetics: reactions occur at the diffusion of the reactant through the solid reaction product layer (porous or non-porous) or through their mixture with the starting material



- Oxidation, metal halogenation, sulfidation, carbon saturation
- Special feature - the formation of a solid film layer on the metal surface,
- Diffusion of metal or non-metal through the product layer
- Characteristic is parabolic growth kinetics
($dx/dt = k/x$)
- The limiting step is the diffusion of the reactants with the product layer growing on the solid phase of the reactant

Solid compound + $O_2 \rightarrow$ products

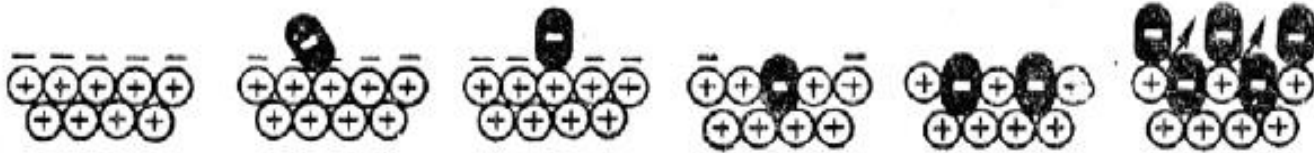
oxidation of metals



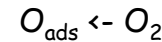
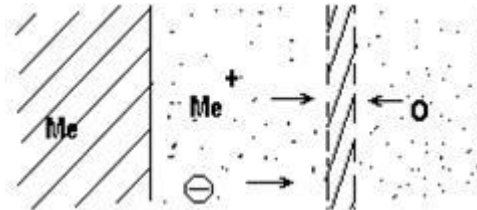
Free energy of the formation of selected oxides in relation to temperature. High negative Gibbs energy indicates more stable oxides;

Solid state reaction

Mechanism of oxidation



Formation of oxide layers at the beginning of corrosion



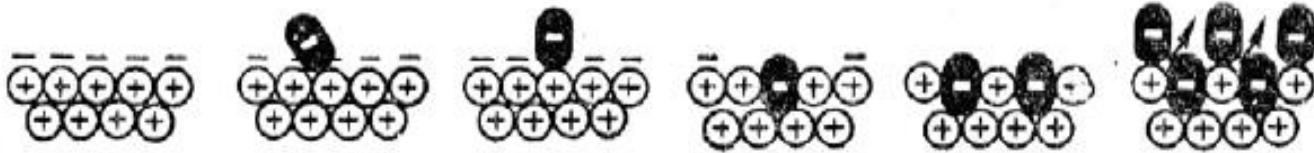
Scheme of oxide layer growth at comparable rates of ion diffusion

The formation of corrosion products is influenced by a series of subsequent and parallel reactions:

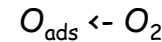
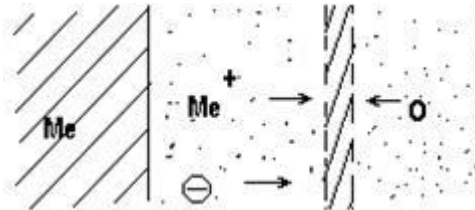
1. Transition of metal in the form of ions and electrons to the oxide layer
2. Movement of Me^{n+} metal ions and electrons in an oxide layer
3. Transmission of oxygen from the gas stream to the oxide surface
4. Oxygen adsorption on the surface
5. Transfer of adsorbed oxygen to an O^{2-}
6. Transport of anions with O^{2-} oxide layer
7. Oxide formation

Solid state reaction

Mechanism of oxidation



Formation of oxide layers at the beginning of corrosion



Scheme of oxide layer growth at comparable rates of ion diffusion

Pilling-Bedworth's criterion:

$$X_{PB} = \frac{\text{Molar volume of oxide}}{\text{Molar volume of metal}}$$



$$X_{PB} = \frac{(\text{molar mass of oxide } M_mO_n) \times (\text{density of metal})}{m \times (\text{molar mass of metal}) \times (\text{density of oxide } M_mO_n)}$$

$$V_{m,MO}/V_{m,M} < 1$$

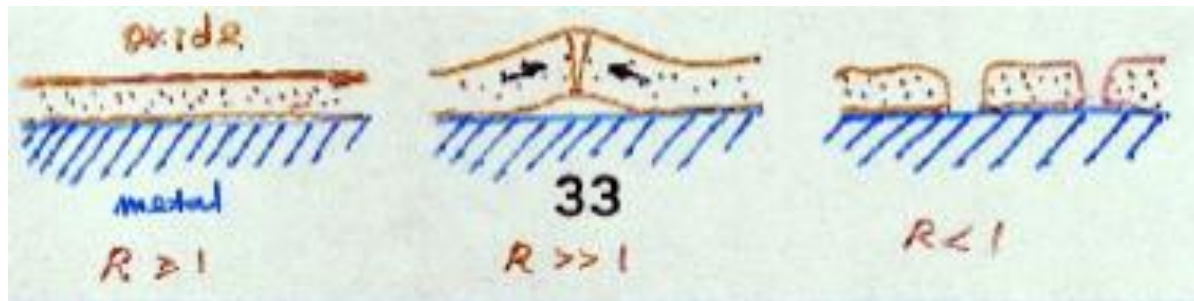
$$V_{m,MO}/V_{m,M} > 1$$

Pilling- Bedworth's ratio (PB)

When $PB < 1$ or $PB > 2$, then the oxide layer is nonprotective (NP) by being non-homogeneous (non-continuous) due to insufficient volume that uniformly covers the surface of the metal. The weight loss is always linear.

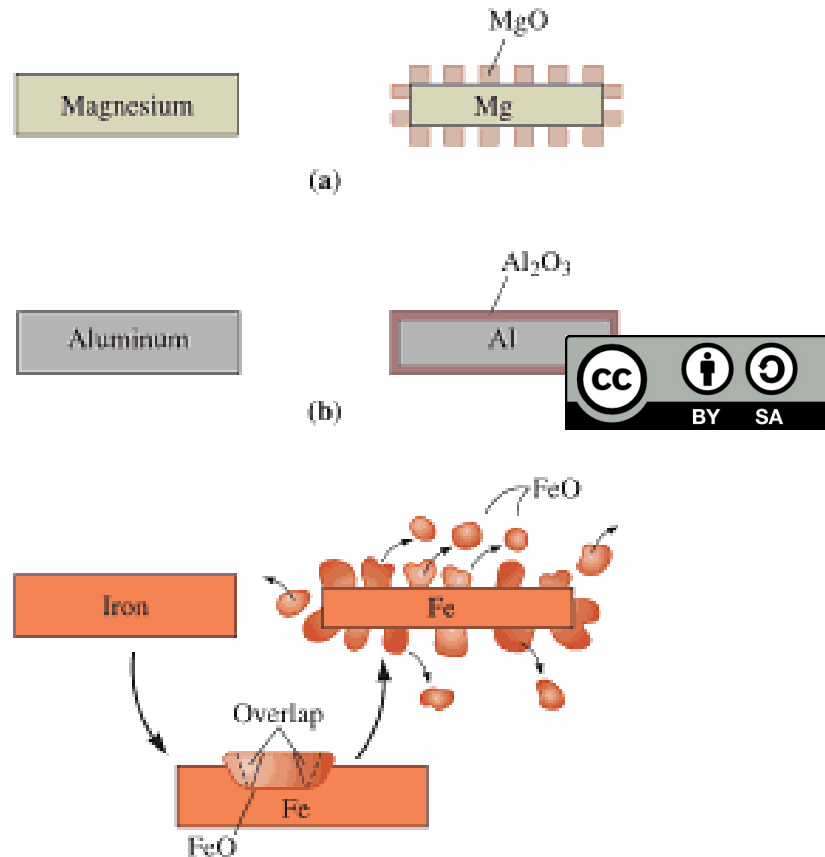
If $1 \leq PB \leq 2$, the oxide layer is protective (P), adherent and strong, fire resistant due to high melting point, non-conductive and non-porous. Diffusions are very slow.

If the $PB = 1$ - the oxidic layer is ideally protective



Pilling - Bedworth's criterion

K	0.45
Na	0.57
Ca	0.64
Mg	0.80
Al	1.28
Cu	1.72
Fe (FeO)	1.78
Fe (Fe ₂ O ₃)	2.15



Three types of oxides can form depending on the ratio of molar volumes of metal and oxides

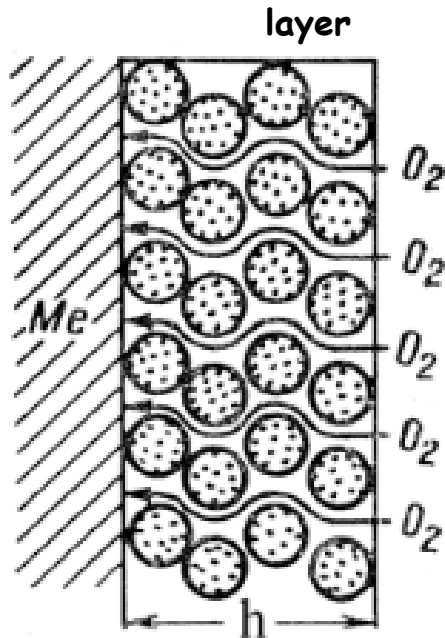
- magnesium forms a porous oxide film
- aluminum forms a protective non-porous oxide film
- iron forms an oxide film that peels off and produces weak protection.

Solid state reaction

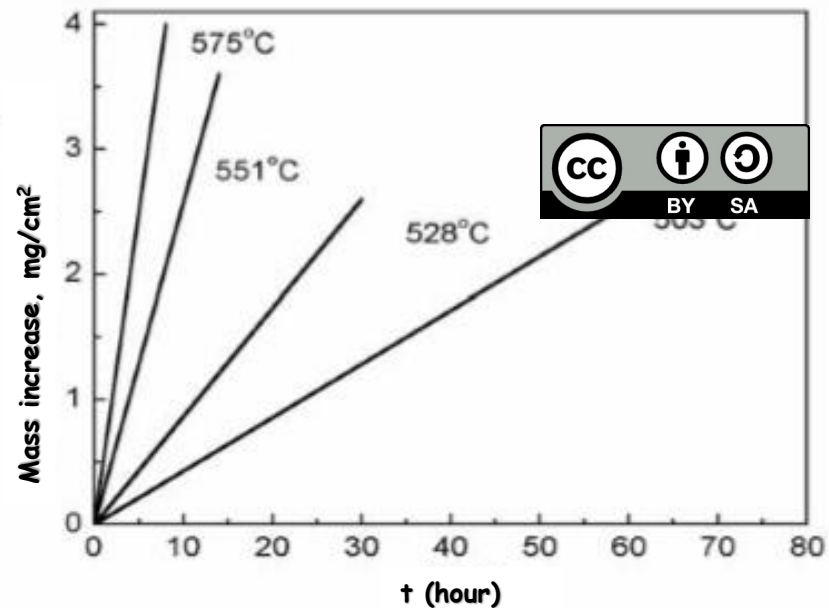
Solid compound + O₂ -> solid compound

Linear growth law of protective layers

$$V_{m,MX}/V_{m,M} < 1$$



Scheme of the process of forming a porous film on metal



Oxidation of pure Mg in an atmosphere of oxygen at different temperatures

Solid state reaction

Solid compound + O₂ -> solid compound

Parabolic growth law of protective layers

$$V_{m,MX}/V_{m,M} > 1$$

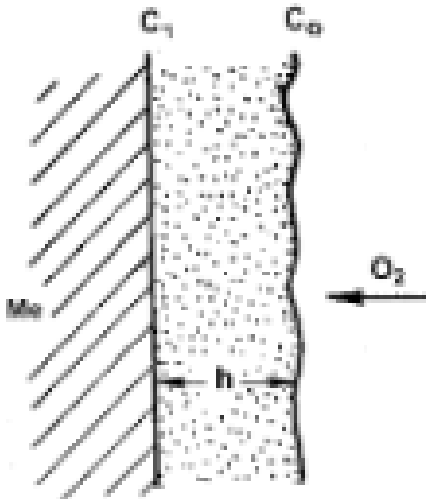
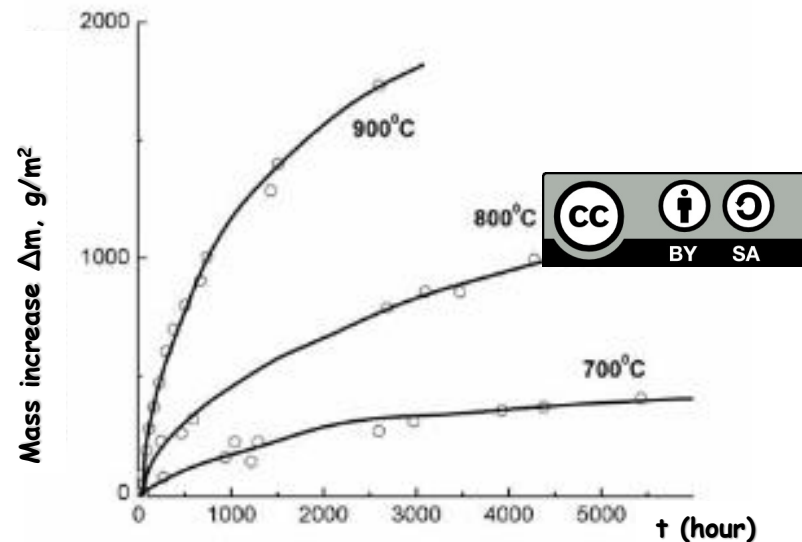


Diagram of oxygen diffusion through the layer during metal oxidation



Oxidation of iron in air at different temperatures

3. Solid compound -> solid compound

Reaction in the solid phase reaction between solid components

Solid-state reactions - reactions involving solid reagents and / or products

Important types of solid-state reactions can be expressed by equations:

1) $T_1 \rightarrow T_2$ (a polymorphic transition, such as graphite in a diamond)



2) $T_1 + T_2 \rightarrow T_3$ (synthesis reaction; such as spinel):
 $\text{MgO} + \text{Al}_2\text{O}_3 \rightarrow \text{MgAl}_2\text{O}_4$;

3) $T_1 + T_2 \rightarrow T_3 + T_4$ (exchange reaction in the solid phase):
 $\text{BaS} + \text{ZnSO}_4 \rightarrow \text{BaSO}_4 + \text{ZnS}$
 $\text{AgCl} + \text{NaI} \rightarrow \text{AgI} + \text{NaCl}$

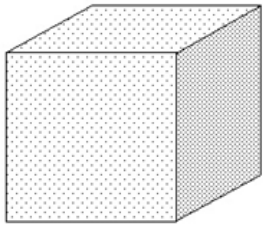
4) $T_1 \rightarrow T_2 \rightarrow T_3$ (the subsequent reaction):



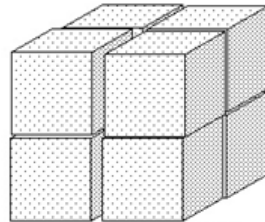
3. Solid compound- > solid compound

Reaction in the solid phase reaction between solid components

Addition: $A + B \longrightarrow C$

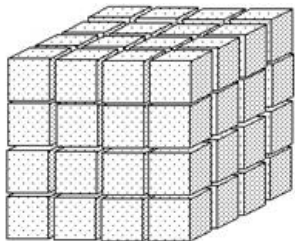


$$A = 6\text{cm}^2$$



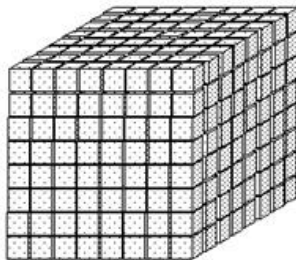
Pieces half the original size.
Twice the surface area

$$A = 12\text{cm}^2$$



Pieces one quarter the original size.
Four times the surface area

$$A = 24\text{cm}^2$$



Pieces one eighth the original size.
Eight times the surface area

$$A = 48\text{cm}^2$$

- Basically, it is the calcination of two solids which react to form the desired product.
 - The full-phase synthesis method is used to prepare a wide range of materials - metal oxides, sulphides, nitrates, aluminosilicates,
 - **disadvantages**
 - High temperatures (500°C) necessary because then the lattice energy is overcome and the cations and anions can diffuse into different positions.
 - Many compounds may decompose at high temperatures.
 - Reactions occur very slowly, but the elevated temperature is accelerated by increasing the diffusion rate
 - Generally, the calcination temperature does not increase to the melting point of the substances, so the reactions are in a solid state.
- The reaction temperature should not exceed 2/3 of the melting point of the compound with the lowest point of Tamman's law.



3. Solid compound- > solid compound

A large number of reactions. Most important for their progress is that all reagents are in a solid state.

An example of the reaction between oxides with the formation of spinels, silicates, tungsten, molybdates,

Special features:

The reaction starts with the contact of solids, the more contacts, the higher reaction rate;

After the formation of a solid product layer, the previous surface closes and for further transformation, diffusion through the product layer is required;

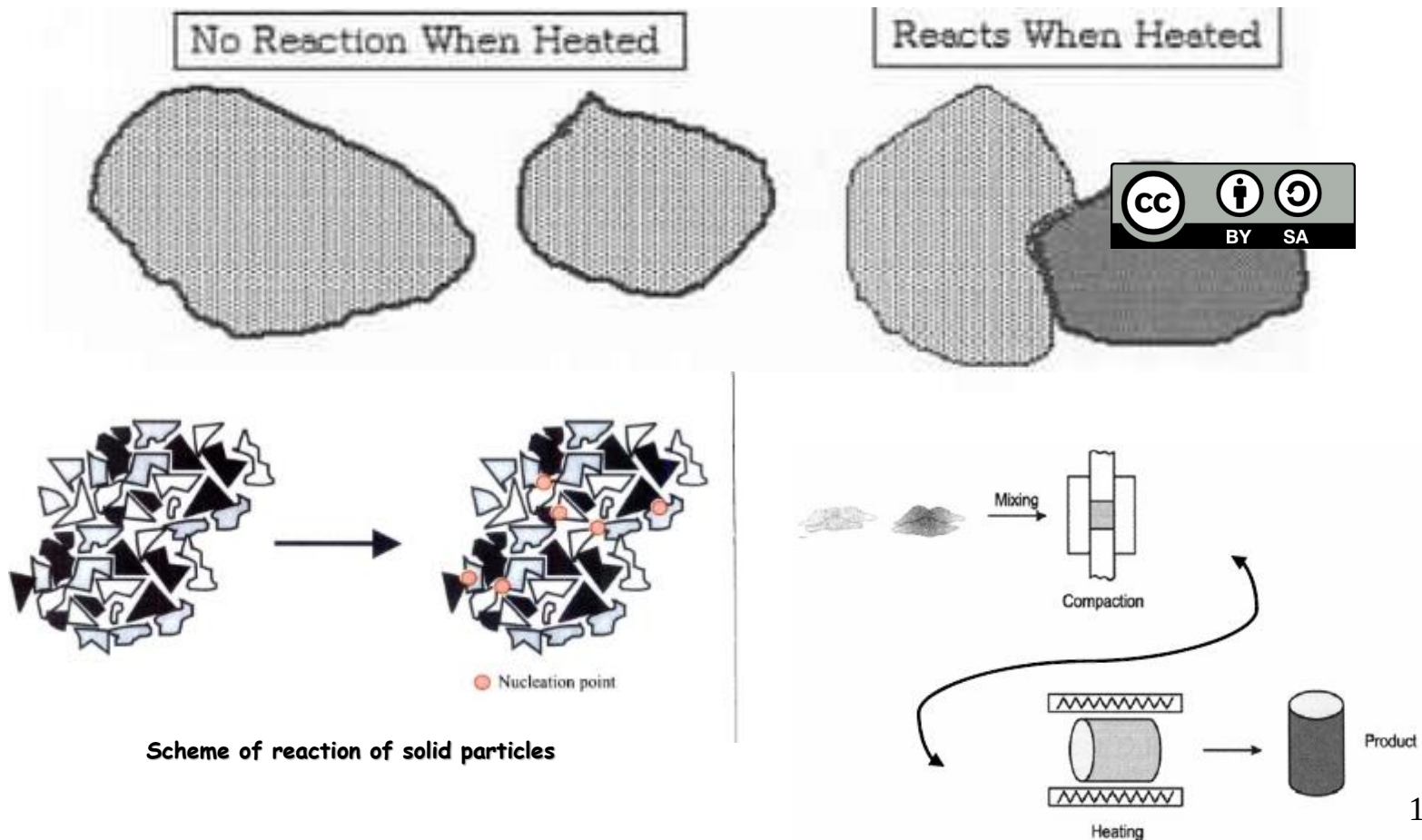
The reaction rate is determined by diffusion of the slowest component;
- The rate of reaction decreases with increasing the reaction product layer.



Solid state mechanisms and reactions

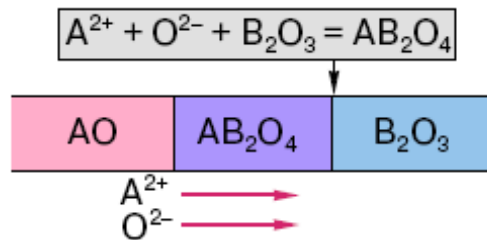
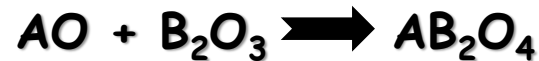
- Addition reactions

The role of the phase interface in the reaction of solids



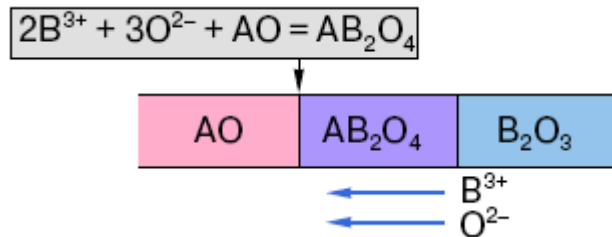
3. Solid compound- > solid compound

Wagner's theory of spinel formation



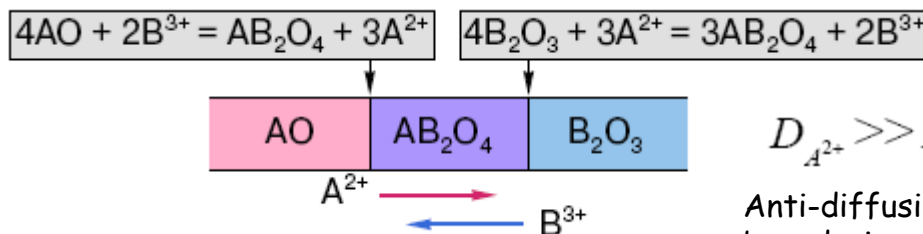
$$D_{A^{2+}} \gg D_{B^{3+}} ; D_{O^{2-}} \gg D_{B^{3+}}$$

Unilateral transfer of AO phase components
reaction is located at the AB₂O₄/B₂O₃ boundary



$$D_{B^{3+}} \gg D_{A^{2+}} ; D_{O^{2-}} \gg D_{A^{2+}}$$

Unilateral transfer of phase component components of B₂O₃; the
reaction is located at the interfacial boundary AB₂O₄/AO



$$D_{A^{2+}} \gg D_{O^{2-}} ; D_{B^{3+}} \gg D_{O^{2-}}$$

Anti-diffusion A and B, the reaction is located at interfacial
boundaries AB₂O₄/AO a AB₂O₄/B₂O₃

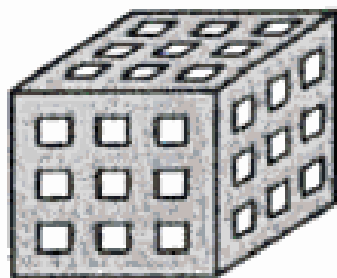
Charge balance in solid phase reactions

- 3Mg^{2+} diffuse against 2Al^{3+}
- $\text{MgO}/\text{MgAl}_2\text{O}_4$ boundary
- $2\text{Al}^{3+} - 3\text{Mg}^{2+} + 4\text{MgO} \rightarrow \text{MgAl}_2\text{O}_4$
- $\text{MgAl}_2\text{O}_4/\text{Al}_2\text{O}_3$ boundary
- $3\text{Mg}^{2+} - 2\text{Al}^{3+} + 4\text{Al}_2\text{O}_3 \rightarrow 3 \text{MgAl}_2\text{O}_4$ PR
- Summary reaction
- $4\text{MgO} + 4\text{Al}_2\text{O}_3 \rightarrow 4 \text{MgAl}_2\text{O}_4$
- PR/LR growth rate of the interlayer = 3/1

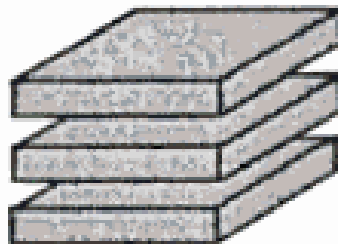


4. Intercalation reaction

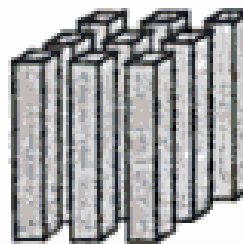
The host structure has a lower dimensionality (layered or chain structures - one-dimensional stacking).



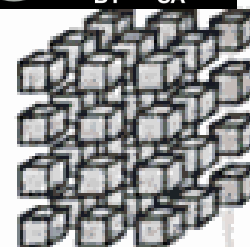
3-Dimensional
(channel)



2-Dimensional
(layer)



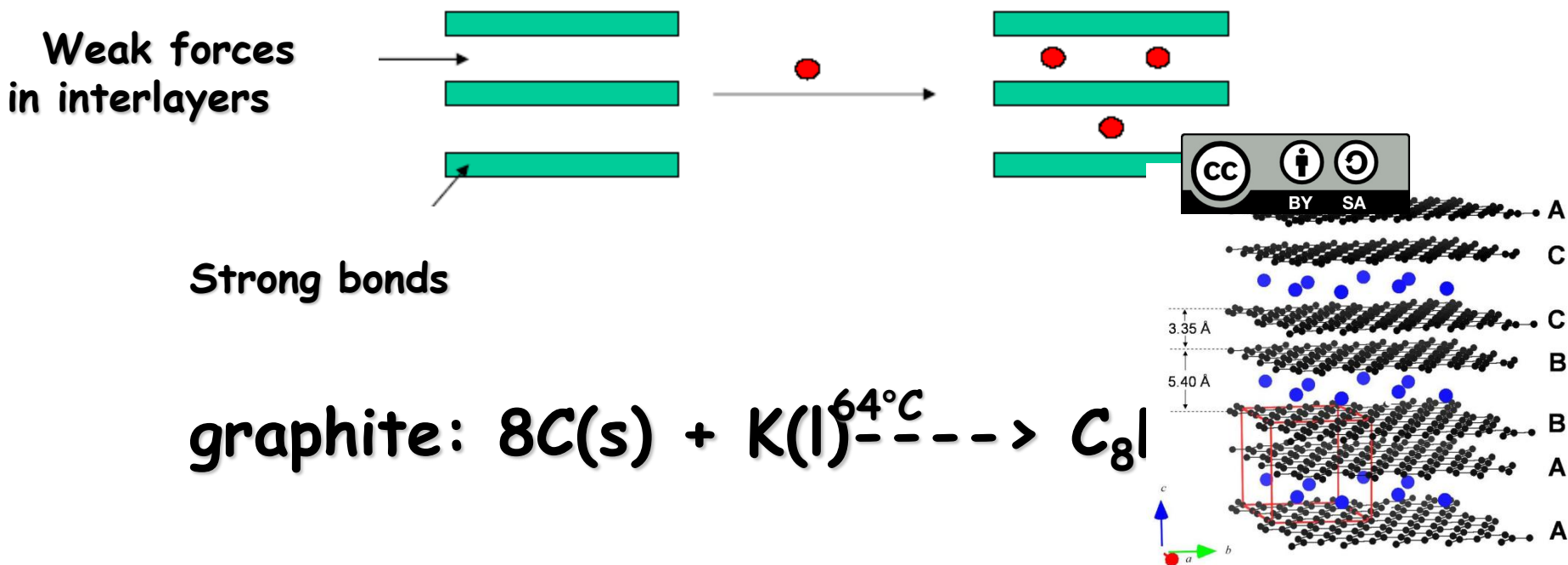
1-Dimensional
(chain)



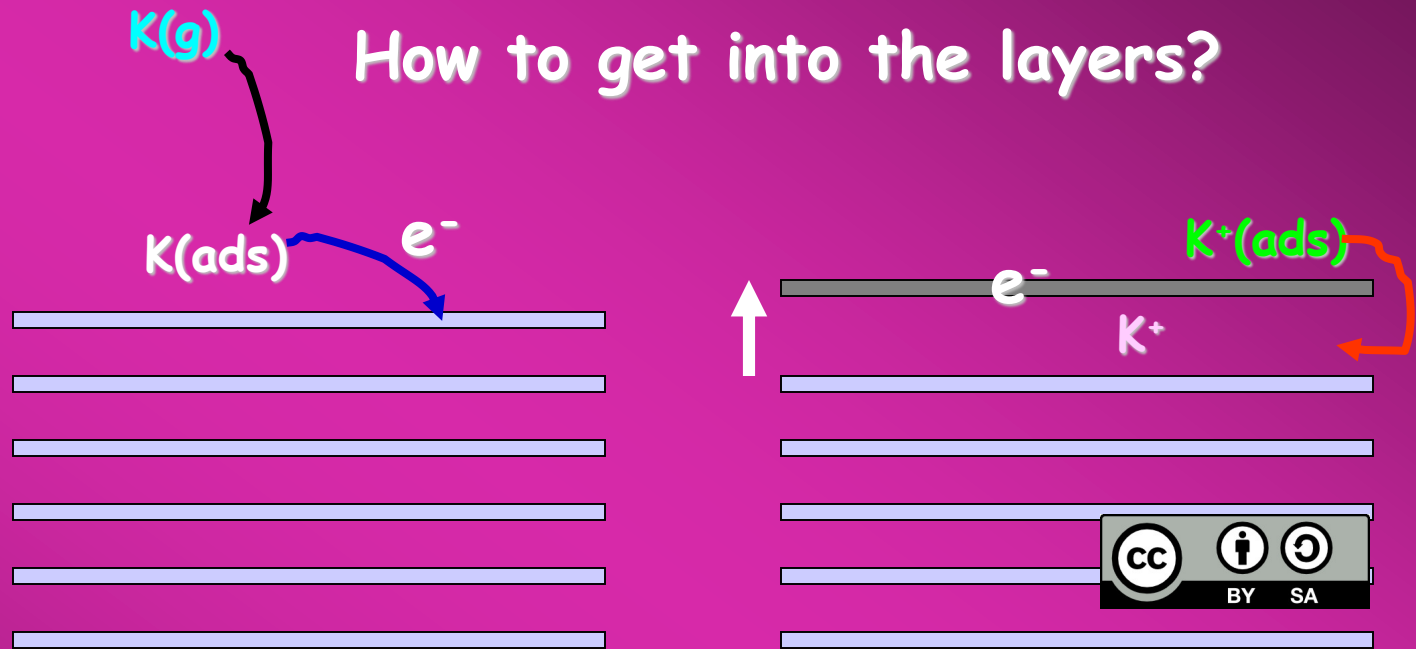
0-Dimensional
(molecular)

Reaction in solid state looks simple

Intercalation of potassium into graphite

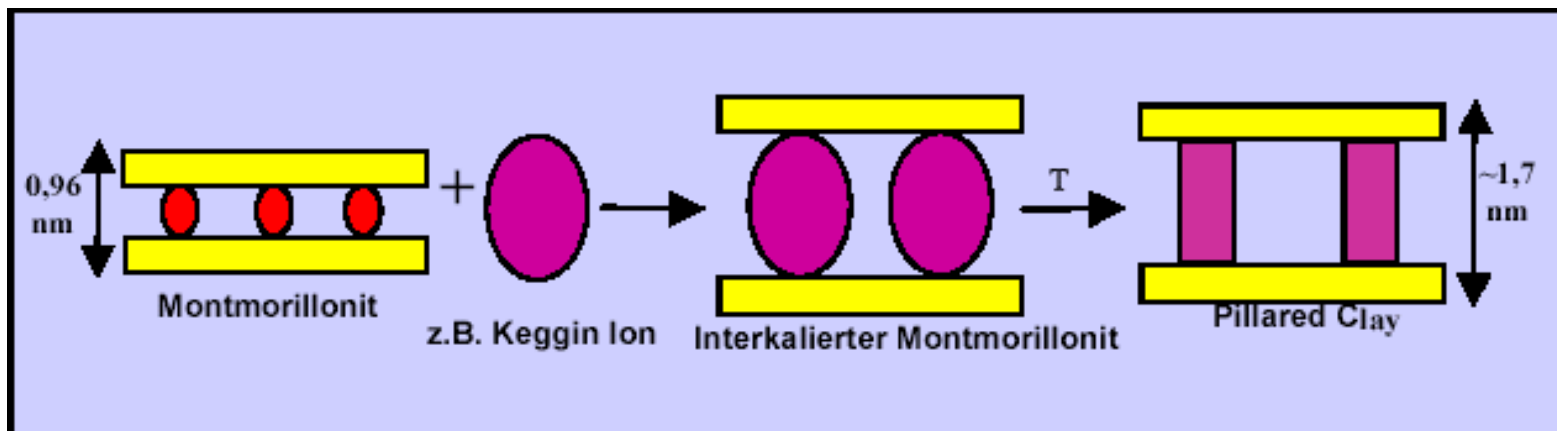
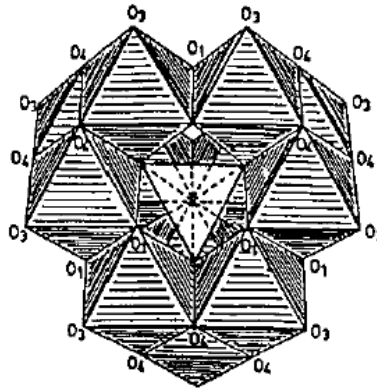


Structure of intercalated graphite C_{24}K .
A/AB/BC/CA.



•By transferring the electron from K to the π^* free graphite band, the layers expand

Pillared clays



Chemistry and Physics of Solids – Lecture 11

THERMAL PROPERTIES OF SOLIDS



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Properties of solids

physical property: response to a specific stimulus, relation is defined by mathematical formula

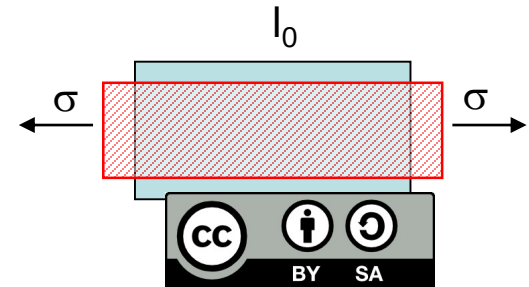
(physical quantities – scalars, vectors, tensors)

Example: elastic deformation of isotropic elastic body

(Hooke's law) $\sigma = E \varepsilon$

tensile stress $\sigma = F/A$ results in strain $\varepsilon = \Delta l/l_0$

→ macroscopic effect



properties are connected with structure of solids (anisotropy, defects)

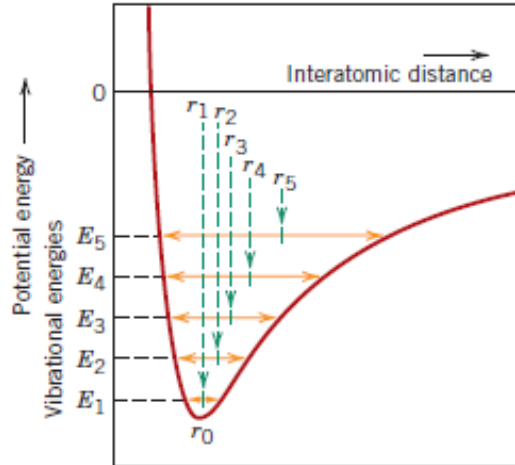
solid = macroscopic system consisting of large number of various particles (atoms, electrons, ...)

macroscopic quantities represent time-averaged values of microscopic quantities → statistical physics

Microstates and macrostate of the system

every particle has a given energy (defined by momentum and position towards surroundings $\rightarrow$ 6 parameters: x, y, z, p_x, p_y, p_z)

microstate – specific microscopic configuration of the system, distribution of particular number of particles to energy levels (allowed stationary state of the system)



microstates with the same energy level differ from each other only in distribution of particles on energy levels, number of particles is identical



macrostate – state of macro system specified by macroscopic parameters (e.g., $p, V, T, \dots$)

particular macrostate can be realized by a large number of microstates with the same energy and different distribution of particles on energy levels

Statistical physics

energy of the system cannot be exactly calculated – obtaining detailed information about microstates of an ensemble consisting of large number of particles and interactions between them is not possible

statistical physics – **properties of macroscopic system are based on properties of particles**

large number of particles in the system → statistical nature of the result
(macroscopic quantities represent time-averaged values of microscopic quantities)

precondition: all microstates are possible with the same probability



→ **looking for a distribution of energy on particular particles in the system realized by the largest number of microstates**

classical statistics (Maxwell-Boltzmann) – particles in the system are distinguishable (e.g., atoms)

quantum statistics – particles cannot be distinguished

Fermi-Dirac – particles with half-integer spin (*fermions*, e.g., electrons)

Bose-Einstein – particles with integer spin (*bosons*, e.g., photons)

Maxwell-Boltzmann statistics

ensemble of N independent, distinguishable, and non-interacting particles (atoms),
distribution over various energy states in thermal equilibrium

internal energy

$$U = \sum_j n_j E_j$$

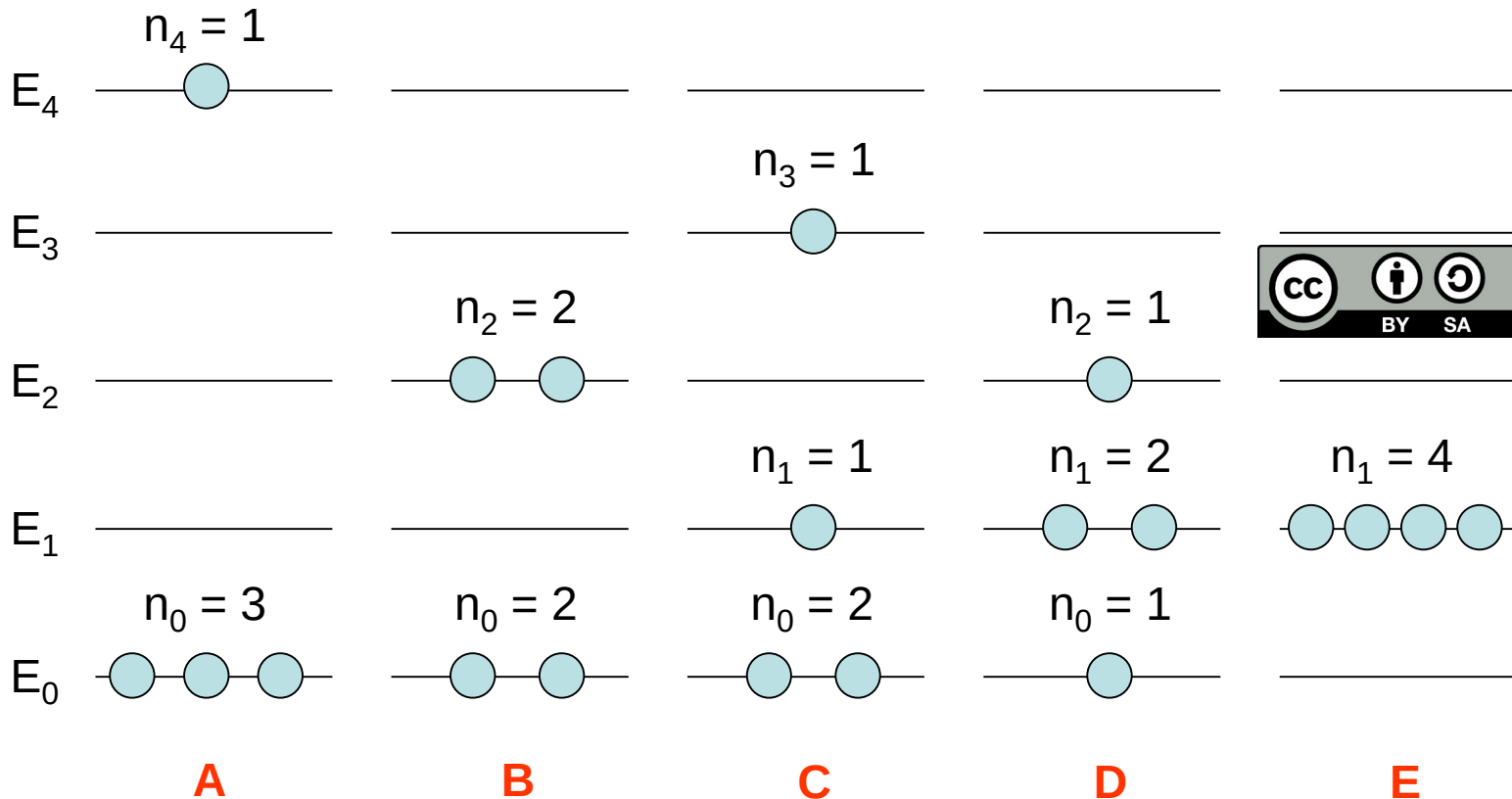
E_j – energy of particular atom on j -th energy level; n_j – number of atoms with energy E_j (occupation number)



$$N = \sum_j n_j$$

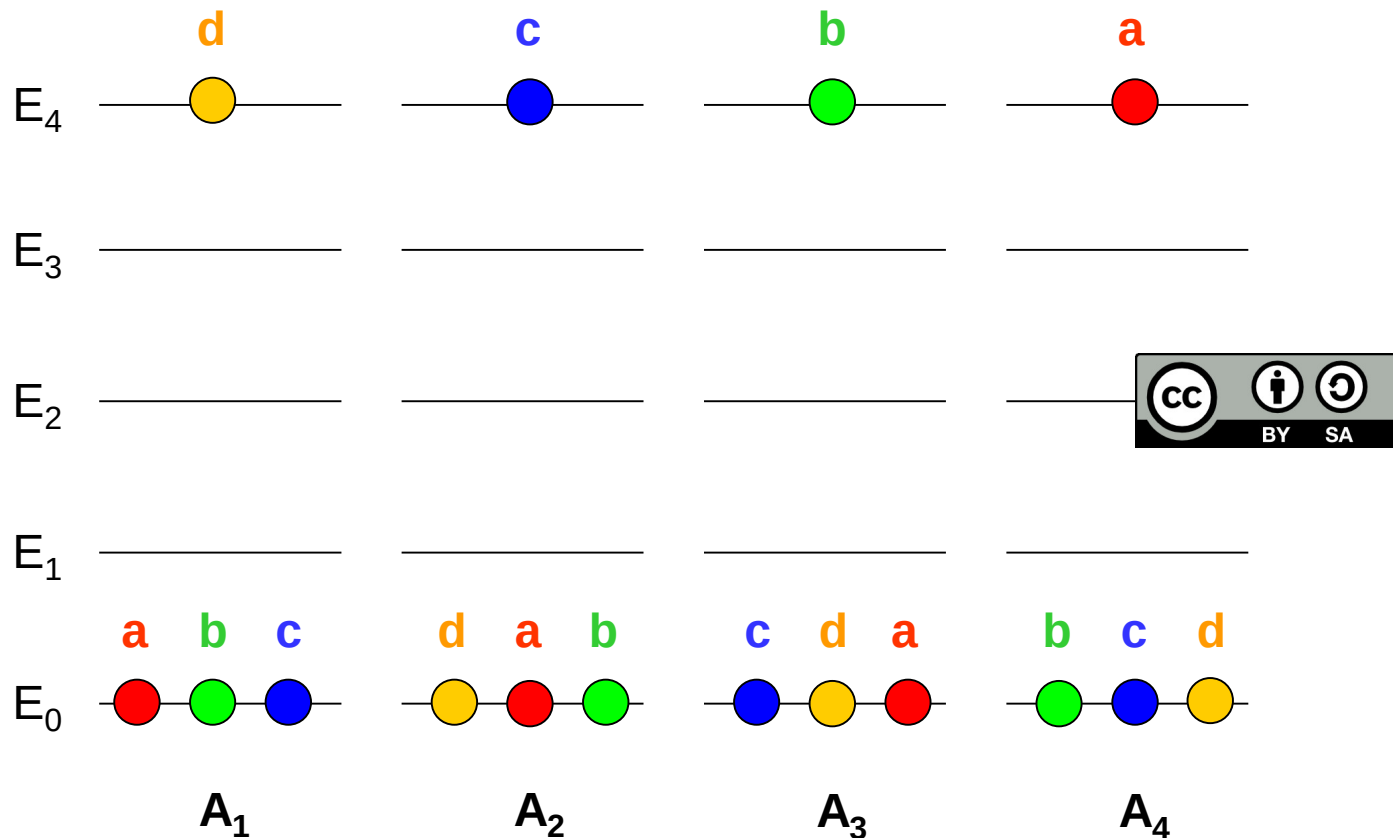
There is large number of possible distributions of N atoms on energy levels but probability of realizing particular distributions is different!

Example: ensemble with internal energy $U = 4$ consisting of 4 distinguishable identical atoms ($N = 4$) contains 5 energy levels, energy difference between adjacent levels is equal to one ($E_0 = 0, E_1 = 1, E_2 = 2, E_3 = 3, E_4 = 4$), number of atoms on particular energy level is not limited



possible distributions of energy, 5 distributions (A-E) satisfy the macrostate ($U = 4$)

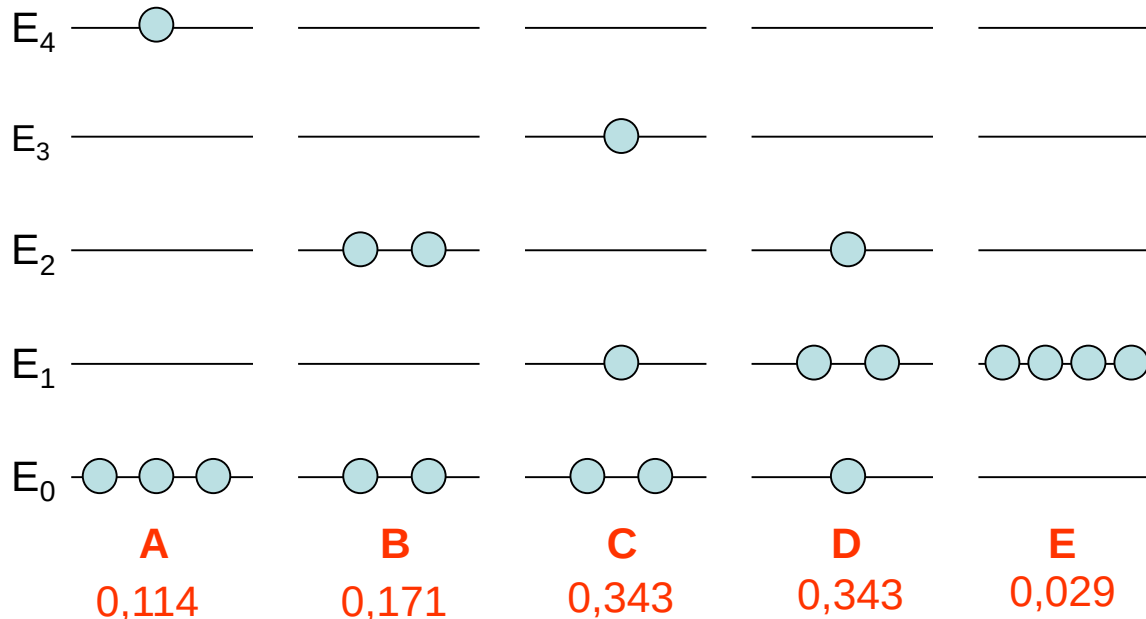
atoms are distinguishable, number of microstates in particular energy distributions has to be determined



4 microstates (A_1 - A_4) correspond to energy distribution A

number of microstates corresponding to a particular energy distribution

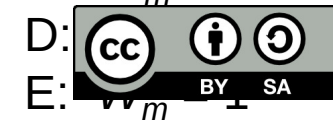
$$W_m = \frac{N!}{\prod_j n_j!}$$



A: $W_m = \frac{4!}{1!3!} = 4$

B: $W_m = 6$

C: $W_m = 12$



→ 35 microstates in 5 energy distributions

probability of energy distribution occurrence in the system

$$P = \frac{W_m}{\sum W_m}$$

energy distributions C and D are the most probable (the largest number of microstates)

number of microstates in particular energy distributions → Gaussian curve

system containing large number of atoms ($\sim 10^{23}$) $\rightarrow \Sigma W_m \sim 10^{28}$, extremely narrow and high Gaussian curve, maximum corresponds to the most probable distribution of microstates

finding occupation number n_j for which the W_m function is maximized (at defined total energy and number of particles)

$$W_m = \frac{N!}{\prod_j n_j!} \quad U = \sum_j n_j E_j \quad N = \sum_j n_j \quad (U \text{ and } N \text{ are constant})$$

(solution using Lagrange multipliers – not shown here)



$\rightarrow$ **Maxwell-Boltzmann distribution** (f_{MB})

$$n_j = N \frac{\exp\left(-\frac{E_j}{kT}\right)}{\sum_j \exp\left(-\frac{E_j}{kT}\right)} = f_{MB} \quad \text{partition function } Q = \sum_j \exp\left(-\frac{E_j}{kT}\right)$$

f_{MB} gives occupation numbers n_j for energy levels E_j at temperature T for the most probable distribution of microstates in the system

Thermal properties of solids

→ response to application of heat

heat absorption → increase in temperature

heat capacity

→ increase in dimension

thermal expansion

heat transfer to lower-temperature regions

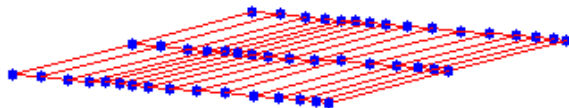
thermal conductivity

→ based on vibrations of atoms around equilibrium position

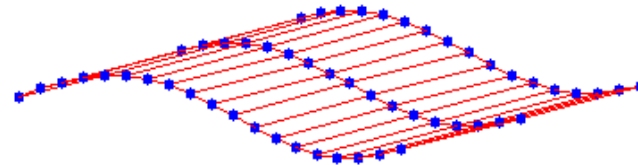


ordered oscillations of atoms in crystal → travelling lattice waves are produced (small amplitudes, high frequencies);

quantized energy of lattice oscillations → energy quantum = phonon



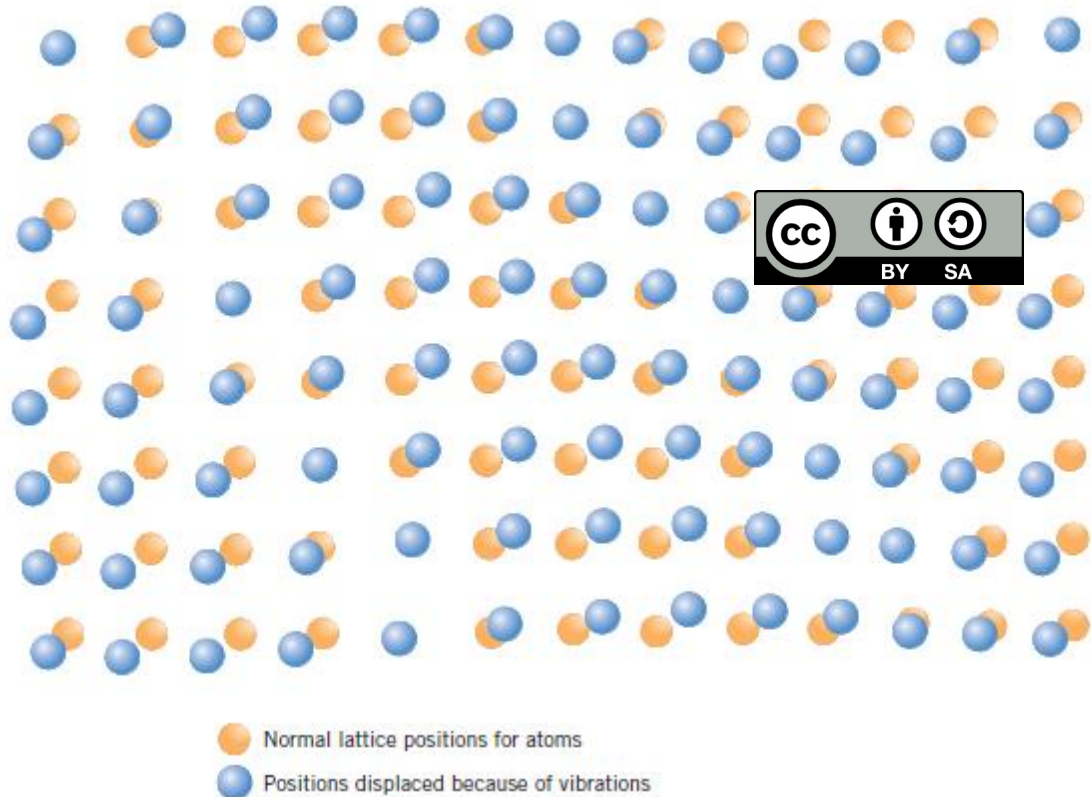
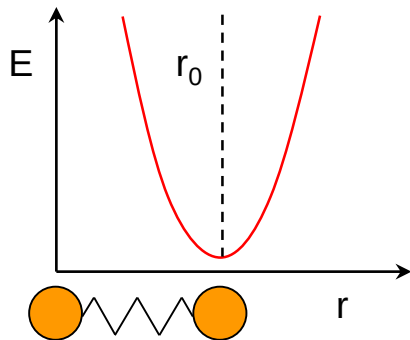
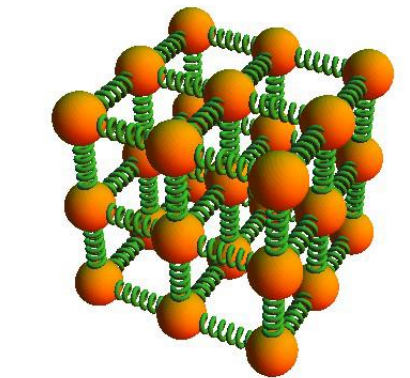
longitudinal wave



transversal wave

crystal consisting of discrete atoms (harmonic oscillators) connected by interatomic bonding, ordered periodic structure

oscillation of adjacent atoms $\rightarrow$ minimum wavelength $\lambda_{min} = 2 r_0$ (r_0 – equilibrium interatomic distance) and maximum frequency of lattice waves $\nu_{max} = \nu_s/2r_0$ (ν_s – speed of sound in solid, $\nu_{max} \sim 10^{13} \text{ s}^{-1}$)



generation of lattice waves in crystal due to atomic vibrations

Vibrations of atoms

Simple harmonic oscillator

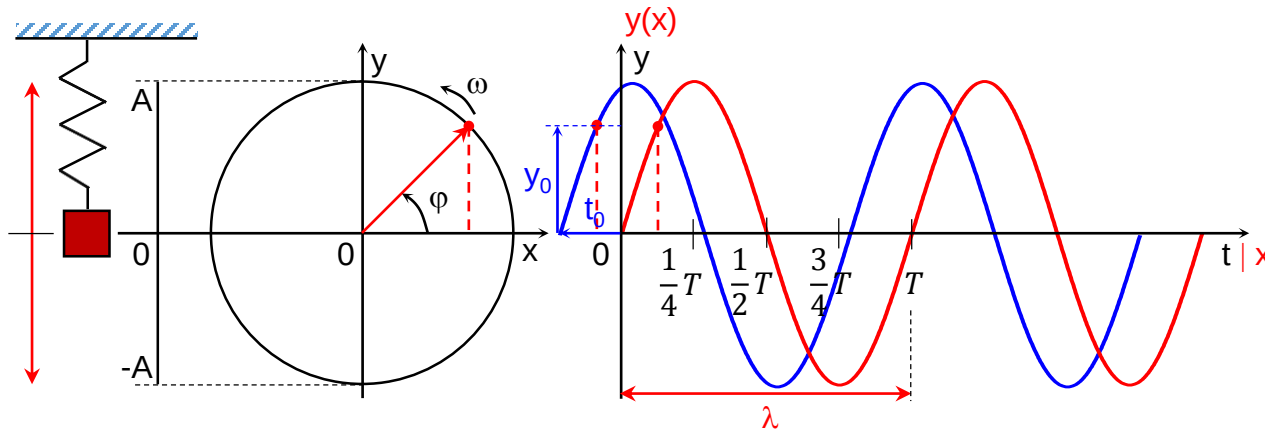
particle moving with an acceleration towards a fixed (equilibrium) point on the straight line and whose magnitude is proportional to the displacement

restoring force $F = ma = m \frac{\partial^2 y}{\partial t^2} = -Ky$ (m - internal mass, K - stiffness constant)

$$y(t) = y_0 \cos(\omega t) + \frac{v_0}{\omega} \sin(\omega t) \rightarrow y(t) = A \cos(\omega t - \varphi)$$

A - amplitude, φ - phase, angular frequency $\omega = \sqrt{\frac{K}{m}} = 2\pi f = \frac{2\pi}{T}$, T - time period,

velocity $v(t) = \frac{\partial y}{\partial t} = -A\omega \sin(\omega t - \varphi)$



→ **one-dimensional traveling wave** $\psi(x, t) = A \cos(kx - \omega t + \varphi)$

$k = \frac{2\pi}{\lambda}$ - spatial angular frequency (wavenumber), λ - wavelength

Wave propagation and scattering in crystal

slightly different equations are used for wave description:

in one dimension $\psi(x, t) = A \cos[2\pi(kx - vt) + \varphi]$

in three dimensions $\psi(\vec{r}, t) = A \cos[2\pi(\vec{k} \cdot \vec{r} - vt) + \varphi]$

or $\psi(\vec{r}, t) = \exp[i(\vec{k} \cdot \vec{r} - \omega t)]$

(ν - frequency, $2\pi\nu = \omega$; $\vec{r}$ - position vector; $\vec{k}$ - wave vector with direction identical with the direction of wave propagation and magnitude $|\vec{k}| = \frac{2\pi}{\lambda}$)



scattering – wave ψ scatters to another wave ψ' with another wave vector $\vec{k}$ but with the same frequency

scattering amplitude is determined by an integral $\int d\vec{r} \psi'^* V \psi$

quantity V describes some physical property (e.g., electron density, charge density, lattice potential, ...) and is periodic function of space

periodic function in one dimension

$V(x) = V(x \pm a)$, a – lattice periodicity (interatomic distance)

periodic function $V(x)$ may be represented as a Fourier series

$$V(x) = \sum_{n=-\infty}^{\infty} V_n \exp\left[i\left(\frac{2\pi nx}{a}\right)\right]$$

integer $n \geq 0$, Fourier coefficient V_n may be found by multiplying by $\exp\left[-i\left(\frac{2\pi mx}{a}\right)\right]$ and integrating over the spatial period

$$\int_0^a \exp i \left[\frac{2\pi(n-m)x}{a} \right] dx = a\delta_{m,n}$$

$\delta_{m,n} = 1$ for $m = n$ and $\delta_{m,n} = 0$ for $m \neq n$ (Kronecker's delta)

$$V_n = \frac{1}{a} \int_0^a V(x) \exp \left[-i \left(\frac{2\pi nx}{a} \right) \right] dx$$

analogously, a three-dimensional periodic function $V(\vec{r})$ may be invariant under translation in the lattice

$$V(\vec{r} + \vec{T}) = V(\vec{r}) , \quad \text{where} \quad \vec{T} = n_1 \vec{u}_1 + n_2 \vec{u}_2 + n_3 \vec{u}_3$$

$(\vec{u}_1, \vec{u}_2, \vec{u}_3)$ - primitive lattice translation vectors, n_1, n_2, n_3 - set of integers)



Reciprocal lattice

introduce a set of primitive reciprocal lattice vectors $\vec{g}_1, \vec{g}_2, \vec{g}_3$ such that

$$\vec{g}_i \cdot \vec{u}_j = 2\pi\delta_{i,j} \quad i = 1, 2, 3, \quad j = 1, 2, 3$$

$$\vec{g}_1 = \frac{\vec{u}_2 \times \vec{u}_3}{\vec{u}_1 \cdot (\vec{u}_2 \times \vec{u}_3)}, \quad \vec{g}_2 = \frac{\vec{u}_3 \times \vec{u}_1}{\vec{u}_1 \cdot (\vec{u}_2 \times \vec{u}_3)}, \quad \vec{g}_3 = \frac{\vec{u}_1 \times \vec{u}_2}{\vec{u}_1 \cdot (\vec{u}_2 \times \vec{u}_3)}$$

each vector $\vec{g}_1, \vec{g}_2$, and $\vec{g}_3$ is perpendicular to two translation vectors in real lattice, therefore

$$\vec{g}_1 \cdot \vec{u}_1 = 2\pi, \quad \vec{g}_2 \cdot \vec{u}_1 = 0, \quad \vec{g}_3 \cdot \vec{u}_1 = 0$$

$$\vec{g}_1 \cdot \vec{u}_2 = 0, \quad \vec{g}_2 \cdot \vec{u}_2 = 2\pi, \quad \vec{g}_3 \cdot \vec{u}_2 = 0$$

$$\vec{g}_1 \cdot \vec{u}_3 = 0, \quad \vec{g}_2 \cdot \vec{u}_3 = 0, \quad \vec{g}_3 \cdot \vec{u}_3 = 2\pi$$



a general reciprocal lattice vector is expressed as linear combination of primitive reciprocal lattice vectors with integer coefficients

$\vec{G} = j_1 \vec{g}_1 + j_2 \vec{g}_2 + j_3 \vec{g}_3$ - is described by set of integers j_1, j_2, j_3

when integers have a common integer divisor (e.g., 2,4,6) $\rightarrow \vec{G}$ is reducible

no common integer divisor (e.g., 1,2,3) $\rightarrow \vec{G}$ is irreducible

Fourier expansion of periodic function $V(\vec{r})$

$$V(\vec{r}) = \sum_{\vec{G}} V_G \exp(i\vec{G} \cdot \vec{r})$$

V_G - set of Fourier coefficients; periodicity is obvious since

$$V(\vec{r} + \vec{T}) = \sum_{\vec{G}} V_G \exp[i\vec{G} \cdot (\vec{r} + \vec{T})] = \sum_{\vec{G}} V_G \exp(i\vec{G} \cdot \vec{r}) \exp(i\vec{G} \cdot \vec{T})$$

$$\begin{aligned} \exp(i\vec{G} \cdot \vec{T}) &= \exp[i(j_1 \vec{g}_1 + j_2 \vec{g}_2 + j_3 \vec{g}_3) \cdot (n_1 \vec{u}_1 + n_2 \vec{u}_2 + n_3 \vec{u}_3)] \\ &= \exp[i2\pi(j_1 n_1 + j_2 n_2 + j_3 n_3)] \end{aligned}$$



integer sum $j_1 n_1 + j_2 n_2 + j_3 n_3 \rightarrow \exp(i\vec{G} \cdot \vec{T}) = 1$

$$V(\vec{r} + \vec{T}) = \sum_{\vec{G}} V_G \exp(i\vec{G} \cdot \vec{r}) = V(\vec{r})$$

Fourier series of periodic function of space contains only components $V_G \exp(i\vec{G} \cdot \vec{r})$ corresponding to reciprocal lattice vectors $\vec{G} = j_1 \vec{g}_1 + j_2 \vec{g}_2 + j_3 \vec{g}_3$

Fourier series of periodic function $V(\vec{r})$ cannot contain other points in reciprocal space

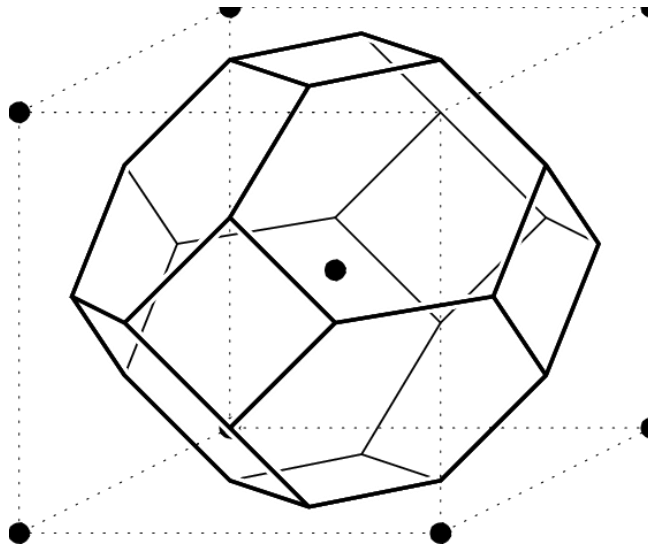
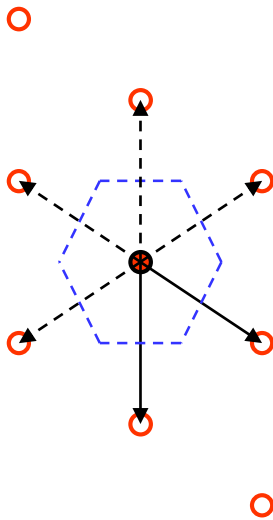
one-dimensional case of basic unit cell $\rightarrow$ interval $0 < x < a$

analogous volume unit in three-dimensional case $\rightarrow$ **Wigner-Seitz cell**

definition: point in the crystal is selected as origin (O); all points $\vec{r}$ in Wigner-Seitz cell are closer to origin O than to any other point obtained by its translation through all possible translation vectors $\vec{T}$

boundary of Wigner-Seitz cell $\rightarrow$ polyhedron; every point on polyhedron face has a corresponding point on an opposite face that may be reached by primitive lattice translation vector

alternative construction of Wigner-Seitz cell: drawing lines from a site atom to all other atoms occupying the same basis in other lattice  atom to all other atoms occupying the same basis in other lattice producing perpendicular bisecting planes of these lines $\rightarrow$ the atom is surrounded by polyhedron



Wigner-Seitz cell
constructed in BCC
structure

Relationship between reciprocal and direct lattices

set of points in direct lattice described by vectors $\vec{r}$ originating at point O and satisfying the equation

$$\vec{G} \cdot \vec{r} = 2\pi \rightarrow \hat{G} \cdot \vec{r} = \frac{2\pi}{\vec{G}} \quad (\vec{G} - \text{irreducible reciprocal lattice vector}, \hat{G} - \text{unit vector})$$

linear equation of the form $G_x X + G_y Y + G_z Z = 2\pi$ defines a plane in direct lattice

at distance $d = \frac{2\pi}{|\vec{G}|}$ from origin O and its normal is oriented along $\vec{G}$



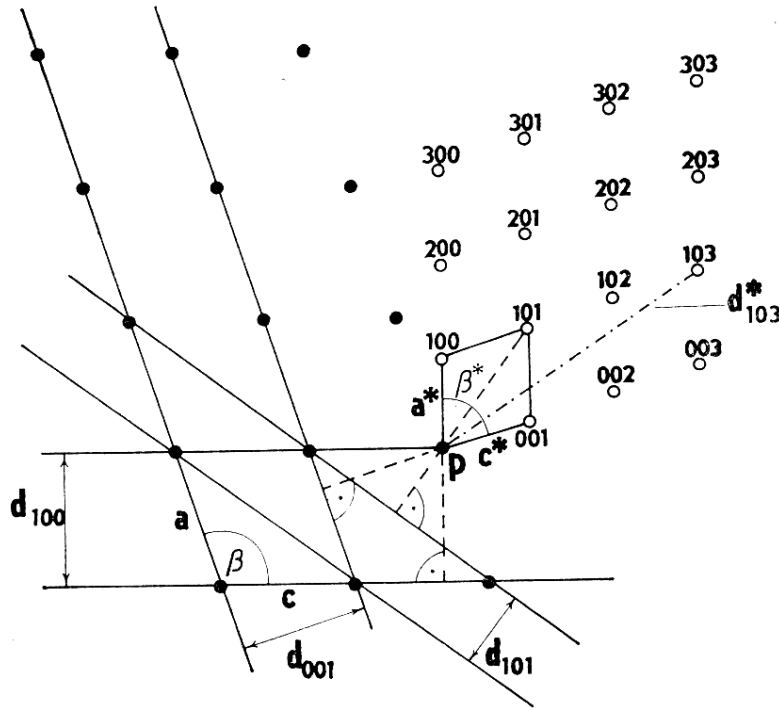
infinite set of parallel planes: $\vec{G} \cdot \vec{r} = 2\pi N \rightarrow \hat{G} \cdot \vec{r} = \frac{2\pi N}{\vec{G}}$ ($\vec{G}$ - reducible, N - any integer)

spacing between successive planes $\rightarrow d = \frac{2\pi}{|\vec{G}|}$ ($\vec{G}$ - irreducible)

intersection of plane defined by $\vec{G} \cdot \vec{r} = 2\pi$ and axes defined by vectors $\vec{g}_1, \vec{g}_2, \vec{g}_3$

$$\vec{G} \cdot \vec{r} = \frac{2\pi j_1}{h} = 2\pi \quad \text{for } \vec{r} = \frac{\vec{u}_1}{h} \rightarrow j_1 = h ; \text{ analogously for } j_2 = k \text{ and } j_3 = l$$

$\rightarrow$ planes with Miller indices $(hkl) \rightarrow$ **X-ray diffraction**



direct lattice is defined by vectors $\vec{a}$, $\vec{b}$, and $\vec{c}$; reciprocal lattice can be defined by vectors $\vec{a}^*$, $\vec{b}^*$, and $\vec{c}^*$

vector $\vec{a}^*$ is perpendicular to plane defined by vectors $\vec{a}$ and $\vec{b}$, etc.

each vector in reciprocal lattice is perpendicular to a set of parallel planes in direct lattice



$$d_{hkl} = \frac{2\pi}{|\vec{G}|}, \text{ where } \vec{G} = h \vec{g}_1 + k \vec{g}_2 + l \vec{g}_3$$

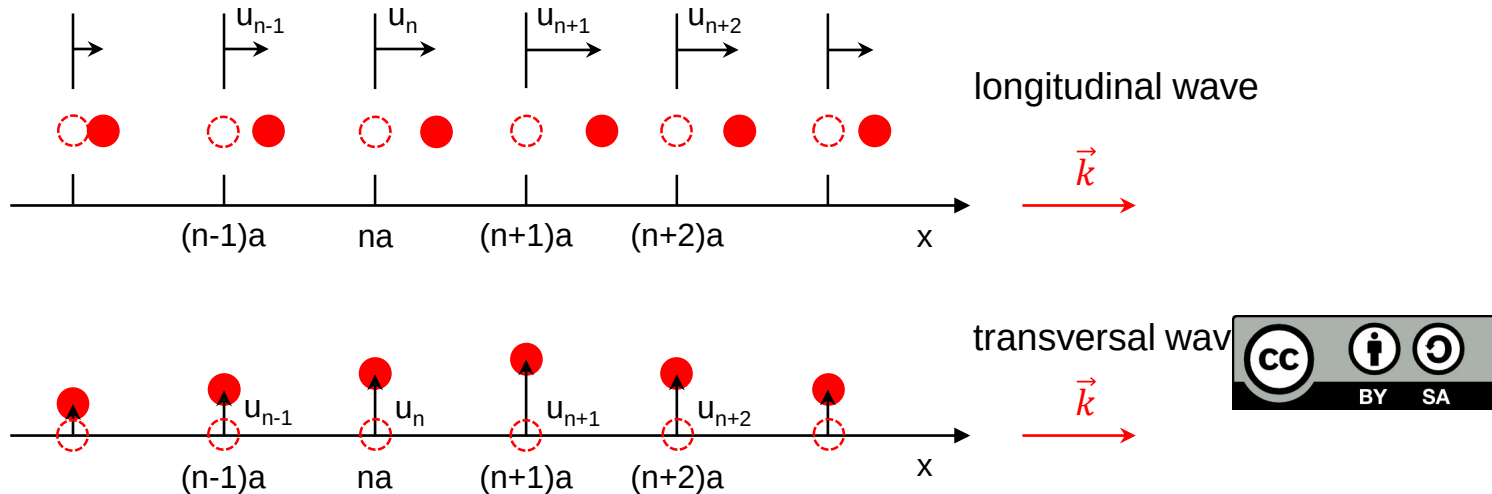
Interaction of waves with ordered arrangement of atoms

structure in reciprocal space analogous to Wigner-Seitz cell in real space (lattice of reciprocal lattice points in wave vector space ($\vec{k}$ -space))

→ **first Brillouin zone** → propagation of waves in solid

Vibrations of atoms in one-dimensional monoatomic lattice

assumption: elastic vibrations of crystal with one atom in primitive cell $\rightarrow$ chain of N identical atoms separated from each other by distance a



lattice with longitudinally excited wave $\rightarrow$ coordinate of n -th atom with amplitude of displacement $u_n(t)$

$$x_n(t) = na + u_n(t), \quad n = 1, 2, \dots, N$$

equations of motion (K - stiffness constant, M - mass of atom)

$$M \frac{\partial^2 u_n}{\partial t^2} = K(u_{n+1} - u_n) - K(u_n - u_{n-1}), \quad n = 1, 2, \dots, N$$

lattice wave representing an excitation, in which successive oscillators bear definite phase relationship to the preceding oscillator

$$u_n(t) = A_j \exp[i(k_j n a - \omega_j t)]$$

periodic boundary condition $u_n(t) = u_{n+N}(t)$

can be satisfied when the relative phase is an integer multiple of $2\pi \rightarrow$ wave vector is given by

$$k_j = \frac{2\pi j}{Na} \quad \text{where } j = 1, 2, \dots, N$$



equation of atoms motion

$$-M\omega_j^2 A_j = K A_j [\exp(ik_j a) + \exp(-ik_j a) - 2]$$

$\rightarrow$ angular frequency as a function of wave vector

$$\omega_j = \sqrt{\frac{4K}{M}} \left| \sin \frac{k_j a}{2} \right|$$

for large values of $N \rightarrow k_1$ (and ω_1) can be made arbitrarily small

maximum excitation frequency occurs for $k_j = \pm \frac{\pi}{a}$ (i.e., for $j = \frac{N}{2}$)

$$\omega_{max} = 2\sqrt{\frac{K}{M}}, \text{ for solids } \omega_{max} \approx 10^{14} \text{ rad s}^{-1}$$

$\rightarrow$ lattice frequencies are broadened into a band from 0 to ω_{max}

j varies from $-\frac{N}{2}$ to $\frac{N}{2}$, the allowed range of wave vectors k from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$

(first Brillouin zone) $\rightarrow$ waves travelling in either direction can be independently treated

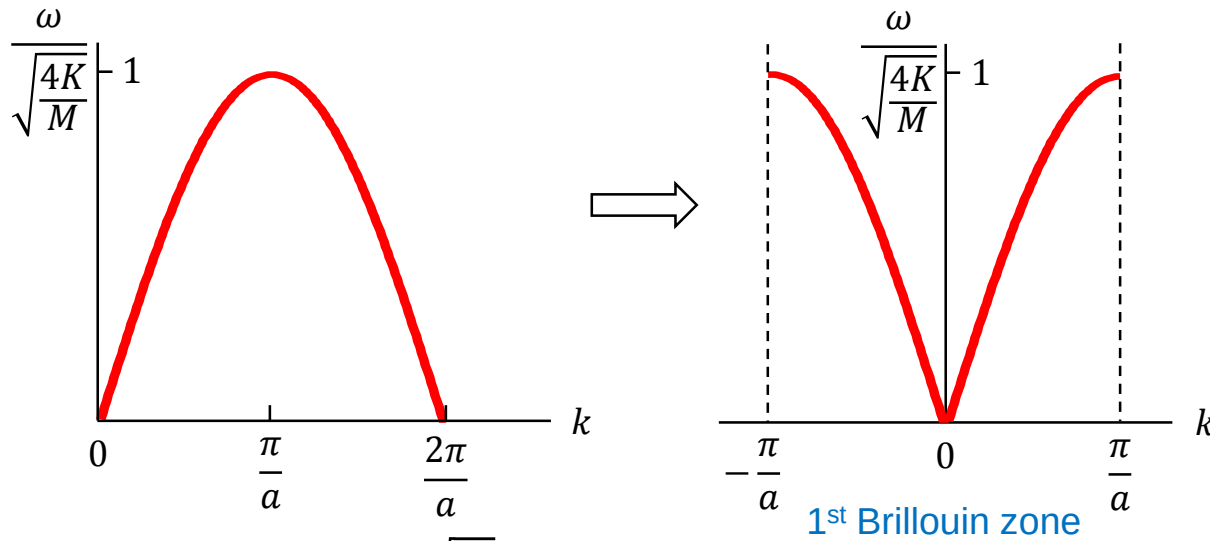


subscript j can be omitted in the limit of large $N \rightarrow$ **dispersion relation** is obtained

$$\omega(k) = 2\sqrt{\frac{K}{M}} \left| \sin \frac{ka}{2} \right|$$

Note: number of possible values of k equals the number of cells in the lattice (N)

linear dispersion relation for low k : $\omega(k) = |k|a\sqrt{\frac{K}{M}} = |k|v_s$, v_s interpreted as speed of sound (in solids $10^3 - 10^4 \text{ m s}^{-1}$)



dispersion relation $\omega(k)/\sqrt{\frac{4K}{M}}$ for the excitations of the one-dimensional mono



Group velocity

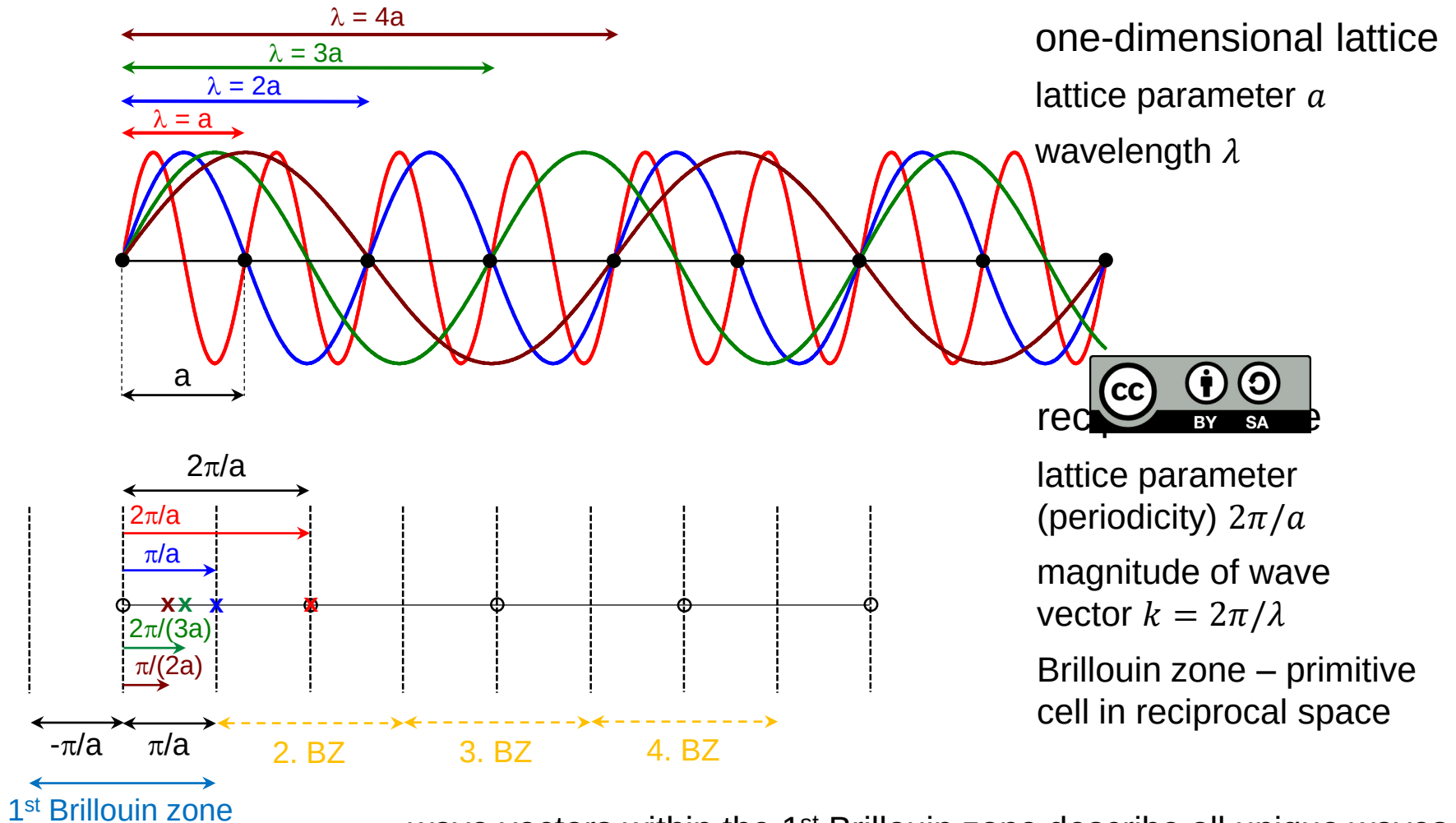
pulse of excitations propagating along the chain travels with velocity

$$v_g = \frac{\partial \omega}{\partial k} = v_s \cos \frac{ka}{2} \text{sgn}(k) \quad , \quad \text{sgn}(k) = 1 \text{ for } k > 0 \text{ and } \text{sgn}(k) = -1 \text{ for } k < 0$$

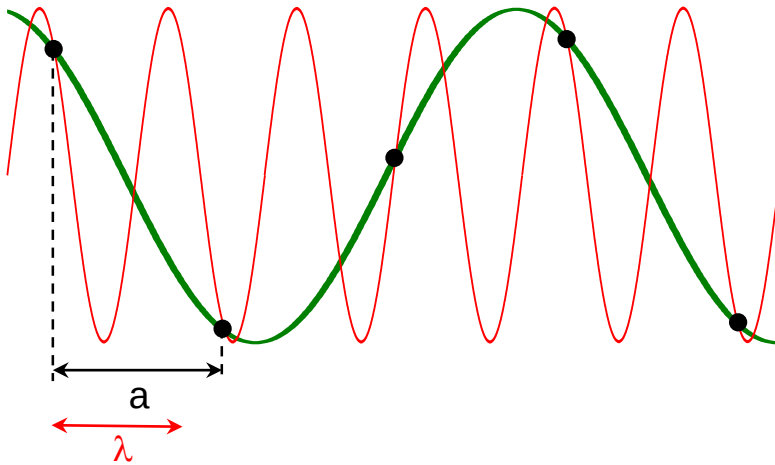
slope of dispersion curve vanishes at the zone boundaries ($k = -\frac{\pi}{a}$ and $k = \frac{\pi}{a}$)

group velocity $v_g = 0$ here

Brillouin zone and waves in solid



wave vectors within the 1st Brillouin zone describe all unique waves interacting with ordered solid (represented by direct lattice); the waves with $\lambda = 2a$ and $\lambda = a$ cannot be distinguished



the red wave contains the same information as the green one

lattice waves with wavelength shorter than interatomic spacing would be meaningless

zero group velocity at Brillouin zone boundaries $\rightarrow$ Bragg scattering of lattice

wave at $|k| = \frac{\pi}{a} = \frac{2\pi}{\lambda}$, wavelength $\lambda = 2a$

for $|k| = \frac{\pi}{a}$ adjacent atoms are 180° out of phase, travelling wave cannot move $\rightarrow$ standing wave is obtained

phase difference of adjacent atoms larger than π is possible but cannot be distinguished from other one (for example, relative phase shift of 1.2π and 4.2π is identical with that of -0.8π and 0.2π , respectively)

waves with long wavelength: $ka \rightarrow 0$, $\lambda \gg a \rightarrow$ lattice can be treated as continuum



Heat capacity

internal energy of the system: kinetic and potential energy of all particles and other structure components (atoms/ions, electrons, defects); cannot be measured directly

heat capacity: ability of substance to absorb heat from surroundings in dependence on temperature (defined as ratio of the added heat per unit amount of solid to the resulting temperature change)

$$c_p = \left(\frac{\partial U}{\partial T}\right)_p, c_v = \left(\frac{\partial U}{\partial T}\right)_v$$

$$c_p - c_v = \left[p + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_p$$



Dulong-Petit law

molar heat capacity of elements (as crystalline solids) are close to a constant value

$c_v \sim 25 \text{ J mol}^{-1} \text{ K}^{-1}$ (excepting some elements such as Be, B, C, and Si)

vibrational energy of atom in three perpendicular directions (x, y, z) is $3kT$

$U = 3NkT = 3RT$ ($N = 6.023 \cdot 10^{23} \text{ mol}^{-1}$, $k = 1,381 \cdot 10^{-23} \text{ J K}^{-1}$, $R = 8,314 \text{ J mol}^{-1} \text{ K}^{-1}$)

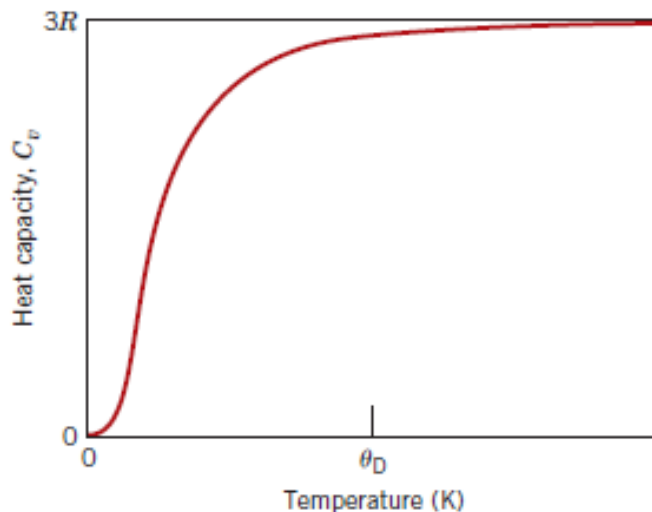
$$c_v = \left(\frac{\partial U}{\partial T}\right)_v = 3R$$

Discrepancy in comparison with experimental measurements

1) no contribution of free electrons is observed in crystals of metals

→ at least one electron from every atom, mean translational kinetic energy $3kT/2$ (ideal gas), contribution of electrons to internal energy of metal $U_{el} = 3RT/2$ (per mol); molar heat capacity of metals should be $c_v = 3R + 3R/2 = 9R/2$

2) at low temperatures (< 150 K) c_v is dependent on temperature – changes with T^3



θ_D – Debye temperature

cannot be explained by  physics

→ dynamics of crystal structures is modelled using quantum mechanics

vibrational energy of atoms is described by concept of atoms as linear harmonic oscillators

(Einstein model, Debye model)

Einstein model of solid

Presumptions:

- every atom in lattice represents independent 3D quantum harmonic oscillator (discrete energy levels, 3 harmonic oscillators perpendicular to each other)
 N atoms $\rightarrow 3N$ independent oscillators, $E_n = (n + \frac{1}{2}) h \nu$, $n = 0, 1, 2, \dots, \infty$ (quantum number)
- all atoms oscillate with the same frequency at given temperature
- distribution of energy according to Maxwell-Boltzmann statistics



$$U = \sum_j E_j n_j = N \frac{\sum_j E_j \exp\left(-\frac{E_j}{kT}\right)}{Q}, \text{ after rearrangement } U = NkT^2 \frac{\partial \ln Q}{\partial T}$$

N atoms $\rightarrow 3N$ linear harmonic oscillators

$$U = 3NkT^2 \frac{\partial \ln Q}{\partial T} \rightarrow \text{determination of partition function } Q \text{ is needed for calculation of internal energy } U$$

energy of atom in crystal is sum of potential energy in equilibrium position and energy of vibrational motion around the equilibrium position

$$E_j = E_0 + E_n$$

after substitution in partition function, rearrangement, and differentiating (not shown here):

$$\frac{\partial \ln Q}{\partial T} = \frac{E_0}{kT^2} + \frac{h\nu}{2kT^2} + \frac{1}{\exp\left(\frac{h\nu}{kT}\right) - 1} \frac{h\nu}{kT^2}$$

internal energy of crystal



$$U = 3NE_0 + \frac{3}{2}Nh\nu + \frac{3Nh\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1}$$

molar heat capacity

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v = 3Nk \left(\frac{h\nu}{kT}\right)^2 \frac{\exp\left(\frac{h\nu}{kT}\right)}{\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^2}$$

$$U = 3NE_0 + \frac{3}{2}Nh\nu + \frac{3Nh\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1}$$

at high temperatures $kT \gg h\nu$, $\exp\left(\frac{h\nu}{kT}\right) \sim 1 + \frac{h\nu}{kT} + \frac{1}{2}\left(\frac{h\nu}{kT}\right)^2 + \frac{1}{3}\left(\frac{h\nu}{kT}\right)^3 + \dots$

$$U = 3NE_0 + \frac{3}{2}Nh\nu + 3NkT \quad \text{and} \quad c_v = \left(\frac{\partial U}{\partial T}\right)_v = 3Nk = 3R \quad (\text{Dulong-Petit law})$$



at low temperatures $h\nu \gg kT$, $\exp\left(\frac{h\nu}{kT}\right) \gg 1$

$$U = 3NE_0 + \frac{3}{2}Nh\nu + \frac{3Nh\nu}{\exp\left(\frac{h\nu}{kT}\right)}$$

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v = 3R\left(\frac{h\nu}{kT}\right)^2 \exp\left(-\frac{h\nu}{kT}\right)$$

exponential dependence of heat capacity on temperature does not correspond to experimental measurements – $f(T^3)$

too simplifying presumptions

(atoms as independent oscillators, oscillation of all atoms with the same frequency)

Debye model

interactions between oscillating atoms in the lattice → crystal approximated as elastic continuum (continuum mechanics can be used)

lattice waves travelling through the crystal, continuous frequency spectrum resembling quadratic function with upper limit – maximum frequency ν_{max}

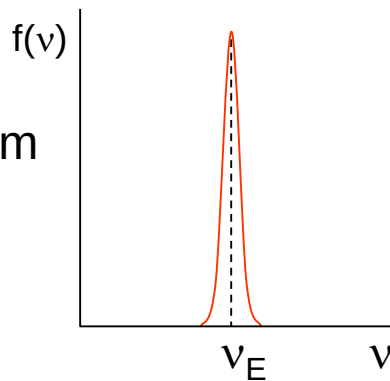
$f(\nu) = a \nu^2$ (a – constant depending on velocity of longitudinal and transversal waves)

$3N$ possible frequencies for N atoms in the crystal

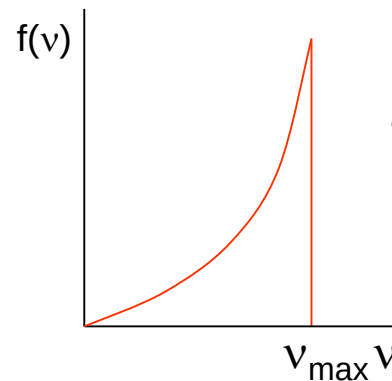


$$\int_0^{\nu_{max}} f(\nu) d\nu = \int_0^{\nu_{max}} a \nu^2 d\nu = 3N$$

phonon spectrum



Einstein model



Debye model

$$f(\nu) = \frac{9N}{\nu_{max}^3} \nu^2$$

energy of phonons within frequency range $< \nu, \nu + d\nu >$ is $E f(\nu) d\nu$

$$U = \int_0^{\nu_{\max}} E f(\nu) d\nu, \text{ where } E = \frac{h\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1} \quad (\text{mean energy of linear oscillator})$$

substitutions $x = \frac{h\nu}{kT}$ and $d\nu = \frac{kT}{h} dx \rightarrow U = \frac{9NkT^4}{\theta_D^3} \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx$

$$\theta_D = \frac{h\nu_{\max}}{k} \quad \text{Debye temperature}$$



important parameter characterizing the crystal structure; increases with decreasing molar mass (θ_D : C 2230 K, Fe 470 K, Pb 105 K)

$$c_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{9NkT^4}{\theta_D^3} \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

at high temperatures $T \gg \theta_D$, $e^x \sim 1+x$

$$U = \frac{9NkT^4}{\theta_D^3} \int_0^{\theta_D/T} x^2 dx = \frac{9NkT^4}{\theta_D^3} \frac{1}{3} \left(\frac{\theta_D}{T} \right)^3 = 3NkT$$

$$c_V = \left(\frac{\partial U}{\partial T} \right)_V = 3Nk = 3R \quad (\text{Dulong-Petit law})$$

at low temperatures $\theta_D \gg T$ a $\theta_D/T \rightarrow \infty$



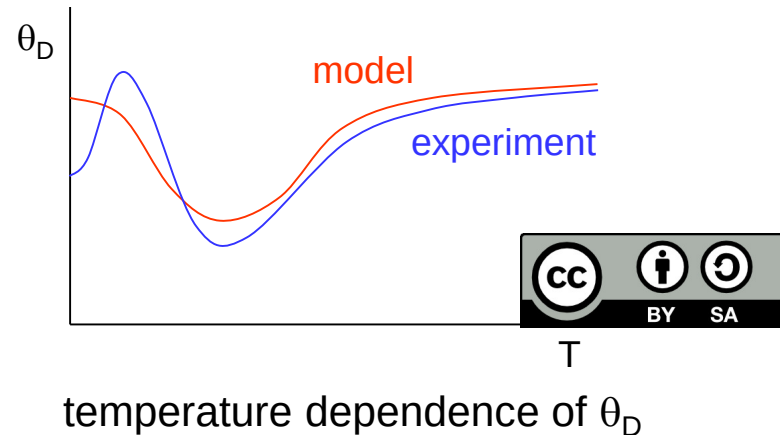
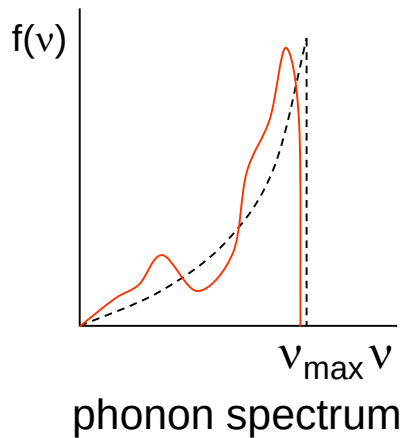
$$U = \frac{9NkT^4}{\theta_D^3} \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{9NkT^4}{\theta_D^3} \frac{\pi^4}{15} = \frac{3NkT^4 \pi^4}{5\theta_D^3} \quad \text{and} \quad c_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{12\pi^4 R}{5} \left(\frac{T}{\theta_D} \right)^3$$

Contribution of free electrons to molar heat capacity

$$c_V(el) = \frac{\pi^2 R}{2} \frac{T}{T_F} \quad \text{Fermi temperature } T_F \sim 5 \cdot 10^4 \text{ K, at common temperatures } c_V(el) \sim R/300$$

More accurate models

phonon spectrum derived from elastic continuum (quadratic function) was used in Debye model → calculation based on dynamics of particular crystal structure (e.g., Born-Kármán model)



Debye temperature is dependent on temperature and pressure, contribution of free electrons to heat capacity is more appreciable at low temperatures:

$$c_v(\text{phonons}) = f(T^3), \quad c_v(\text{electrons}) = f(T)$$

anharmonic effects during oscillation of atoms: $E_r = E_{r0} + A (r - r_0)^2 + B (r - r_0)^3 + \dots$

only harmonic oscillations → infinite free path of phonons, no interactions between phonons, no thermal expansion

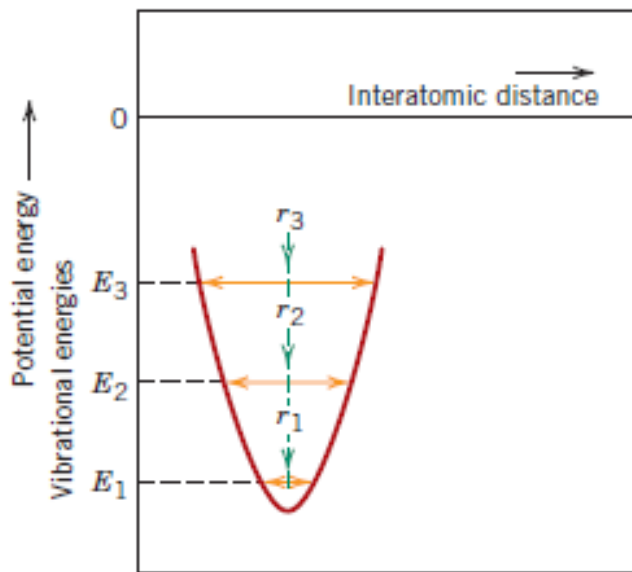
Thermal expansion

most solids expand upon heating and contract when cooled

change in length with increasing temperature: $l = l_0[1 + \alpha(T - T_0)]$

$$\frac{\Delta l}{l_0} = \alpha \Delta T \quad \alpha - \text{linear coefficient of thermal expansion}$$

thermal expansion is connected with dynamics of crystal structure



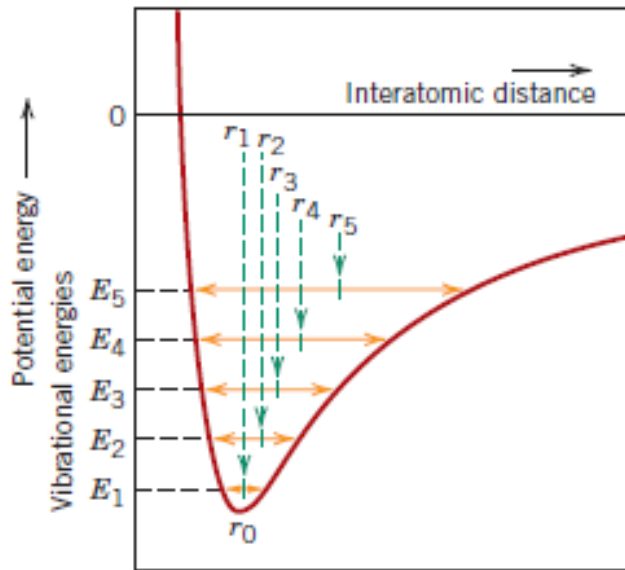
energy in dependence of
distance – minimum at $T = 0 \text{ K}$ ($r = r_0$)

energy of oscillation atoms increases with increasing temperature – atoms attain higher energy levels ($E_1, E_2, E_3, \dots$) with equilibrium interatomic distances $r_1, r_2, r_3, \dots$

symmetric dependence $E_r = f(r^2) \rightarrow$ no change in mean interatomic distance

(thermal expansion cannot be explained)





anharmonic components are involved

$$E_r = E_{r_0} + A (r - r_0)^2 + B (r - r_0)^3 + \dots$$

→ Morse potential

(mean interatomic distance increases with increasing temperature)

solids with strong chemical bonds
(covalent, ionic) → slight thermal expansion



linear coefficient of thermal expansion (10^{-6} K^{-1}): ceramic materials 0.5 – 15,
metals 5 – 25, polymers 50 – 400

volume coefficient of thermal expansion $\frac{\Delta V}{V_0} = \alpha_v \Delta T$

affected by anisotropy of crystal structure; in isotropic materials $\alpha_v \sim 3\alpha$

$$c_p - c_v = \frac{\alpha_v^2 v_0 T}{\beta} \quad (v_0 - \text{molar volume, } \beta - \text{compressibility})$$

Thermal conductivity

ability of solid to transfer heat between regions with different temperature

heat flux density $\vec{q} = \lambda \text{ grad}(T)$ (Fourier's law)

(heat flux density is oriented along temperature gradient)

λ - thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)

common values: metals 20 – 400, ceramic materials 2 – 50, polymers ~ 0.3

$$q = -\lambda \frac{dT}{dx} \quad (\text{analogous to diffusion, first Fick's law})$$



Heat transfer in solids – energy carriers

phonons (insulators), electrons (metals), excitons (electron-hole pairs), photons (at high temperatures)

thermal conductivity of metals is proportional to electric conductivity

$$\lambda_e = L \sigma T \quad (\text{Wiedemann-Franz law})$$

L – constant (Lorentz number), theoretical value of $L = 2,44 \cdot 10^{-8} \text{ } \Omega \text{WK}^{-2}$

Resistance to thermal transfer

thermal conductivity is attributed mainly to moving electrons and lattice waves (phonons)

resistance of crystal to heat flux (analogy of electrical resistance) impedes equalization of temperatures

- interactions between energy carriers (phonon-phonon, electron-electron, phonon-electron)
- scattering of energy carriers by point and line defects
- scattering of energy carriers by surface of crystal and grain

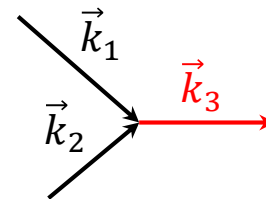


Example: three-phonon process

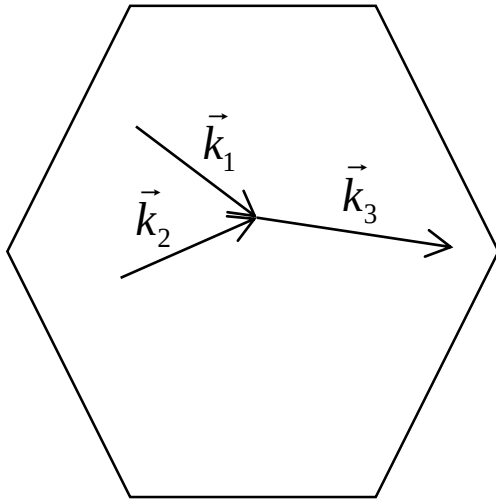
phonon-phonon interaction produces another phonon, overall energy and quasi-momentum of the system have to be preserved

frequency $\nu_1 + \nu_2 = \nu_3$

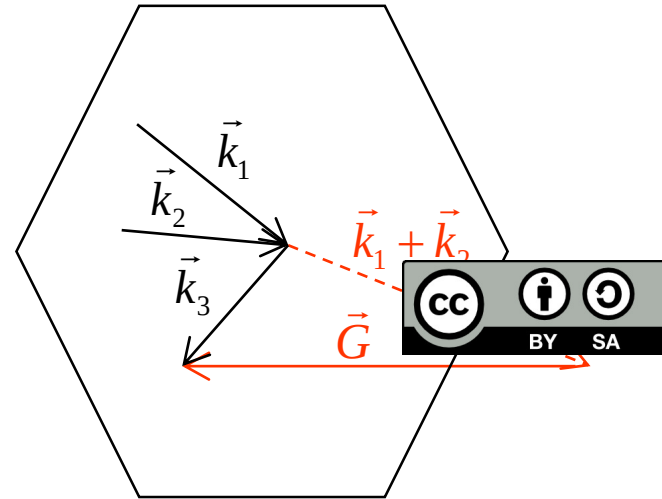
wave vectors $\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{G}$
($\vec{G}$ - reciprocal lattice vector)



overall crystal wave vector must be preserved $\rightarrow$ reciprocal lattice vector $\vec{G}$ restores the net crystal wave vector to the first Brillouin zone when the final phonon wave vector $\vec{k}_3$ lies outside the zone



N-process



U-process

N-process (normal) – direction of energy propagation (phonon flux) is not changed, $\vec{G} = 0$

U-process (umklapp) – change in direction of energy propagation, $\vec{G} \neq 0$, reciprocal lattice vector serves to bring the wave vector back inside the first Brillouin zone

Thermal stress and thermal shock

thermal expansion/contraction due to temperature changes can result in compressive and tensile strains in solid → undesirable plastic deformation (ductile metals, polymers) or fractures (brittle materials)

1) stress caused by restraining thermal expansion

proportional to $E\alpha\Delta T$ (E – modulus of elasticity)

2) stress caused by temperature gradients in solid

temperature distribution inside the solid depends on size, shape, thermal conductivity, and rate of heating or cooling → temperature differences between exterior and interior regions result in different thermal expansion and compressive or tensile stresses within the solid



thermal shock resistance is given by thermal and mechanical properties

proportional to $\frac{\sigma_{cr}\lambda}{E\alpha}$ (σ_{cr} – critical stress)

Example: enhancement of thermal shock resistance by changing the linear coefficient of thermal expansion of glass

common soda-lime glass $\alpha \sim 9 \cdot 10^{-6} \text{ K}^{-1}$, borosilicate (Pyrex) glass $\alpha \sim 3 \cdot 10^{-6} \text{ K}^{-1}$

Chemistry and Physics of Solids - Lecture 12

ELECTRICAL PROPERTIES OF SOLIDS



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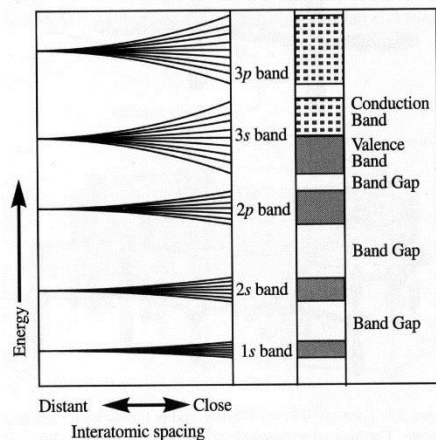
EUROPEAN UNION
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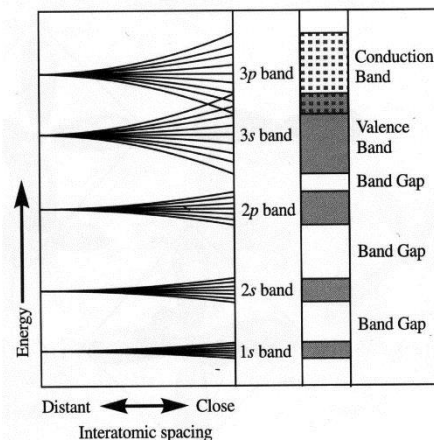
electrical conduction – gradient of outer electric field results in motion of charge carriers (electrons, ions, holes)

electrical conductivity $\sigma = e \mu_n n + e \mu_p p$ $[\Omega^{-1} \text{ m}^{-1}]$

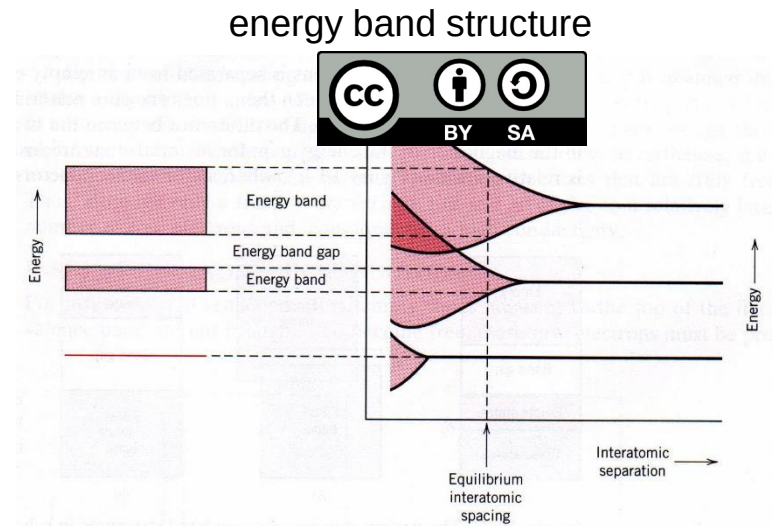
Metals (conductors) $\sigma = 10^6 - 10^7 \Omega^{-1} \text{ m}^{-1}$



Na: $1s^2 2s^2 2p^6 3s^1$



Mg: $1s^2 2s^2 2p^6 3s^2$



valence electrons can move freely within the crystal, even weak electric field induces electron motion and charge transfer

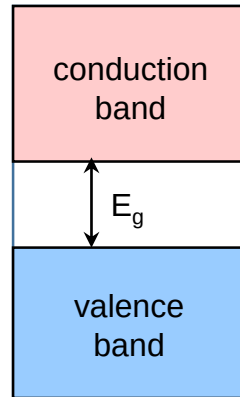
Semiconductors

$$\sigma = 10^{-6} - 10^5 \Omega^{-1} \text{ m}^{-1}$$

valence band completely filled with electrons, separated from empty conduction band by relatively narrow band gap ($E_g < 3 \text{ eV}$)

possible excitation of electrons to conduction band

charge carriers – electrons and holes



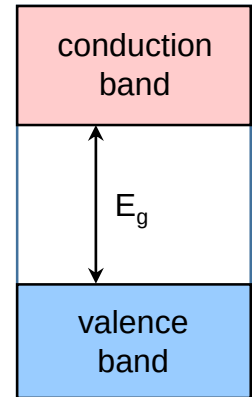
Insulators (dielectrics)

$$\sigma = 10^{-9} - 10^{-13} \Omega^{-1} \text{ m}^{-1}$$

valence band completely filled with electrons, separated from empty conduction band by wide bandgap ($E_g > 3 \text{ eV}$)

electrons cannot be excited to conduction band

polarization by applied electric field



Superconductors $\sigma = 10^{23} - 10^{25} \Omega^{-1} \text{ m}^{-1}$

some metals, alloys, and intermetallic compounds, sudden drop in electrical resistance at very low temperatures (T_c up to about 20 K), attractive interactions between electrons (Cooper pairs), “high-temperature” oxide superconductors ($T_c > 90 \text{ K}$)

Ionic conductors

some ionic crystals, solid electrolytes; ions as charge carriers; in some materials relatively high conductivity at common temperatures → superionic conductors ($\sigma = 10^1 - 10^2 \Omega^{-1} \text{ m}^{-1}$)

Electrical properties of metals

metallic bonding – electrostatic attraction between cloud of delocalized (“conduction”) electrons and positively charged metal ions → sharing of free electrons among lattice cations (electron gas)

applied electric field accelerates electron motion

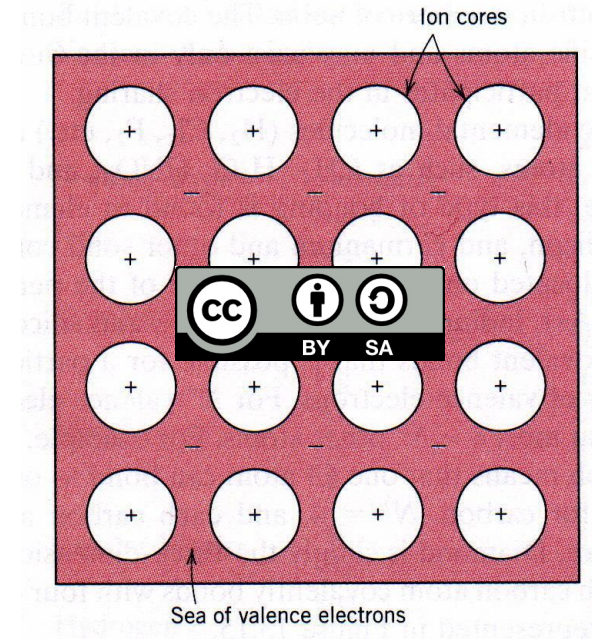
hindrances of free motion of electrons:

- scattering due to collisions with oscillating lattice cations
- scattering on lattice defects (vacancies, line defects, impurity atoms, grain boundaries)
- scattering due to interactions between electrons

oscillations of atoms and concentration of defects increase with increasing temperature

→ **electrical conductivity of metals decreases with increasing temperature**

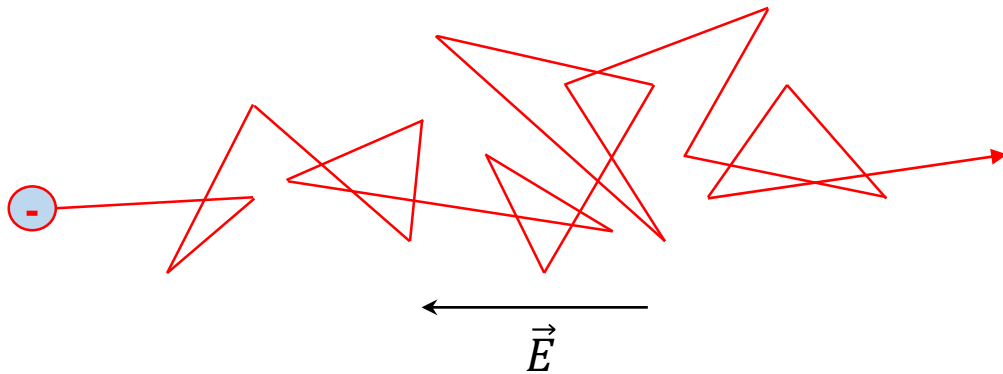
properties of metals are explained using quantum mechanics (Sommerfeld model of free electrons in metals)



Ohm's law

absence of electric field: electrons move in all directions, sum of velocities is zero

applied electric field: acceleration and scattering of moving electrons (deflection and randomizing velocity of electrons) → drift of electrons against direction of the electric field



only collisions of moving electrons with lattice atoms, impurities and defects are considered, classical mechanics can be applied (Drude model)



force acting on electron in external electric field $F = -eE = -m_e a$

electron acceleration within time between two collisions (velocity Δv is maximum at time τ)

$$a = \frac{\Delta v}{\tau}, \quad \Delta v = \frac{e E \tau}{m_e}$$

mean electron velocity between two collisions $v_D = \frac{\Delta v}{2} = \frac{e E \tau}{2m_e} = \frac{e}{2m_e} \frac{U}{l} \tau$

(difference in electric potential U (voltage) at ends of conductor with length l : $U = E l$)

current through a conductor with cross-section area A at concentration of electrons n

$$I = n A e v_D = \frac{n A e^2 E \tau}{2m_e} = \frac{n e^2 \tau A}{2m_e l} U = \frac{1}{R} U$$

Ohm's law derived from concept of free electrons in metals

$$\frac{1}{R} = \frac{n e^2 \tau A}{2m_e l} , \quad U = \frac{1}{R} I$$

electrical conductivity

$$\sigma = \frac{n e^2 \tau}{2m_e} \quad [\Omega^{-1} m^{-1}]$$



mobility of charge carriers (electrons)

$$\mu_n = \frac{e \tau}{2m_e} \quad [m^2 V^{-1} s^{-1}]$$

resistivity

$$\rho = \frac{1}{n e \mu_n} \quad [\Omega m]$$

$$\frac{1}{\rho} = \sigma = n e \mu_n$$

Fermi-Dirac quantum statistics

ensemble of N indistinguishable particles with half-integer spin (electrons) occupying energy levels $E_j; j = 1, \dots, s$

only one particle is allowed in each energy state

degenerate energy levels $\rightarrow$ group of energy sublevels (slightly different energy states) $g_j; j = 1, \dots, s$

(g_j = degeneracy of j -th level, larger number of possible energy states compared to atoms)

degeneracy of energy level $E_s \rightarrow g_s$ sublevels occupied by n_s electron



each sublevel is either occupied by one electron or empty (according to Pauli exclusion principle)

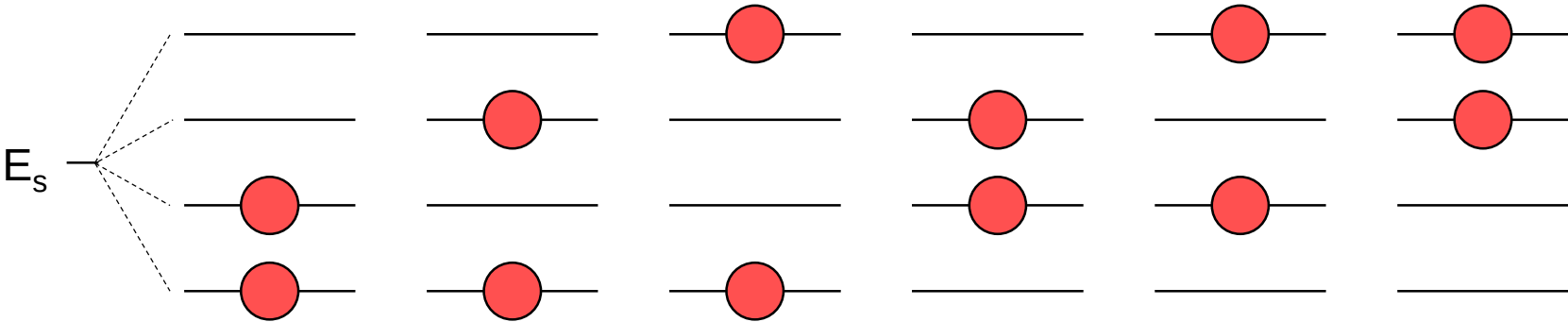
$\rightarrow n_s$ sublevels occupied, $(g_s - n_s)$ sublevels remain unoccupied, $g_s \geq n_s$

number of microstates in energy level E_s (i.e., number of independent ways for distributing n_s electrons in energy level E_s)

$$W_s = \frac{g_s!}{n_s! (g_s - n_s)!}$$

Example: number of microstates in energy level E_s degenerate with 4 sublevels occupied with various number of electrons

degeneracy (g_s)	number of electrons in energy level (n_s)	number of microsities in energy level (W_s)
4	0	1
4	1	4
4	2	6
4	3	4
4	4	1



six possible microstates in energy level E_s degenerate with four sublevels occupied by two electrons ($g_s = 4, n_s = 2, W_s = 6$)

number of microstates for realizing energy distribution in macrostate involving all possible energy levels E_j (arrangements in particular energy levels are independent on each other)

$$W = \prod_j \frac{g_j!}{n_j! (g_j - n_j)!}$$

the most probable distribution corresponds to the largest number of microstates realizing the macrostate → finding the maximum value of W when overall energy and number of particles are preserved

$$U = \sum_j n_j E_j \quad N = \sum_j n_j \quad (U \text{ and } N \text{ are constants})$$



Fermi-Dirac distribution (probability function, f_{FD})

$$\frac{n_j}{g_j} = \frac{1}{\exp\left(\frac{E_j - E_f}{kT}\right) + 1} = f_{FD}$$

probability of occupying the energy level E_j ,

$$0 \leq f_{FD} \leq 1$$

E_f – Fermi energy

Free particle wave

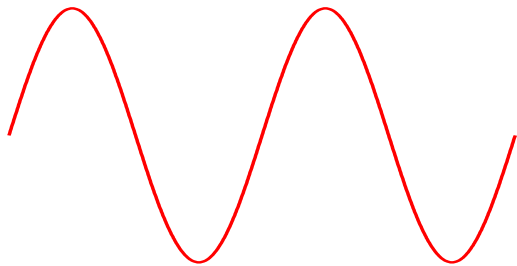
general free-particle wave function (in 1D): $\psi(x, t) = A \exp[i \left(\frac{2\pi}{\lambda} x - \omega t \right)] = A \exp[i(kx - \omega t)]$

complex function can be expanded $\psi(x, t) = A \cos(kx - \omega t) - iA \sin(kx - \omega t)$

associated with momentum $p = \frac{h}{\lambda} = \frac{hk}{2\pi} = \hbar k$ k - wave vector

wave function for electron

$$\psi(x, t) = A \exp[i(kx - \omega t)]$$



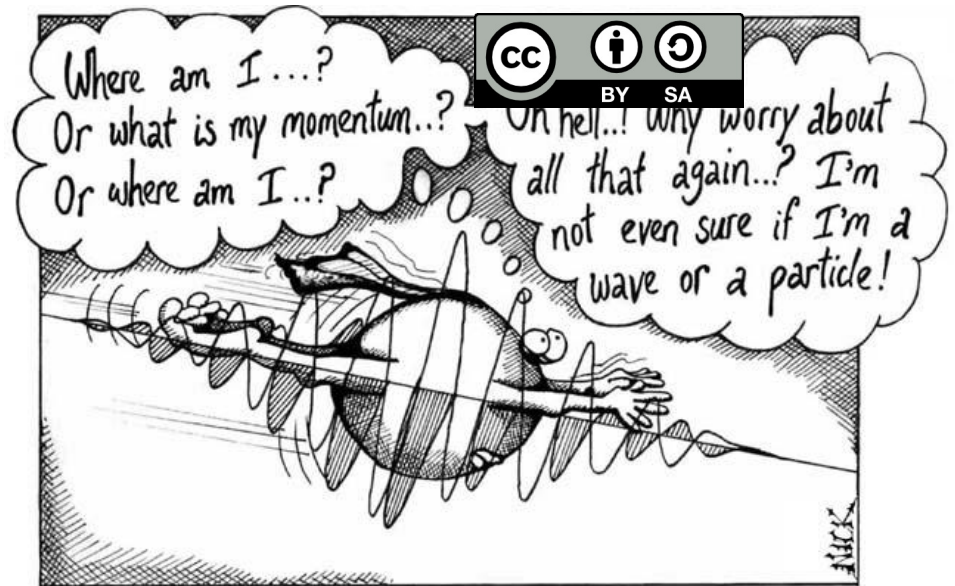
$$\psi(x, t) = A \cos(kx - \omega t)$$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h}$$

p - electron momentum
(de Broglie relationship)

$$\omega = \frac{\omega \hbar}{\hbar} = \frac{E}{\hbar}$$

E - electron energy
(Planck relationship)



Approximations in quantum theory of solids

quantum theory of solids – solution of Schrödinger equation for stationary state
(solid – system of N atoms containing N cores and NZ electrons (Z = atomic number),
interactions between all particles are considered)

wave function $\psi(\vec{r}_1, \dots, \vec{r}_{NZ}; \vec{R}_1, \dots, \vec{R}_N)$, $\vec{r}_k$ and $\vec{R}_i$ - position vectors of electron and core

$$\hat{H}\psi = E\psi$$

Hamiltonian (sum of operators corresponding to kinetic and potential energies of a system)

$$\hat{H} = \hat{T} + \hat{U} = \left[-\frac{\hbar^2}{2m} \Delta + \hat{U} \right] \quad \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \hbar$$


$$\left[-\sum_k \frac{\hbar^2}{2m_e} \Delta_k - \sum_i \frac{\hbar^2}{2m_c} \Delta_i + \frac{1}{2} \sum_{k \neq l} \frac{e_r^2}{r_{kl}} + U_2(\vec{r}_1, \dots, \vec{r}_{NZ}; \vec{R}_1, \dots, \vec{R}_N) + U_3(\vec{R}_1, \dots, \vec{R}_N) \right] \psi = E\psi$$

$$U_1 = \frac{1}{2} \sum_{k \neq l} \frac{e_r^2}{r_{kl}} \quad \text{- potential energy of pair electron interactions,} \quad e_r^2 = \frac{e^2}{4\pi\epsilon_0}$$

U_2 - potential energy of core-electron interactions, U_3 - potential energy of cores

Born-Oppenheimer approximation

system of particles $\rightarrow$ subsystem of electrons and subsystem of cores

$m_e \ll m_c$, electrons move in a field of stationary cores, potential energy of cores $U_3 = 0$

$$\left[-\sum_k \frac{\hbar^2}{2m_e} \Delta_k + \frac{1}{2} \sum_{k \neq l} \frac{e_r^2}{r_{kl}} + U_2(\vec{r}_1, \dots, \vec{r}_{NZ}; \vec{R}_1^0, \dots, \vec{R}_N^0) \right] \psi_e = E_e \psi_e$$

Hartree-Fock approximation

interactions between electrons $\rightarrow$ interaction between a single electron in a field of all other electrons and all cores



potential energy of electron in a field of stationary cores

$$U_2 = \sum_k U_k(\vec{R}_1^0, \dots, \vec{R}_N^0) = \sum_k U_k(\vec{r}_k)$$

potential energy of electron in a field of all other electrons

$$\frac{1}{2} \sum_{k \neq l} \frac{e_r^2}{r_{kl}} = \sum_k U'(\vec{r}_k)$$

a single electron in a potential field of all stationary cores and all other electrons in the system

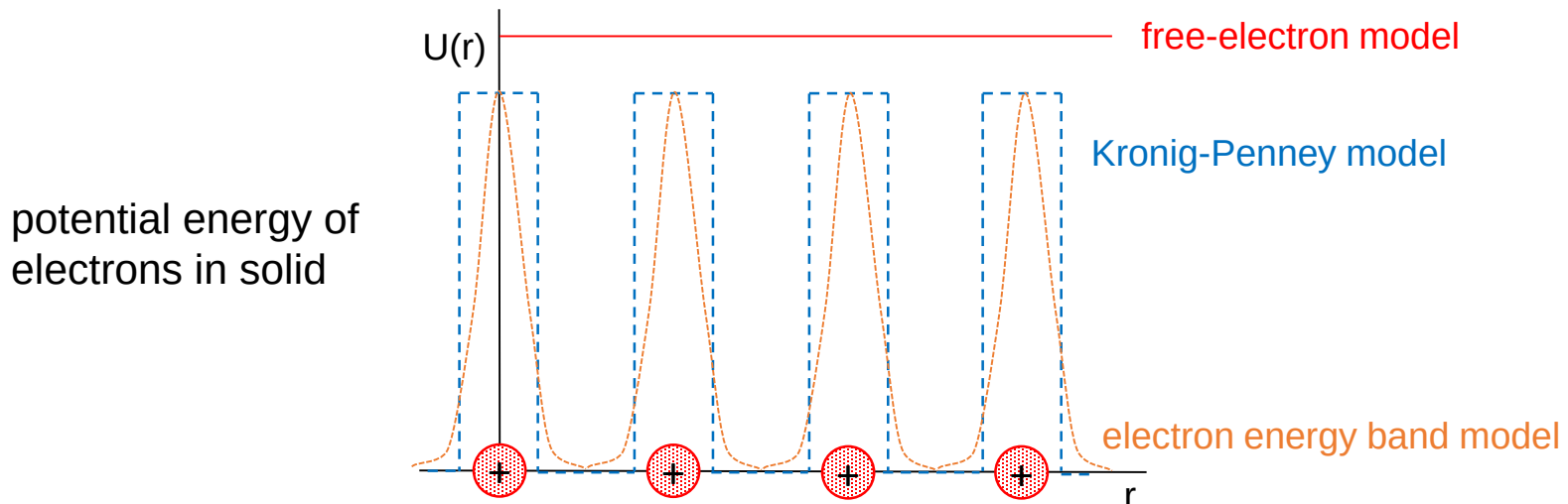
$$\tilde{U}(\vec{r}_k) = U(\vec{r}_k) + U'(\vec{r}_k)$$

$$\left[-\frac{\hbar^2}{2m_e} \Delta_k + \tilde{U}(\vec{r}_k) \right] \psi_k = E_k \psi_k$$

Kronig-Penney model

potential field $\tilde{U}(\vec{r}_k)$ is periodic according to lattice periodicity

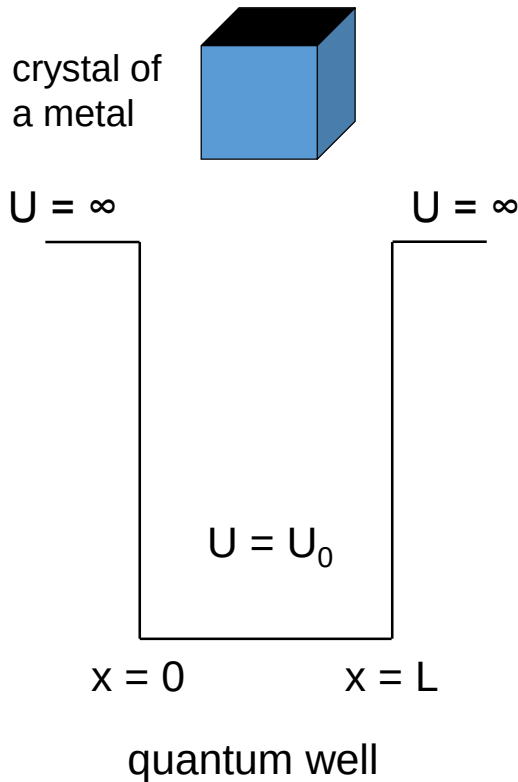
Kronig-Penney model is a simplified model for an electron in one-dim
potential (periodic square wave)



Free-electron model

Presumptions:

- free motion of electrons within a metal (invariable potential energy)
- quantized energy of electrons, Pauli exclusion principle in occupancy of energy levels
- probability of occupying energy levels at $T > 0$ K given by Fermi-Dirac distribution



Schrödinger equation for electron in quantum well



$$\left[-\frac{\hbar^2}{2m_e} \Delta + U_0 \right] \psi = E\psi$$

wave function periodic along x , y , and z axes with periodicity of L (Born-Kármán boundary conditions)

$$\psi(x, y, z) = \psi(x + L, y, z) = \psi(x, y + L, z) = \psi(x, y, z + L)$$

$$\psi(\vec{r}) = A \exp(i\vec{k}\vec{r}) \rightarrow \text{looking for } E \text{ vs. } \vec{k} \text{ relationship}$$

$$\vec{r} - \text{position vector, } \vec{k} - \text{wave vector, } k = \frac{2\pi}{\lambda}, A = \text{const}$$

periodicity of wave function: $\exp(ik_x x) = \exp[ik_x(x + L)] = \exp(ik_x L) \exp(ik_x x)$

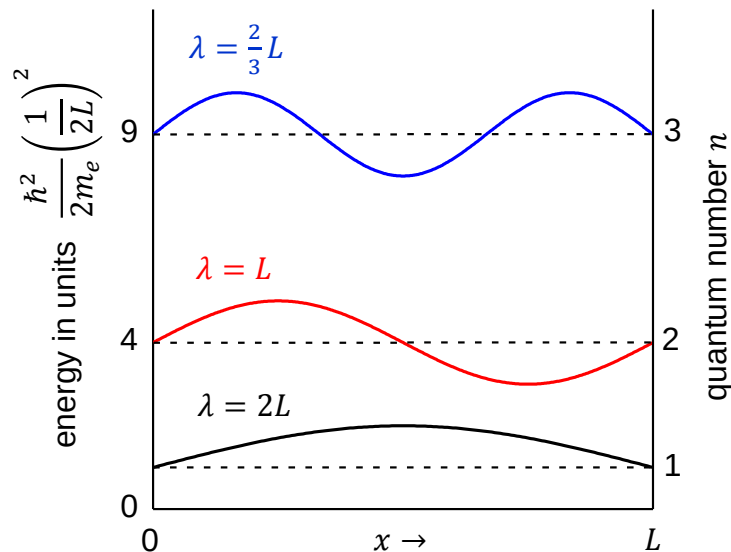
where $\exp(ik_x L) = \cos(k_x L) + i \sin(k_x L) = 1$

wave vector components $k_x L = 2\pi n_x \Rightarrow k_x = 2\pi n_x / L$, $k_y = 2\pi n_y / L$, $k_z = 2\pi n_z / L$

n_x, n_y, n_z - free electron quantum numbers (0, ± 1 , ± 2 , ...)

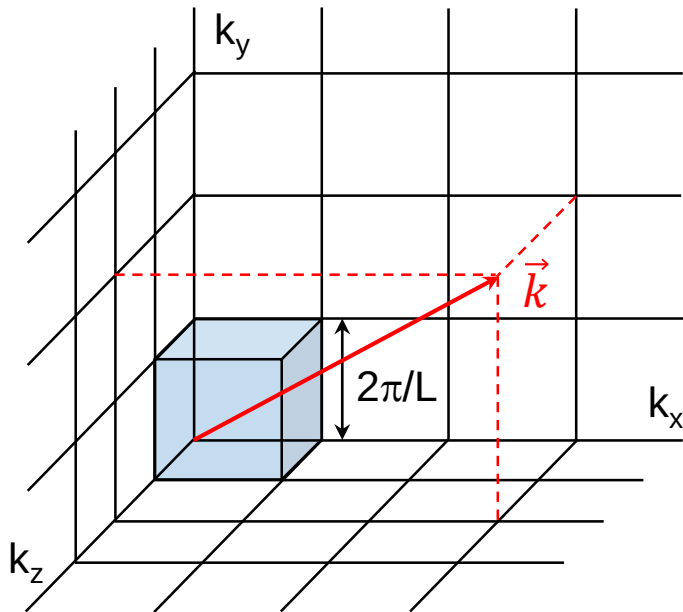
electron energy related to potential energy U_0

$$E = \frac{\hbar^2}{2m_e} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m_e} \left(\frac{2\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2)$$



first three energy levels and wave functions of free electrons; quantum number n gives number of half-wavelengths in the wave function

(adapted from Kittel C., Introduction to Solid State Physics, 8th Edition, John Wiley & Sons, 2005)



one cell in k -space = particular energy level,
which can be occupied by two electrons with
opposite spin
electrons occupy energy states within a sphere
with radius of $k_0 \rightarrow N$ electrons will occupy $N/2$
cells

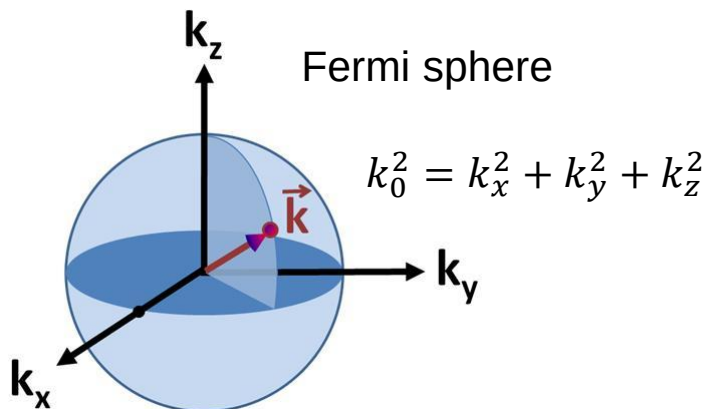
$$\frac{\frac{4}{3}\pi k_0^3}{\frac{8\pi^3}{L^3}} = \frac{L^3 k_0^3}{6\pi^2} = \frac{N}{2} \quad \Rightarrow \quad k_0 = \left(\frac{3\pi^2 N}{L^3} \right)^{\frac{1}{3}}$$



k -space filled with cells of volume $\left(\frac{2\pi}{L}\right)^3$

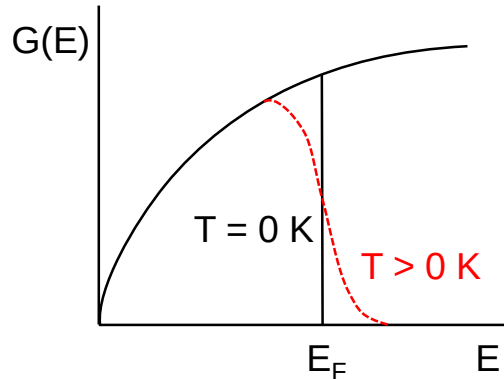
Fermi energy

energy of the highest occupied state at $T = 0$ K



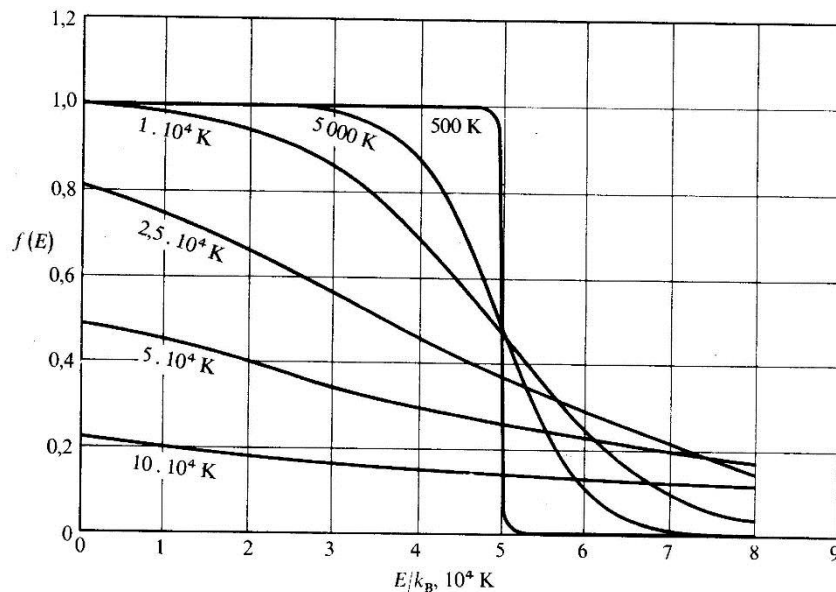
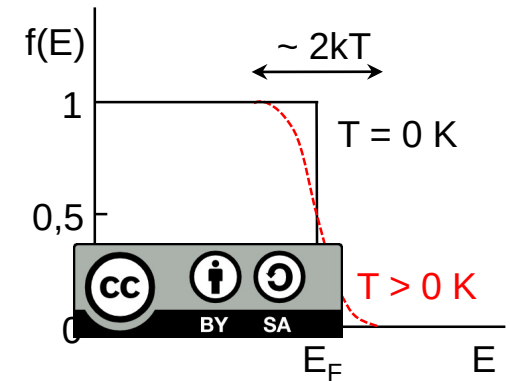
$$E_F = \frac{\hbar^2}{2m_e} \left(\frac{3\pi^2 N}{L^3} \right)^{\frac{2}{3}}$$

density of energy states in dependence on energy – redistribution of electrons in energy levels at $T > 0$ K, some electrons are thermally excited to energy states with $E > E_F$ (total number of electrons does not change)



redistribution of electrons according to Fermi-Dirac statistics

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{kT}\right) + 1}$$



valid up to $T \sim 10^4$ K

Fermi temperature (T_F) can be exceeded at $T \gg 0$, $T_F = E_F/k \rightarrow E - E_F \gg kT$

all electrons under Fermi energy will be thermally excited

Fermi-Dirac distribution at various temperatures

($T_F = E_F/k = 50000$ K; copied from Kittel C., Introduction to Solid State Physics, 8th Edition, John Wiley & Sons, 2005)

Electron motion in periodic potential field

free electron model – invariable potential in whole crystal is expected

3D periodicity of crystal structure → periodic changes in the potential field

$$\left[-\frac{\hbar^2}{2m_e} \Delta + U(\vec{r}) \right] \psi = E\psi$$

periodic change of potential energy $U(\vec{r}) = U(\vec{r} + \vec{t})$, $\vec{t} = t_1 \vec{a}_1 + t_2 \vec{a}_2 + t_3 \vec{a}_3$

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ – primitive lattice vectors



→ solution – Bloch wave function $\psi(\vec{r}) = u_{\vec{k}}(\vec{r}) \exp(i\vec{k}\vec{r})$
(wave function for particle in a periodically repeating environment – electron in crystal)

$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{t})$ - periodic function with the same periodicity as the crystal lattice
dependent on wave vector $\vec{k}$ and the periodic potential field $U(\vec{r})$

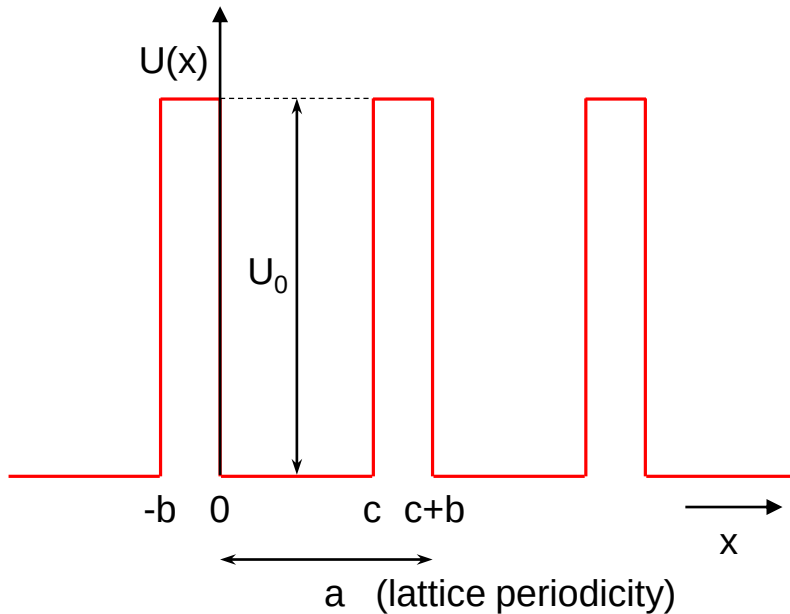
⇒ periodic character of electron energy E

periodic potential energy of electron according to Kronig-Penney model

→ electron energy bands in solid

Kronig-Penney model

one-dimensional periodic potential energy, series of square wells



$$t = a = c + b$$

$$0 < x < c \quad U = 0$$

$$-b < x < 0 \quad U =$$



rearrangement of Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m_e}{\hbar^2} E\psi = 0 \quad 0 < x < c,$$

$$\frac{d^2\psi}{dx^2} + \frac{2m_e}{\hbar^2} (E - U_0)\psi = 0 \quad -b < x < 0$$

function ψ in Schrödinger equation is replaced with one-dimensional Bloch wave function

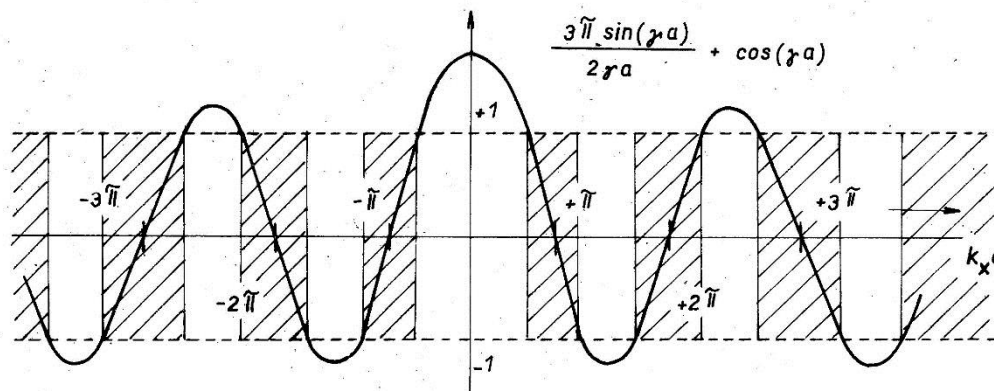
$$\psi(x) = u_{k_x}(x) \exp(ik_x x)$$

(solution is not shown here, it can be seen e.g. in Kittel C., Introduction to Solid State Physics, 8th Edition, John Wiley & Sons, 2005)

→ simplified relationship

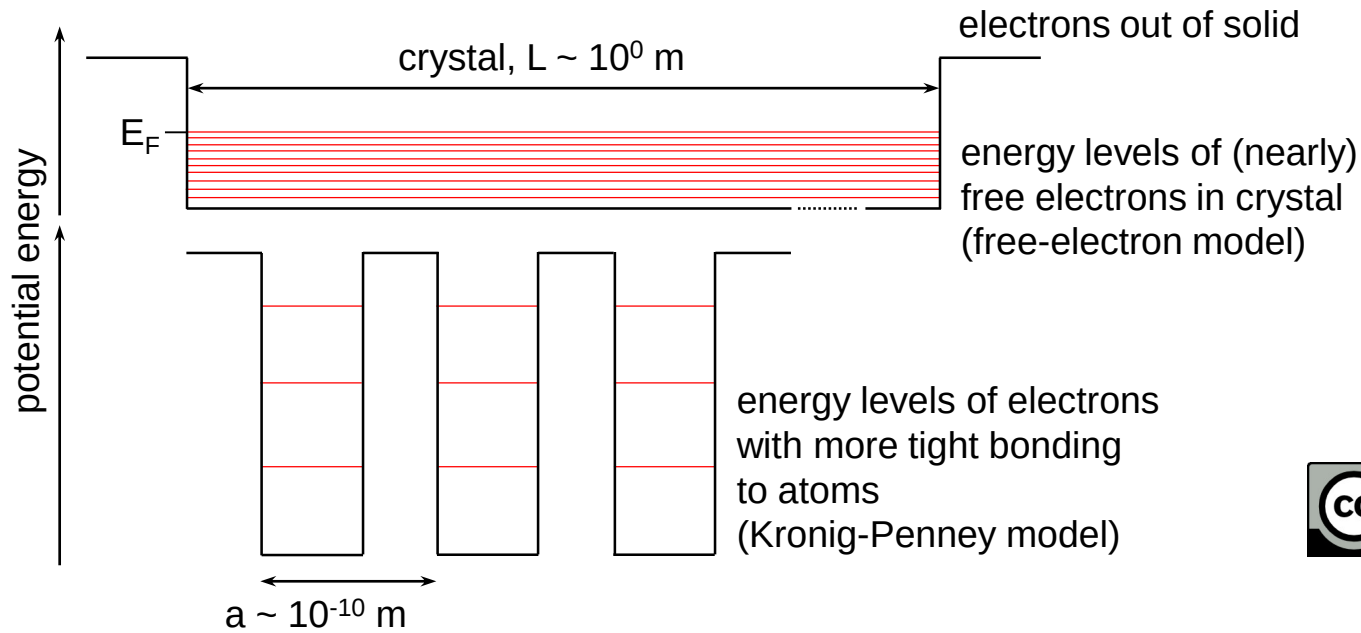
$$P \frac{\sin(\gamma a)}{\gamma a} + \cos(\gamma a) = \cos(k_x a) \quad \gamma^2 = \frac{2m_e E}{\hbar^2} \quad P = \text{konst}$$

$\cos(k_x a)$ may attain only values in the range from -1 to +1, relationship is satisfied only with certain energy values → **allowed energy E** (energy bands)



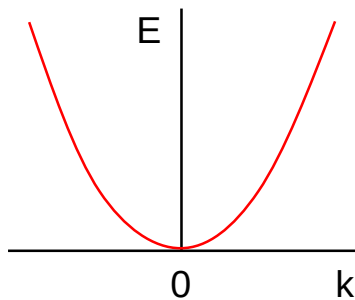
dependence of $\left[\frac{\sin(\gamma a)}{\gamma a} + \cos(\gamma a) \right]$ on $k_x a$ for $P = 3\pi/2$

Energy of electrons and periodic lattice

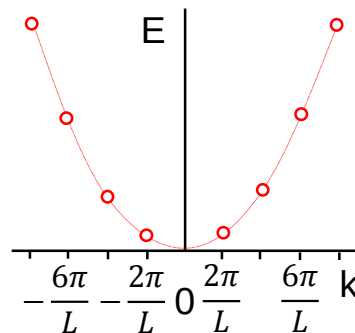


electron energy as a function of wave vector

k^2
 $2m_e$

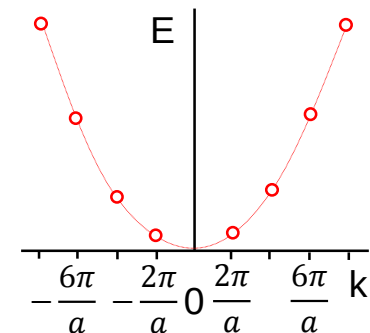


electrons out of solid



free-electron model

allowed energy states

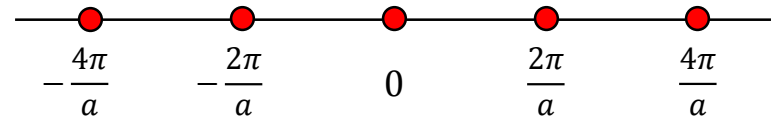


Kronig-Penney model
 $n\pi/a \gg n\pi/L$

reciprocal lattice $\rightarrow$ reflects direct lattice periodicity in reciprocal space
direct lattice periodicity (interatomic distance) $a \rightarrow 2\pi/a$ in reciprocal space

allowed wave vectors $\vec{k}$ (allowed electron energy states) $\rightarrow$ magnitude in reciprocal length units in reciprocal space ($\lambda \rightarrow 2\pi/\lambda$)

one-dimensional reciprocal lattice with periodicity of $2\pi/a$

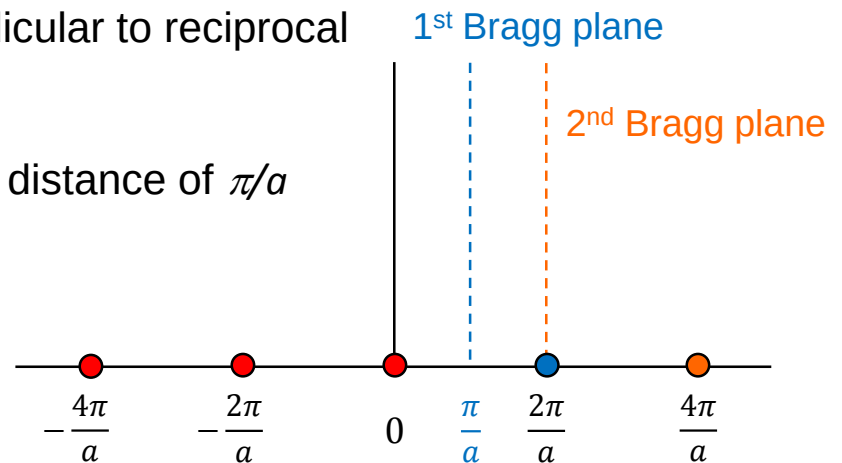


electron motion in solid – traveling wave with wavelength comparable to lattice periodicity $\rightarrow$ diffraction may occur due to interaction of electron with atoms ordered in a lattice



Bragg plane = plane in reciprocal space perpendicular to reciprocal lattice vector bisecting the lattice vector

$\rightarrow$ lattice vector with length of $2\pi/a$ is bisected in distance of π/a

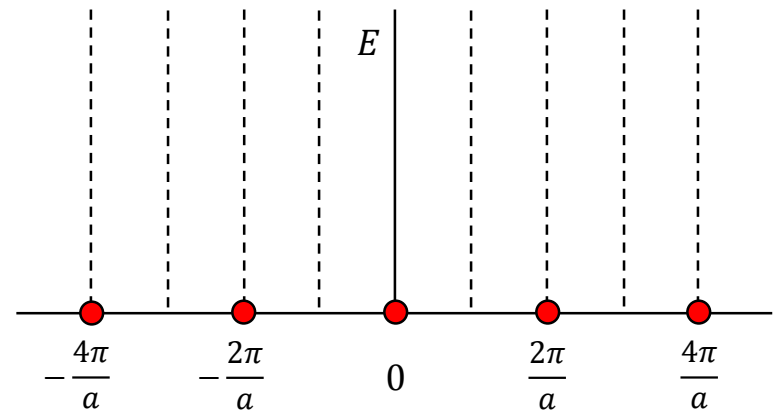


diffraction occurs when wave vector touches the Bragg plane

Bragg's law $n\lambda = 2a \sin \theta$

wave vector meeting the Bragg condition in reciprocal lattice

$$k = \frac{2\pi}{\lambda} \rightarrow k = \frac{n\pi}{a \sin \theta}$$



Bragg planes in one-dimensional reciprocal lattice



interaction of electron waves with periodic lattice $\rightarrow$ diffraction only with particular wave vectors $\vec{k}$, discontinuity at Bragg planes

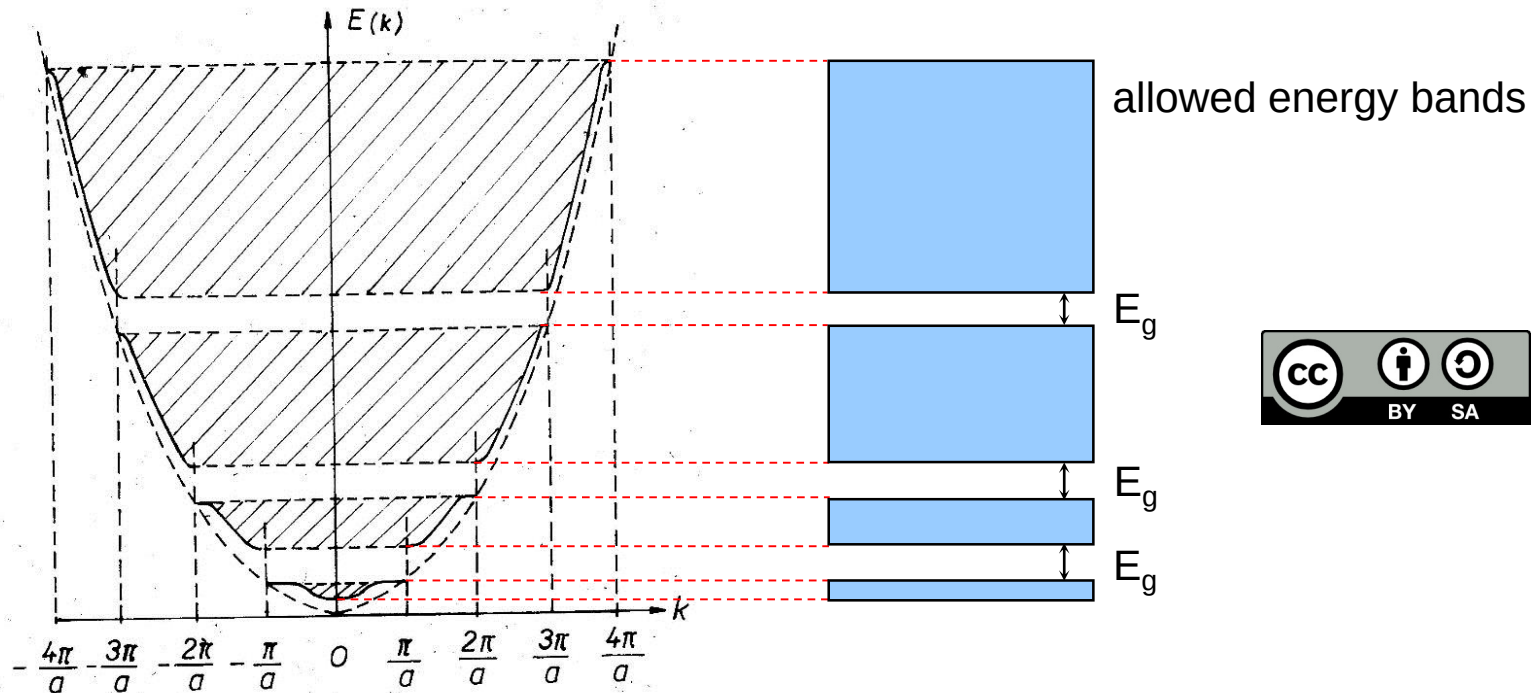
free-electron model

length of electron wave vectors $k = \frac{n\pi}{L}$ considerably shorter compared to lattice periodicity

$\rightarrow$ closely packed energy levels – “continuum”

Brillouin zones

dependence of electron energy E on wave vector $\vec{k}$ is not continuous at $k = \pm \frac{n\pi}{a}$, $n = 1, 2, \dots$



first allowed electron energy band ($n = 1$) for k values in the range from $-\pi/a$ to π/a
 → first Brillouin zone

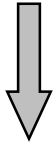
k values in the range from $-2\pi/a$ to $-\pi/a$ and from π/a to $2\pi/a$ → second Brillouin zone

energy bandgap → discontinuity at boundary between zones

repeating of $E(\vec{k})$ function
within reciprocal lattice with
periodicity of $2\pi/a$

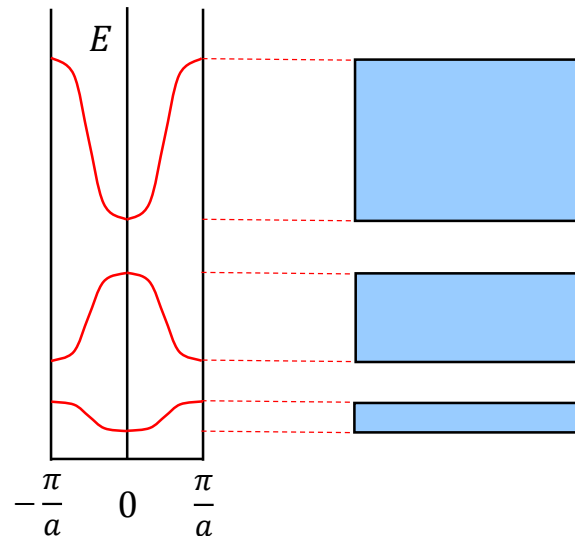
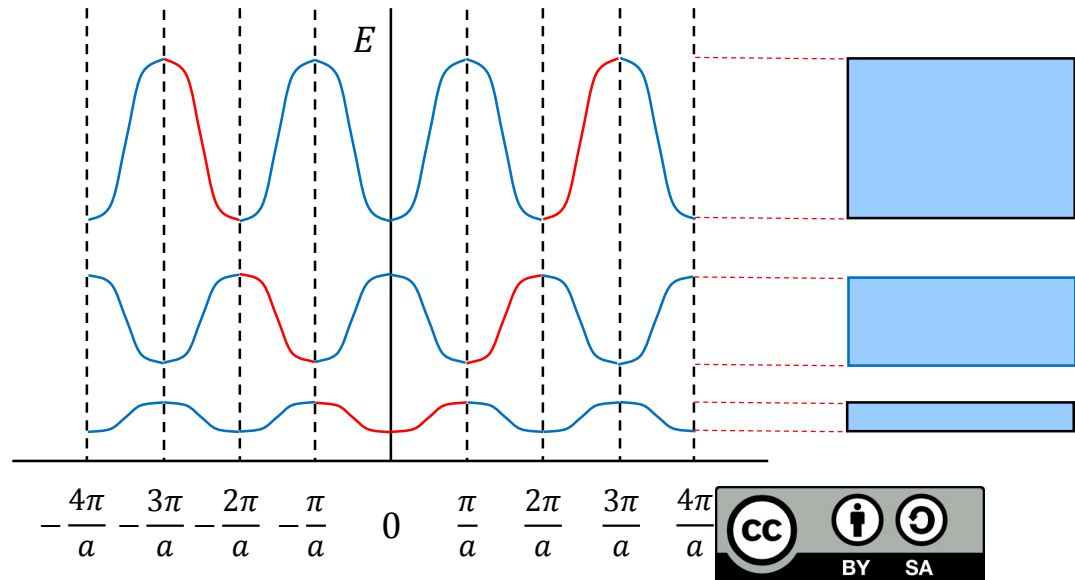
course of the of $E(\vec{k})$ function
represents electron energy
band

(extended zone scheme)



reduced zone scheme

shows course of $E(\vec{k})$ function in
reciprocal space between the first
Bragg planes from the origin
(range from $-\pi/a$ to $\pi/a \rightarrow 1. \text{ BZ}$)
represents information about
interaction between wave vectors
and periodic lattice



Origin of energy gap

wave traveling along the x-axis: $\psi_{trav} = \exp(ikx)$ or $\psi_{trav} = \exp(-ikx)$

electron density for traveling wave is invariant as $\rho \sim |\psi_{trav}|^2 = \exp(ikx) \exp(-ikx) = 1$

wave with wave vector $k = \pm \frac{\pi}{a} \rightarrow$ equal parts of wave travel to the left and to the right, wave vectors satisfy the Bragg condition, waves are reflected to travel in opposite direction

each subsequent Bragg reflection = reversing the direction of traveling $\rightarrow$ standing wave

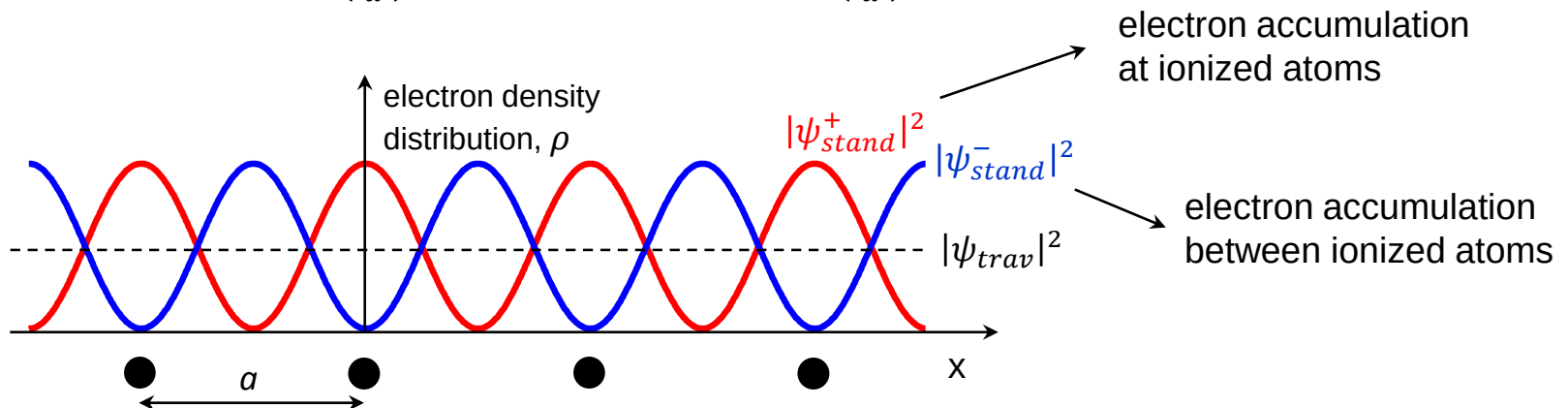
$$\psi_{stand}^+ = \exp\left(i \frac{\pi x}{a}\right) + \exp\left(-i \frac{\pi x}{a}\right) = \sqrt{2} \cos\left(\frac{\pi x}{a}\right)$$

$$\psi_{stand}^- = \exp\left(i \frac{\pi x}{a}\right) - \exp\left(-i \frac{\pi x}{a}\right) = i\sqrt{2} \sin\left(\frac{\pi x}{a}\right)$$



difference in electron density distribution of standing waves

$$\rho \sim |\psi_{stand}^+|^2 = 2\cos^2\left(\frac{\pi x}{a}\right), \rho \sim |\psi_{stand}^-|^2 = 2\sin^2\left(\frac{\pi x}{a}\right)$$

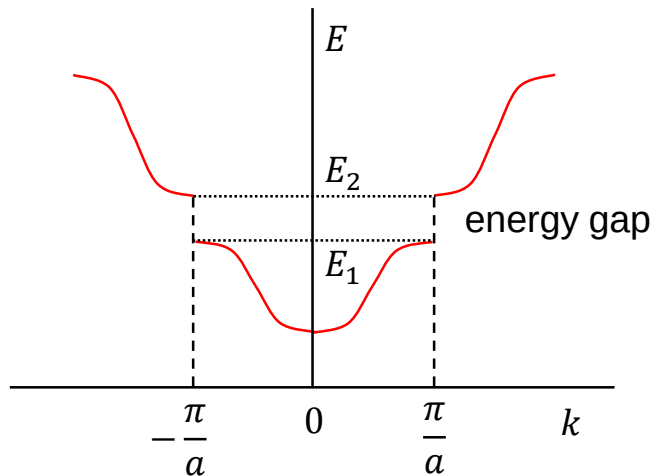


attractive interactions between ionized atoms and electrons $\rightarrow$ negative potential energy of electrons

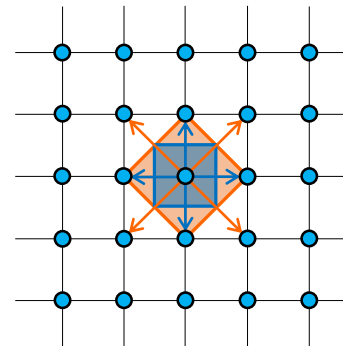
therefore $E_1(\psi_{stand}^+) < E_2(\psi_{stand}^-)$

$$E_2 - E_1 = E_g$$

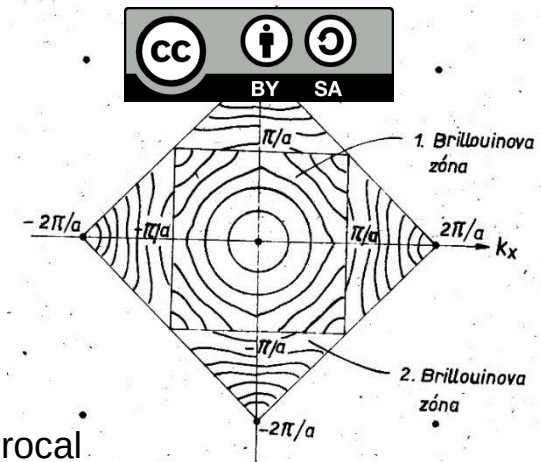
there is no other solution for $k = \pm \frac{\pi}{a}$, no electron can attain energy between E_1 and E_2



length of wave vector $k < \pi/a \rightarrow$ free motion of electron within crystal



Brillouin zones in reciprocal 2D square lattice



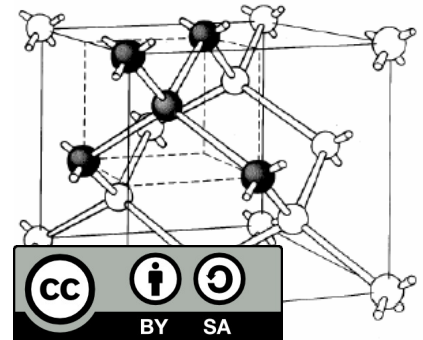
deformation of lines with constant energy close to 1st BZ boundary – at the boundary ($k = \pm \pi/a$) there are two values of electron energy E

Semiconductors

covalent bonds between atoms → completely filled valence band, empty conduction band, narrow band gap ($E_g < \sim 3 \text{ eV}$)

elemental semiconductors (Si, Ge) – covalent bonding, diamond cubic crystal structure

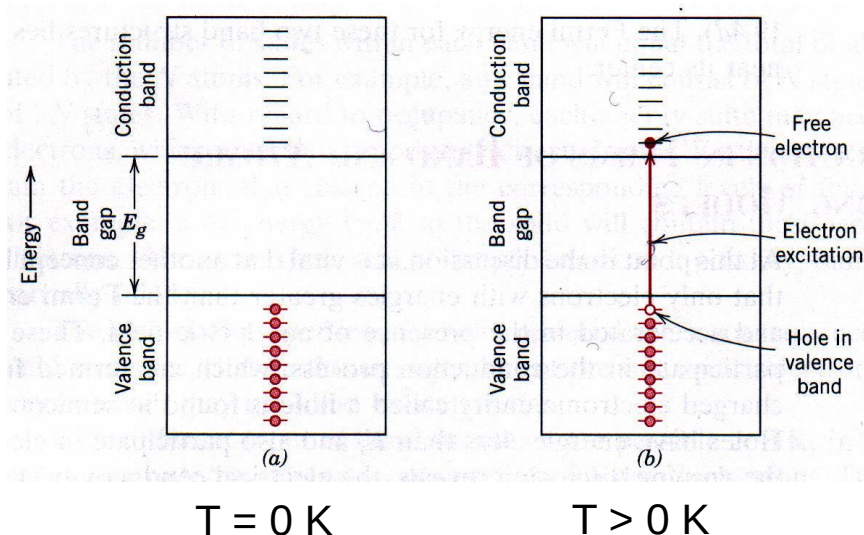
compound semiconductors – polar covalent bonding, sphalerite-like crystal structure



$A^{III}B^V$ (GaAs, AlAs, InP, ...)

$A^{II}B^{VI}$ (CdS, ZnTe, ...)

Intrinsic semiconductors

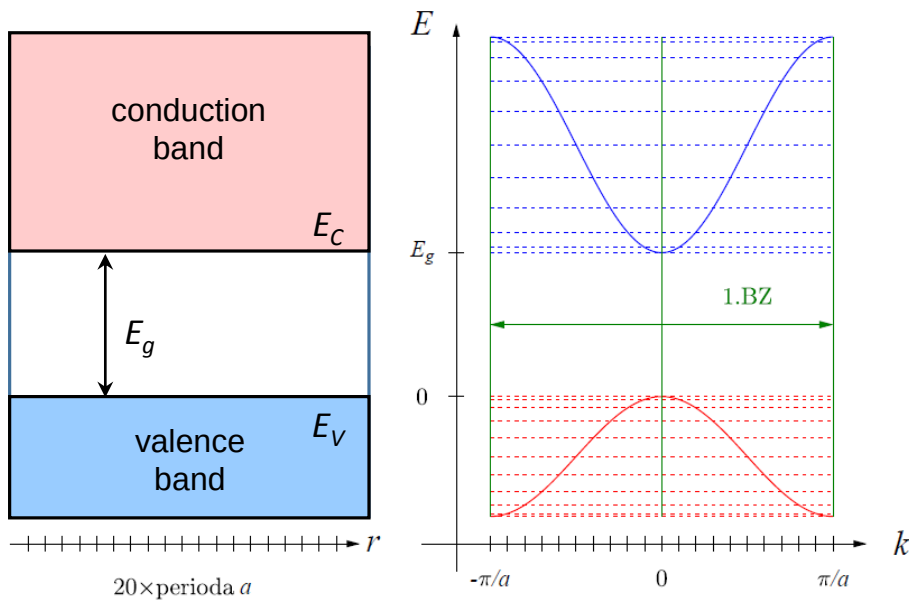


excitation of electrons (e^-) into conduction band → electrical conductivity

vacant electron state in valence band - holes (h^+); moving other valence electron to fill the incomplete bond → holes motion (contribution to conductivity)

electron + hole = exciton (quasiparticle)

equilibrium between generation of electron-hole pairs and their recombination



the lowest energy state in conduction band (E_C) – electron with potential energy $E \geq E_C$ is accelerated by external electric field $\rightarrow$ kinetic energy

the highest energy state in valence band (E_V) – potential energy of electron $E \leq E_V$; increasing in hole potential energy = increasing in potential energy of electron in valence band

band gap $E_g = E_C - E_V$

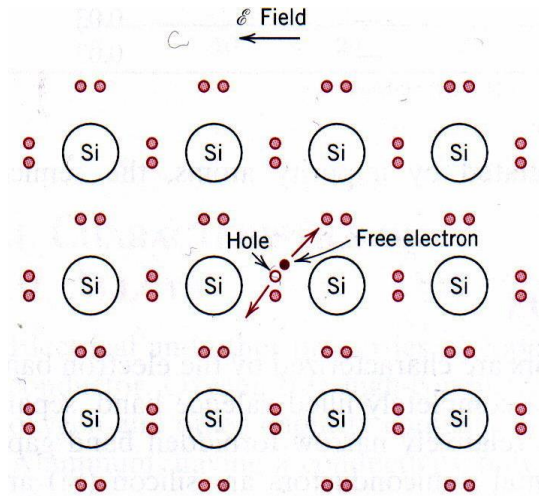


energy band structure of semiconductor and dispersion relation in reciprocal space within the first Brillouin zone

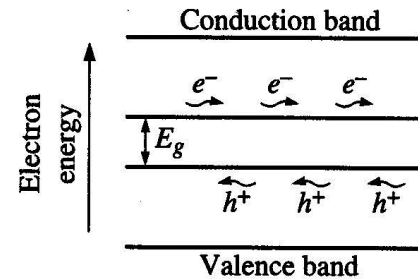
probability of electron energy state occupation at $T = 0$ K: $f(E_V) = 1, f(E_C) = 0$

$$\frac{1}{\exp\left(\frac{E_C - E_F}{kT}\right) + 1} = 1 - \frac{1}{\exp\left(\frac{E_V - E_F}{kT}\right) + 1} \quad \text{satisfied only for } E_F = \frac{E_C + E_V}{2}$$

$\rightarrow$ in semiconductors $f(E_F) = 0.5$



two types of charge carrier, motion of electrons due to applied electric field



electrical conductivity: $\sigma = \sigma_n + \sigma_p = n e \mu_n + p e \mu_p$

intrinsic sem



$= p_i$

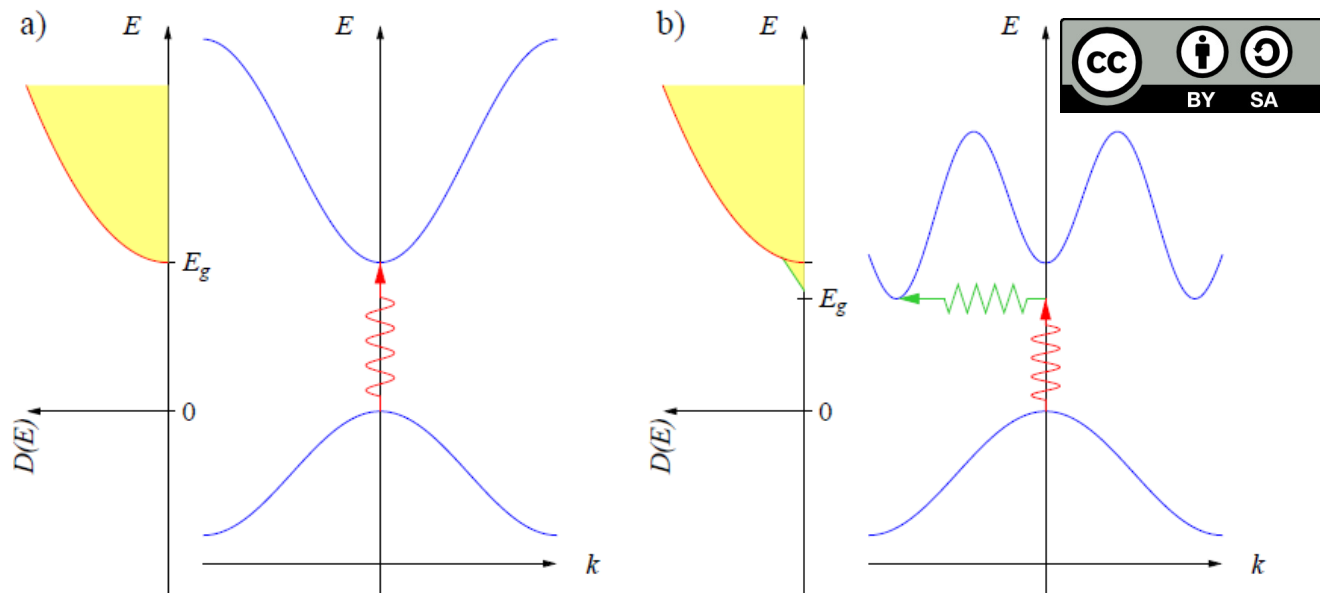
semiconductor	E_g [eV]	σ [$\Omega^{-1} \text{ m}^{-1}$]	μ_n [$\text{m}^2 \text{ V}^{-1} \text{ s}^{-1}$]	μ_p [$\text{m}^2 \text{ V}^{-1} \text{ s}^{-1}$]
Si	1,11	$4 \cdot 10^{-4}$	0,14	0,05
Ge	0,67	2,2	0,38	0,18
GaP	2,25	-	0,05	0,002
GaAs	1,42	10^{-6}	0,85	0,45
InSb	0,17	$2 \cdot 10^4$	7,7	0,07
CdS	2,40	-	0,03	-
ZnTe	2,26	-	0,03	0,01

Direct and indirect band gaps

minimum energy state in conduction band and maximum energy state in valence band are each characterized by a certain crystal momentum (wave vector) in the first Brillouin zone

direct band gap: electrons and holes in both bands have the same wave vectors, excitation of electron without change in wave vector

indirect band gap: electron cannot shift from the highest energy state in valence band to the lowest energy state in conduction band without change in wave vector; phonon-assisted transition is necessary



photon absorption in semiconductors with direct and indirect band gaps

(copied from J. Soubusta, Fyzika pevných látek SLO/PL, Univerzita Palackého v Olomouci, 2012)

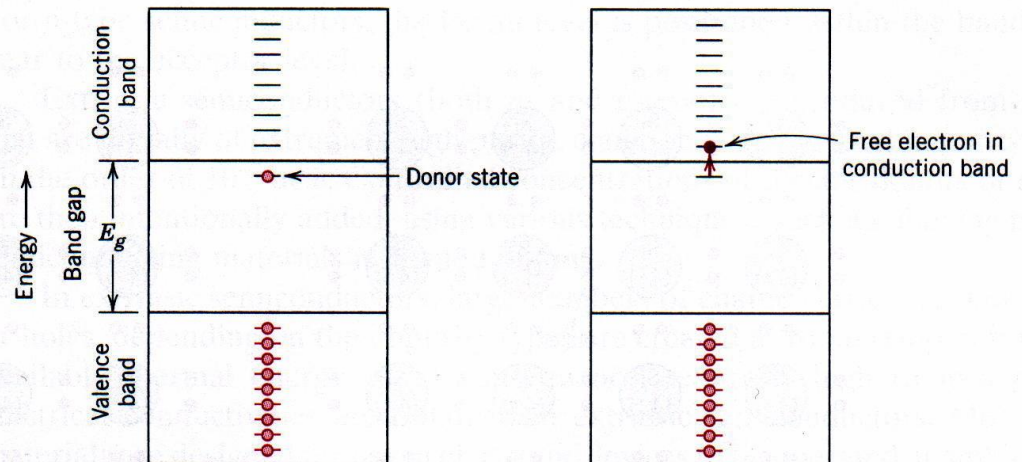
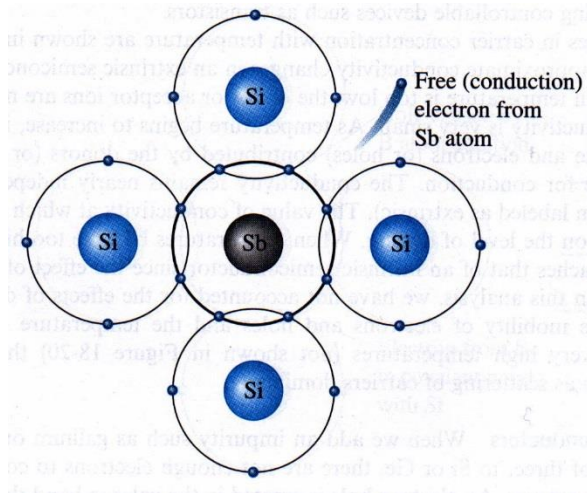
Extrinsic semiconductors

electrical conductivity is affected by substitutional defects in crystal lattice (impurity atoms with other number of valence electrons – donors or acceptors of electrons)

both donors and acceptors of electrons are present in the semiconductor → conductivity is determined by type of substitutional defects with higher concentration

n-type semiconductor

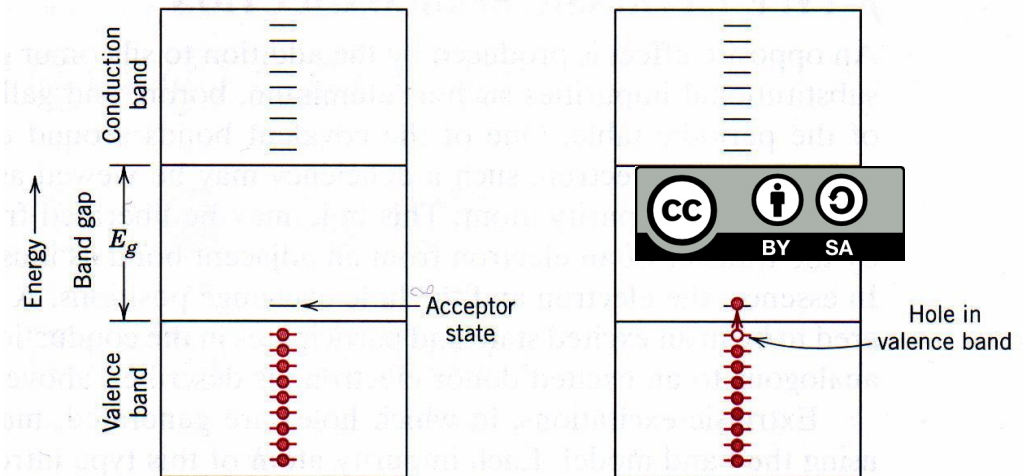
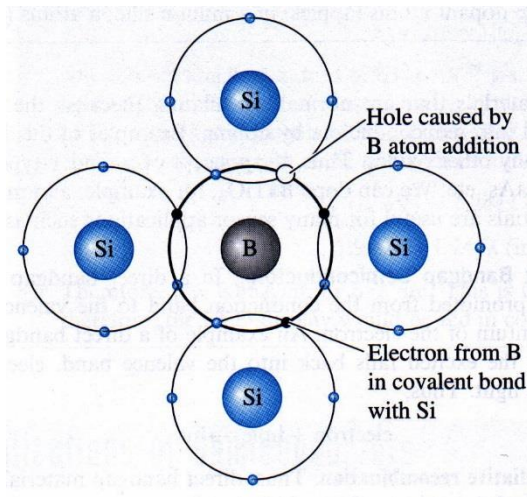
donor impurity level within the semiconductor band gap close to conduction band, low energy needed for ionization of donor atoms



p-type semiconductor

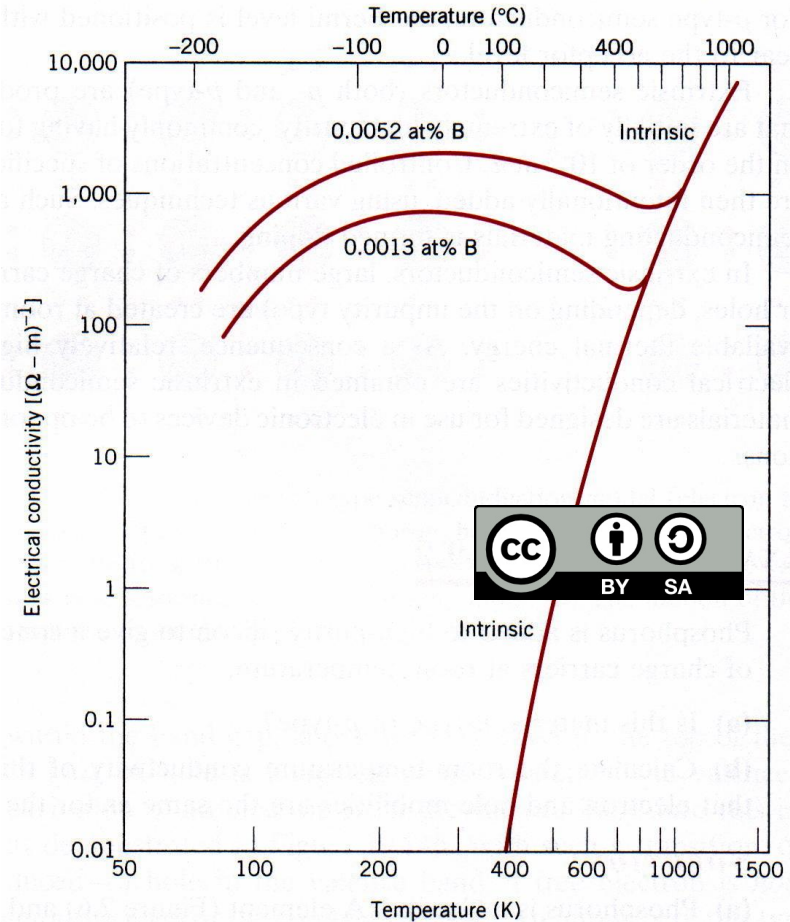
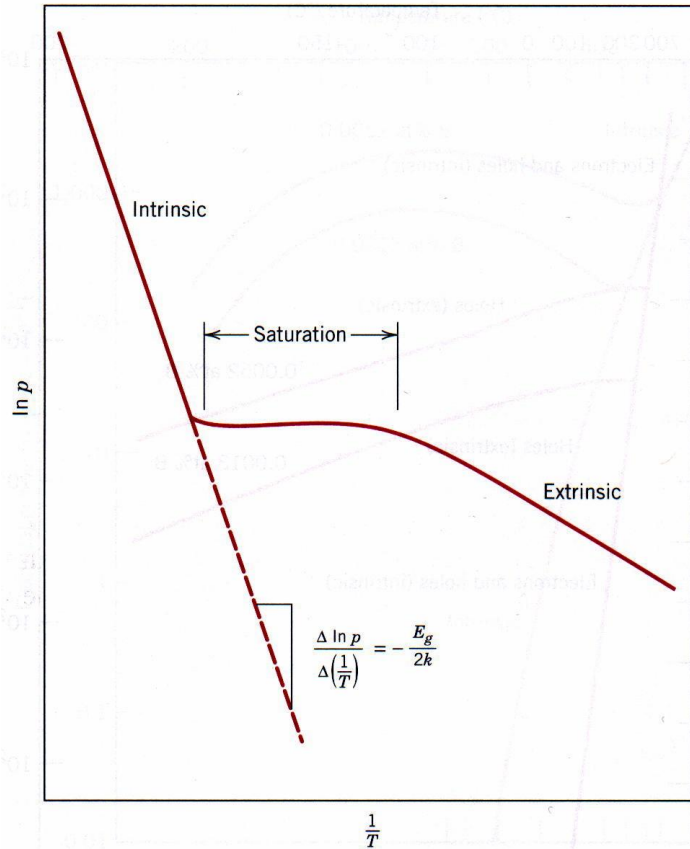
acceptor impurity level within the semiconductor band gap close to valence band; covalent bonding around each acceptor atom is deficient in an electron → electron from valence band can be excited to this hole and hole in valence band is created

acceptor atoms in a sufficient concentration in the crystal → holes as major charge carrier in the semiconductor



electrical neutrality of extrinsic semiconductors in absence of external electric field – electrons in conduction band and holes in valence band are connected with ionized donor and negatively charged acceptor atoms, respectively

high concentration of dopants → degenerate semiconductors with electrical conductivity similar to conducting materials



temperature dependence of electrical conductivity for p-type semiconductor (boron-doped silicon)

(copied from W.D. Callister, Jr., Materials Science and Engineering, An Introduction. Fifth Edition, John Wiley & Sons, Inc., 2000)

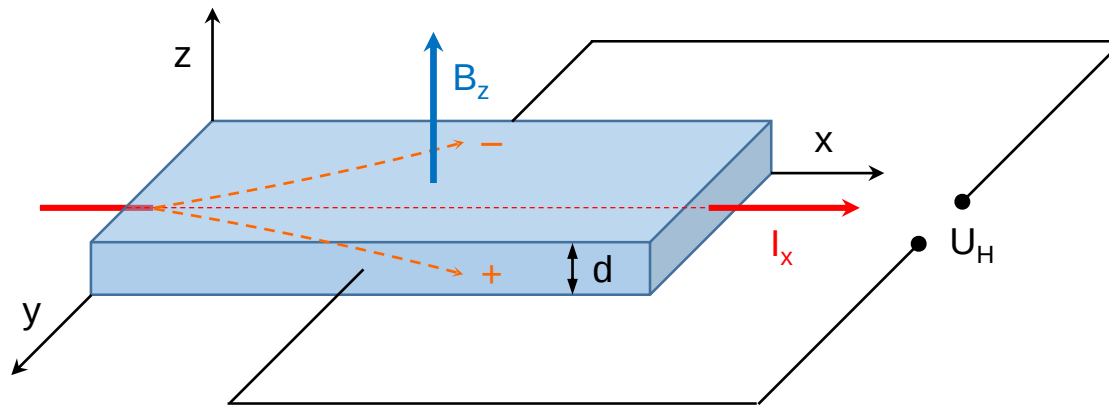
slight changes in electrical conductivity after saturation of all acceptor atoms with electrons from valence band up to intrinsic semiconductor conductivity turns up

Hall effect

displacement of moving charges in magnetic field → majority charge carrier type, its concentration and mobility can be determined

applied magnetic field is perpendicular to direction of charged particle motion; force on the particles perpendicular to both magnetic field and particle motion directions is exerted

Hall voltage is generated on specimen sides to compensate the magnetic field




$$U_H = \frac{R_H I_x B_z}{d}$$

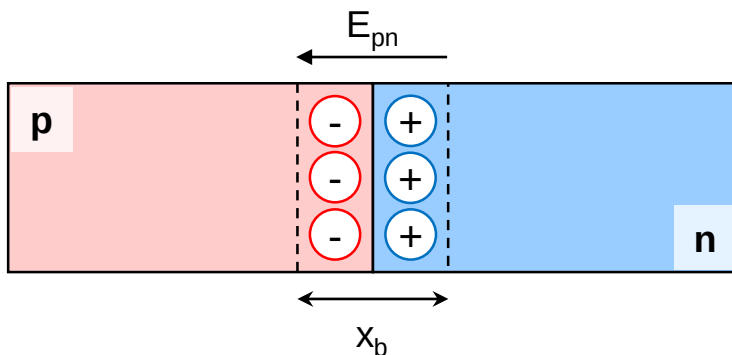
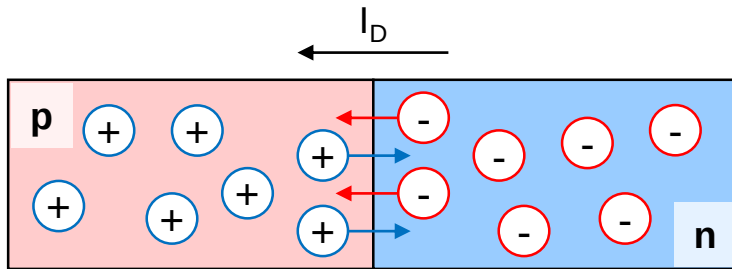
R_H – Hall coefficient, represents reciprocal density of moving charge carriers

$$R_H = -\frac{1}{n e} \quad (\text{n-type semiconductor}) \qquad R_H = \frac{1}{p e} \quad (\text{p-type semiconductor})$$

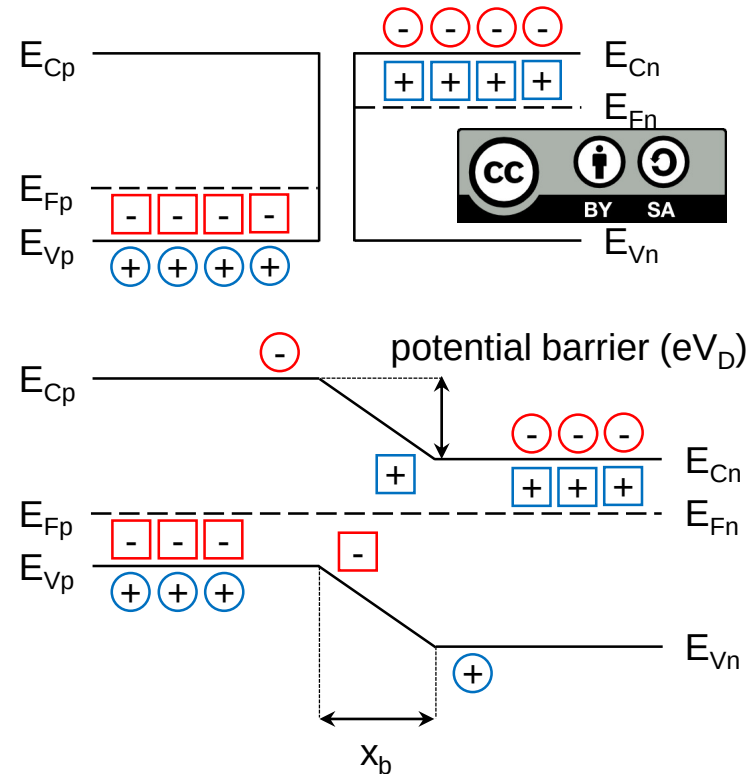
p-n junction

diffusion of major charge carriers across interface between n- and p-type semiconductors → diffusion current due to gradient of charge carries concentration

ionized donors remaining in n-type part, recombination of electrons with holes forming negatively charged ions in p-type part → space charge region is formed close to interface, generated electric field E_{pn} counteracts the diffusion current



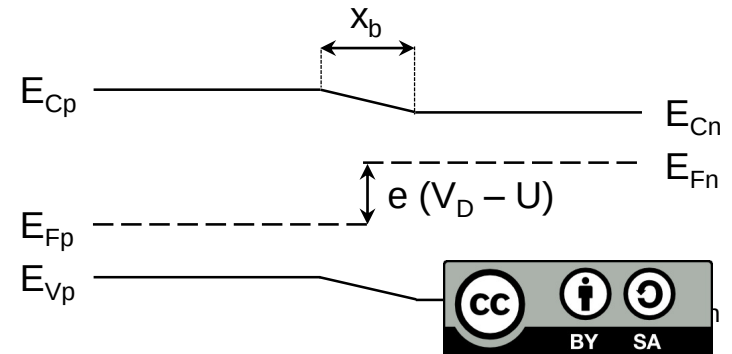
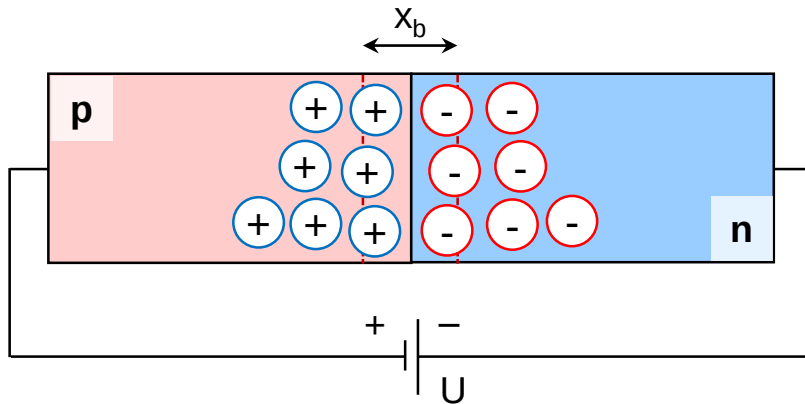
diffusion voltage V_D in space charge region at p-n junction



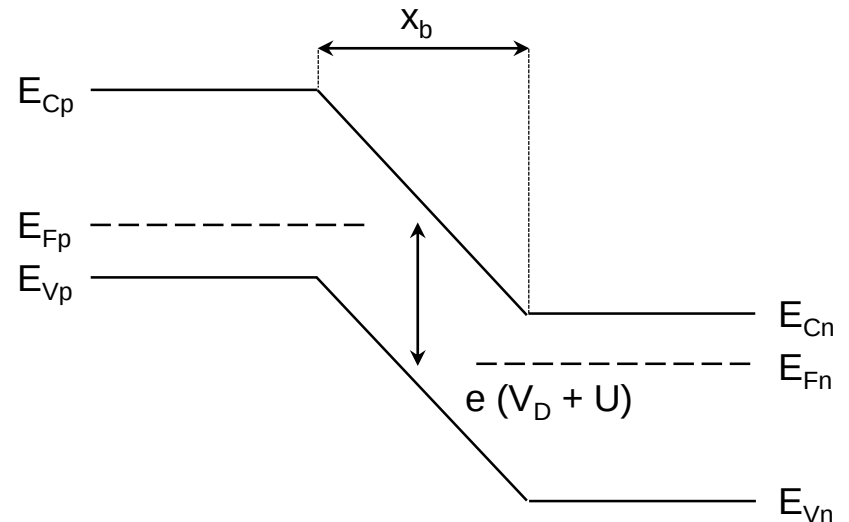
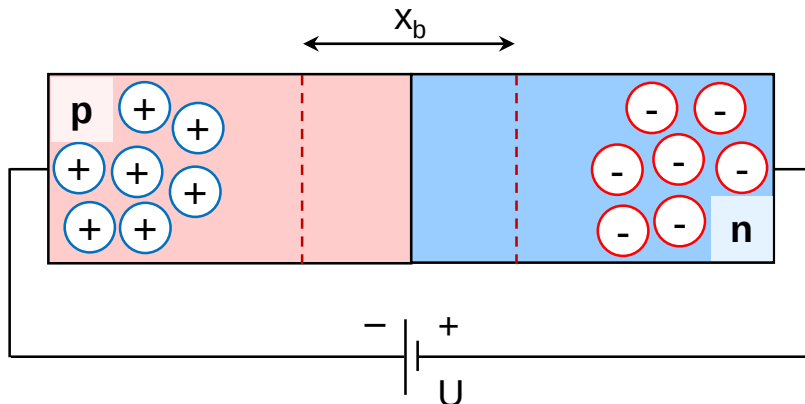
p-n junction diode

electrical resistance of p-n junction is dependent on current direction

forward bias: lower potential barrier, charge carriers are attracted to the junction → increased current and low electrical resistance



reverse bias: charge carriers drawn away from the junction → decrease in diffusion current, insulating character of p-n junction



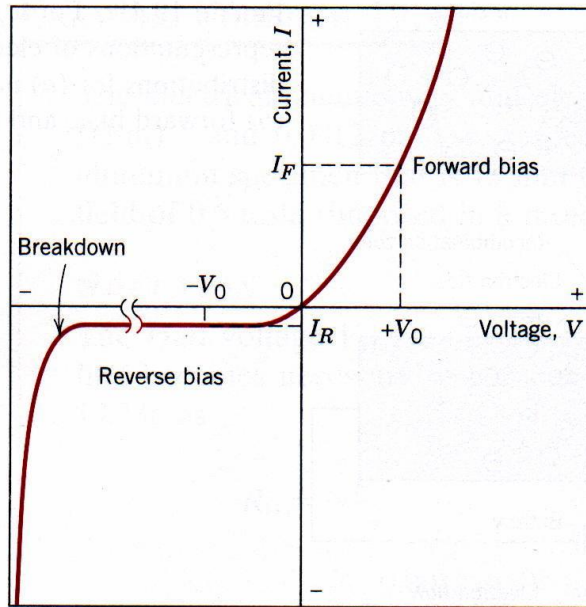
Current-voltage characteristics of p-n junction

$$I = I_R \left[\exp\left(\frac{eU}{kT}\right) - 1 \right]$$

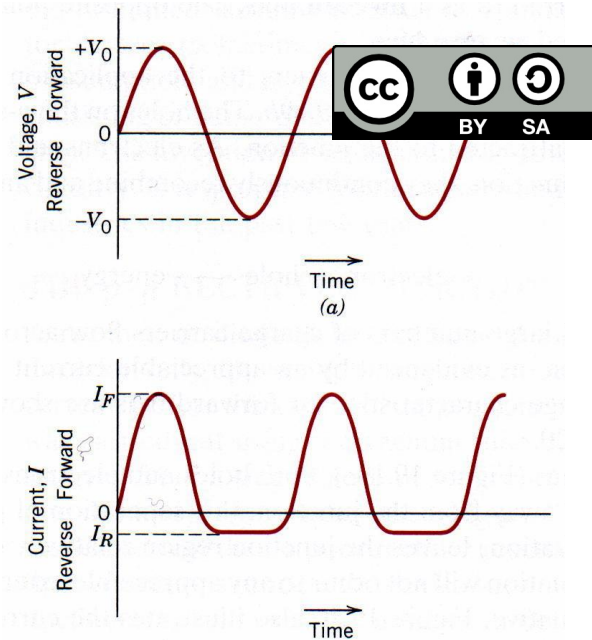
I_R – residual current, $U > 0$ in forward bias, $U < 0$ in reverse bias

breakdown at high reverse bias voltage, large numbers of charge carriers are generated

(Zener diode with heavy doping of p-n junction: very thin space charge region, tunnelling of electrons from valence band of p-type part to conduction band of n-type part at relatively low breakdown voltage → voltage stabilization in circuits)



current-voltage characteristics of p-n junction



current rectification by p-n junction

Interaction of p-n junction with electromagnetic radiation

electron excitation from valence to conduction band due to interaction with photon ($h\nu > E_g$)

Photoconductivity

increase in electrical conductivity of solid due to absorption of electromagnetic radiation

irradiation of p-n junction in reverse bias → generation of electrons and holes resulting in current increase in electrical circuit

photodiode: conversion of electromagnetic radiation into electric current, light detection

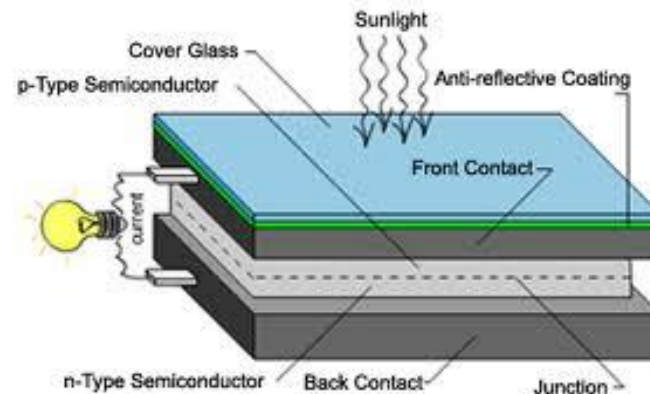
Photovoltaic effect

voltage generation in solid exposed to electromagnetic irradiation due to separation

separation of electrons and holes across p-n junction yields forward (photo)voltage between terminals of irradiated diode; electrons pass through the circuit → energy of radiation is transformed into electrical energy



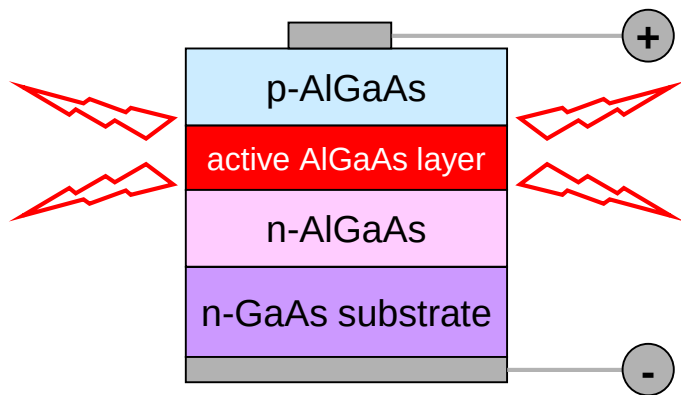
silicon photovoltaic panel



p-n junction as light source

electroluminescence – photon production due to radiative recombination of electrons and holes ($h\nu \sim E_g$)

Light emitting diodes: diode in forward bias, recombination of electrons and holes at p-n junction



structure of AlGaAs LED

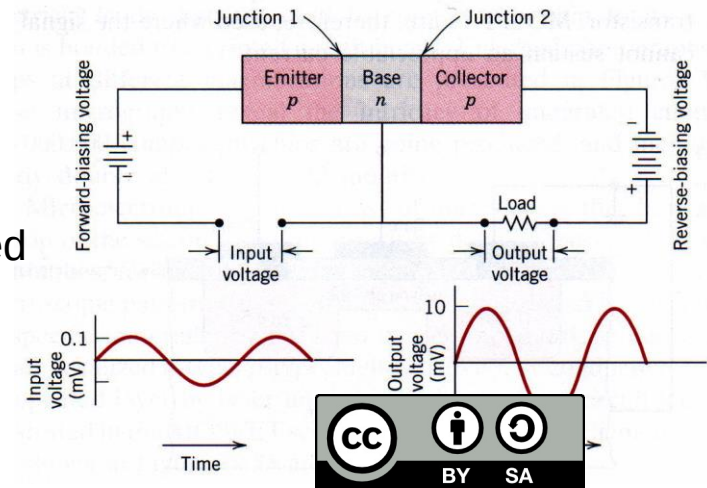
semiconductor	wavelength (nm)	efficiency (%)	power (lm W ⁻¹)
GaAs _{0.6} P _{0.4}	650	0,2	0,15
GaAs _{0.35} P _{0.65} :N	630		1
GaAs _{0.14} P _{0.86} :N	585		1
GaP:N	565	0,4	2,5
GaP:Zn-O	700	2	0,40
AlGaAs	650	4 – 16	2 – 8
AlInGaP	620	6	20
AlInGaP	585	5	20
AlInGaP	570	1	6
SiC	470	0,02	0,04
GaN	450	2	0,6

Combination of p-n junctions: transistor

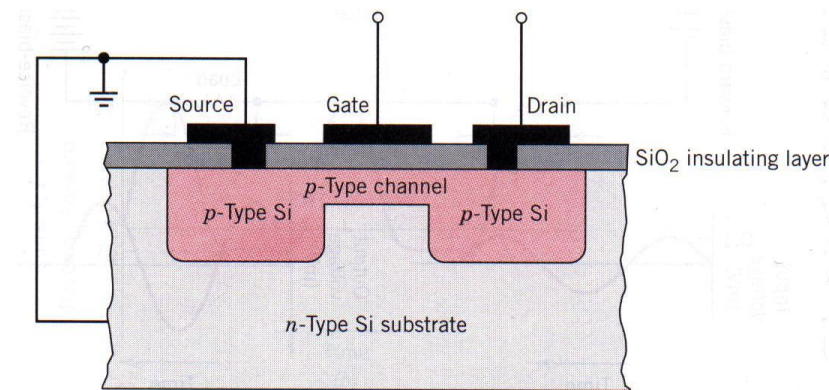
very thin base part sandwiched between emitter and collector parts with other type of conductivity (p-n-p or n-n-n configuration)

most of charge carriers from emitted pass through the base into collector, electric current between base and collector (p-n junction in reverse bias) is increased

→ output voltage amplification



MOSFET (metal-oxide-semiconductor field-effect-transistor)



small islands of one type semiconductor (connected with narrow channel) within substrate of other type semiconductor

flow of charge carriers from source to drain is controlled by electric field on gate connected over thin insulating oxide layer

small alteration in the field at the gate results in large variation in current between source and drain → amplification of source signal; much smaller gate current compared to base current in junction transistor

Dielectrics

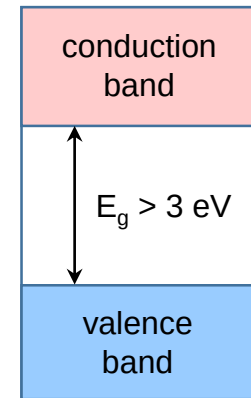
valence band completely filled with electrons

empty conduction band, wide bandgap

electrons cannot be excited into conduction band

no free motion of electrons through the solid, negligible electrical conductivity → insulators

applied electric field → change in charge distribution (polarization)



Electrical insulators



perfect insulator – absence of electrical conductivity; real insulators contain slight amount of mobile charge carriers

strong external electric field ($> 10^6 \text{ V cm}^{-1}$) → breakdown (sudden increase in electrical current)

(tearing bound electrons away from atoms and subsequent collisions of accelerated electrons with other atoms → avalanche breakdown, formation of conductive paths, disruptive discharge → permanent physical changes in the solid)

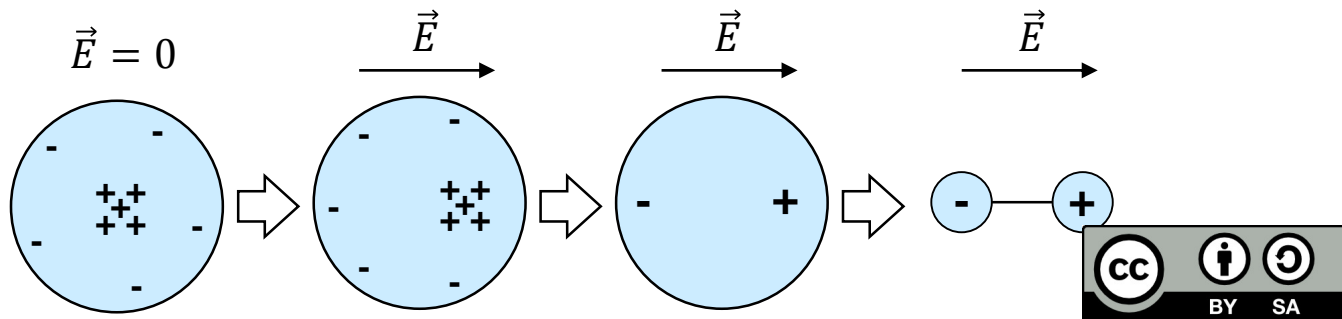
dielectric strength $E_{br} = U_{br}/d$ (U_{br} – breakdown voltage, d – specimen thickness)

All insulators are dielectrics but not every dielectric is insulator.

Electric polarization

interaction of dielectric with applied electric field $\rightarrow$ change in charge distribution within the dielectric

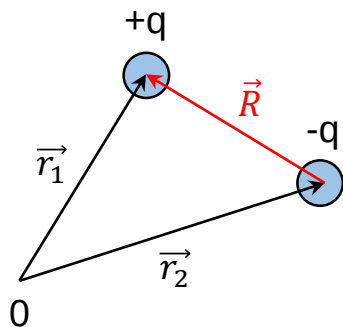
charged particles in atoms (protons, electrons) $\rightarrow$ displacement of electron cloud center relative to nucleus in applied electric field, electric dipole is created



electric dipole = point charges separated by a distance $|\vec{R}|$

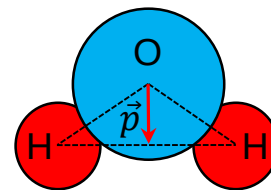
dipole moment

$$\vec{p} = q\vec{r}_1 - q\vec{r}_2 = q(\vec{r}_1 - \vec{r}_2) = q\vec{R}$$



non-polar dielectric = dielectric without permanent dipoles

polar molecules and groups: $\vec{p} \neq 0$ in absence of external electric field, random orientation



molecule of water

dipole moment

$$p = 6,1 \cdot 10^{-30} \text{ C m}$$

Macroscopic polarization

dipole moments are aligned with an external electric field

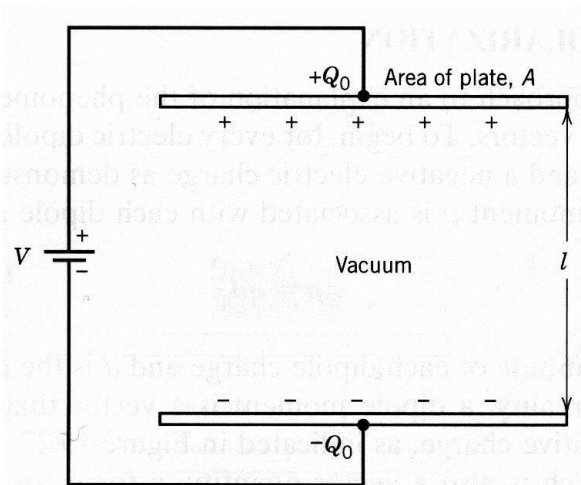
total dipole moment (density of electric dipole moments, polarization): $\vec{P} = \frac{\sum \vec{p}_i}{dV}$

electric displacement field $\vec{D} = \epsilon \vec{E} = \epsilon_0 \vec{E} + \vec{P}$ [C m⁻²]

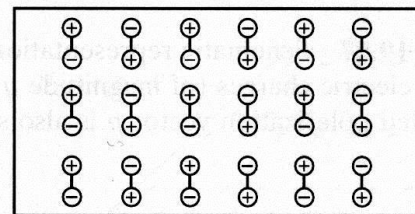
linear dielectrics (isotropic, relatively weak electric field $\vec{E}$): $\vec{P} = \epsilon_0 \kappa \vec{E} = \epsilon_0 (\epsilon_r - 1) \vec{E}$

ϵ – permittivity; $\epsilon_0 = 8,85 \cdot 10^{-12}$ F m⁻¹ – vacuum permittivity, κ - electric susceptibility

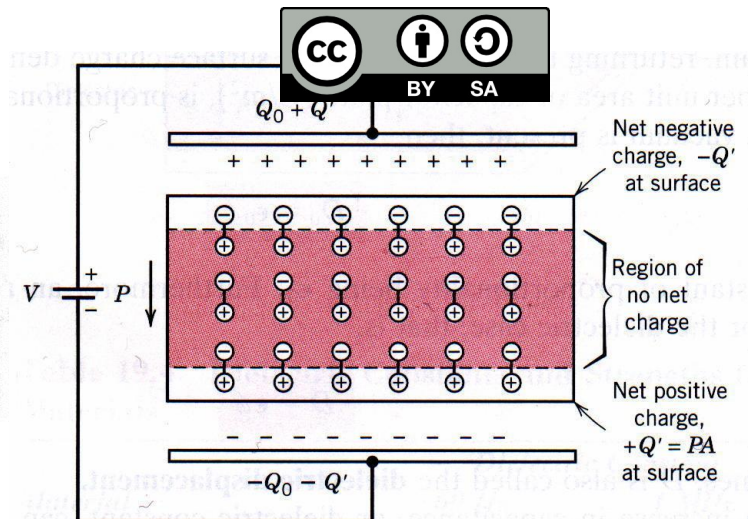
relative permittivity $\epsilon_r = 1 + \kappa = \epsilon / \epsilon_0 > 1$



charging of capacitor plates in vacuum



dipole arrangement in a non-polarized dielectric



increase in charge density resulting from polarization of a dielectric

electric field in dielectric decreases, capacitance of the capacitor increases ($C = \epsilon A / l$)

Types of polarization

solid with identical elementary dipoles $\vec{p}$ induced by local electric field $\vec{E}_{loc}$

$$\vec{p} = \alpha \vec{E}_{loc} \quad \alpha - \text{polarizability}$$

polarization $\vec{P} = N\vec{p}$, N = number of dipoles in a unit volume

Electronic polarization

distortion of atomic electron cloud by electric field, found in all dielectrics, very fast response to applied electric field

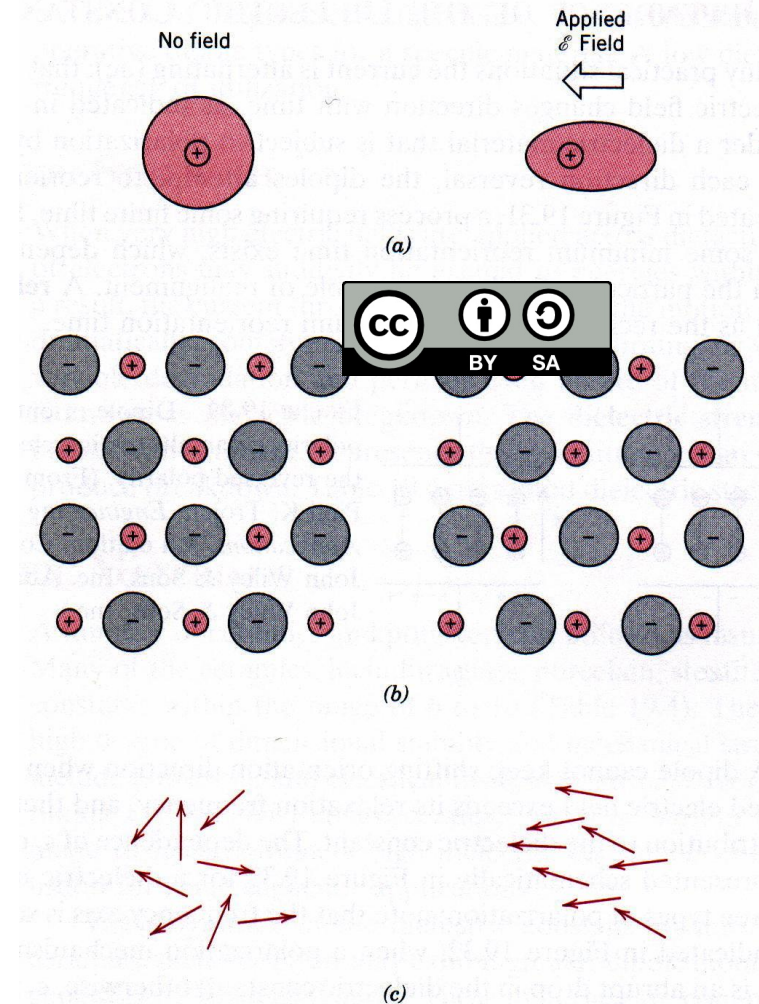
Ionic polarization

relative displacement of charged ions in response to electric field, increase in net dipole moment, found in ionic crystals

Orientation polarization

found in substances with permanent dipole moments, alignment of permanent dipoles parallel to applied electric field, rather restricted in solids

$$\text{total polarization } \vec{P} = \vec{P}_e + \vec{P}_i + \vec{P}_o$$

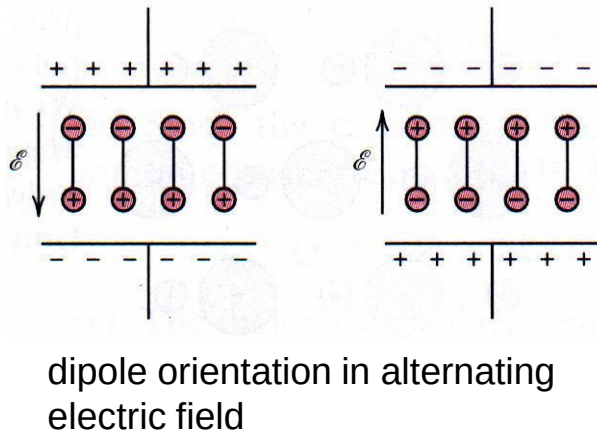


Polarization in alternating electric field

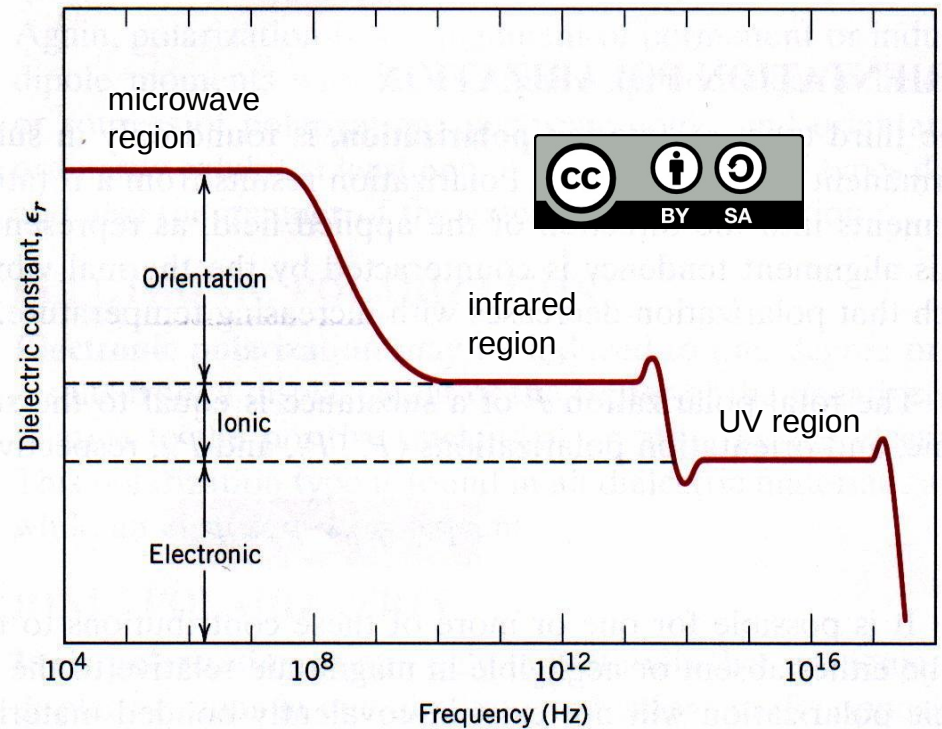
polarization is dependent on externally applied electric field: $\vec{P} = (\epsilon_r - 1)\epsilon_0\vec{E}$

certain time is necessary for dipole alignment in applied electric field (depends on type of polarization)

alternating electric field $\rightarrow$ there is minimum reorientation time for each polarization type (reciprocal reorientation time = relaxation frequency)



dipole cannot keep shifting orientation direction when frequency of alternating field exceeds the relaxation frequency



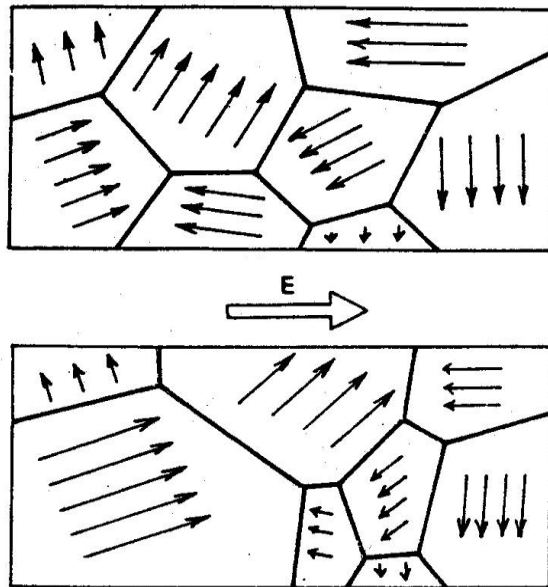
variation of relative permittivity with frequency of alternating electric field

Ferroelectrics

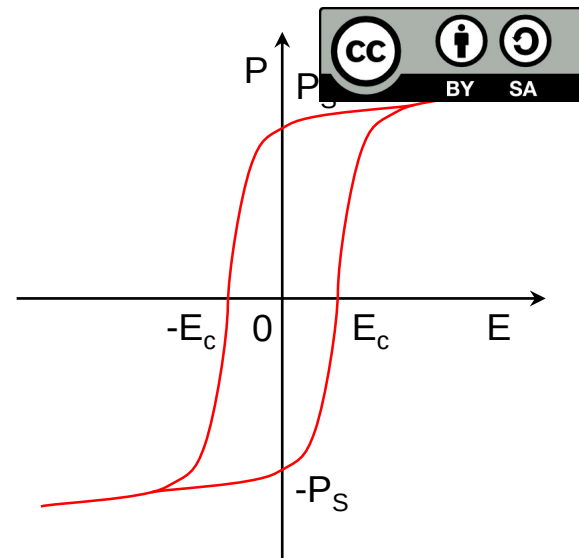
dielectrics with spontaneous polarization within a certain temperature range, $\vec{P}_s \neq 0$ at $\vec{E} = 0$

domain structure – small regions with parallel alignment of dipole moments; ferroelectric domains with dipole moments parallel to applied electric field increase in size to the detriment of other ones → increasing electric field results in alignment of all dipole moments $\vec{P}_s$ parallel to $\vec{E}$

spontaneous polarization can be removed by coercive electric field (E_c) and reversed by suitably strong electric field applied in opposite direction → hysteresis loop



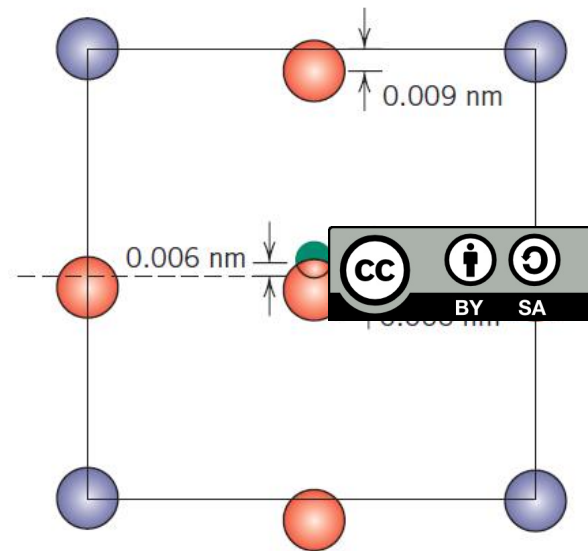
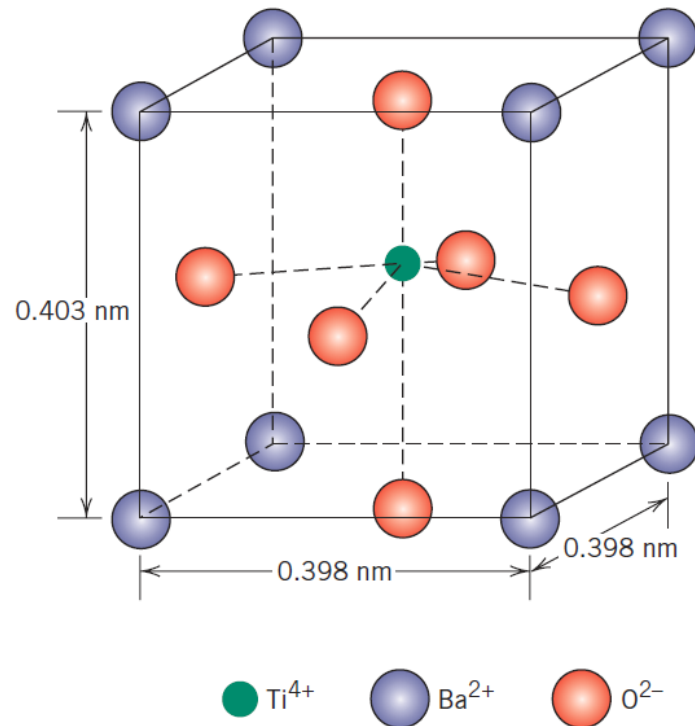
change in domain structure during polarization of ferroelectric solid



change in total polarization of ferroelectric solid with applied electric field

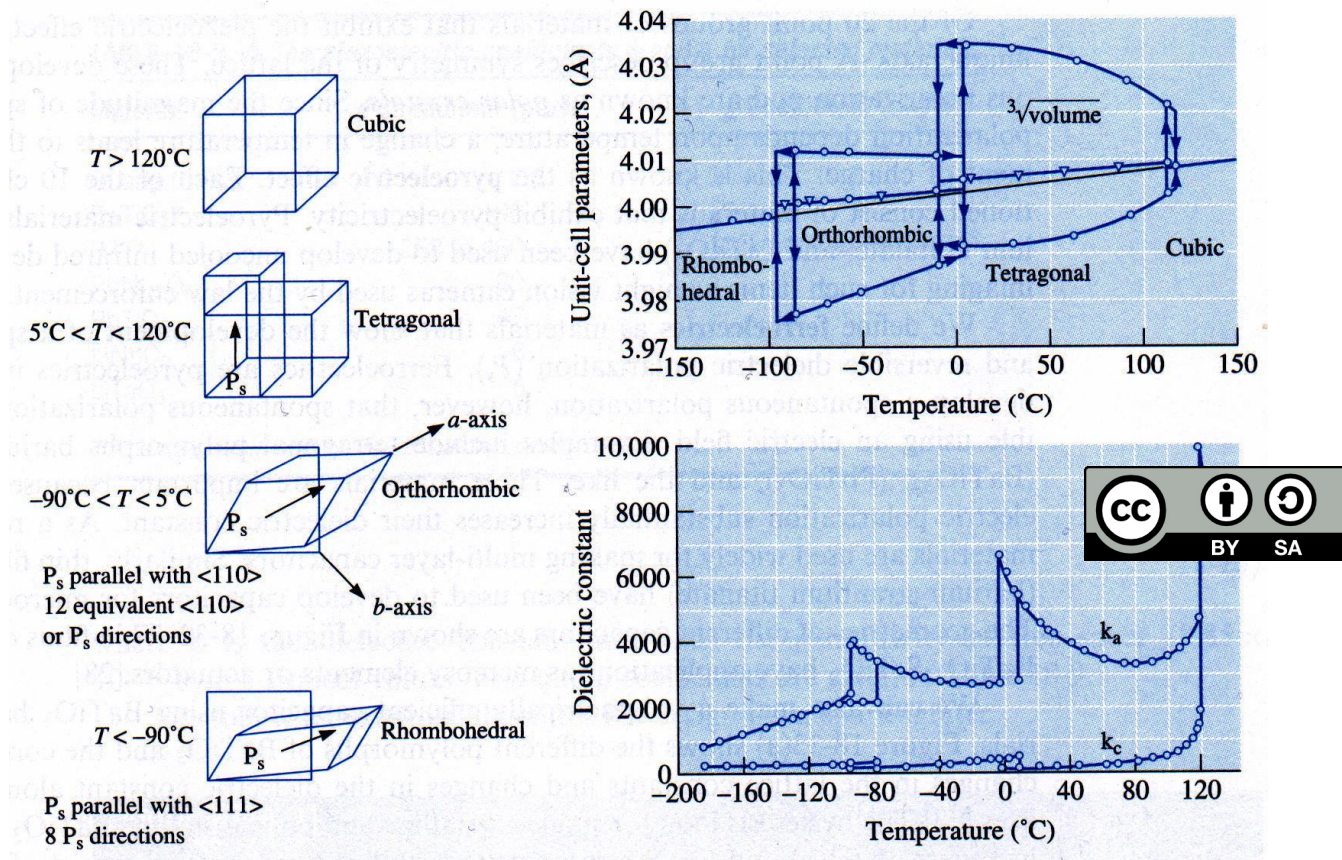
barium titanate (BaTiO_3): permanent dipole moment in unit cell caused by relative displacement of O^{2-} and Ti^{4+} ions from their symmetrical positions in cubic perovskite structure at $T < 120^\circ\text{C}$ (ferroelectric Curie temperature T_c)

rearrangement to regular cubic structure at $T > T_c$, loss of ferroelectric properties, paraelectric behavior



(copied from W.D. Callister, Jr., Materials Science and Engineering, An Introduction. 7th Edition, John Wiley & Sons, Inc., 2007)

ferroelectric phases of BaTiO₃ and orientation of spontaneous polarization vector $\vec{P}_s$

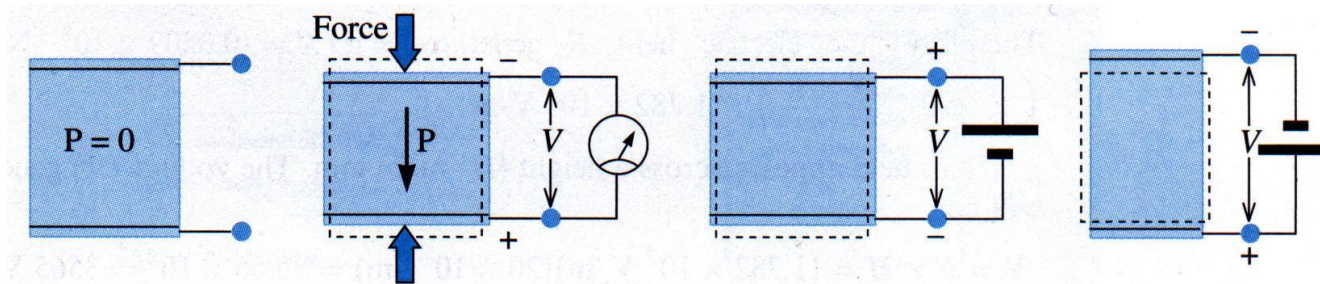


(copied from z D.R. Askeland, P.P. Phulé, The Science and Engineering of Materials (4th Edition). Thomson Brooks/Cole 2003)

Note: antiferroelectrics – the same relative displacement of adjacent atoms from their symmetrical positions but in opposite direction; oppositely oriented dipole moments cancel each other, total polarization is zero (for example, PbZrO₃, NaNbO₃)

Piezoelectrics

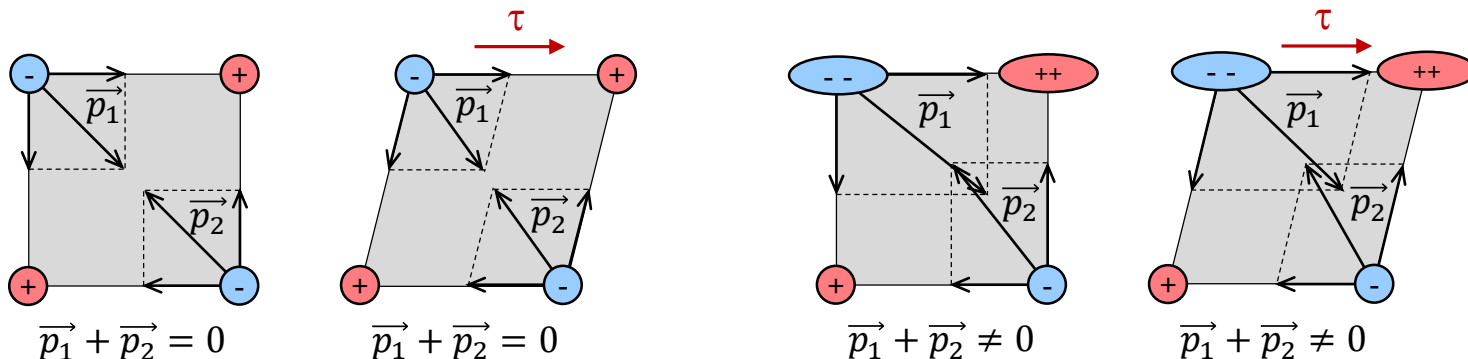
piezoelectric effect: polarization change in response to applied mechanical stress $\rightarrow$ variation of surface charge density upon crystal faces caused by change in dipole density in the bulk



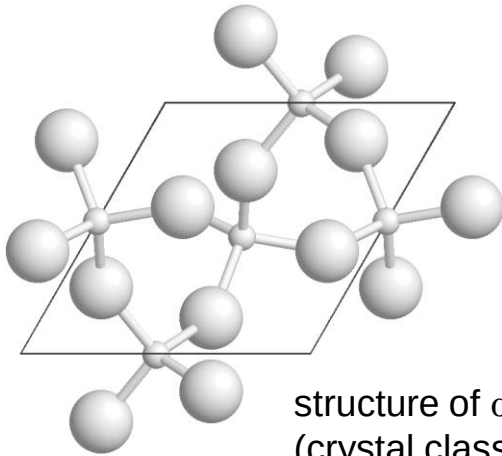
Note: displacement of ions in crystal lattice by external electric field $\rightarrow$ strain in direction of the electric field = electrostriction



piezoelectric effect only in structures without a center of symmetry (20 non-centrosymmetric crystal classes: 1, 2, m , 222, $mm2$, 4, $\bar{4}$, 422, $4mm$, $\bar{4}2m$, 3, 32, $3m$, 6, $\bar{6}$, 622, $6mm$, $\bar{6}2m$, 23, $\bar{4}3m$)



contribution of ionic dipole moments to overall polarization after applying mechanical stress in centrosymmetric and non-centrosymmetric crystal structures



structure of α -SiO₂
(crystal class 32)

$P = d\tau$ d – piezoelectric coefficient (third-order tensor)

All ferroelectrics exhibit piezoelectric effect.
Piezoelectric effect can also be exhibited by some crystals which are not ferroelectric.

piezoelectrics: BaTiO₃, PbTiO₃, PbZrO₃, Pb(Zr_{1-x}Ti_x)O₃ (PZT), LiNbO₃, SiO₂ (quartz), ZnO, ...



Pyroelectrics

crystals with temperature dependent spontaneous polarization – shifting of positively and negatively charged ions in crystal lattice results in changing of polarization and surface charge density

all pyroelectrics are piezoelectric (10 polar crystal classes: 1, 2, m, mm2, 3, 3m, 4, 4mm, 6, 6mm)

$$\Delta \vec{P} = \vec{\pi} \Delta T \quad \pi - \text{pyroelectric coefficient } [\text{C m}^{-2} \text{ K}^{-1}]$$

pyroelectrics: BaTiO₃, LiNbO₃, LiTaO₃

Ionic conductors

solid electrolytes – compounds with ionic bonding, solid solutions

motion of ions through a solid (diffusion) in applied electric field → ionic conductivity

total electric conductivity includes both electronic and ionic conductivity

materials with high ionic conductivity at common temperatures → superionic conductors
($\sigma = 10^{-1} - 10^2 \Omega^{-1} \text{ m}^{-1}$)

properties:

- structure enabling motion of ions (structure with cation or anion deficiency – vacancies, empty interstitial positions)
- low energy barriers for ion jumping between free positions in the structure ($\sim 0.1 \text{ eV}$)
- continuous paths for ion motion



cation conductors:

Na^+ $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ (β -alumina), $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($0 < x < 3$, NASICON)

Ag^+ AgI , RbAg_4I_5

Li^+ LiCoO_2 , LiMnO_2 , $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (c-LLZO)

H^+ $\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$

anion conductors:

F^- PbF_2 , CaF_2 , LaF_3

O^{2-} $\text{Y}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$ (YSZ), $\text{Ca}_x\text{Zr}_{1-x}\text{O}_{2-x}$, some perovskites ($\text{Ba}_2\text{In}_2\text{O}_5$, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3-y}$)

Chemistry and Physics of Solids - Lecture 13

MAGNETIC AND OPTICAL PROPERTIES OF SOLIDS



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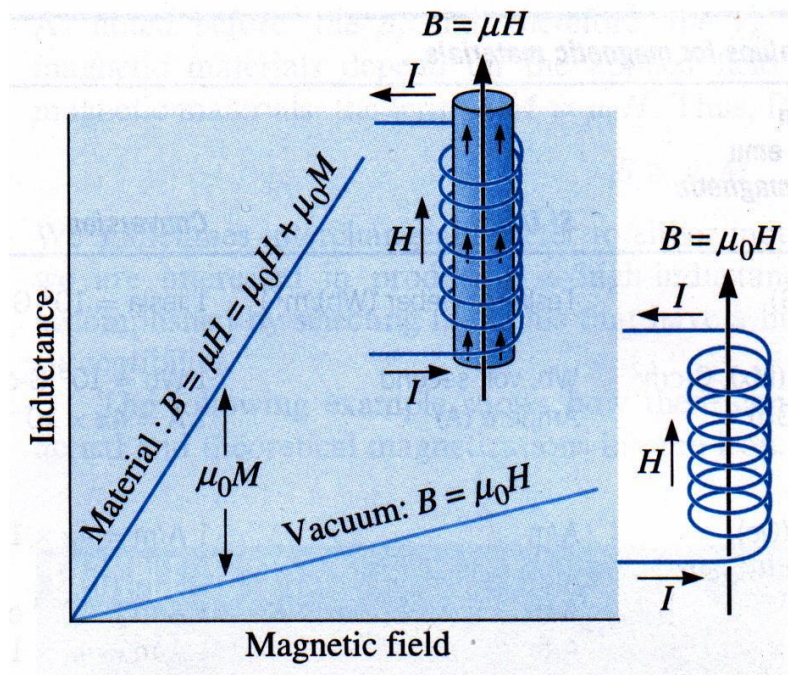


Magnetic properties of solids

interaction between solid and magnetic field → internal magnetic field in the solid is generated

magnetization (M) – magnetic moment in a unit volume of solid inserted into externally applied magnetic field with strength of H (sum of magnetic dipole moments associated with individual electrons)

magnetic induction or **magnetic flux density** (B) – force acting on moving electric charge (magnitude of internal magnetic field strength within solid exposed to external magnetic field)



$$\vec{B} = \mu \vec{H} = \mu_0 \vec{H} + \mu_0 \vec{M}$$



permeability of vacuum $\mu_0 = 1,257 \cdot 10^{-6} \text{ H m}^{-1}$
($\epsilon_0 \mu_0 = 1/c^2$)

relative permeability $\mu_r = \mu / \mu_0$

magnetic susceptibility $\chi = \mu_r - 1$

$$\vec{M} = \chi \vec{H}$$

units:

magnetic field strength $H = \text{A m}^{-1}$ (Henry)

magnetic induction $T = \text{kg s}^{-2} \text{ A}^{-1}$ (Tesla)

Elementary magnetic moments

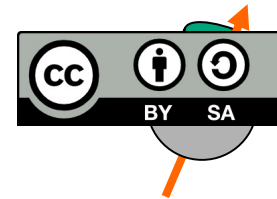
each solid contains moving charged particles → magnetic dipole moments are generated

- spin of electrons (spin magnetic moments)
- orbital motion of electrons around nucleus (orbital magnetic moments)
- spin of nuclei (spin magnetic moment of nucleus $\ll$ electron magnetic moments)

Spin magnetic moment of electron

$$|\vec{\mu}_s| = 2|\vec{\mu}_B|[s(s+1)]^{1/2} \quad s - \text{spin quantum number, } s = 1/2$$

$$|\vec{\mu}_B| = \frac{e\hbar}{2m_e} = 9.273 \cdot 10^{-24} \text{ J T}^{-1} \quad \text{Bohr magneton}$$



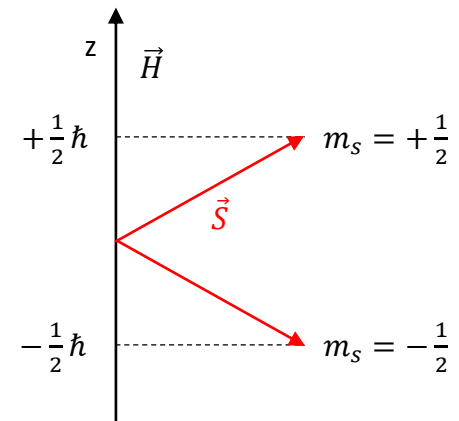
spin angular momentum

quantized values, $(2s + 1)$ possible orientations in magnetic field
→ 2 orientations of spin angular momentum $\vec{S}$ with norm of

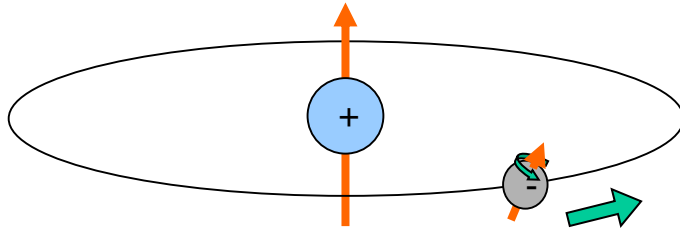
$$|\vec{S}| = \hbar[s(s+1)]^{1/2}$$

two values of secondary spin quantum number $m_s = \pm 1/2$

(spin z-projection $s_z = \hbar m_s$)



Orbital magnetic moment of electron



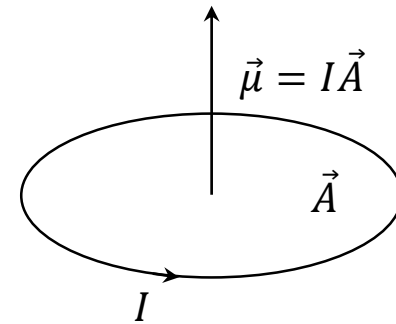
current $I = e/\tau$ [C s⁻¹ = A s s⁻¹ = A]

orbital magnetic moment

$$\vec{\mu}_e = \frac{e}{2m_e} \vec{L}$$

$\vec{L}$ - angular momentum for the electron orbital motion, quantized values $|\vec{L}| = \hbar[l(l+1)]^{1/2}$
 (l - orbital quantum number)

$$|\vec{\mu}_e| = \frac{e\hbar}{2m_e} [l(l+1)]^{1/2} \quad \frac{e\hbar}{2m_e} = |\vec{\mu}_B|$$



current loop generating magnetic field
 with magnetic moment along its axis of
 rotation

vector of loop area $\vec{A}$ is defined
 according to current direction



vector $\vec{L}$ has $(2l + 1)$ possible orientation in magnetic field

$n = 1$ (s) $l = 0 \rightarrow m_l = 0$, spherical symmetry of s orbital

$n = 2$ (p) $l = 1 \rightarrow 3$ orientations ($m_l = -1, 0, 1 \rightarrow p_x, p_y, p_z$)

$n = 3$ (d) $l = 2 \rightarrow 5$ orientations ($m_l = -2, -1, 0, 1, 2 \rightarrow d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, d_{z^2}$)

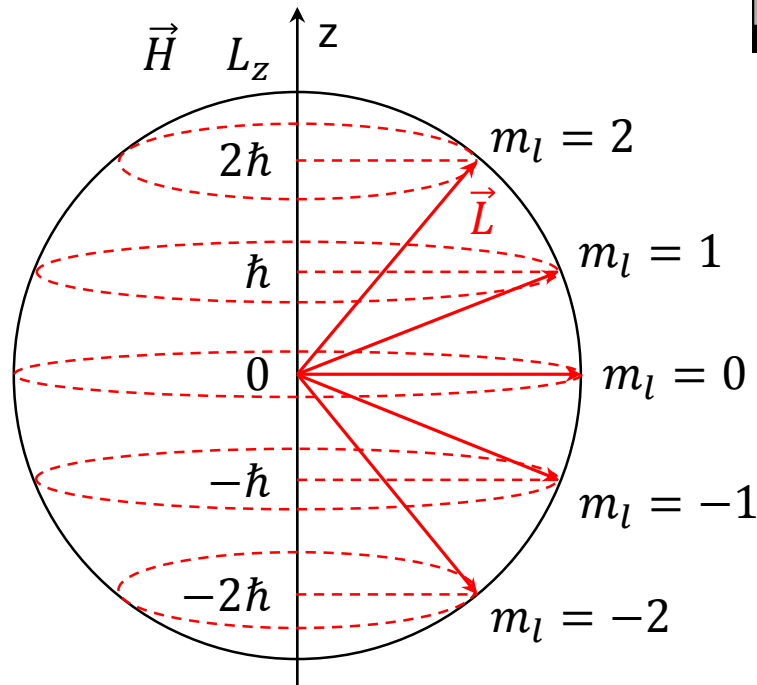
atom in magnetic field oriented along the z-axis

- magnetic field induces precession of vector $\vec{L}$
- mean value of L_x and L_y components is zero, component $L_z = m_l \hbar$
- precession angles between vector $\vec{L}$ and z-axis are quantized

$$\cos \alpha = \frac{m_l}{[l(l + 1)]^{1/2}}$$

$$|\vec{L}| = \hbar[l(l + 1)]^{1/2}$$

quantization of orbital angular momentum $\vec{L}$ ($l = 2$)



Total magnetic moment of electron

interaction of spin angular momentum and orbital angular momentum

→ total angular momentum of electron $\vec{J} = \vec{L} + \vec{S}$

$|\vec{J}| = \hbar[j(j+1)]^{1/2}$ j – total angular momentum quantum number of electron

$j = l + s, l + s - 1, \dots, l - s$ (for example, $l = 1, s = 1/2, j = 3/2$ and $1/2$)

Multi-electron atom

total orbital quantum number and total spin quantum number $L = \sum m_l, S = \sum m_s$

spin-orbital interaction (LS coupling) → $J = L + S, L + S - 1, \dots, L - S$ (total angular momentum quantum number)



term symbols (spectroscopic state of atom) $(2S+1)L_J$

spin multiplicity $(2S + 1)$ = number of possible states of J for given L and S (multiplet)

Example: term of iron atom in a ground state

Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ **[Ar] $3d^6 4s^2$** $\boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow\downarrow}$

all orbitals excepting the 3d one are fully occupied, 3d orbital contains 6 electrons

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2} = 2 \rightarrow (2S + 1) = 5 \quad J = 4, 3, 2, 1, 0$$

$$L = 2 + 1 + 0 - 1 - 2 + 2 = 2 \rightarrow \text{spectroscopic symbol D}$$

3d shell over half full → maximum J value $J = |L + S| = 4$

(shell up to half full → minimum J value $J = |L - S|$)

shell just half full → $L = 0, J = S$)

} $\Rightarrow {}^5D_4$

total magnetic moment of atom = sum of all orbital and spin magnetic moments (vectors)

$$|\vec{\mu}_{at}| = g|\vec{\mu}_B|[J(J+1)]^{1/2}$$

g – Landé factor (normalization of vectors $\vec{\mu}_e$ and $\vec{\mu}_s$ coupling) given by

$$g(L, S, J) = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

spin magnetic moments within the atom cancel each other → only orbital magnetic moments are effective: $S = 0, J = L, g = 1$

orbital magnetic moments within the atom or ion cancel each other → only spin magnetic moments are effective: $L = 0, J = S, g = 2$



coupling of electron magnetic moments within solid determines its magnetic behavior

5 types of magnetism:

diamagnetism

paramagnetism

ferromagnetism

antiferromagnetism

ferrimagnetism

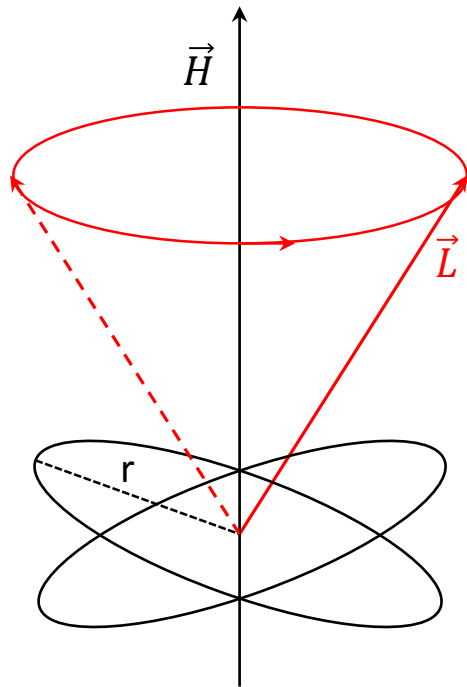
Diamagnetism

non-permanent, very weak form of magnetism present in all substances

induced by change in orbital motion of electrons in an external magnetic field

diamagnetic materials: cancellation of all orbital and all spin magnetic moments of electrons resulting in zero magnetic dipole of atoms, optimum energy of electron motion states

external magnetic field induces precession of orbital angular momentum around the external field direction (Larmor precession) → additional current loop is created



angular frequency of Larmor precession

$$\omega_L = \frac{eH\mu_0}{2m_e}$$

magnetic susceptibility of diamagnetic solid consisting of N atoms

$$\chi = -\frac{Ne^2r^2\mu_0}{6m_e} < 0$$

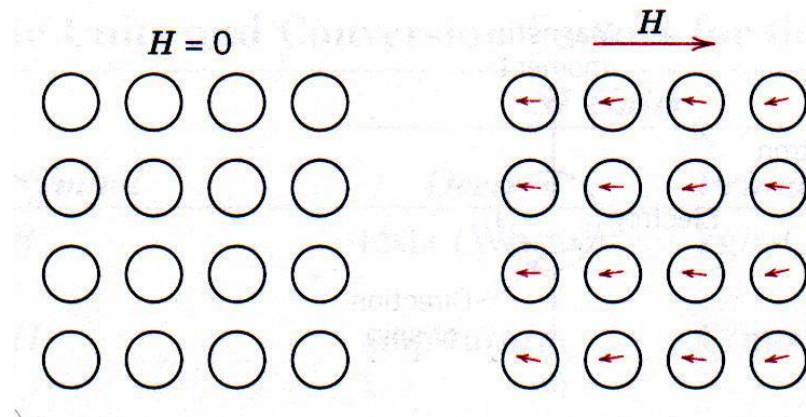
(dependent only on radius of electron motion path, independent on temperature)



application of external magnetic field increases energy of electrons and induces magnetic moment oriented in opposite direction

→ diamagnetic materials repel the external field

negative and very slight magnetic susceptibility $\chi \sim$ from -10^{-6} to -10^{-4}



Examples of diamagnetic substances:

H_2 molecules, inert gases

metals (Cu, Au)

covalent crystals (pairing of valence electrons – diamond, Si, Ge, SiO_2)

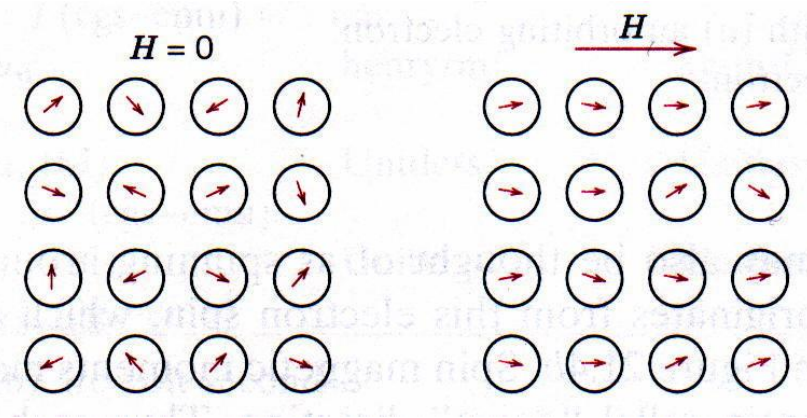
ionic crystals (electron transfer to acquire inert gas configuration – NaCl)

Paramagnetism

atoms with permanent magnetic moment (unpaired electrons → incomplete cancellation of electron spin and/or orbital magnetic moments)

random orientation of magnetic moments $\vec{\mu}_e$ and $\vec{\mu}_s \rightarrow \vec{M} = 0$ at $\vec{H} = 0$

magnetic moments of unpaired electrons are oriented parallel to external magnetic field → paramagnetic solid attracts the external field, $\chi > 0$ ($10^{-5} - 10^{-4}$)

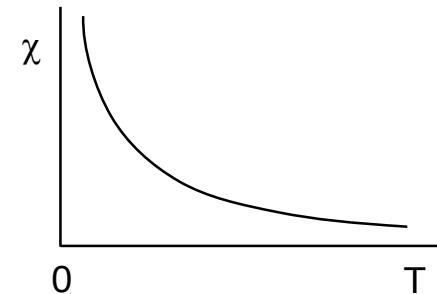


$$\chi = \frac{Ng^2\mu_B^2 J(J+1)}{3kT} \frac{C}{C}$$

$$C = \frac{Ng^2\mu_B^2 J(J+1)}{3k} \quad (\text{Curie constant})$$

atoms in solid are not independent on each other → correction (θ – Weiss constant)

$$\chi = \frac{C}{T - \theta}$$



Examples of paramagnetic solids:

Al, Cr, Ti, Zr

Pauli paramagnetism of free electrons

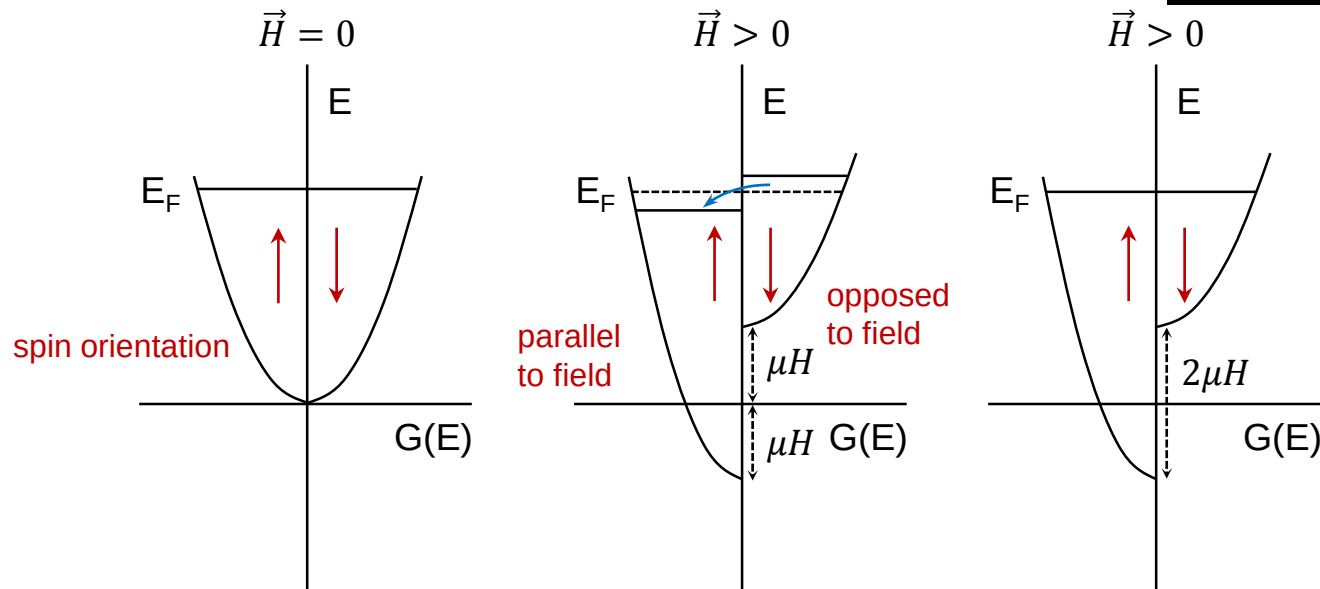
a strong paramagnetism in metals containing unpaired electrons could be expected – not observed in general (e.g., alkaline metals show only weak and temperature independent paramagnetism)

electrons in metal occupy all energy states up to Fermi level E_F

spin-paired electrons are allocated to each energy state $\rightarrow$ equal numbers of spin-up and spin-down electrons (metal would be diamagnetic)

slight energy separation in magnetic field $\rightarrow$ electrons opposed to the field have higher energy than those parallel to the field (difference of μH)

only electrons over Fermi level can reorient their spin in magnetic field

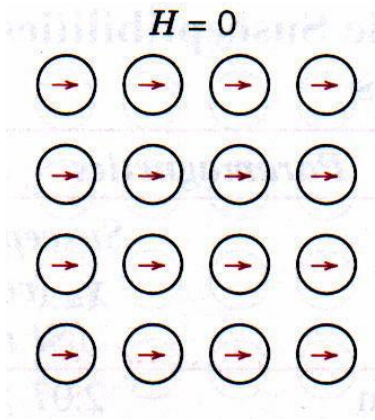


Ferromagnetism

cancellation of orbital magnetic moments, alignment of spin magnetic moments in adjacent atoms due to electron interactions (based on electrostatic repulsion)

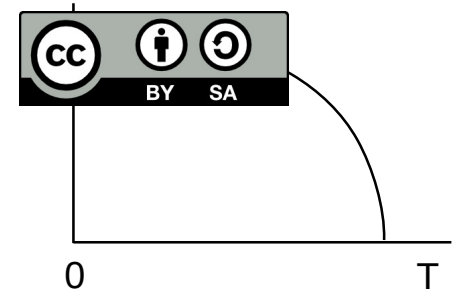
observed only in solids (domain structure), ordered crystal structure is not necessary

strong magnetization even in a weak external magnetic field persist after removing from the field, high magnetic susceptibility ($\chi \gg 1$) – dependent on external magnetic field strength and temperature



$$\chi = \frac{C}{T - T_c}$$

T_c – Curie temperature



alignment of spin magnetic moments in domains is disrupted at $T > T_c$

→ paramagnetic behavior

Examples of ferromagnetic solids (T_c):

Fe (1043 K)

Gd (293 K)

Co (1388 K)

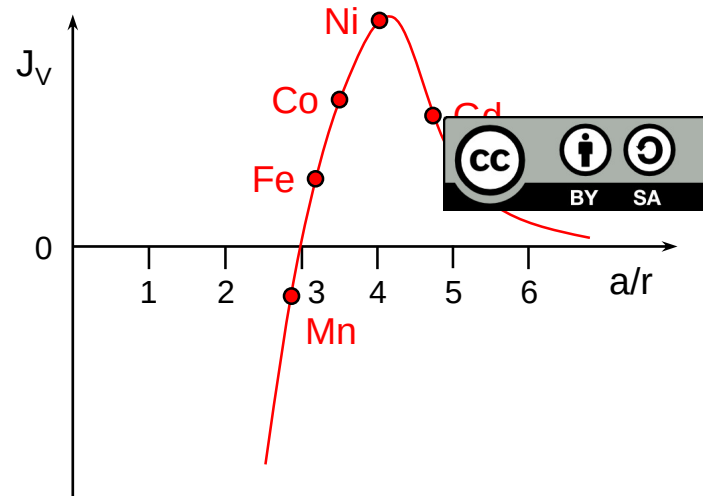
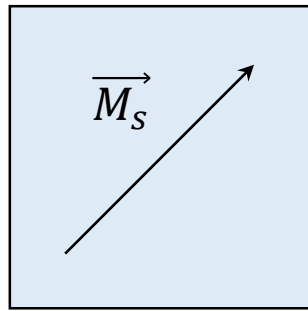
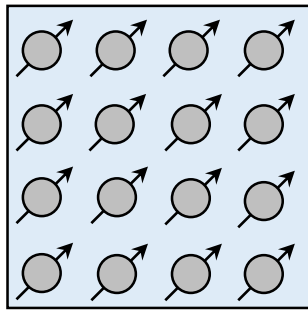
Cu_2MnAl (603 K)

Ni (627 K)

CrO_2 (387 K)

quantum mechanical exchange interactions between bonding electrons in adjacent atoms in a magnetic domain → alignment of spin magnetic moments of atoms → spontaneous magnetization in the domain (vector $\vec{M}_s$); electrostatic energy decreases when all electrons have parallel spins

interactions are characterized by exchange integral J_v , which is dependent on ratio of interatomic distance (lattice parameter) and radius of valence (3d) shell a/r



$$a/r > 3 \rightarrow J_v > 0$$

parallel alignment of spin magnetic moments (ferromagnetic behavior)

$$a/r < 3 \rightarrow J_v < 0$$

antiparallel alignment (antiferromagnetic behavior)

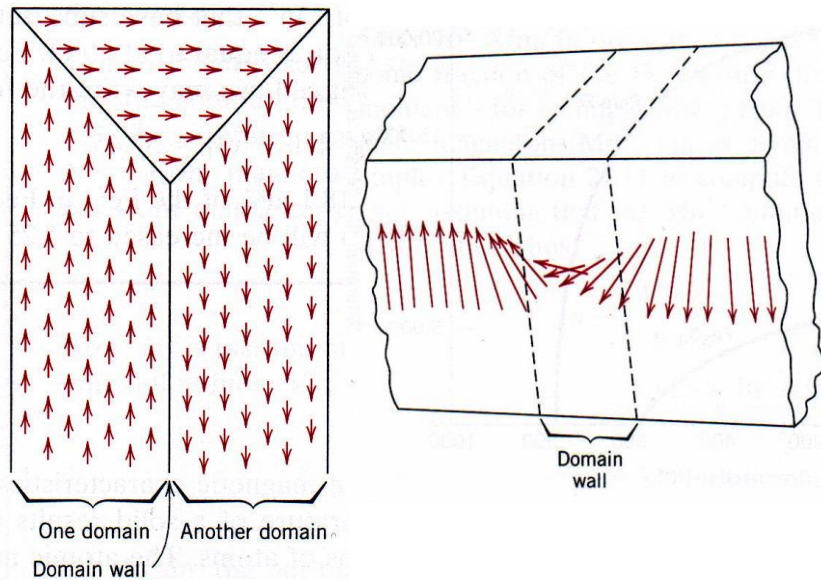
$$a/r \sim 3 \rightarrow J_v \sim 0$$

paramagnetic behavior

Domain structure and magnetization

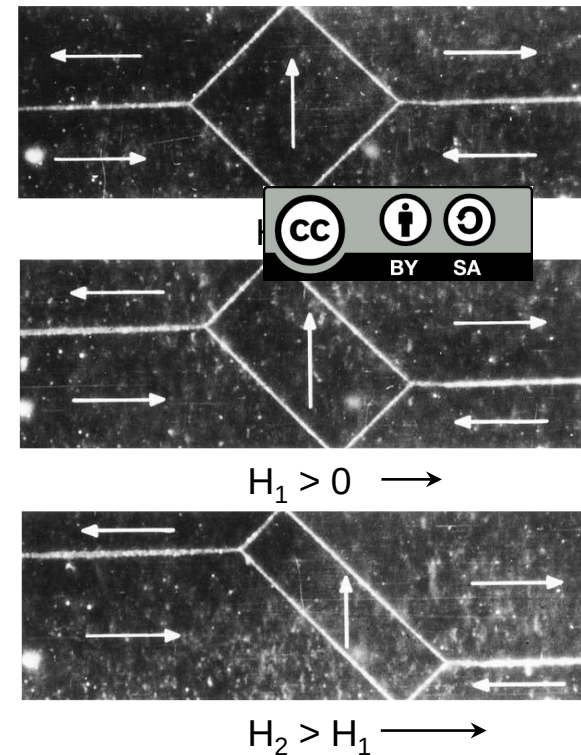
domains with various orientation and magnitude of magnetic moment $\vec{M}_s$, various size of domains ($10^{-3} - 10^3$ mm)

gradual change in magnetic dipole orientations at domain boundaries – domain (Bloch) walls (approximately 300 times wider than lattice parameter), can be shifted within solid



formation of aligned magnetic dipoles into more closure domains is energetically advantageous

(copied from W.D. Callister, Jr., Materials Science and Engineering, An Introduction. 7th Edition, John Wiley & Sons, Inc., 2007)



micrograph of iron single crystal showing magnetic domains and their change in shape when external magnetic field was applied

Magnetization curve and hysteresis loop

initial solid without magnetization: $T < T_C$, $H = 0$, zero magnetization (randomly oriented magnetic dipoles cancel each other)

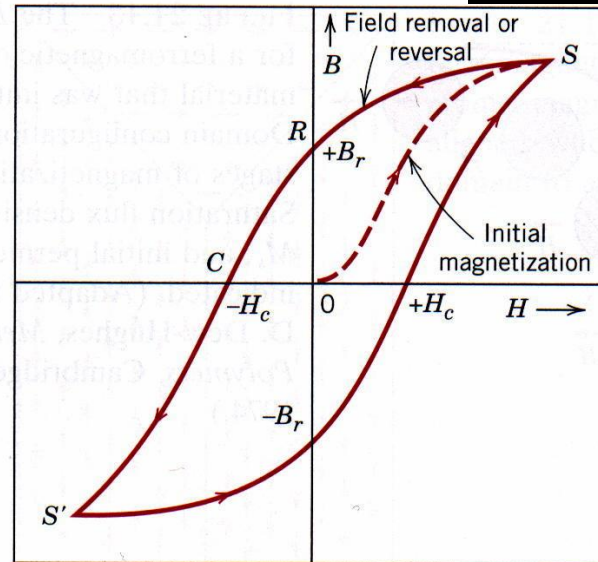
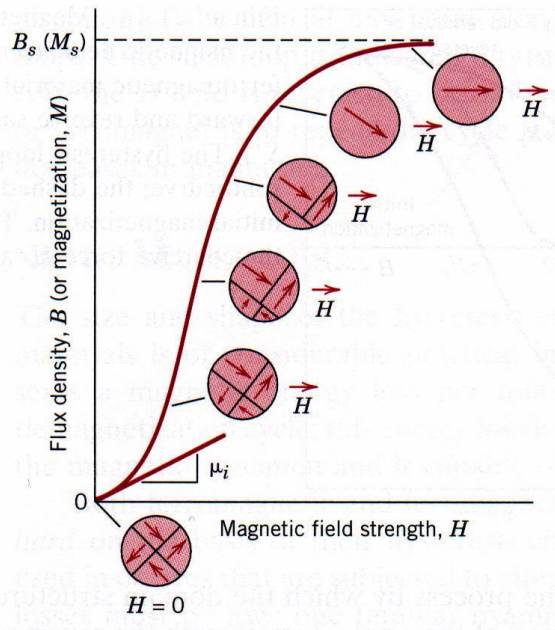
domains with magnetic dipole alignment parallel to external magnetic field ($H > 0$) increase their size, gradual rearrangement of domains with increasing external magnetic field strength

all domains oriented parallel to the external field $\rightarrow$ maximum (saturated) magnetization

external field strength reduction by reversal of field direction: residual magnetization

(remanence) at $H = 0$, external magnetic field in reverse direction to the original field

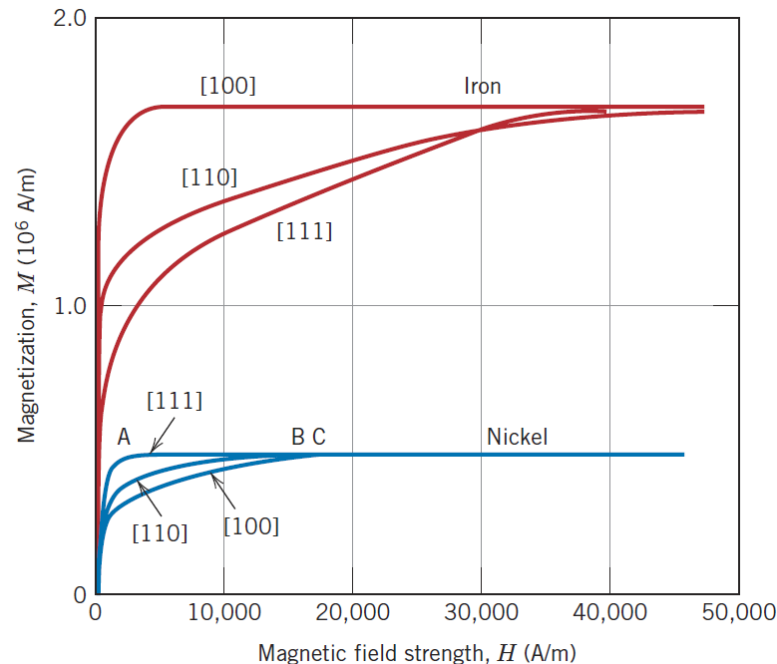
(coercivity) has to be applied for remanence removal; increasing in field strength $\rightarrow$ reverse saturated magnetization; repeated reversal of the external magnetic field $\rightarrow$ hysteresis loop



Effect of anisotropy

magnetization is more easy in certain crystallographic directions – (for example, the direction of easy magnetization for α -Fe single crystal is [100]; achieving saturation magnetization is most difficult in the [111] direction)

magnetostriction – magnetic materials change their dimensions or shape during magnetization; applied external magnetic field changes magnetostrictive strain due to domain walls shift and rearrangement of the materials structure

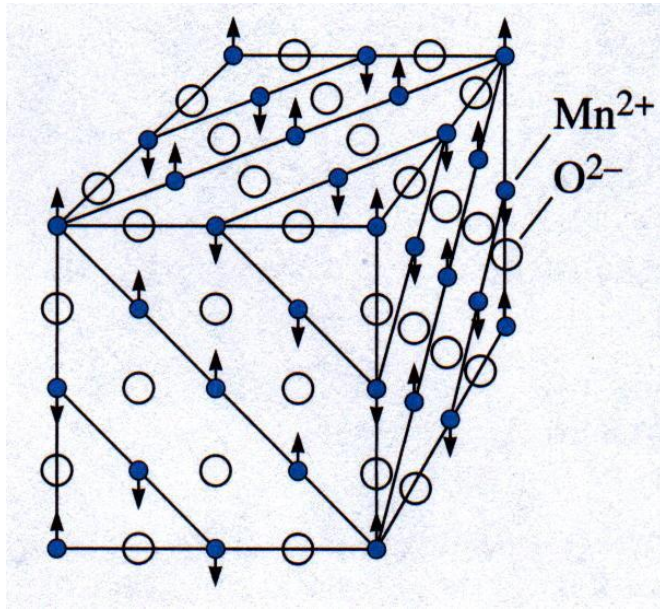


magnetization curves measured in various crystallographic directions for iron and nickel single crystals

(copied from W.D. Callister, Jr., Materials Science and Engineering, An Introduction. 7th Edition, John Willey & Sons, Inc., 2007)

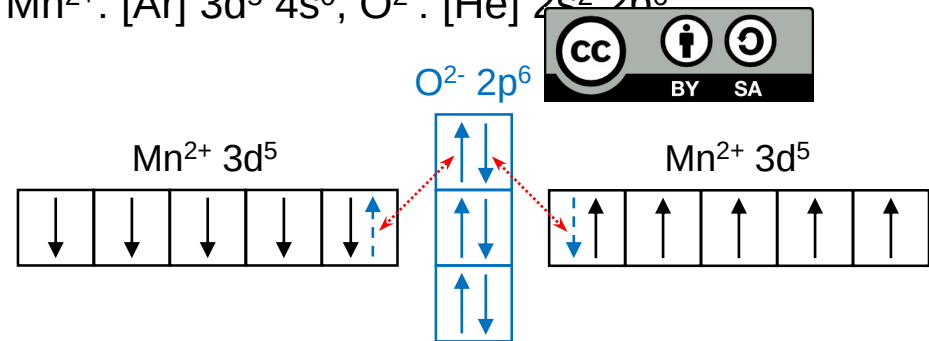
Antiferromagnetism

magnetic moment coupling between adjacent atoms results in antiparallel alignment, their spin magnetic moments are in exactly opposite orientation → complete cancellation, magnetic susceptibility $\chi \sim 10^{-5} - 10^{-3}$, comparable with paramagnetic materials



superexchange interaction: direct interaction between Mn²⁺ cations in Mn²⁺–O²⁻–Mn²⁺ lines is not possible due to separation by non-magnetic O²⁻ anions → interaction through oxygen 2p electrons

Mn²⁺: [Ar] 3d⁵ 4s⁰, O²⁻: [He] 2s² 2p⁶



antiferromagnetic ordering is stable up to temperature limit (Néel temperature T_N)

$T > T_N \rightarrow$ paramagnetic behavior

Examples of antiferromagnetic solids (T_N): MnO (116 K), CoO (291 K), NiO (525)

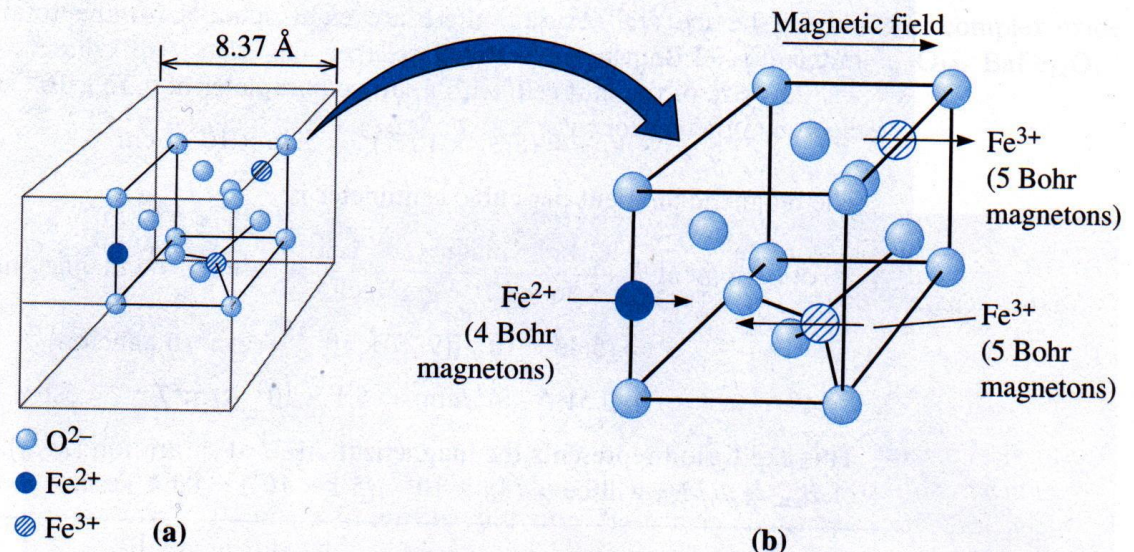
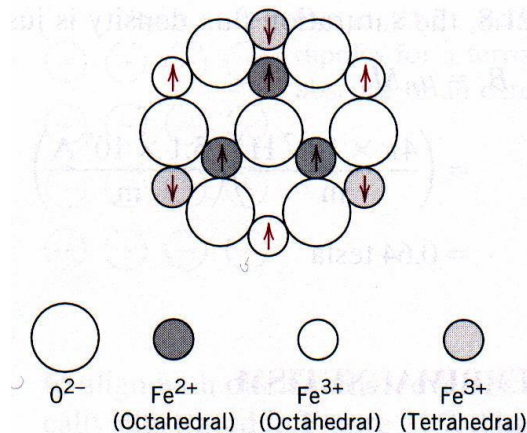
Ferrimagnetism

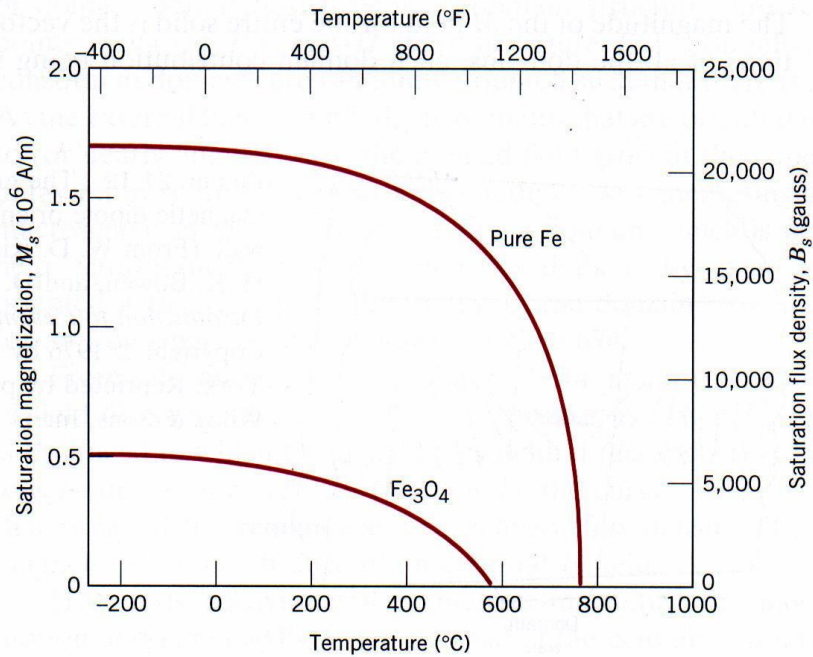
magnetic moment coupling between adjacent atoms results in antiparallel alignment but their spin magnetic moments are not cancelled completely (two subsets of magnetic moments exist, only one has antiparallel spin moments arrangement) → permanent magnetization

similar macroscopic magnetic characteristics like ferromagnetic materials, other source of net magnetic moments

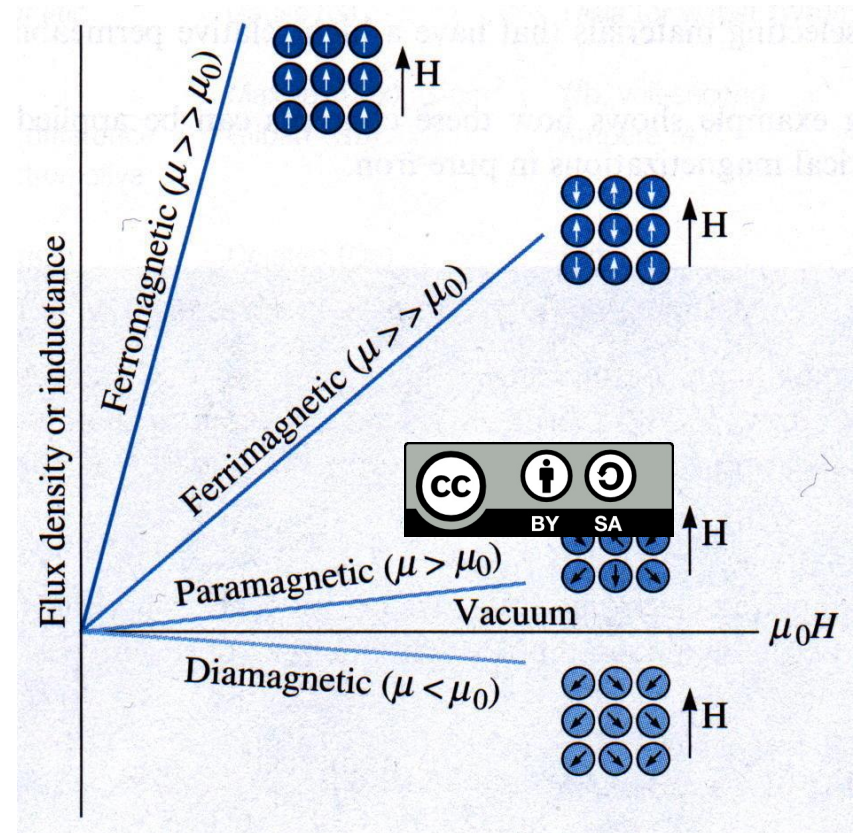
Example: Fe_3O_4 (magnetite) with inverse spinel crystal structure

parallel orientation of spin magnetic moments of Fe^{3+} cations in tetrahedral sites; spin magnetic moments of Fe^{2+} and Fe^{3+} cations have also parallel orientation but in opposite direction to Fe^{3+} cations in tetrahedral sites; spin magnetic moment of Fe^{3+} cations in tetrahedral and octahedral sites → only Fe^{2+} cations contribute to magnetization





saturation magnetization of iron and magnetite dependent on temperature



comparison of magnetic behavior of various materials in external magnetic field

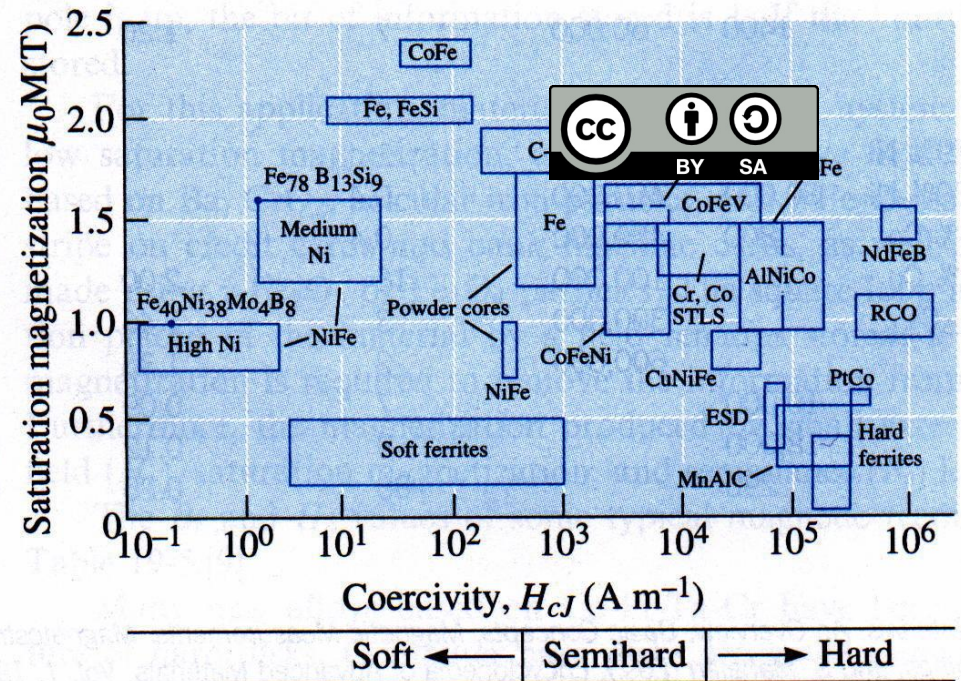
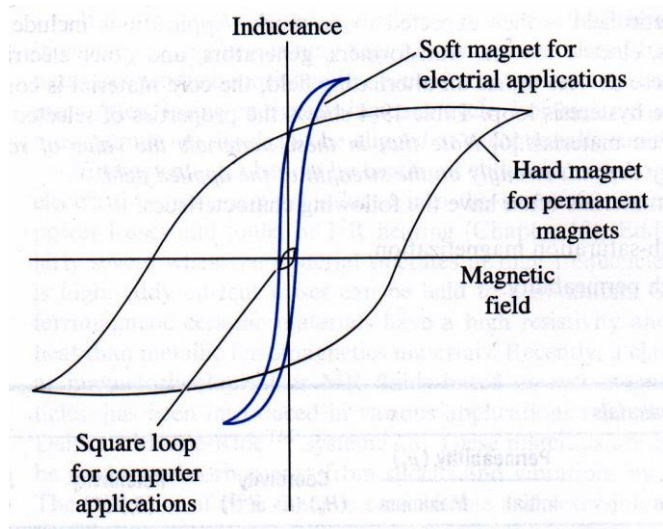
(copied from W.D. Callister, Jr., Materials Science and Engineering, An Introduction, Fifth Edition, John Wiley & Sons, Inc., 2000 and D.R. Askeland, P.P. Phulé, The Science and Engineering of Materials (4th Edition). Thomson Brooks/Cole 2003)

Soft and hard magnetic materials

shape of hysteresis loop shows magnetic behavior of materials

soft magnetic materials: small area of narrow hysteresis loop (low hysteresis energy loss), high initial permeability, low coercivity ($< 100 \text{ A m}^{-1}$)

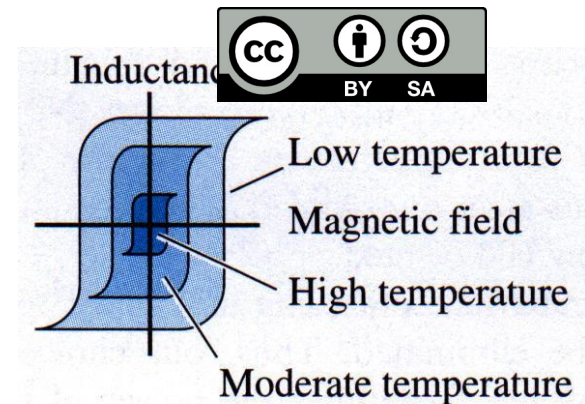
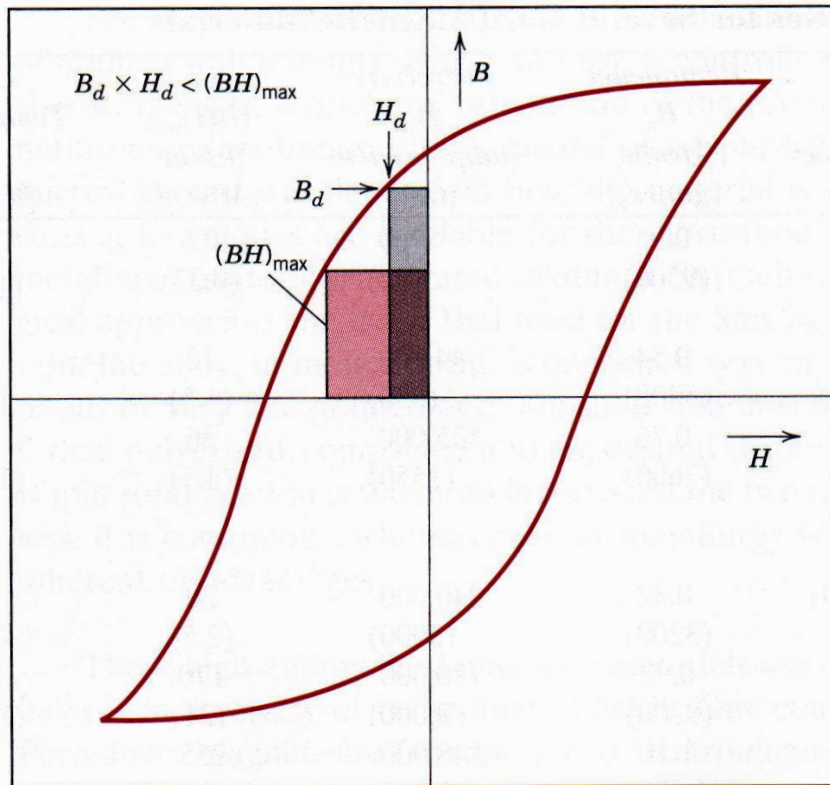
hard magnetic materials (permanent magnets): large area of hysteresis loop, high remanence, coercivity ($> 5 \cdot 10^4 \text{ A m}^{-1}$), saturation magnetization, and resistance to demagnetization



Energy product

area within a loop $\rightarrow$ magnetic energy loss per unit volume of solid per magnetization-demagnetization cycle; remanence, coercivity, and saturation magnetization determine properties and application of magnetic materials

energy product = the largest rectangle area constructed within the second quadrant of the hysteresis loop $|\vec{B} \times \vec{H}|$



Properties of some permanent magnets

material	commercial name	remanence $\mu_0 M_r$ [T]	coercivity $\mu_0 H_c$ [T]	energy product $(BH)_{\max}$ [kJ m ⁻³]	Curie temperature [°C]
Fe-Co	Co-steel	1.07	0.02	6	387
Fe-Co-Al-Ni	Alnico-5	1.05	0.06	4	380
BaFe ₁₂ O ₁₉	Ferrite	0.42	0.31	34	469
SmCo ₅	Sm-Co	0.87	0.80	144	723
Nd ₂ Fe ₁₄ B	Nd-Fe-B	1.23	1.21	290 – 445	312

Soft magnetic materials and their applications

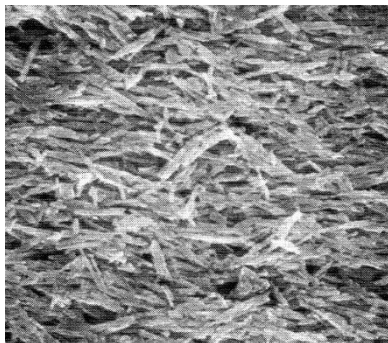
- iron, soft magnetic alloys of iron with other elements (e.g., Ni, Co, Mo, V, Si)
 - cores subjected to alternating magnetic fields (transformers, electric motors, etc.)
- soft magnetic ferrites (ferromagnetic mixed oxides of iron and other elements)
 - spinels – Fe_3O_4 , MFe_2O_4 ($\text{M} = \text{Mn, Ni, Zn, Mg, ...}$) – transformers, antennas, recording heads
 - garnets – iron garnets $\text{M}_3\text{Fe}_5\text{O}_{12}$ ($\text{M} = \text{Y, rare earth elements}$) – microwave applications, e.g., filters, transmitters, transducers (yttrium iron garnet, YIG)

Materials for data storage

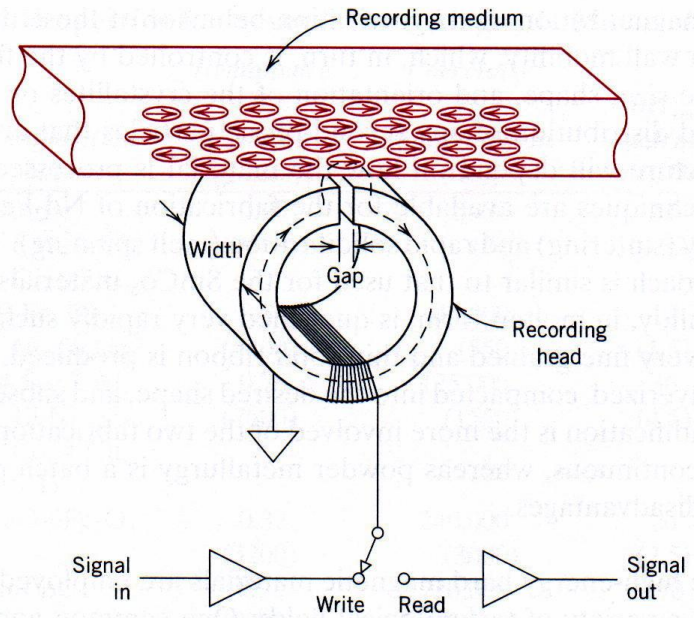


materials with rectangular hysteresis loop, low remanence, saturation magnetization, and coercivity → oriented magnetization of small area (domain) in a given direction persisting after removal of external magnetic field

- Fe, $\gamma\text{-Fe}_2\text{O}_3$, CrO_2 , barium ferrite, $(\text{Mg,Mn})\text{Fe}_2\text{O}_4$, $(\text{Ni,Zn})\text{Fe}_2\text{O}_4$, etc.

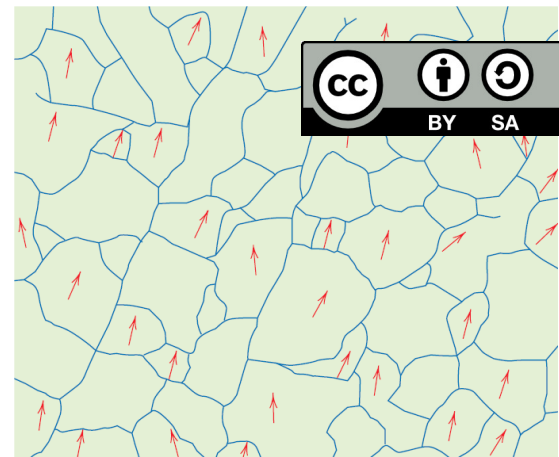
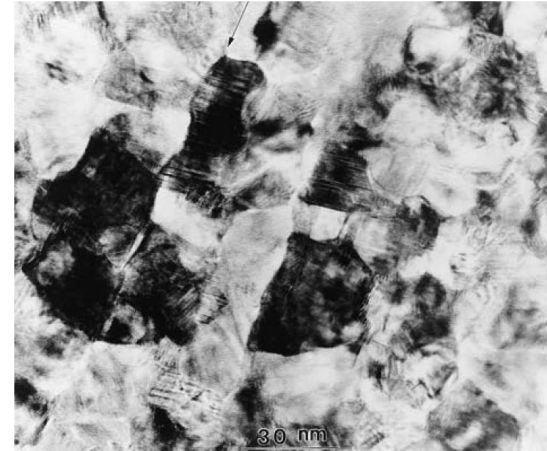


microstructure of magnetic storage disc – small needle-shaped $\gamma\text{-Fe}_2\text{O}_3$ crystals embedded in an epoxy resin are oriented parallel to recording head motion



recording information on magnetic storage medium:
 magnetization of domains by magnetic field
 generated by electric current in recording head /
 reading: magnetized domains induce electric current
 in recording head

(copied from W.D. Callister, Jr., Materials Science and
 Engineering, An Introduction. 7th Edition, John Wiley
 & Sons, Inc., 2007)

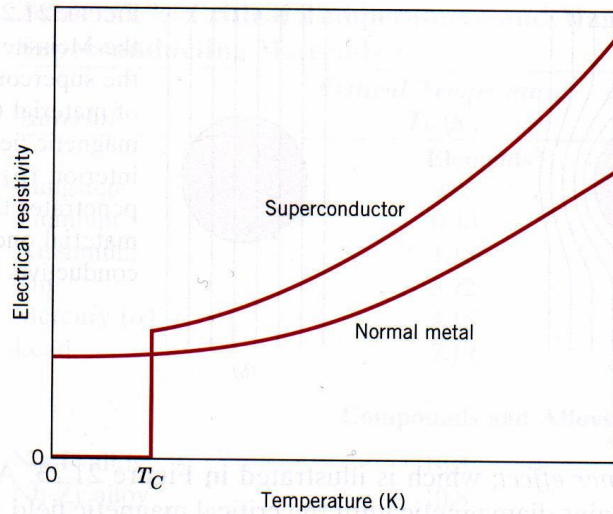


HRTEM image showing microstructure of
 polycrystalline Co-Cr-Pt alloy thin film used
 as high-density magnetic storage medium;
 arrows in grains represent direction of easy
 magnetization

Superconductors

conducting materials (metals) – decrease in electrical resistivity with decreasing temperature

superconductors – sudden drop in resistivity at low temperatures ($R \rightarrow 0$)



discovery of superconductivity in mercury at temperatures under 4.2 K (Kammerling-Onnes, 1911)

superconductivity disappears at $T > T_C$
(superconducting transition or critical temperature)

in external magnetic field – superconductivity up to critical magnetic induction (B_C)



$$B_C(T) = B_C(0) - \left(1 - \frac{T}{T_C}\right)$$

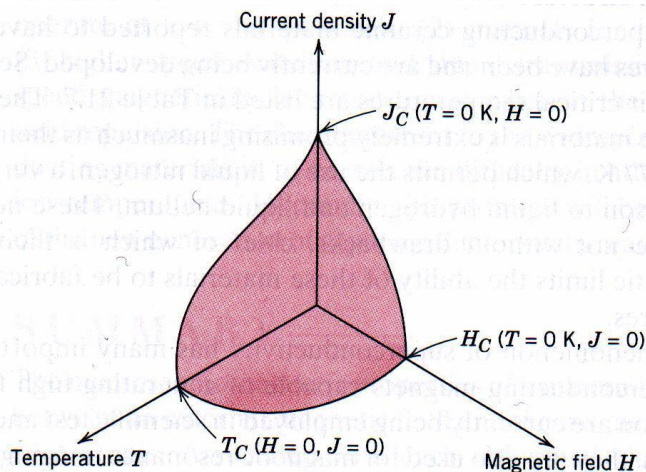
($B_C(0)$ – extrapolation of B_C at $T = 0$ K)

electric current induced by magnetic field → critical current density J_C ($\sim 10^5$ A cm⁻²)

type I superconductors: metals, $T_C < 10$ K,
 $B_C \sim 10^{-4} - 10^{-2}$ T

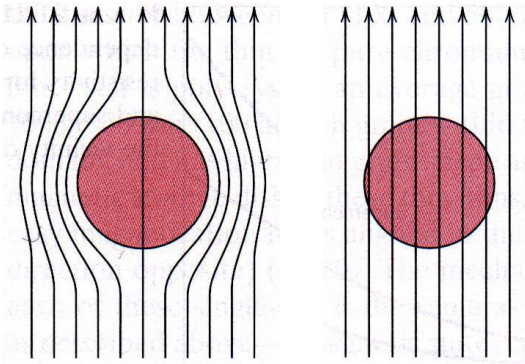
type II superconductors: alloys and intermetallic compounds, $T_C < 20$ K, $B_C \sim 10^1$ T

high-temperature superconductor: ceramic materials (oxides), $T_C \sim 100$ K



Meissner effect

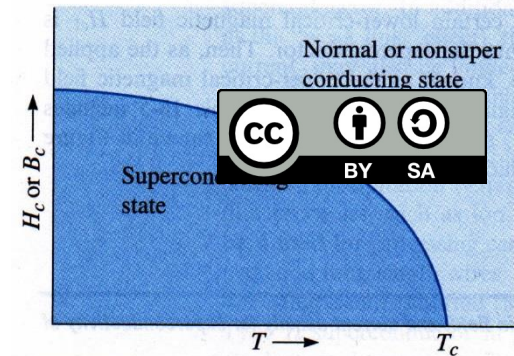
solid in superconducting state is completely diamagnetic and repels the external magnetic field ($B = 0$ within the solid), complete magnetic flux penetration takes place at $B = B_C$



superconducting body excludes magnetic field up to the body becomes normally conducting at $B > B_C$

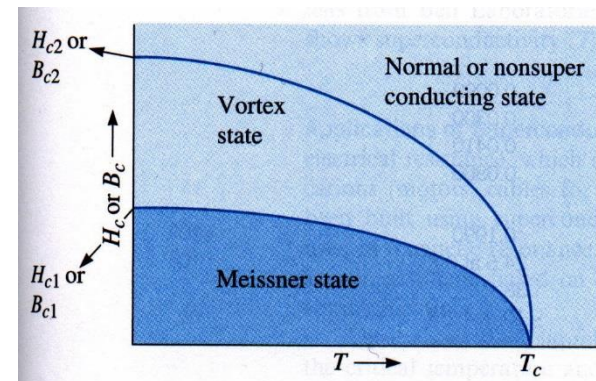
type I superconductors

magnetic field penetrates only very thin surface layer (thickness of $\sim 10^{-7}$ m), transition between superconducting and normal state at $B = B_C$



type II superconductors

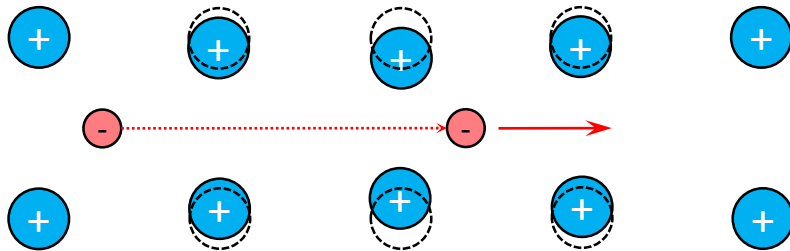
gradual transition from superconducting to normal state, occurs between lower critical and upper critical magnetic field strengths; solid is diamagnetic at $B < B_{C1}$, gradual penetration of magnetic field to solid between B_{C1} and B_{C2} (lamellar structure of solid consisting of superconducting and areas and those with normal conduction – vortex state)



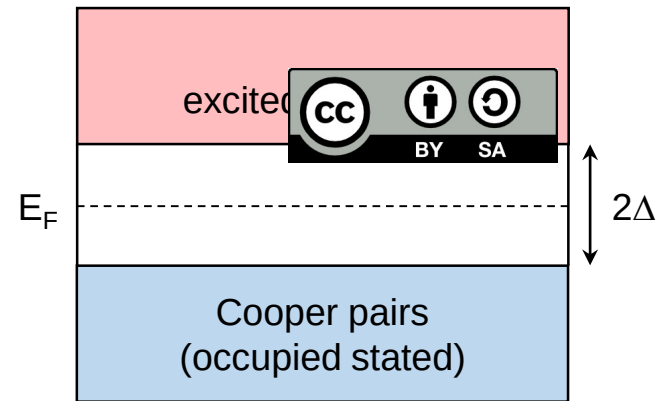
Cooper pairs

BCS theory (Bardeen, Cooper, Schrieffer, 1957) explained superconductivity by interactions between pairs of conducting electrons (Cooper pairs)

electron-phonon interactions (phonon exchange between two electrons) at $T < T_c \rightarrow$ new energy states of electrons $\vec{l}_1 = \vec{k}_1 - \vec{q}$ and $\vec{l}_2 = \vec{k}_2 + \vec{q}$, electrons are attracted to each other the strongest interaction between electrons with opposite spins and wave vectors $\rightarrow$ Cooper pair with total spin of zero (composite boson with long wavelength passing free through a solid)



simplified model of attractive interaction between electron in superconductors: slight local distortion in cation ordering caused by electron passing through a solid creates region of enhanced positive charge; another electron can be attracted to this region to form Cooper pair



paired states of electron with energy lower than Fermi level $\rightarrow$ energy gap

$$2\Delta = 3.53 kT_c$$

one Cooper pair is related to about 10^6 conducting electrons ($T = 0$ K)

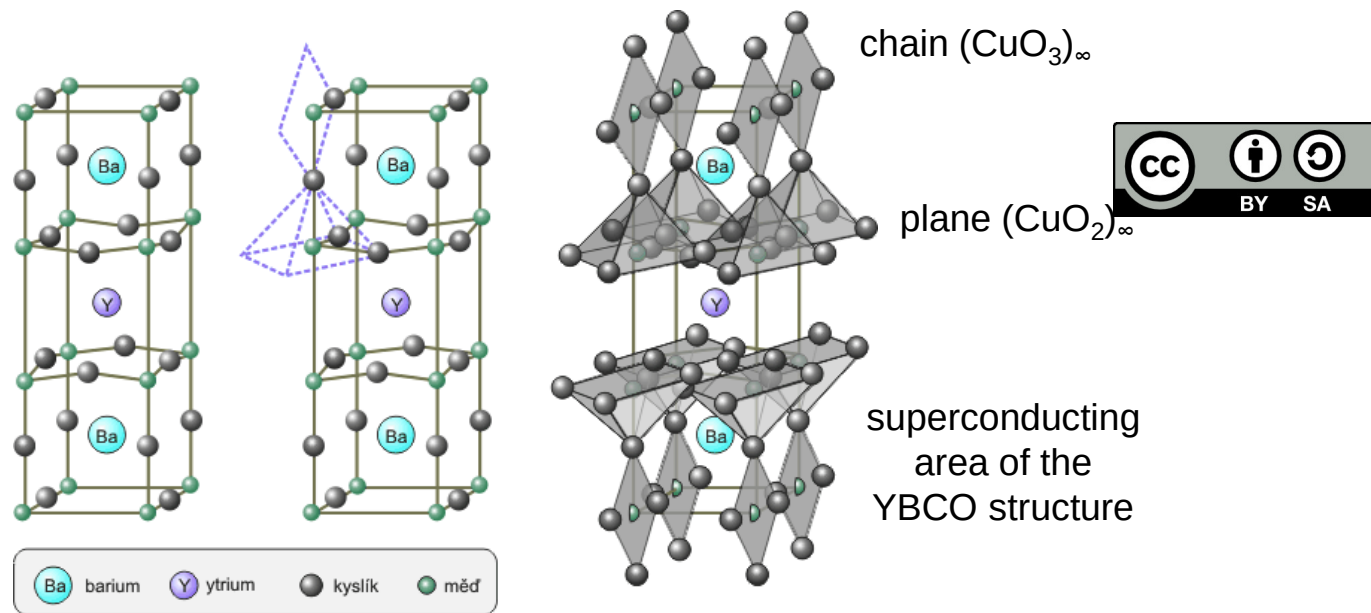
High-temperature superconductors

Ceramic (oxide) materials, $T_c > 30$ K, their superconductivity is not explained by BCS theory

$\text{La}_{5-x}\text{Ba}_x\text{Cu}_3\text{O}_{5(3-y)}$ ($x = 1$ nebo $0,75$, $y > 0$) $T_c = 30$ K

1-2-3 compounds: $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($0 < x < 0,5$) YBCO $T_c = 93$ K

oxides Bi-Sr-Ca-Cu-O (110 K), Tl-Ba-Ca-Cu-O (125 K), Hg-Ba-Ca-Cu-O (153 K)

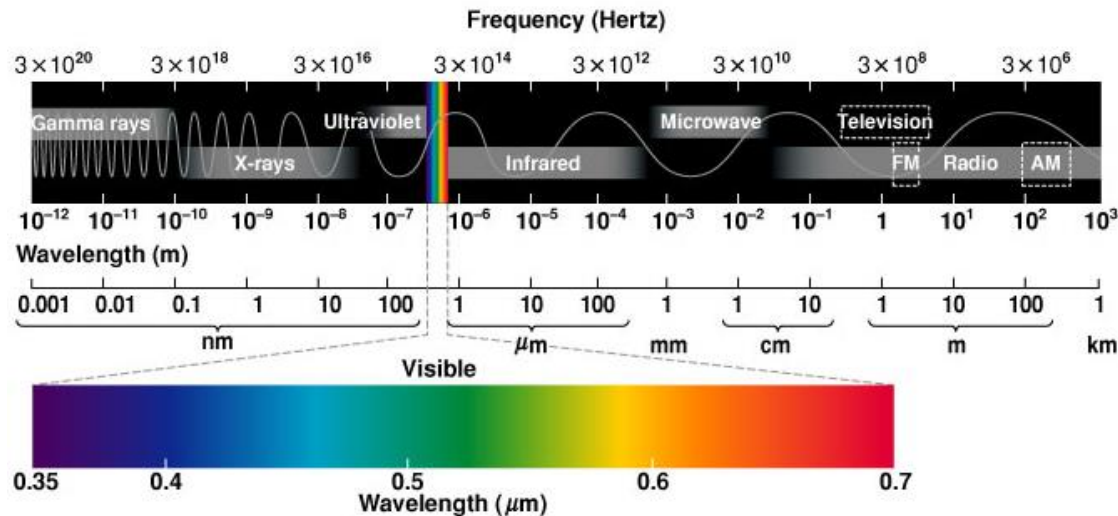


YBCO unit cell and ordering of oxygen atoms; oxygen content in the YBCO structure affects superconducting behavior

(copied from http://www.aldebaran.cz/bulletin/2004_36_hts.html)

Optical properties of solids

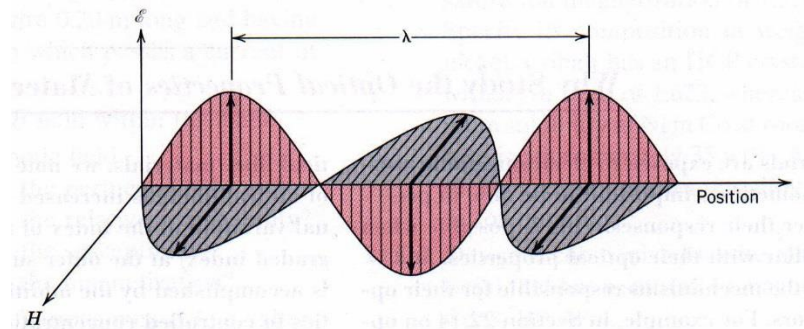
response of solid exposed to electromagnetic radiation, namely in the visible region



wave-particle duality

synchronized oscillation of continuous electric and magnetic fields, transverse wave with electric and magnetic vectors (perpendicular to each other) oscillating perpendicular to direction of wave and energy propagation

stream of discrete particles (photons) with energy of $E = h\nu = hc/\lambda$



Maxwell's equations → propagation of electromagnetic wave within a solid

$$\text{rot } \vec{E} = -\mu_0\mu_r \frac{\partial \vec{H}}{\partial t} \quad (\text{Faraday's law of induction})$$

$$\text{rot } \vec{H} = \frac{\partial \vec{D}}{\partial t} + \vec{j} \quad (\text{Ampère's circuital law})$$

$$\text{div } \vec{D} = \rho \quad (\text{Gauss's law})$$

$$\text{div } \vec{H} = 0 \quad (\text{Gauss's law for magnetism})$$

($\vec{j}$ - current density, ρ - free charge density)



Maxwell's equations can be used when wavelength of electromagnetic wave is much longer compared to dimensions of non-homogeneities in solid (visible light $\lambda \sim 10^{-7}$ m, lattice parameters $\sim 10^{-9}$ m)

Note: divergence and rotation operators

divergence of vector match a vector field $\vec{v}(x, y, z)$ with a scalar field $s(x, y, z)$ – associates a scalar with every point of a vector field (giving a quantity of vector's field source at each point)

$$\text{div } \vec{v} = \nabla \cdot \vec{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$$

rotation (or curl) of vector match a vector field $\vec{v}(x, y, z)$ with another vector field $\vec{u}(x, y, z)$

$$\text{rot } \vec{v} = \nabla \times \vec{v} = \left(\frac{\partial v_z}{\partial y} - \frac{\partial v_y}{\partial z} \right) \vec{i} + \left(\frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x} \right) \vec{j} + \left(\frac{\partial v_y}{\partial x} - \frac{\partial v_x}{\partial y} \right) \vec{k}$$

Material relations (parameters of solid, in which electromagnetic wave propagates)

electromagnetic field of low intensity (non-linear response cannot be induced) and nonmagnetic, homogeneous, and isotropic material are expected

$$\rightarrow \mu_r = 1, \rho = 0, \vec{D} = \varepsilon_0 \varepsilon_r \vec{E}, \vec{j} = \sigma \vec{E}$$

permittivity (ε), permeability (μ), and conductivity (σ) are scalars (in general, they are tensors of second order)

$$\text{rot } \vec{E} = -\mu_0 \frac{\partial \vec{H}}{\partial t}$$

$$\text{rot } \vec{H} = \varepsilon_0 \varepsilon_r \frac{\partial \vec{E}}{\partial t} + \sigma \vec{E}$$

$$\text{div } \vec{E} = 0$$

$$\text{div } \vec{H} = 0$$



for electric component of electromagnetic field (magnetic component need not be considered and $\vec{H}$ was excluded) it can be written

$$\text{rot rot } \vec{E} = -\mu_0 \frac{\partial}{\partial t} \left(\varepsilon_0 \varepsilon_r \frac{\partial \vec{E}}{\partial t} + \sigma \vec{E} \right)$$

wave equation for electric field intensity is obtained after rearrangement

$$\frac{\partial^2 \vec{E}}{\partial x^2} + \frac{\partial^2 \vec{E}}{\partial y^2} + \frac{\partial^2 \vec{E}}{\partial z^2} - \sigma \mu_0 \frac{\partial \vec{E}}{\partial t} - \mu_0 \epsilon_0 \epsilon_r \frac{\partial^2 \vec{E}}{\partial t^2} = 0$$

solution in the form of harmonic planar wave

$$\vec{E}^*(\vec{r}, t) = \vec{E}_0 \exp \left[i \omega \left(t - \frac{\vec{s} \cdot \vec{r}}{v} \right) \right] \quad \rightarrow \quad \vec{E}(\vec{r}, t) = \vec{E}_0 \cos(\vec{k} \cdot \vec{r} - \omega t + \varphi)$$

(ω - angular frequency, $\vec{s}$ - unit vector parallel to wave propagation direction, $\vec{E}_0$ - amplitude, v - phase velocity, φ - phase offset)



$\vec{E}^*(\vec{r}, t)$ - complex quantity, only real part is meaningful

in a non-conducting medium ($\sigma = 0$)

$$\frac{1}{v^2} = \mu_0 \epsilon_0 \epsilon_r$$

in vacuum ($\epsilon_r = 1$) $v = c = 1/(\epsilon_0 \mu_0)^{1/2}$

refractive index (in non-conducting solids) $n = c/v$, $n^2 = \epsilon_r$

conducting solid ($\sigma \neq 0$) absorbs electromagnetic radiation, for solution of wave equation in the form of planar wave the phase velocity has to fulfil the following condition

$$\frac{1}{v^2} = \mu_0 \epsilon_0 \epsilon_r - i \frac{\mu_0 \sigma}{\omega}$$

complex refractive index n^* and complex permittivity ϵ^* has to be defined

$$n^* = n - i\kappa, \quad n^* = c/v$$

and then

$$\epsilon_r = n^2 - \kappa^2, \quad \frac{\sigma}{\epsilon_0 \omega} = 2n\kappa$$

(κ – mass attenuation coefficient)

complex relative permittivity

$$\epsilon^* = \epsilon_1 - i\epsilon_2$$

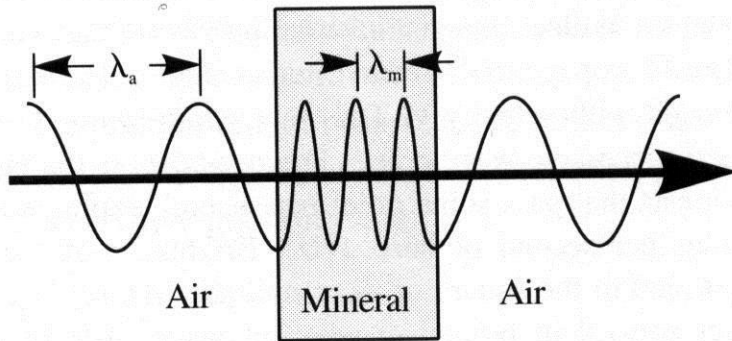
$$\epsilon_1 = \epsilon_r = n^2 - \kappa^2$$

$$\epsilon_2 = \frac{\sigma}{\epsilon_0 \omega} = 2n\kappa$$



Refraction

wave propagation speed differs in various media



frequency remains unchanged, wavelength is changing ($\lambda = v/\nu$)

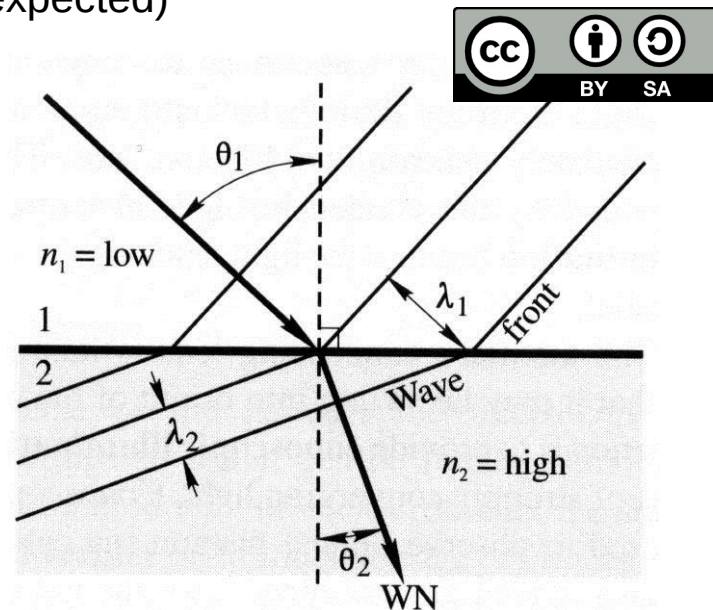
interference of waves with different wavelength
→ change in direction of wave propagation

(transparent and non-conducting solid is expected)

Snell's law

(refraction angle related to incidence angle – change in angle of wave propagation direction to surface normal when light enters other medium)

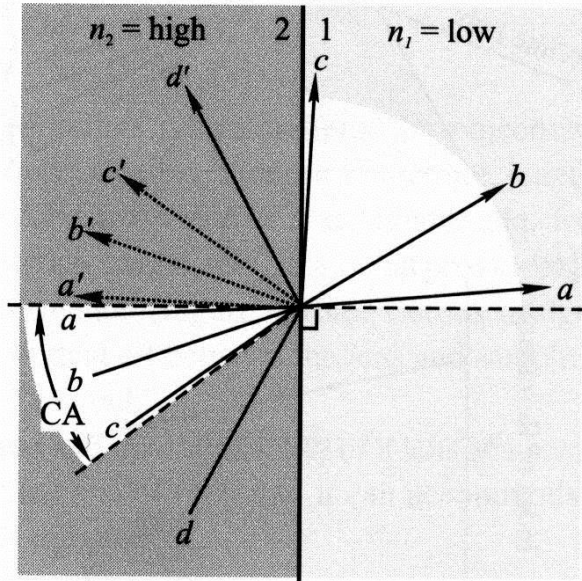
$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2}{n_1}$$



(WN – wave normal)

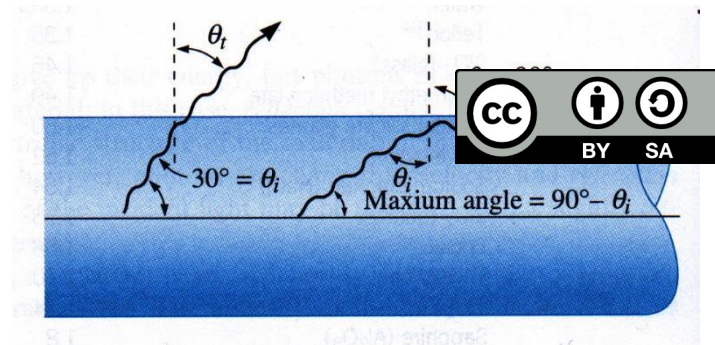
Total internal reflection

refraction with refractive angle above 90° is not possible; when light enters a medium with lower refractive index, the radiation passes through interface only when incidence angle is smaller than critical angle; radiation will be completely reflected at interface for $\theta_i > CA$

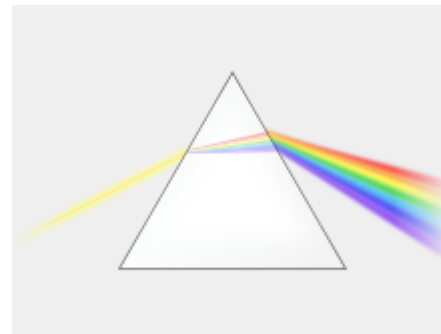


critical angle can be calculated from

$$\sin(CA) = n_1/n_2$$



refractive index decreases with
increasing radiation wavelength
→ dispersion of light



Light polarization

electromagnetic wave propagation: transverse oscillations related to propagation direction, vectors of electric and magnetic components are perpendicular to each other but they can turn around the direction of wave propagation

$$\vec{E}(\vec{r}, t) = \vec{E}_0 \cos(\vec{k} \cdot \vec{r} - \omega t + \varphi)$$

$$\vec{B}(\vec{r}, t) = \vec{B}_0 \cos(\vec{k} \cdot \vec{r} - \omega t + \varphi)$$

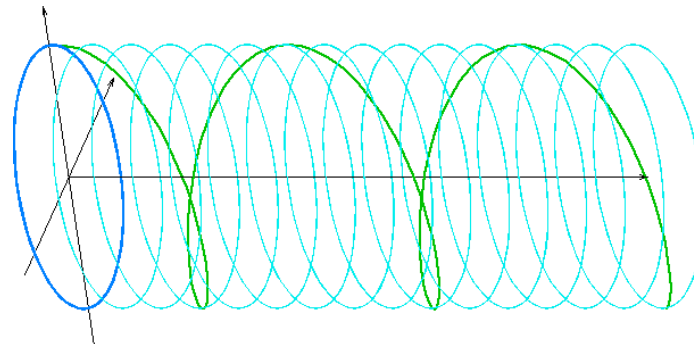
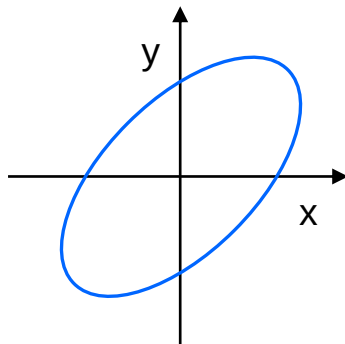
($\vec{E}_0$, $\vec{B}_0$ - amplitude of wave, $\vec{k}$ - wave vector parallel to propagation direction, $\vec{r}$ - position vector, ω - angular frequency, t - time, φ - phase offset)

only one component vector is needed (usually $\vec{E}$ is chosen)



unpolarized light: in plane perpendicular to wave propagation direction (x-y plane) the $\vec{E}(\vec{r}, t)$ vector has a random orientation depending on time

polarized light: in x-y plane the terminal point of $\vec{E}(\vec{r}, t)$ vector creates a defined curve depending on time



Understanding polarization of waves: interference of linearly polarized waves

two linearly polarized electromagnetic waves (terminal point of $\vec{E}(\vec{r}, t)$ vector oscillates in plane along the direction of propagation) with the same frequency and wavenumber are polarized parallel to x and y axes and propagate in direction parallel to z axis

$$\vec{E}(z, t) = \vec{x}_0 E_1 \cos(kz - \omega t + \varphi_1) + \vec{y}_0 E_2 \cos(kz - \omega t + \varphi_2)$$

($\vec{x}_0, \vec{y}_0$ - unit vectors parallel to x and y axes, E_1, E_2 - wave amplitudes, φ_1, φ_2 - phase offsets)

parametric equations of a curve, which is created by terminal point of $\vec{E}(\vec{r}, t)$ vector in x-y plane depending on time ($z = 0$)

$$E_x(t) = \cos(\omega t + \varphi_1) = E_1(\cos \omega t \cos \varphi_1 - \sin \omega t \sin \varphi_1)$$

$$E_y(t) = \cos(\omega t + \varphi_2) = E_2(\cos \omega t \cos \varphi_2 - \sin \omega t \sin \varphi_2)$$



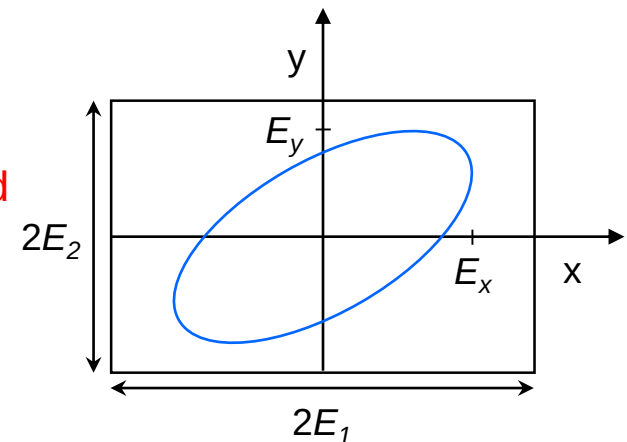
final electric field intensity $\vec{E}$ is given by vector sum of E_x and E_y intensities; the equations can be solved when

$$\begin{vmatrix} \cos \varphi_1 & -\sin \varphi_1 \\ \cos \varphi_2 & -\sin \varphi_2 \end{vmatrix} \neq 0$$

→ equation of ellipse – **elliptically polarized wave is created**

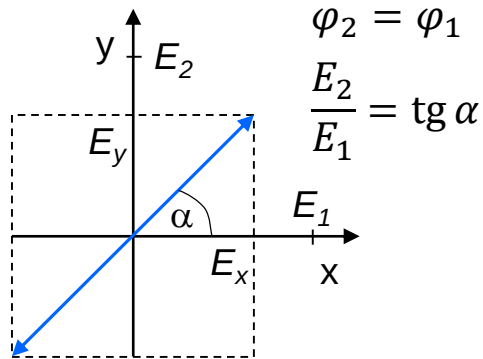
$$\left(\frac{E_x(t)}{E_1}\right)^2 + \left(\frac{E_y(t)}{E_2}\right)^2 - 2\frac{E_x(t)E_y(t)}{E_1E_2}\cos\varphi = \sin^2\varphi$$

$$(E_x(t) \leq E_1, E_y(t) \leq E_2, \varphi = \varphi_2 - \varphi_1)$$

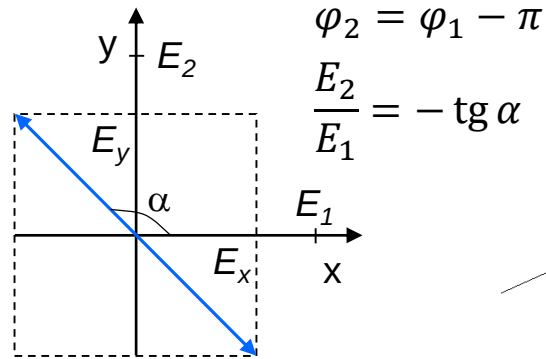


Linearly polarized light

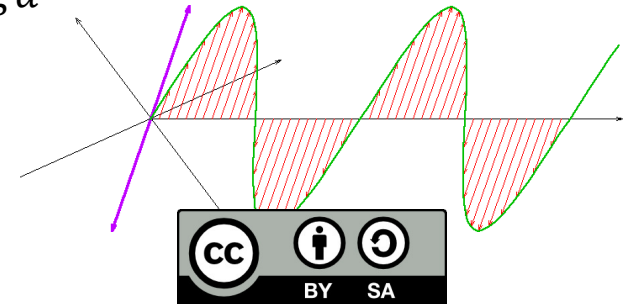
limiting case of elliptically polarized light, terminal point of vector $\vec{E}$ oscillates in a plane, angle of turn in x-y plane is determined by ratio of E_1 and E_2 amplitudes



right-handed orientation

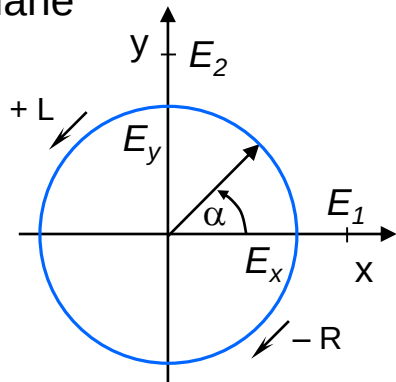


left-handed orientation



Circularly polarized light

limiting case of elliptically polarized light, terminal point of vector $\vec{E}$ creates a circle in x-y plane



$$E_1 = E_2$$

$$\varphi_2 = \varphi_1 \pm \frac{\pi}{2}$$

$$\alpha = \omega t + \varphi_1$$

$$E_x(t) = E_1 \cos(\omega t + \varphi_1)$$

$$E_y(t) = E_2 \cos(\omega t + \varphi_1 \pm \frac{\pi}{2}) = \mp E_2 \sin(\omega t + \varphi_1)$$

– right-handed orientation (R), + left-handed orientation (L)

(orientation of turn in reverse to direction of light propagation)

Polarization of light in solid

homogeneous, non-conducting, magnetically isotropic, and electrically anisotropic solid is expected → magnitude and direction of polarization depends on direction of electric field propagation

$$\vec{D} = \varepsilon_0 \sum \varepsilon_{ij} \vec{E} \quad i = x, y, z \quad j = x, y, z$$

$$\begin{pmatrix} D_x \\ D_y \\ D_z \end{pmatrix} = \varepsilon_0 \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

ε_{ij} – tensor of relative permittivity (symmetric, $\varepsilon_{ij} = \varepsilon_{ji}$ → 6 independent

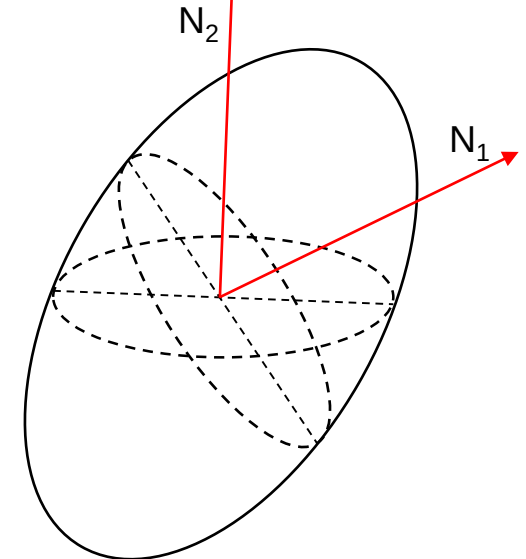


$$\frac{x^2}{\varepsilon_{xx}} + \frac{y^2}{\varepsilon_{yy}} + \frac{z^2}{\varepsilon_{zz}} = 1$$

ellipsoid of wave normals, in general two circular cross-sections can be found

only one speed of electromagnetic wave propagation (v_1, v_2) in direction parallel to circular cross-section normal (N_1, N_2)

→ no more than two optic axes can be found in crystal



Optically isotropic solids

three equivalent crystallographic directions, perpendicular to each other (cubic crystals, amorphous materials)

Optically anisotropic solids

- *uniaxial*

two or more equivalent crystallographic directions in one plane (rhombohedral, tetragonal, and hexagonal crystals)

incident light is split into two rays with linear polarization perpendicular to each other; propagation of the first ray (ordinary – o) is described by Snell's law,  propagation of the other one (extraordinary – e) is dependent on the angle between propagation direction and optic axis (variable refractive index)

speed of propagation $v_o > v_e$ – positive uniaxial crystal, $v_o < v_e$ – negative uniaxial crystal, maximum difference in direction perpendicular to optic axis

incident light parallel to optic axis is not split – no birefringence is observed

- *biaxial*

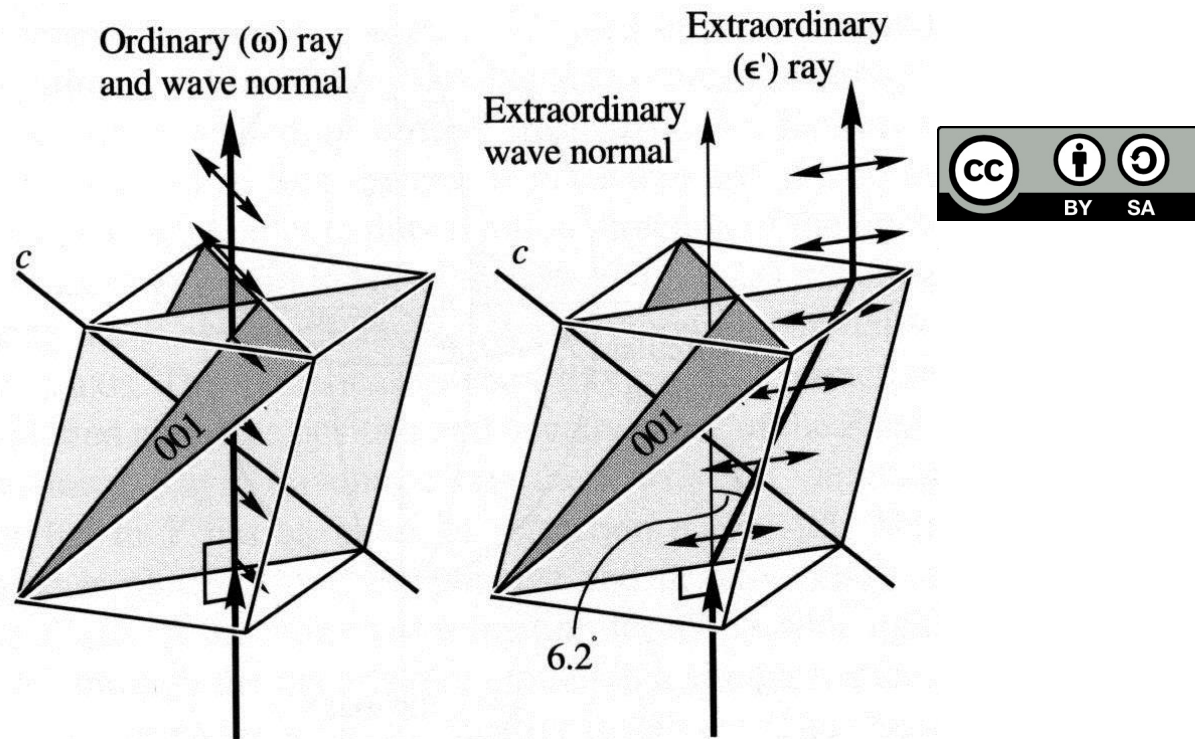
no equivalent crystallographic directions (orthorhombic, monoclinic, and triclinic crystals)

incident light is split into three rays, there are three refractive indexes (n_o , n_{e1} , n_{e2}) in the crystal

Birefringence in calcite crystal

ordinary ray – behavior like in an isotropic solid (the same speed of propagation in all direction, no refraction at perpendicular incidence), linear polarization alongside the plane perpendicular to optic axis

extraordinary ray – different speed of propagation in various directions, refraction even at perpendicular incidence, linear polarization parallel to plane defined by optic axis (c) and both rays (at 589 nm $n_o = 1.658$, $n_e = 1.486$)

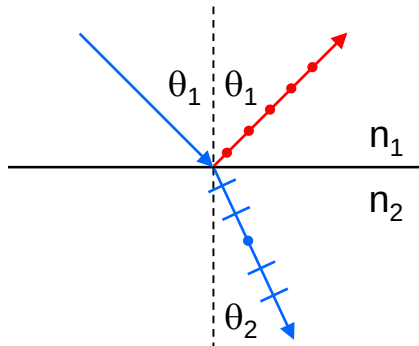


(copied from W.D. Nesse: Introduction to Mineralogy. Oxford University Press, New York 2000)

Production of polarized light

- *polarization by reflection*

unpolarized light with certain angle of incidence (Brewster's angle) is reflected from the surface to obtain linearly polarized light – polarization is perpendicular to plane of incidence



$$n_1 < n_2$$

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \text{ (Snell's law)}$$

Brewster's angle is given by equation

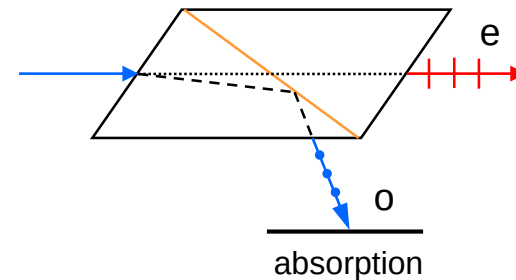
$$\theta_1 + \theta_2 = \frac{\pi}{2}$$

$$\tan \theta_1 = \frac{n_2}{n_1}$$



- *polarization by birefringence*

Nicol prism is used (rhombohedral calcite crystal is cut and rejoined), linearly polarized extraordinary ray is obtained

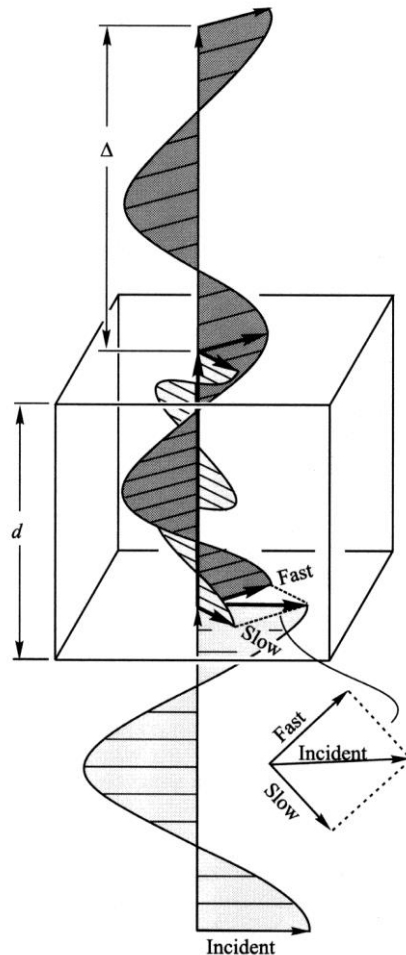


- *polarization by total internal reflection*

Fresnel rhomb – circularly polarized light is obtained from linearly polarized light with incident angle of $\pi/4$ due to phase shift of $\pi/2$ between parallel and perpendicular components

Waveplate (optical retarder)

birefringent crystals with surfaces cut perpendicular to optic axis, incident linearly polarized light is split into two waves (parallel and perpendicular to optic axis) with different speed of propagation



phase shift of outgoing waves

$$|\Delta\varphi| = \frac{2\pi}{\lambda} |n_e - n_o| d = \frac{2\pi}{\lambda} \Delta$$

(λ – light wavelength in vacuum, n_e , n_o – refraction index of ordinary and extraordinary rays, d – waveplate thickness)

half-wave plate

$$\Delta = \left(k + \frac{1}{2}\right) \lambda \rightarrow \text{phase shift } \Delta\varphi = \pi$$

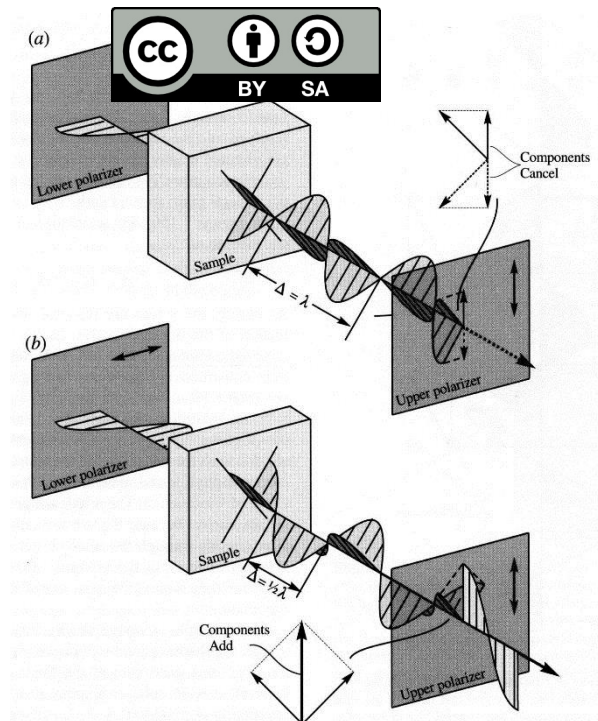
light with linear polarization perpendicular to incident light is obtained

(k – positive integer)

quarter-wave plate

$$\Delta = \left(k + \frac{1}{4}\right) \lambda \rightarrow \text{phase shift } \Delta\varphi = \frac{\pi}{2}$$

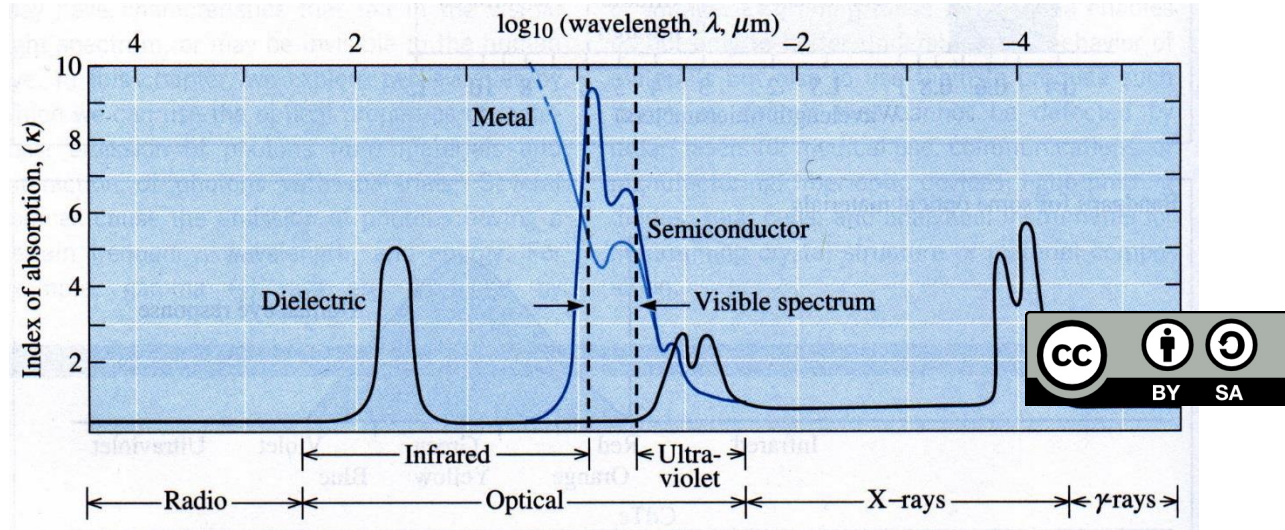
circularly polarized light is obtained



Absorption of electromagnetic radiation in solids

index of absorption is dependent on radiation wavelength

$$\kappa = \frac{\alpha \lambda}{4\pi n} \quad (\alpha - \text{linear absorption coefficient, } \lambda - \text{radiation wavelength in vacuum, } n - \text{refractive index})$$



Metals: easy excitation of electrons to higher energy states, absorption and reemission of photons, transparent to high-frequency radiation

Semiconductors: photons absorption due to electrons excitation from valence to conduction band (intrinsic semiconductors, $h\nu > E_g$) or electrons excitation from (alternatively to) impurity levels within the band gap (extrinsic semiconductors, $h\nu < E_g$)

Dielectrics: usually transparent to visible light, absorption due to presence of electron levels within the band gap (color centers – impurities, vacancies) or excitons generation

→ other effects (luminescence, stimulated emission of radiation)

Solid-state lasers

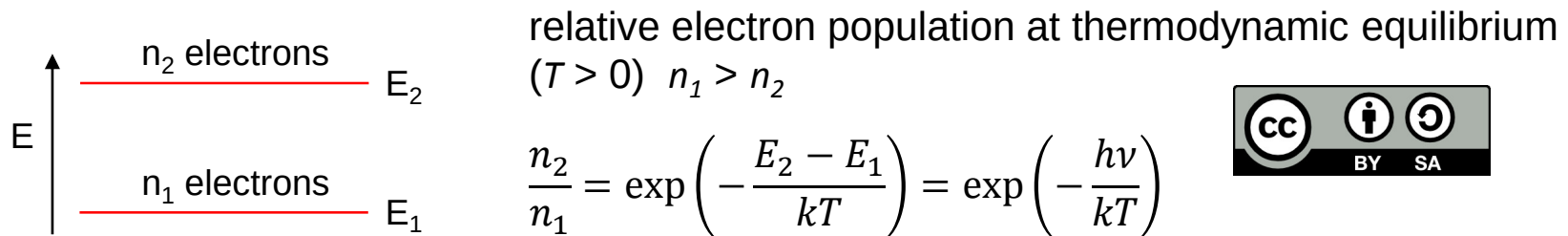
LASER = Light Amplification by Stimulated Emission of Radiation

produced radiation – monochromatic, coherent, high intensity, high collimation

Stimulated emission

transition of electrons between discrete energy levels ($E_2 > E_1$, $E_2 - E_1 = h\nu$)

electron decay from excited to ground state → spontaneous emission, photon is generated



electron pumping to higher energy level (energy absorption) → population inversion with $n_2 > n_1$ can be created; during irradiation more photons is generated than lost by absorption

propagation of light in the active medium leads to increase in light intensity

$$I = I_0 \exp(n_2 - n_1) Kl ; K = 2/(n_2 - n_1)$$

(I_0 - incident light intensity, l - light path within the active medium)

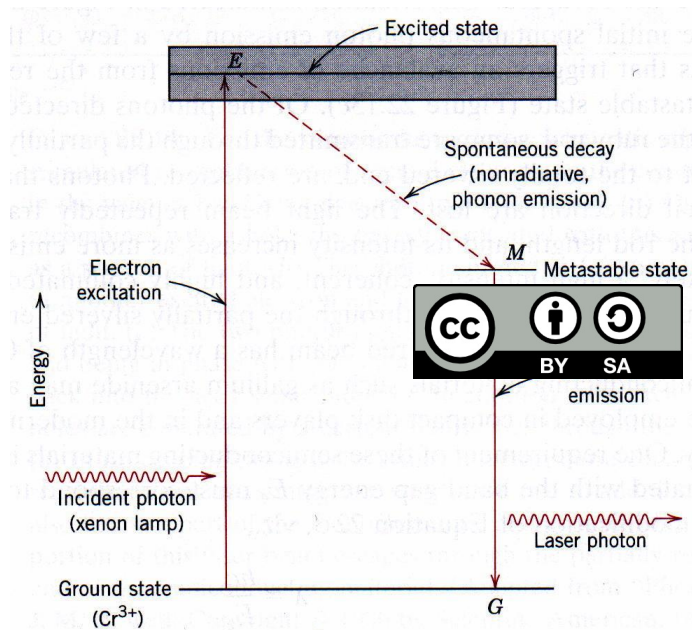
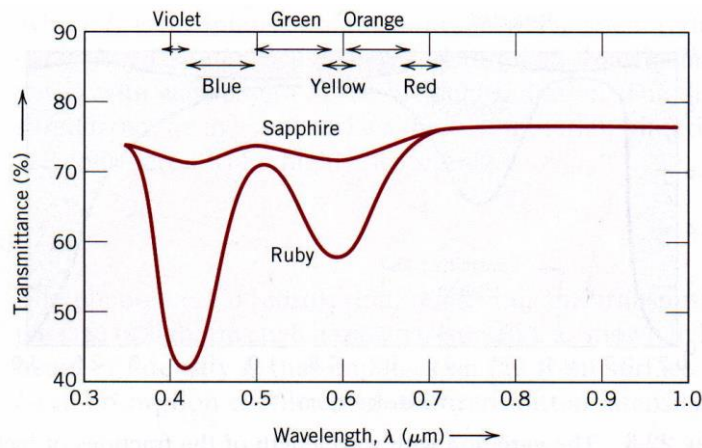
reflection on mirrors → amplification due to interference of incident and reflected waves

resonance frequency $\nu = n \frac{v}{2l}$ (v - light propagation speed, n - integer, l - active medium length)

Ruby laser

ruby – single crystal of Al_2O_3 (leuco sapphire) containing Cr^{3+} cations as substitutional defects

light absorption at 407 and 556 nm $\rightarrow$ excitation of Cr^{3+} 3d electrons to higher energy levels (three-level laser)



electrons stay on metastable levels for longer time (up to 3 ms) $\rightarrow$ population inversion

photon with suitable frequency causes electron excitation or decay with the same probability $\rightarrow$ stimulated emission occurs

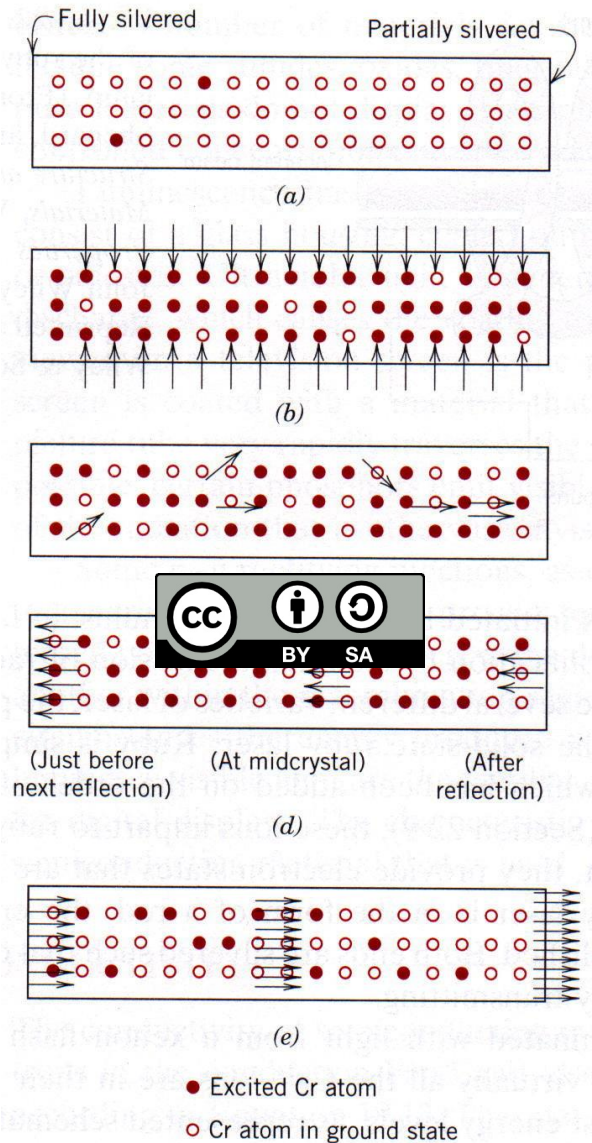
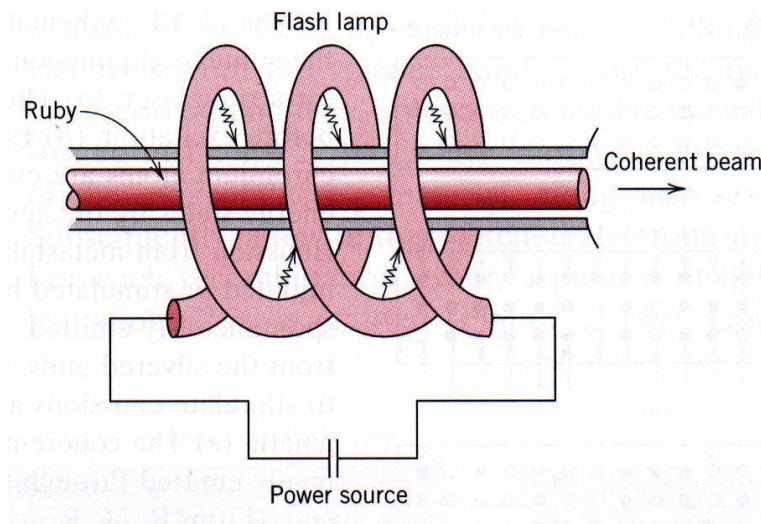
photon with the same energy, direction, and phase shift like the stimulating photon is emitted

active medium – ruby single crystal, rod with flat, parallel, highly polished, and silvered ends (one totally reflecting and one partially transmitting mirrors)

excitation radiation – xenon flash lamp

photons produced by stimulated emission repeatedly pass through the rod in axial direction; light is amplified and transmitted through the partially silvered end

wavelength of ruby laser light is 694 nm



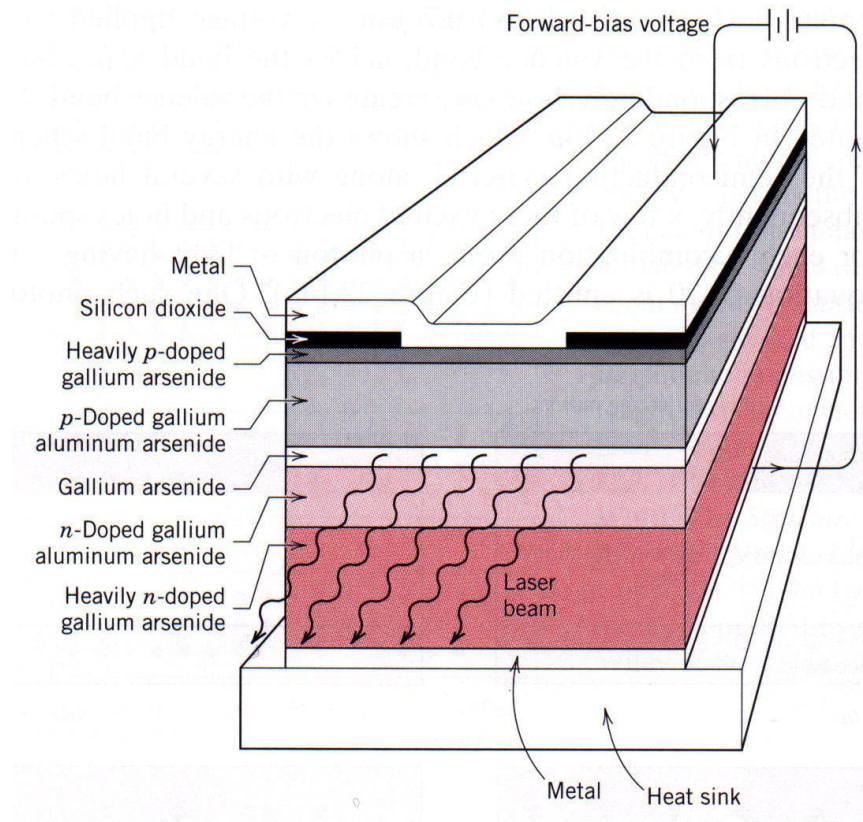
(copied from W.D. Callister, Jr., Materials Science and Engineering, An Introduction. 7th Edition, John Wiley & Sons, Inc., 2007)

Semiconductor lasers (laser diodes)

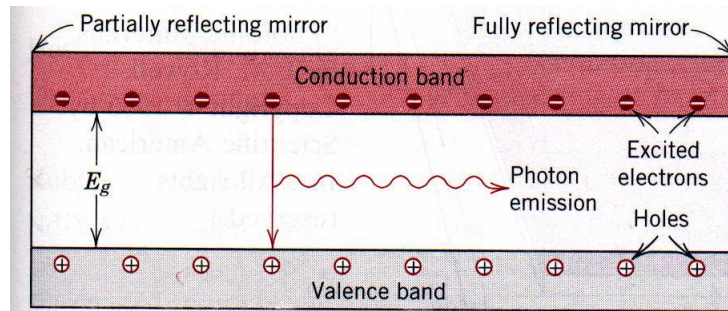
analogs of LED diodes, more complex structure consisting of thin layers with various composition and electronic properties

applied voltage ensures that there is a steady source of excited electrons and holes, population inversion can be created

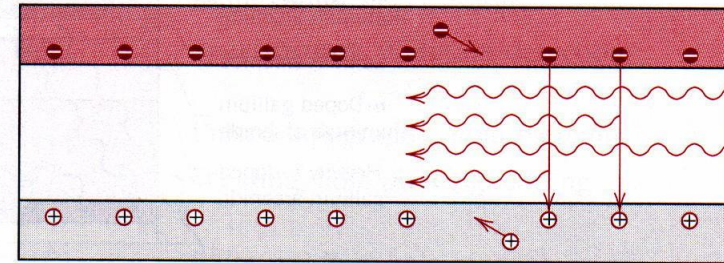
photons are emitted due to recombination of electron-hole pairs, stimulated emission takes place to obtain laser beam



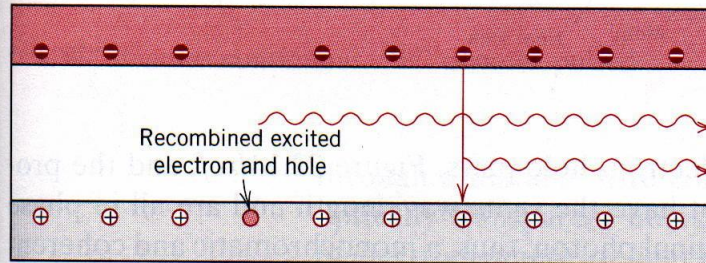
structure of GaAs semiconducting laser



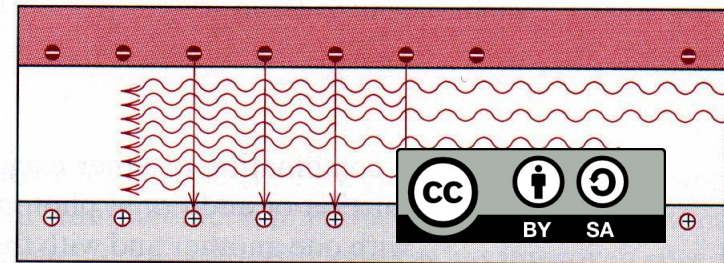
(a)



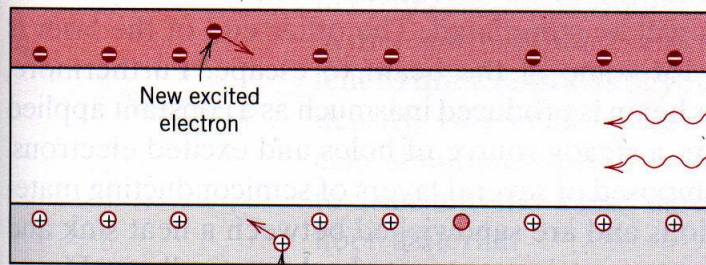
(d)



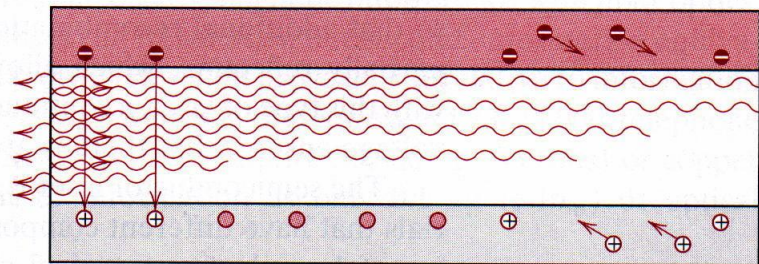
(b)



(e)



(c)



(f)

production of laser beam by stimulated photon emission due to recombination of excited electrons-hole pairs: photon emitted by spontaneous recombination stimulates avalanche recombination of other pairs, light is amplified as it is reflected on mirrors, new electron-hole pairs are generated by electric current passing through p-n junction

Chemistry and Physics of Solids – Lecture 14

MECHANICAL PROPERTIES OF SOLIDS



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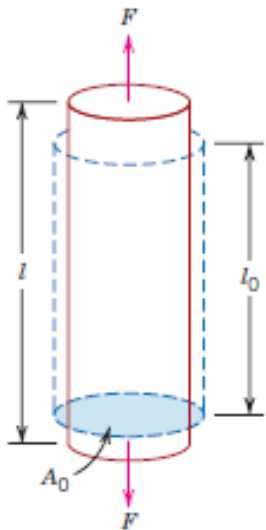
EUROPEAN UNION
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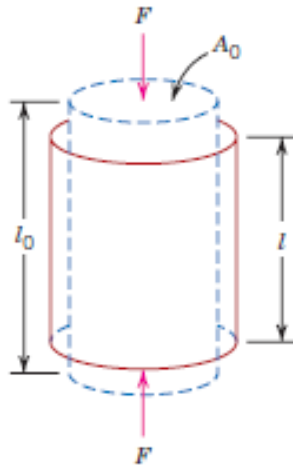
Mechanical behavior of solids – response to an applied load or force

relation between outer load and inner bonding forces → deformation

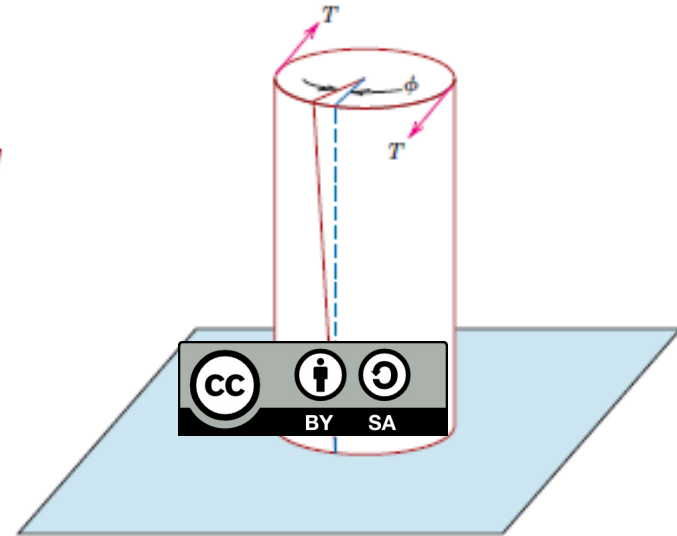
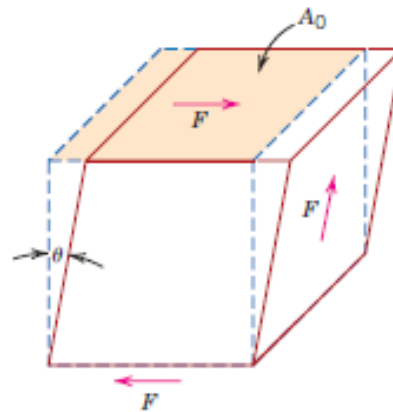
stress = force applied to a unit area [$\text{N m}^{-2} = \text{Pa}$]



tensile or compressive load (σ)
force acts perpendicular to area
→ elongation or contraction



shear load (τ)
force acts parallel to area
→ shear deformation

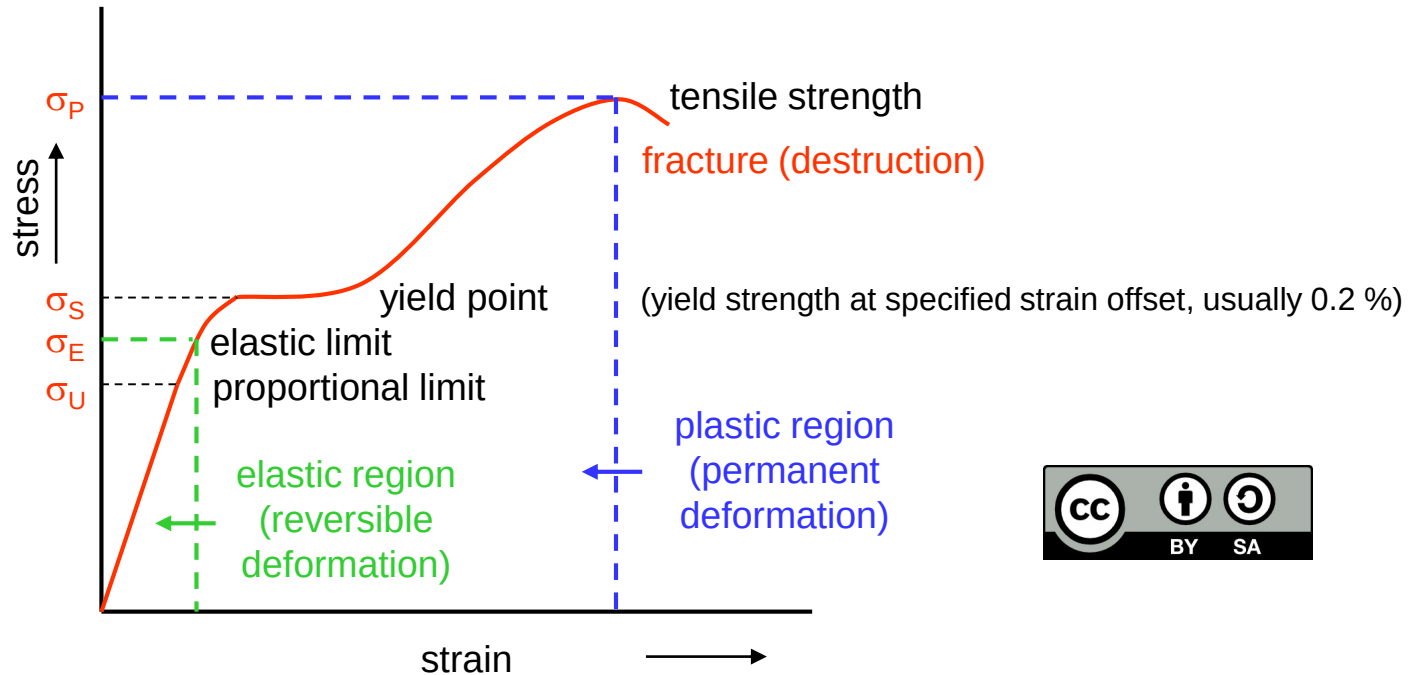


torque → torsional deformation

continuous changes in cross-sectional area are ignored → **engineering stress** – average applied force is related to initial cross-sectional area

dimensional change = strain; **engineering strain** – final length is related to original length

General stress-strain curve



Important mechanical properties:

elasticity: ability of reversible deformation (material returns to original size and shape after releasing the applied outer forces)

ductility: ability to undergo significant plastic deformation before fracture (very slight or no plastic deformation upon fracture → brittle materials)

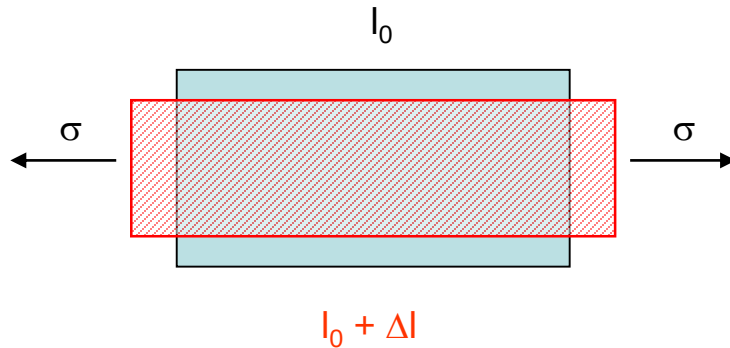
strength: resistance to fracture (limit state of tensile stress leading to tensile failure); yield strength – the lowest stress producing a permanent deformation

toughness: ability to absorb energy up to fracture (tough material is both strong and ductile)

Elasticity

isotropic elastic body (polycrystalline compact materials, metals, plastics, etc.)
tensile stress results in elastic deformation (strain)

$$\sigma = F/A \rightarrow \varepsilon = (l - l_0)/l_0 = \Delta l/l_0$$



up to proportional limit σ_U the stress is related to the strain by **Hooke's law**

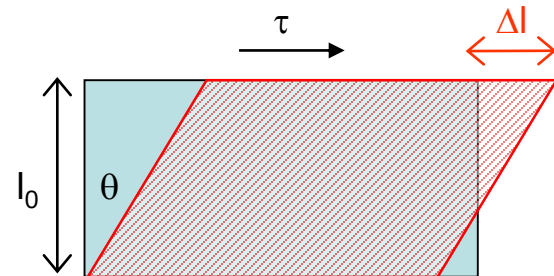
$$\sigma = E \varepsilon$$

(E – modulus of elasticity, values in order of 10^{10} Pa)



shear stress $\tau = F'/A$ results in a shear strain $\gamma = \Delta l/l_0 = \tan \theta$

stress strain relation (Hooke's law) $\tau = G \gamma$
(G – shear modulus)



$$\frac{E}{G} = 2(\nu + 1) \quad \nu = \left| \frac{\varepsilon_y}{\varepsilon_x} \right|$$

Poisson's ratio ($\varepsilon_y, \varepsilon_x$ – relative deformations in perpendicular and parallel directions to the direction of tensile stress, resp.)
the ν values range mostly between 0 and 0,5

Note: Tensors

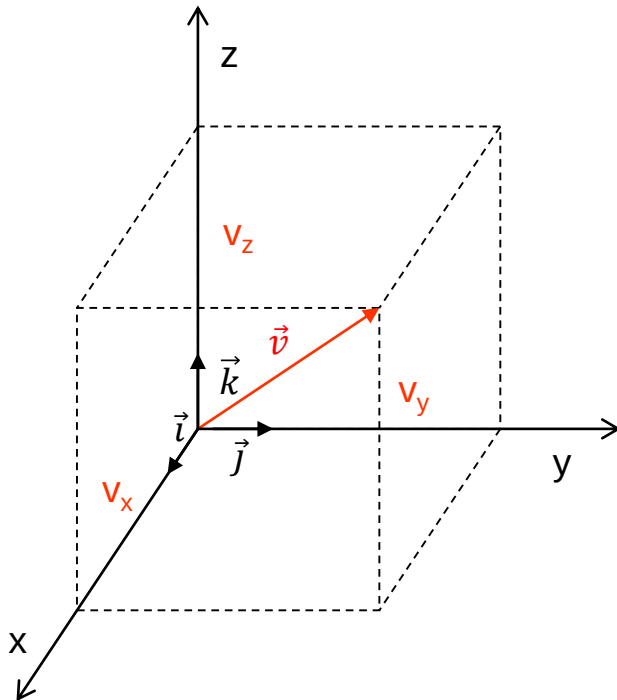
scalar – quantity defined by a single real number (magnitude) → zero-order tensor

vector – quantity defined by magnitude and direction → first-order tensor

in three-dimensional Cartesian coordinate system the vector $\vec{v}$ is defined by triples of scalar components v_x, v_y, v_z

$$\vec{v} = v_x \vec{i} + v_y \vec{j} + v_z \vec{k}$$

($\vec{i}, \vec{j}, \vec{k}$ – vectors of unit length pointing along the directions of positive x, y, and z axes, respectively)



magnitude (length) of the vector $\vec{v}$

$$v = |\vec{v}| = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

General relation between two vectors:

vector quantity defined by components (v_1, v_2, v_3) is a function of other vector quantity (u_1, u_2, u_3) , it can be expressed as a linear combination of the u_1 , u_2 , and u_3 components

$$\begin{aligned}v_1 &= T_{11}u_1 + T_{12}u_2 + T_{13}u_3 \\v_2 &= T_{21}u_1 + T_{22}u_2 + T_{23}u_3 \\v_3 &= T_{31}u_1 + T_{32}u_2 + T_{33}u_3 \\ \mathbf{v}_i &= T_{ij} \mathbf{u}_j\end{aligned} \quad T_{ij} = \begin{vmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{vmatrix}$$



T_{ij} – second-order tensor, defined by 9 components, each of them has a geometric and physical meaning (examples: surface tension, thermal conductivity)

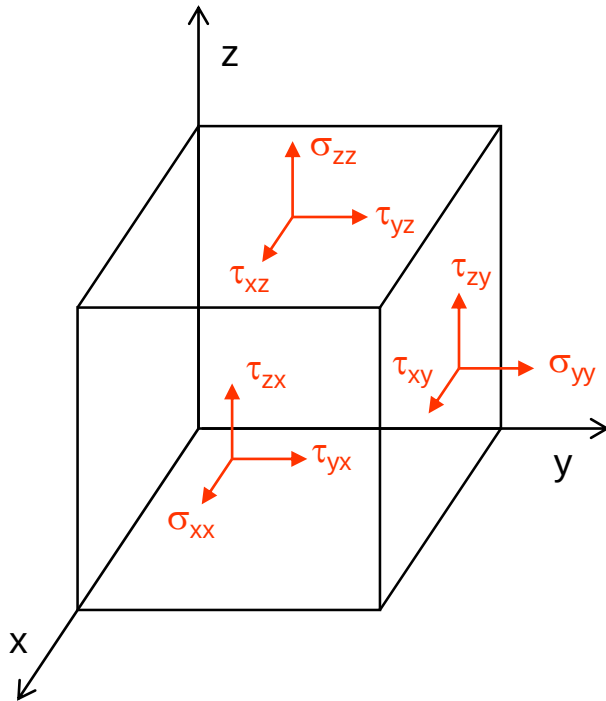
relation between vector and 2nd-order tensor $v_i = T_{ijk} Q_{jk} \rightarrow$ 3rd-order tensor T_{ijk} (27 components)

relation between vector and 3rd-order tensor or between two 2nd-order tensors $\rightarrow$ 4th-order tensor, etc.

elastic moduli are 4th-order tensors

Elastic deformation of anisotropic solid

anisotropic solid (crystal) – both stress and strain are 2nd-order tensors
 (force acts on a surface with defined orientation, deformation is related to an oriented surface)
 in general it can be described by 36 elastic coefficients



9 independent stresses can act on the crystal
 (components express either tensile or shear forces)

σ_{xx} tensile stress in the x axis direction in the plane perpendicular to the x axis

τ_{yx} shear stress in the y axis direction in the plane perpendicular to the x axis

τ_{zx} shear stress in the z axis direction in the plane perpendicular to the x axis

etc.



$$T_{ij} = \begin{pmatrix} \sigma_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \sigma_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_{zz} \end{pmatrix}$$

stress tensor T_{ij} is symmetric

$$\tau_{yx} = \tau_{xy}, \tau_{yz} = \tau_{zy}, \tau_{zx} = \tau_{xz}$$

→ stress in anisotropic solid is described by 6 independent stress components $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \tau_{yz}, \tau_{xz}$ and τ_{xy}

deformation of Cartesian coordinate system in the crystal

position vector $\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$ is changed to $\vec{r}' = x\vec{x}' + y\vec{y}' + z\vec{z}'$

change in point position after deformation: $\vec{R} = \vec{r}' - \vec{r} = x(\vec{x}' - \vec{i}) + y(\vec{y}' - \vec{j}) + z(\vec{z}' - \vec{k})$

lengths of $\vec{i}$, $\vec{j}$, and $\vec{k}$ vectors as well as angles between them are changed, changes in positions can be expressed as a function of vector $\vec{r}$

$$\vec{R} = (xe_{xx} + ye_{yx} + ze_{zx})\vec{i} + (xe_{xy} + ye_{yy} + ze_{zy})\vec{j} + (xe_{xz} + ye_{yz} + ze_{zz})\vec{k}$$

$$R(\vec{r}) = u(\vec{r})\vec{i} + v(\vec{r})\vec{j} + w(\vec{r})\vec{k}$$

$$e_{xx} = \frac{\partial u}{\partial x} \quad e_{xy} = \frac{\partial v}{\partial x} \quad e_{xz} = \frac{\partial w}{\partial x}$$

$$e_{yx} = \frac{\partial u}{\partial y} \quad e_{yy} = \frac{\partial v}{\partial y} \quad e_{yz} = \frac{\partial w}{\partial y}$$

$$e_{zx} = \frac{\partial u}{\partial z} \quad e_{zy} = \frac{\partial v}{\partial z} \quad e_{zz} = \frac{\partial w}{\partial z}$$

→ strain tensor D (CC BY SA)
tensor of second order)

$$D_{ij} = \begin{Bmatrix} \varepsilon_{xx} & \gamma_{xy} & \gamma_{xz} \\ \gamma_{yx} & \varepsilon_{yy} & \gamma_{yz} \\ \gamma_{zx} & \gamma_{zy} & \varepsilon_{zz} \end{Bmatrix}$$

$$\varepsilon_{xx} = e_{xx} \quad \gamma_{xy} = e_{xy} + e_{yx}$$

$$\varepsilon_{yy} = e_{yy} \quad \gamma_{xz} = e_{zx} + e_{xz}$$

$$\varepsilon_{zz} = e_{zz} \quad \gamma_{yz} = e_{yz} + e_{zy}$$

physical meaning of the components:

ε_{xx} , ε_{yy} , ε_{zz} – changes in lengths of coordinate axes

γ_{xy} , γ_{xz} , γ_{yz} – changes in angles between coordinate axes after deformation

Hooke's law in anisotropic solid

relation between stress and strain tensors

$$\mathbf{T}_{ij} = \mathbf{C}_{ijkl} \mathbf{D}_{kl}$$

C_{ijkl} – elastic moduli, symmetric tensor of fourth order (81 components)

number of components is reduced due to symmetry, as $C_{ijkl} = C_{jikl} = C_{ijlk} = C_{klij}$

(from 81 to 36, only 21 components are independent)



increasing symmetry of crystal lattice results in decreasing number of independent components

determination of elastic moduli – speed of sound measurements in certain crystallographic directions

(for example, in cubic crystals the speed of sound is measured in crystallographic directions [100], [110], and [111])

Plasticity

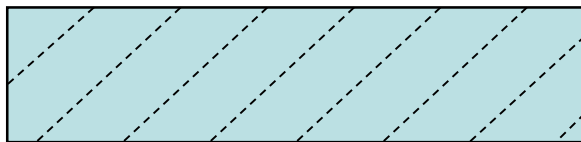
elastic deformation – reversible and homogeneous, outer load causes a slight shift of atoms from their equilibrium positions

plastic deformation – permanent and non-homogeneous, some atoms are shifted of at least one interatomic distance to new positions

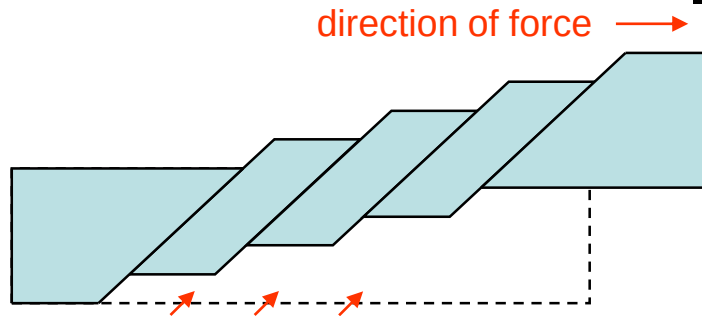
shift of atoms in certain crystallographic directions and planes with the most dense atomic packing is preferred; stress causes slip (a small slice of crystal is moved sideways) or mechanical twinning (a part of crystal attains different orientation)



plastic deformation by slip



planes most closely packed with atoms



slip planes

plastic deformation and slip in zinc single crystal exposed to strain stress

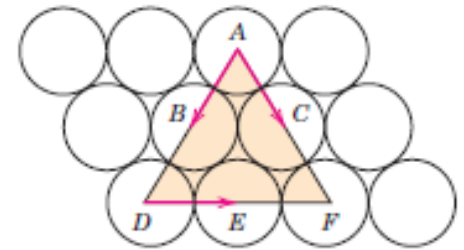
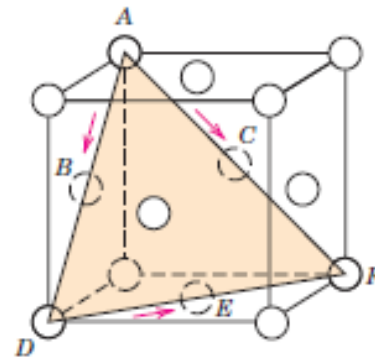


Example:

Face-centered cubic crystal structure:

the (111)-type planes are closely packed with atoms, slip can occur along the $[1\bar{1}0]$ -type directions; their combination results in 12 slip systems

4 independent (111)-type planes and 3 independent $[1\bar{1}0]$ -type directions in each of them



Body-centered cubic crystal structure:

close packing of atoms in the (110)-type planes, slip can occur along the $[1\bar{1}1]$ -type directions, their combination results in 12 slip systems

6 independent (110)-type planes and 2 independent $[1\bar{1}1]$ -type directions in each of them

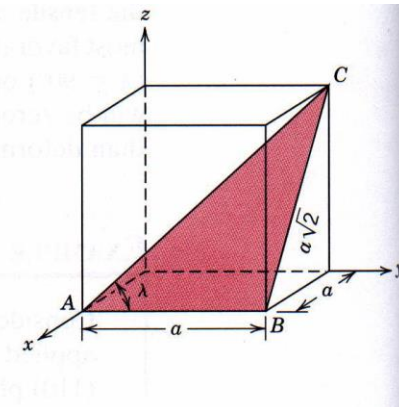
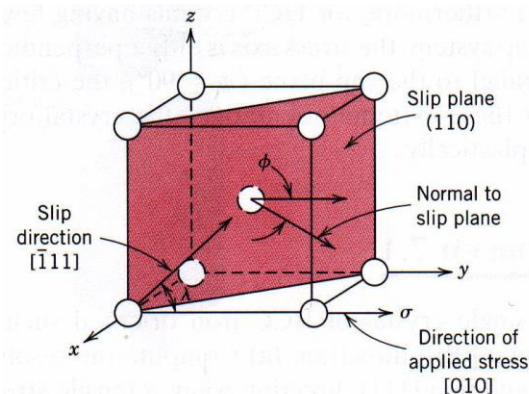


Table 7.1 Slip Systems for Face-Centered Cubic, Body-Centered Cubic, and Hexagonal Close-Packed Metals

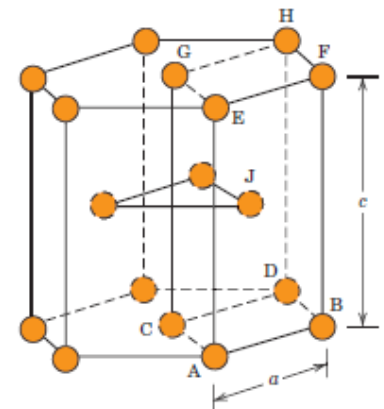
<i>Metals</i>	<i>Slip Plane</i>	<i>Slip Direction</i>	<i>Number of Slip Systems</i>
Face-Centered Cubic			
Cu, Al, Ni, Ag, Au	$\{111\}$	$\langle\bar{1}10\rangle$	12
Body-Centered Cubic			
α -Fe, W, Mo	$\{110\}$	$\langle\bar{1}11\rangle$	12
α -Fe, W	$\{211\}$	$\langle\bar{1}11\rangle$	12
α -Fe, K	$\{321\}$	$\langle\bar{1}11\rangle$	12
Hexagonal Close-Packed			
Cd, Zn, Mg, Ti, Be	$\{0001\}$	$\langle11\bar{2}0\rangle$	3
Ti, Mg, Zr	$\{10\bar{1}0\}$	$\langle11\bar{2}0\rangle$	3
Ti, Mg	$\{10\bar{1}1\}$	$\langle11\bar{2}0\rangle$	6



(copied from W.D. Callister, Jr.: Materials Science and Engineering, An Introduction. 7th Edition, John Wiley & Sons, Inc., 2007)

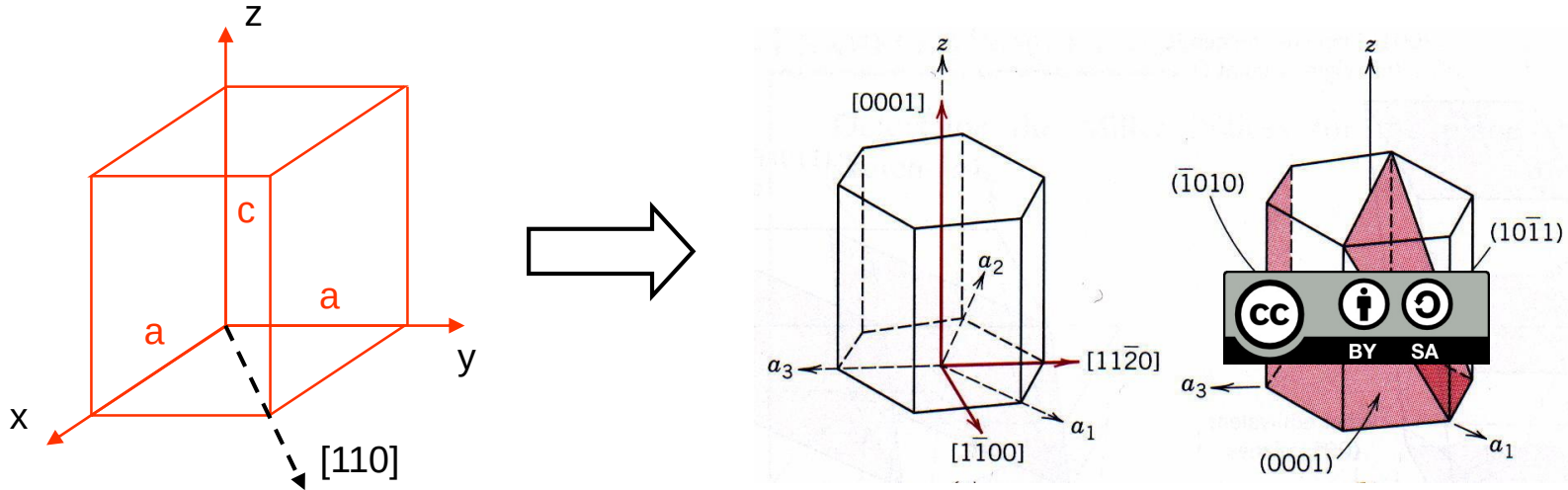
metals with FCC and BCC crystal structure having large number of slip systems are ductile (plastic deformation is possible along the various systems)

metals with HCP crystal structure are quite brittle as they have few slip systems



Note: Indices of crystallographic planes and directions in hexagonal crystals

Miller-Bravais system with 4 coordination axes can be used in hexagonal crystals; 3 axes (a_1 , a_2 , a_3) with angle of 120° between them in the basal plane and z axis perpendicular to this plane. Miller indices (hkl) are changed to (hkil), where $h+k+i=0$, i.e., $i = -(h+k)$.



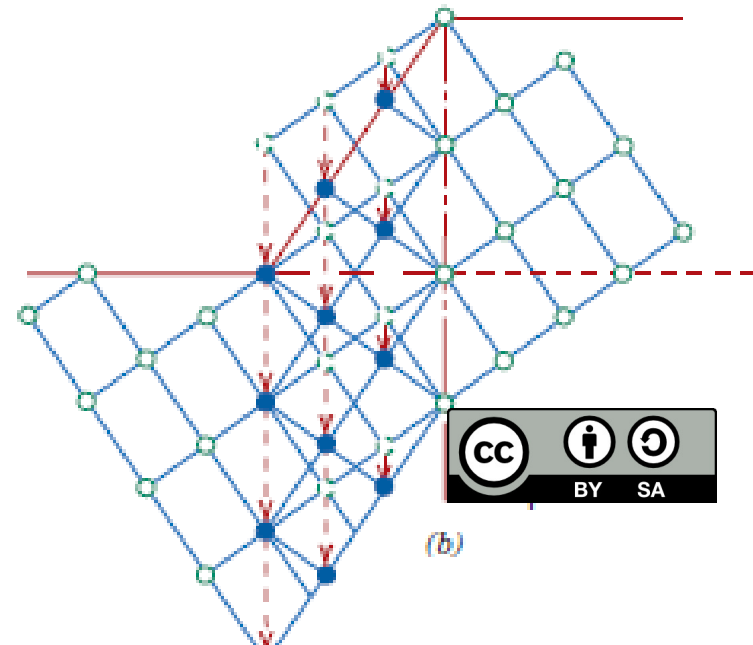
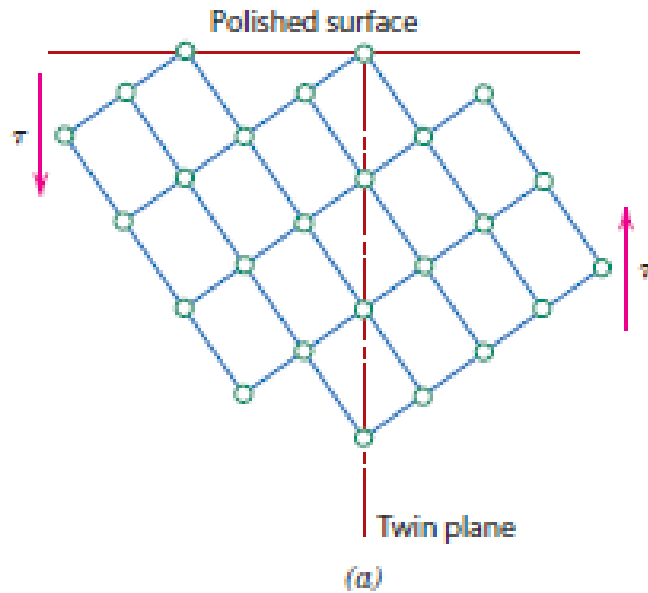
Transformation of crystallographic direction $[uvw]$ to four-index $[u'v'tw']$ system

$$u' = \frac{n}{3}(2u - v) \quad v' = \frac{n}{3}(2v - u) \quad t = -(u' + v') \quad w' = nw$$

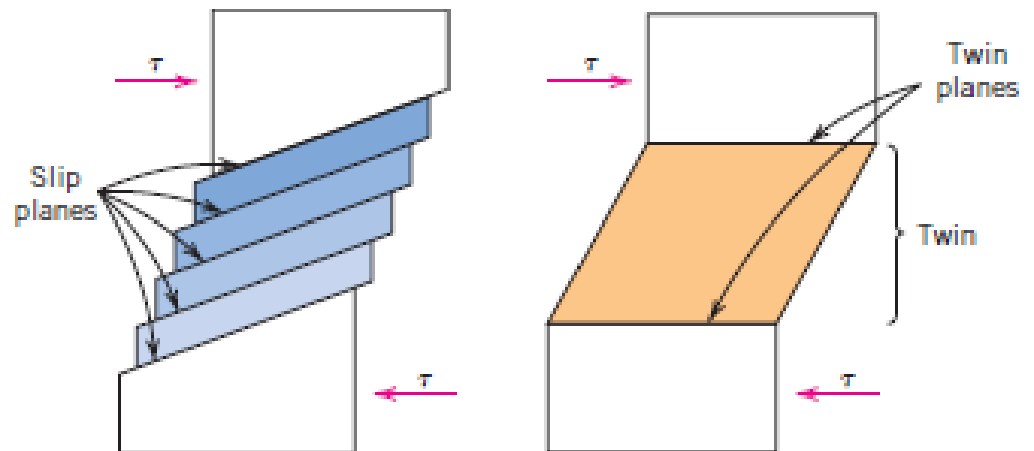
(n is the factor sometimes needed to make the new indices into smallest integers)

Transformation of $[110]$ direction: $u = \frac{n}{3}(2 - 1) \quad v = \frac{n}{3}(2 - 1) \quad t = -(1 + 1) \quad w = n \cdot 0 \Rightarrow [11\bar{2}0]$

Plastic deformation by twinning

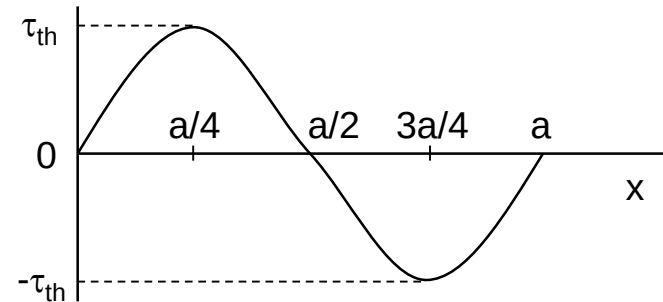
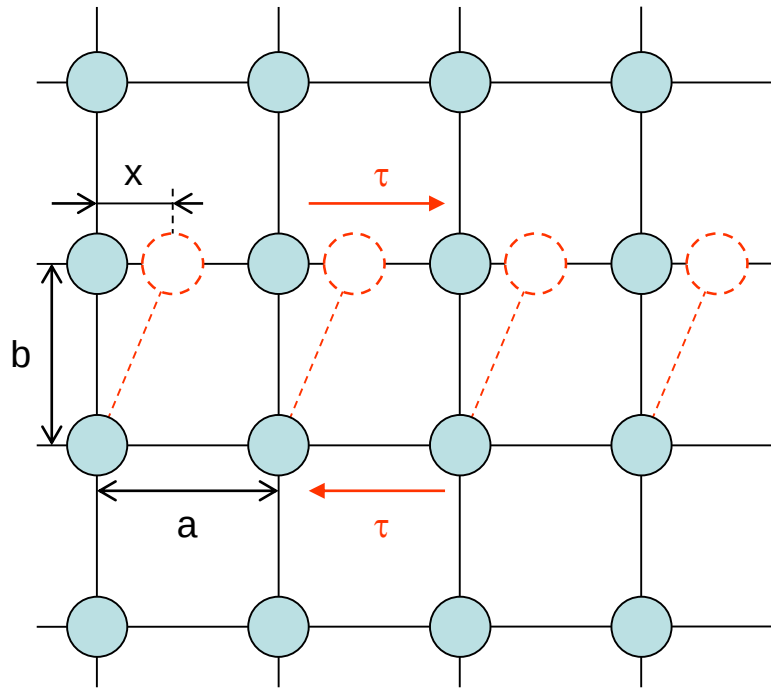


shear forces produce atomic displacement; atoms on one side of a twin plane are located in mirror image positions of atoms on the other side



Theoretical shear stress for slip initiation

atoms are shifted in x direction after attaining the τ_{th} value to new positions at distance of lattice parameter a



τ_{th} corresponds to shear stress at $x = a/4$ and reverse shear stress at $x = 3a/4$ (atoms are attracted to neighboring position)

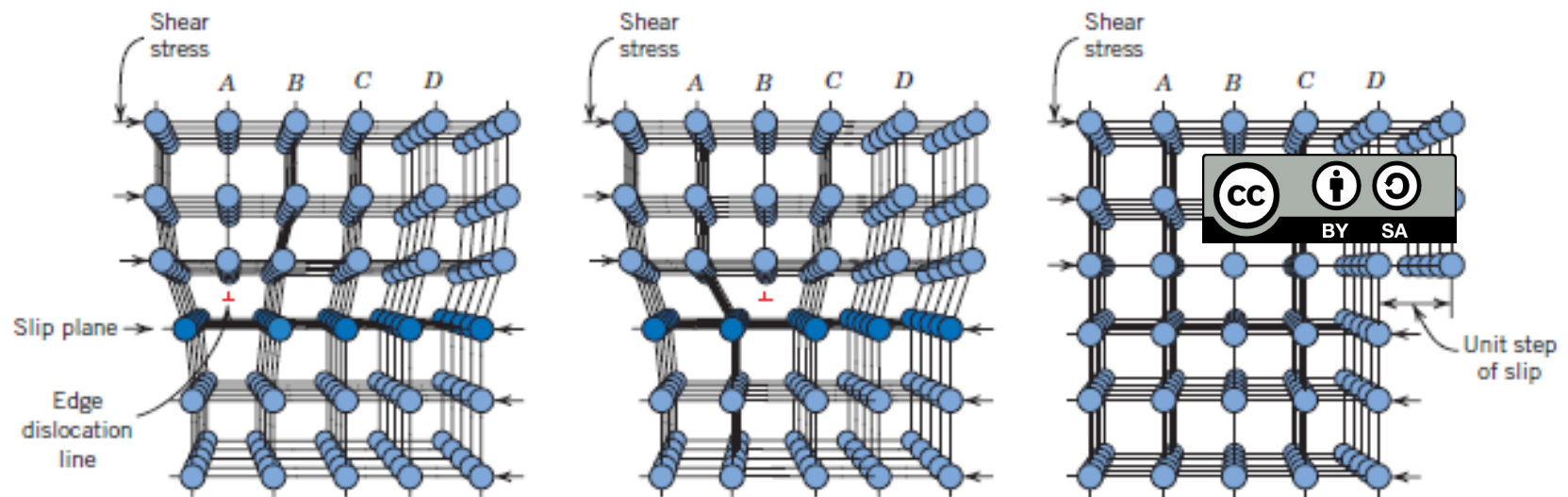
forces are balanced in a middle interatomic position at $x = a/2$

$$\tau(x) = \tau_{th} \sin \frac{2\pi x}{a} \quad \text{for } x \ll a \text{ it can be substituted as } \tau(x) = \tau_{th} \frac{2\pi x}{a}$$

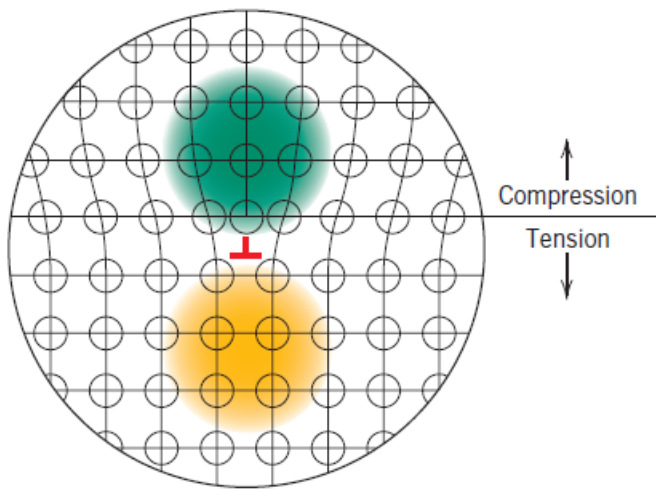
$$\text{Hooke's law can be applied at slight deformation: } \tau(x) = G \frac{x}{b} \rightarrow \tau_{th} = \frac{G}{2\pi} \frac{a}{b}$$

for metals with cubic crystal structure $a = b$, $G \sim 10^{10} \text{ N m}^{-2} \rightarrow \tau_{\text{th}} \sim 10^9 \text{ N m}^{-2}$, measured values of slip-initiating shear stress are much lower ($10^7 - 10^8 \text{ N m}^{-2}$)

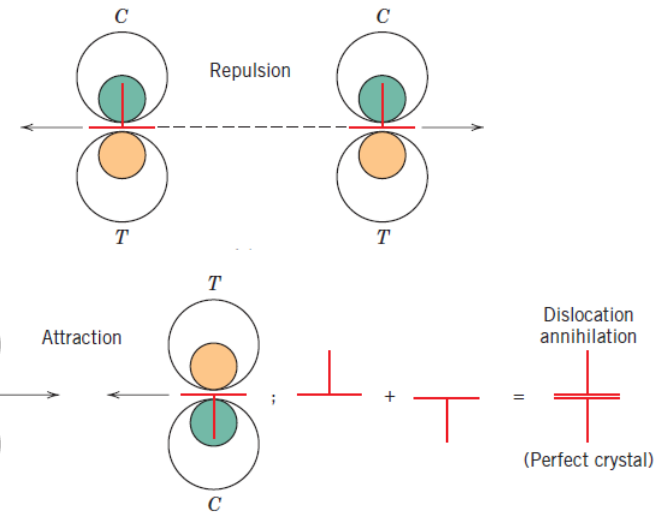
real crystals contain defects (applied stress can cause movement of dislocations and generation of the new ones)



atomic rearrangements accompanying the movement of an edge dislocation caused by shear stress $\rightarrow$ a step corresponding to magnitude of of Burgers vector $\vec{b}$ is formed on the crystal surface

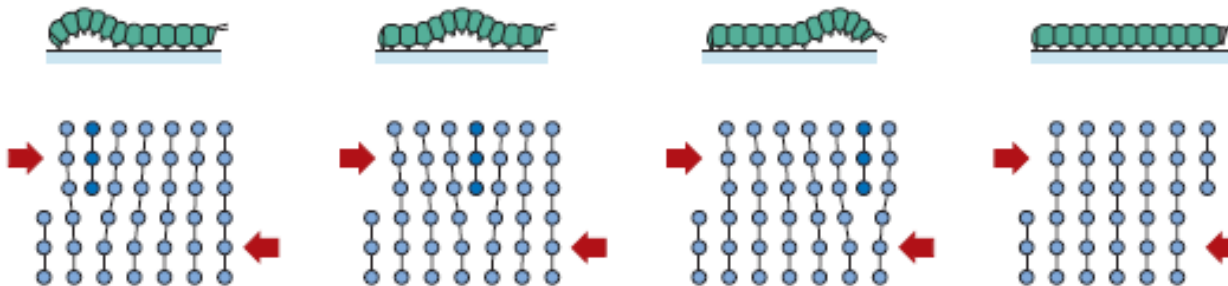


atomic lattice distortion around the dislocation line → compressive, tensile, and shear lattice strains imposed on neighboring atoms

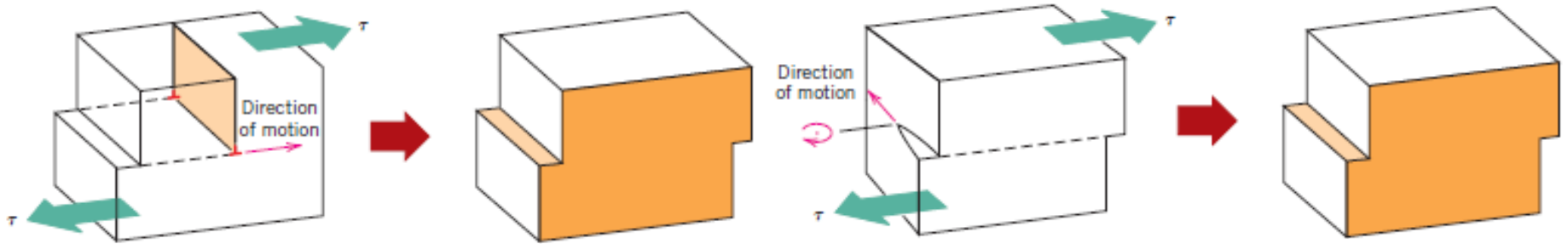


edge dislocations of the same sign and lying in the same slip plane repulse each other

edge dislocations of opposite sign and lying in the same slip plane attract each other and annihilate upon meeting



dislocation motion in crystal needs much lower shear stress compared to shifting whole layer of atoms

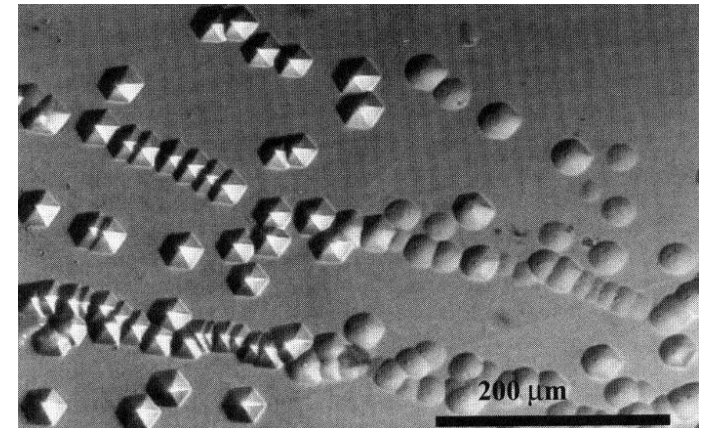


formation of a step on crystal surface by motion of the edge and screw dislocations



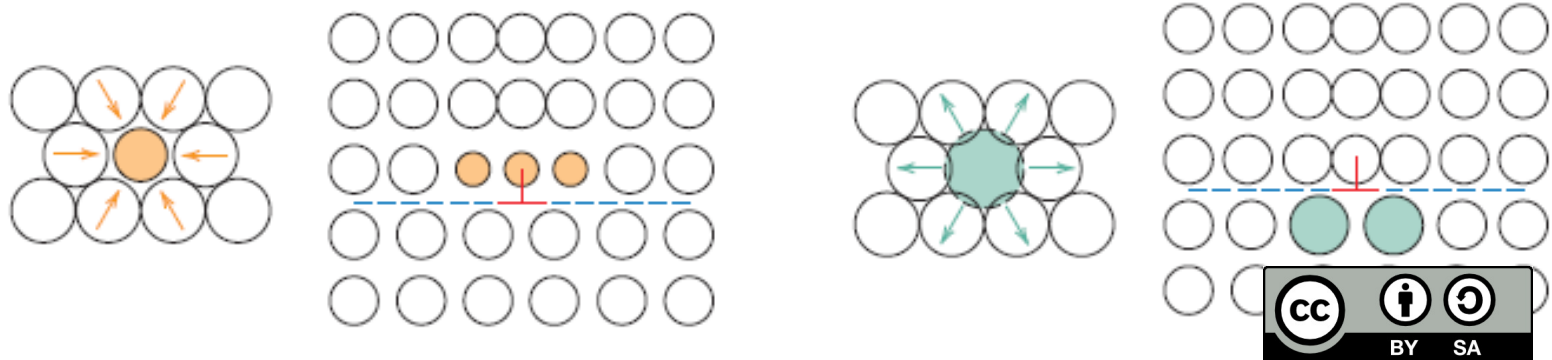
steps formed on surface of crystals exposed to plastic deformation are too high in comparison with magnitude of Burgers vector (approximately 10^4 dislocations should pass through the slip plane to reach the observed steps height)

→ a source of multiple dislocations has to exist in the crystals under stress



micrograph of SiC single crystal surface – spots show positions, at which dislocations intersect the surface

dislocation lines pass through regions, in which their motion is difficult or disabled, for example due to presence of impurity atoms:



substitutional impurity atoms of different size cause tensile and compressive lattice strains imposed on host atoms; interactions between dislocations and impurities result in partial compensation of impurity-dislocation lattice strains, dislocation motion is restricted

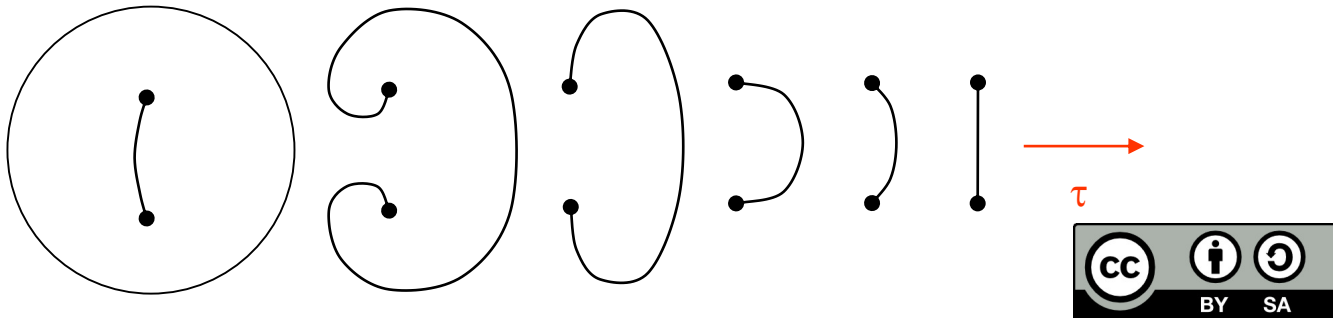
→ resistance to slip is increased, greater stress must be applied for continuing plastic deformation (strengthening of the material)

or

→ dislocation is anchored in such site and its motion is disabled, multiple dislocations can be generated in the slip plane

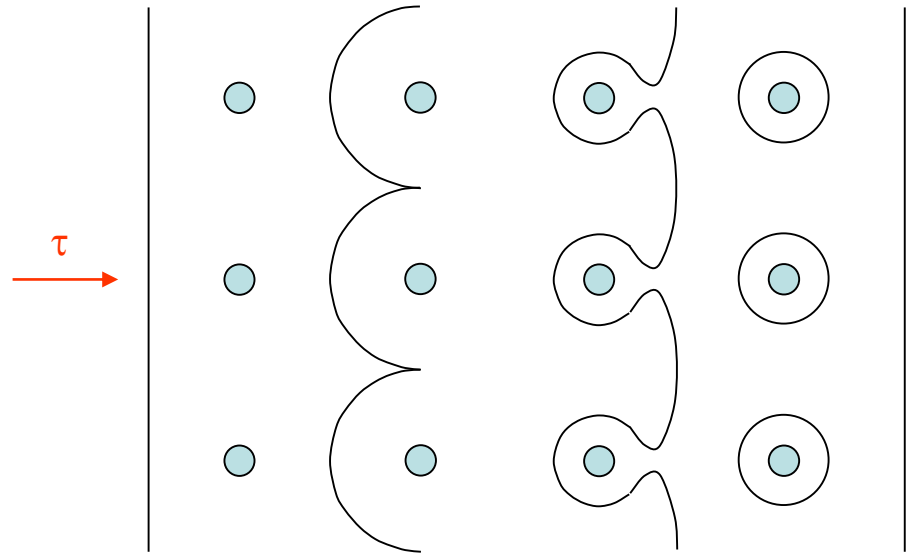
Frank-Read source

straight dislocation in slip plane is pinned in two ends, shear stress exerted on the slip plane results in a force acting perpendicularly to the dislocation line, which is lengthened and curved, until the segments spiralling around the pinning points collide and cancel; expanding dislocation loop as well as new dislocation line between pinning points are formed



Köhler-Orovan mechanism of dislocation multiplication

dislocation line moving over impurity defects in slip plane is gradually curved to form dislocation loop around each defect but its motion continues in a given direction



stress needed to move dislocation within a plane of atoms (Peierls-Nabarro stress)

$$\tau_{PN} = G \exp\left(-\frac{2\pi W}{b}\right) \quad W = \frac{a}{1-\nu} \quad (\text{dislocation width})$$

(G – shear modulus, b – interatomic spacing, a – interplanar spacing, ν - Poisson's ratio)

$\tau_{PN} \sim 10^2 \text{ N m}^{-2}$, too low value in comparison with slip-initiating shear stress ($10^7 - 10^8 \text{ N m}^{-2}$)
perfect structure of crystal with very slight concentration of dislocations is expected

Strengthening



plastic deformation depends on mobility of dislocations

dislocation concentration in plastically deformed materials increases (generation of multiple dislocations)

dislocations outside the slip plane do not move, active dislocations moving in slip plane have to overcome those with different orientation

impurity defects complicate the dislocations motion

→ increasing applied stress is needed to continue in plastic deformation

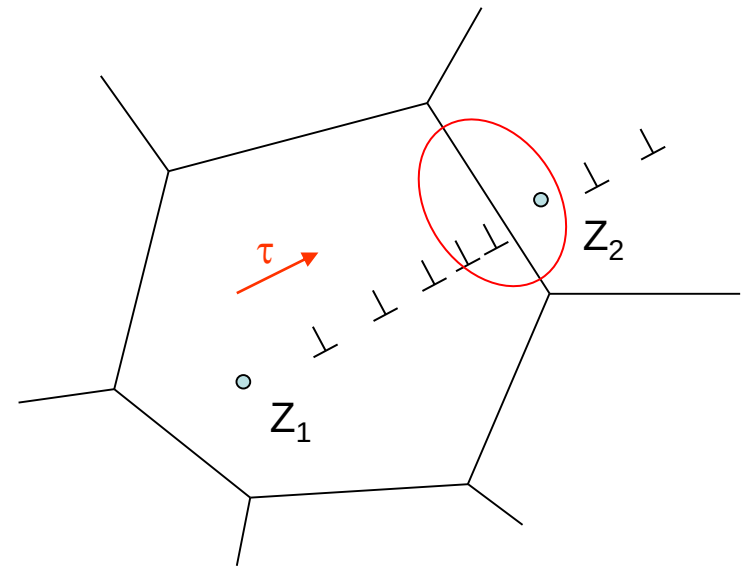
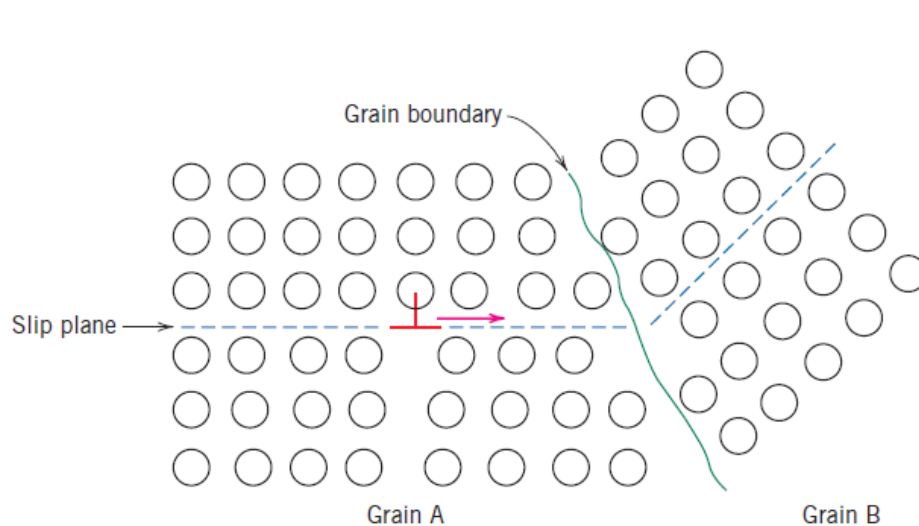
polycrystalline materials: strengthening by grain boundaries

grain boundaries represent barriers to dislocation motion (slip planes are discontinuous and change directions across the boundary)

→ accumulation of dislocations in front of the grain boundary

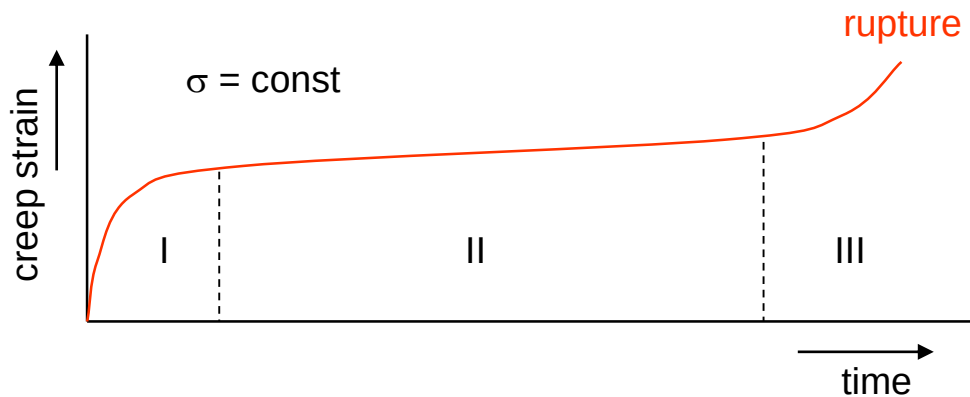
lattice strain at the grain boundary

- generation of the multiple dislocations is gradually reduced up to disabling the source (strengthening within the grain)
- new source of multiple dislocations can be activated in neighboring grains
- slip in other slip planes can be induced



Creep

plastic deformation under long-term static mechanical stress resulting in fracture
often observed at higher temperatures ($T > 0.3 T_m$)



high-temperature creep

$$\varepsilon = \alpha t + \beta t^n$$

α, β - cons



I. primary (transient) creep: continuously decreasing creep rate; stress initially induces motion of dislocations and generation of multiple dislocations but strengthening occurs with increasing concentration of dislocations

II. secondary (steady-state) creep: constant creep rate; balance between strain strengthening and recovery (recovery – material becomes softer and retains ability to be deformed; dislocations climb out of the slip plane, grains change shape, etc.)

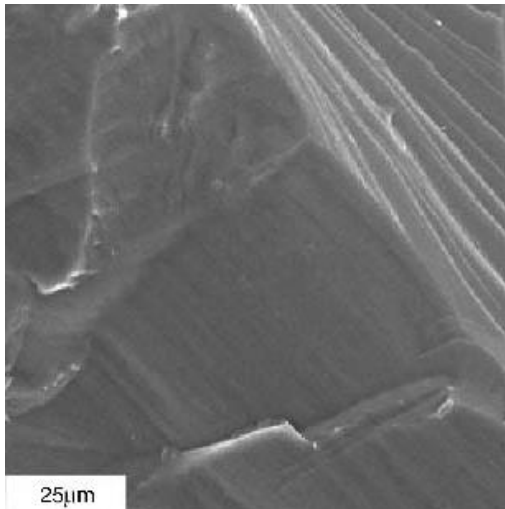
III. tertiary creep: creep rate acceleration and rupture due to microstructural changes (grain boundary separation, formation of internal cracks, cavities and voids)

Fracture

separation of material into two or more pieces under action of stress, new surfaces are formed

elastic materials with only narrow region of plastic deformation → **brittle fracture**; fracture surface is relatively flat, in single crystals often cleavage along definite crystallographic plane with low Miller indices

materials exhibiting considerable plastic deformation → **ductile fracture**; extensive deformation (necking) before fracture, undulated fracture surface



cleavage fracture in silicon
single crystal



brittle fracture in steel

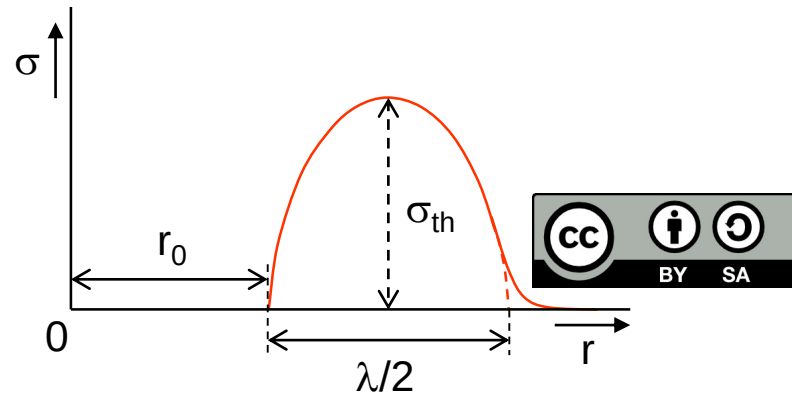
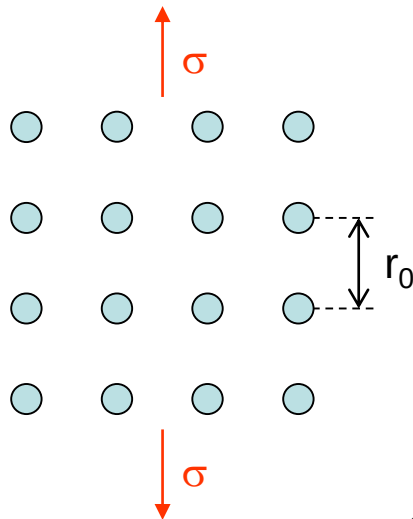


ductile (cup-and-cone)
fracture in aluminum

Theoretical strength

tensile stress σ_{th} necessary for separation of a body into two parts

brittle crystal with defect-free structure exhibiting no plastic deformation and tensile stress acting normal to a crystallographic plane are expected; theoretical strength is related to interatomic forces



$$\sigma = \sigma_{th} \sin \frac{2\pi(r - r_0)}{\lambda} \quad , \text{ in elastic region} \quad \sigma = E \frac{r - r_0}{r_0}$$

$$\sigma_{th} \sin \frac{2\pi(r - r_0)}{\lambda} = E \frac{r - r_0}{r_0}$$

elastic strain energy (W_D) consumed for fracture of a completely brittle material corresponds to surface energy of created two new surfaces (2γ)

$$W_D = \int_{r_0}^{r_0 + \lambda/2} \sigma dr = \int_{r_0}^{r_0 + \lambda/2} \sigma_{th} \sin \frac{2\pi(r - r_0)}{\lambda} dr = \sigma_{th} \frac{\lambda}{\pi}$$

for $(r - r_0) \ll r_0$ $\sin \frac{2\pi(r - r_0)}{\lambda} \sim \frac{2\pi(r - r_0)}{\lambda}$

$$\sigma_{th} \frac{\lambda}{\pi} = 2\gamma \quad \rightarrow \quad \lambda = \frac{2\gamma\pi}{\sigma_{th}}$$

$$\sigma_{th} = \sqrt{\frac{E\gamma}{r_0}}$$

values of E , γ , and r_0 can be obtained from experimental measurements and theoretical strength σ_{th} can be calculated

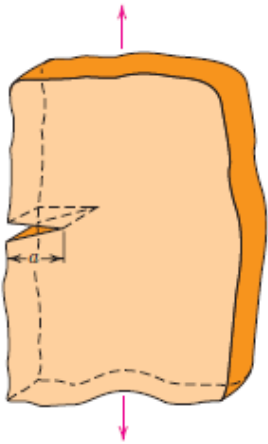
$\sigma_{th} \sim 10^{10} \text{ N m}^{-2} \rightarrow$ observed fracture strength values are much lower ($\sim 10^8 \text{ N m}^{-2}$)



Critical stress

fracture stress is affected by microscopic flaws and cracks in the material

defects are always present under normal conditions at the surface and in the interior, applied stress can also induce their formation and growth (e.g., accumulation of dislocations or vacancies), crack propagation is observed



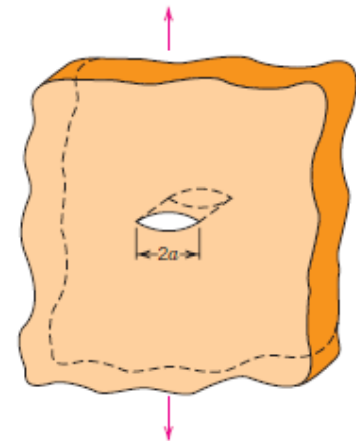
elastic strain in material act against the applied stress but it diminishes around the microscopic crack, the applied stress is concentrated at the crack tip



Griffith criterion: release of elastic strain energy has to be greater than energy increment connected with creation of new surfaces

critical stress calculation:

elastic body of unit thickness contains elliptical crack with length of $2c$ is expected



release of elastic strain energy at crack length increase dc :

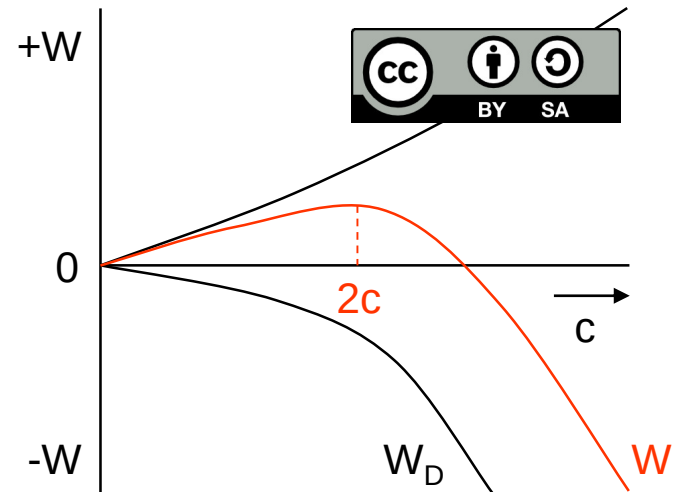
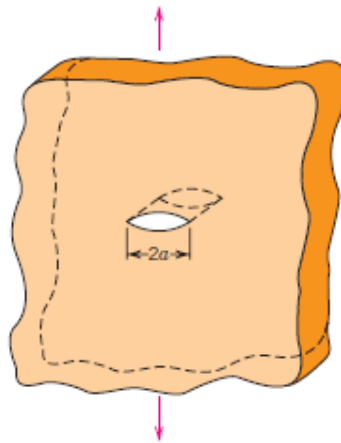
$$dW_D = -\frac{2\pi c \sigma^2}{E} dc$$

increase in surface energy at crack length increase dc : $dW_p = 4\gamma dc$

crack starts to propagate after reaching critical length of $2c$, total energy ($W_D + W_p$) is maximum when W_D and W_p are balanced:

$$\frac{dW_D}{dc} + \frac{dW_p}{dc} = 0$$

$$\sigma_{cr} = \sqrt{\frac{2\gamma E}{\pi c}}$$



Griffith formula was derived for tensile stress acting in a thin layer, stress oriented along the layer normal was neglected

critical crack length for brittle materials
 $2c \sim 10^{-7} \text{ m}$

Ductile fracture

tensile strength increases in materials exhibiting plastic deformation ($\sigma_p > \sigma_s$)

plastic deformation energy associated with crack extension has to be taken into account

$$\sigma_{kr} = \sqrt{\frac{2(\gamma + \gamma_{pl})E}{\pi C}}$$

γ_{pl} – local plastic deformation energy at the tip and around the crack, it is dependent on temperature (at very low temperatures $\gamma_{pl} \rightarrow 0$, at higher temperatures $\gamma_{pl} \gg \gamma$)

cross-section area decreases with increasing tensile stress up to material rupture



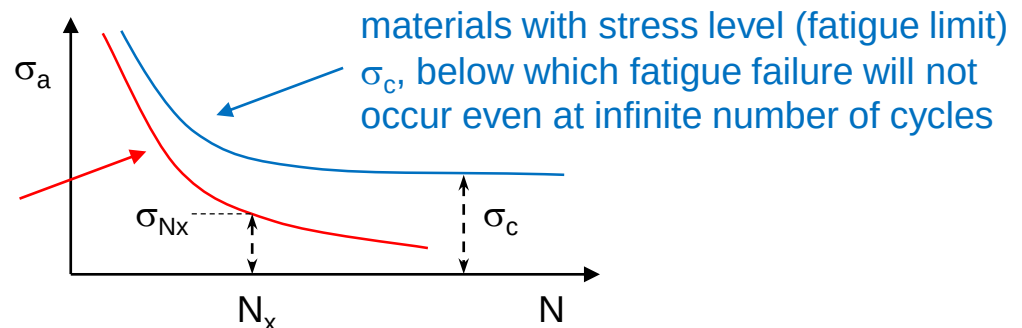
Fatigue

repeated stress or strain cycling decreases tensile strength (fracture even at $\sigma < \sigma_s$)

oscillation movement of dislocations → interactions, limited mobility in some areas, mosaic structure of material, increased probability of cracks formation

stress amplitude vs. number of cycles to failure (Wöhler curve)

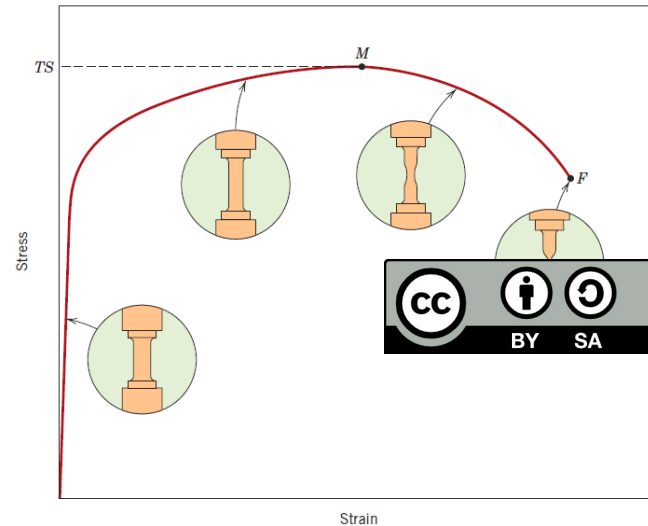
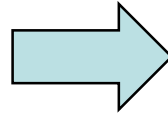
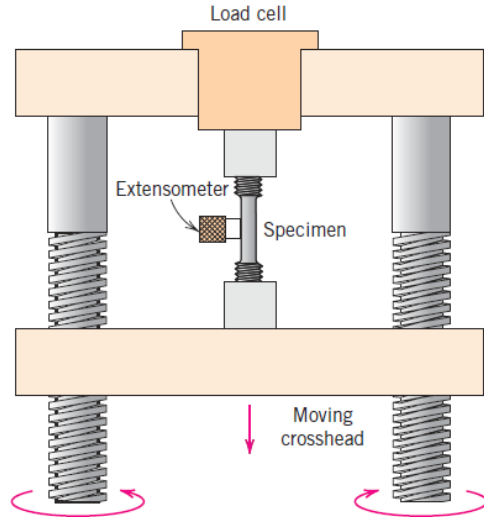
materials without fatigue limit, failure will occur at any stress level σ_a (fatigue strength) after specified number of cycles; fatigue life is defined as number of cycles N_x at specified stress level σ_{Nx}



Stress-strain tests

Tension test

specimen is elongated by moving crosshead, load cell and extensometer measure the magnitude of applied load and elongation



Bending test

specimen is placed on two supports and bent in its midpoint; the flexural strength gives a measure of the amount of bending that an object can sustain without fracture

Impact fracture testing

specimen with machined V-notch is used, the load is applied as an impact blow from a weighted pendulum hammer that is released from a position at fixed height; energy consumed for fracture is evaluated

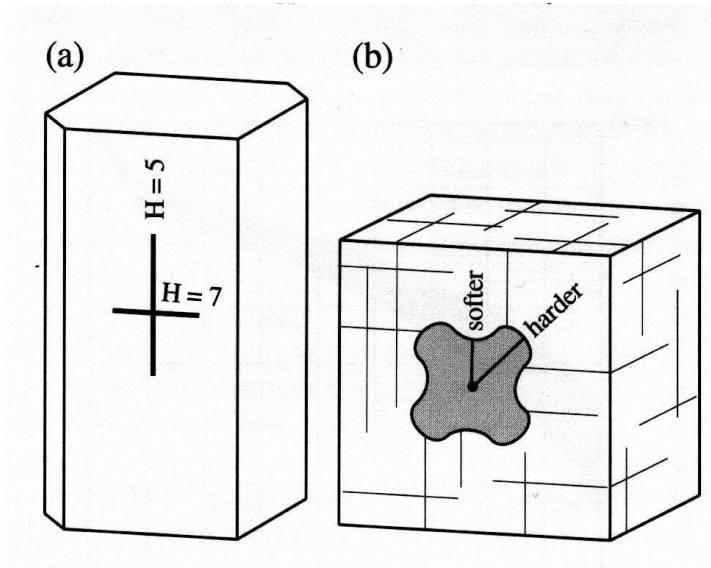
Hardness

resistance of material to localized plastic deformation (e.g., small dent or scratch)

there is no general dependence between applied force and hardness

many parameters can affect the test (anisotropy of crystal structure → measured crystallographic plane, lattice defects, single crystal vs. polycrystalline material, material homogeneity and microstructure, etc.), difficult definition of hardness – various methods are used

often is measured by forcing a chosen solid (indenter) into the material to be tested



(a) kyanite (Al_2SiO_5)

(b) halite (NaCl)

Mohs scale

qualitative ordinal scale consisting of 10 minerals characterizing scratch resistance of minerals through the ability of harder material to scratch the softer one

Mohs hardness	mineral	chemical formula
10	diamond	C
9	corundum	$\alpha\text{-Al}_2\text{O}_3$
8	topaz	$\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$
7	quartz	SiO_2
6	orthoclase feldspar	KAlSi_3O_8
5	apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$
4	fluorite	CaF_2
3	calcite	CaCO_3
2	gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
1	talc	$\text{Mg}_3\text{Si}_4\text{O}_{10} \cdot \text{Mg}(\text{OH})_2$

minerals in Mohs scale do not represent a linear dependence in absolute hardness, therefore, Mohs scale was rearranged and 5 synthetic hard materials were added

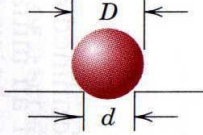
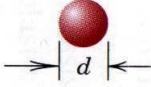
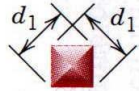
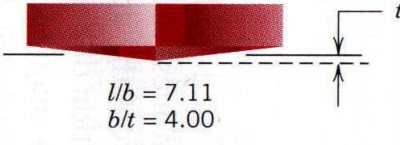
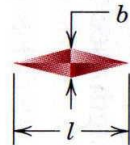
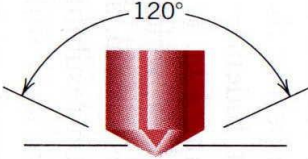
Mohs scale	rearranged scale	material	chemical formula	Vickers hardness [GPa]
10	15	diamond natural (bort)	C	90 – 100,6
-	14	diamond synthetic (carbonado)	C	80 – 90
-	13	boron nitride (cubic)	β -BN	70 – 80
-	12	boron carbide	$B_{12}C_3 - B_{13}C_2$	40 – 48
-	-	silicon carbide	SiC	38 – 41
-	11	boron	B	34 – 36
-	10	titanium carbide	TiC	30 – 34
9	9	corundum	α -Al ₂ O ₃	20 – 24
-	-	tungsten carbide	WC	15 – 18,5
8	8	topaz	Al ₂ SiO ₄ (F,OH) ₂	14,0 – 18,0
7	7	quartz	α -SiO ₂	10,0 – 12,5
-	6	magnetite	Fe ₃ O ₄	6,0 – 8,5
6	-	orthoclase feldspar	KAlSi ₃ O ₈	4,5 – 7,14
-	5	scheelite	CaWO ₄	5,5 – 7,0
5	-	apatite	Ca ₅ (PO ₄) ₃ (OH,F,Cl)	2,5 – 5,4
4	4	fluorite	CaF ₂	1,64 – 2,6
-	3	galena	PbS	1,10 – 1,5
3	-	calcite	CaCO ₃	0,56 – 1,05
-	2	halite (rock salt)	NaCl	0,3 – 0,9
2	-	gypsum	CaSO ₄ ·2H ₂ O	0,35 – 0,8
1	1	talc	Mg ₂ Si ₄ O ₁₀ ·Mg(OH) ₂	0,024 – 0,11



Indentation methods for hardness determination

hardness of materials to deformation is expressed as relation between applied load and area or depth of penetration; indenters of various shapes made from specified materials are used

Table 6.4 Hardness Testing Techniques

Test	Indenter	Shape of Indentation		Load	Formula for Hardness Number ^a
		Side View	Top View		
Brinell	10-mm sphere of steel or tungsten carbide			P	$HB = \frac{2P}{\pi D [D - \sqrt{D^2 - d^2}]}$
Vickers microhardness	Diamond pyramid			P	
Knoop microhardness	Diamond pyramid			P	$HK = 14.2P/l^2$
Rockwell and Superficial Rockwell	Diamond cone $\frac{1}{16}, \frac{1}{8}, \frac{1}{4}, \frac{1}{2}$ in. diameter steel spheres	 	 	60 kg 100 kg 150 kg } Rockwell 15 kg 30 kg 45 kg } Superficial Rockwell	

^a For the hardness formulas given, P (the applied load) is in kg, while D , d , d_1 , and l are all in mm.

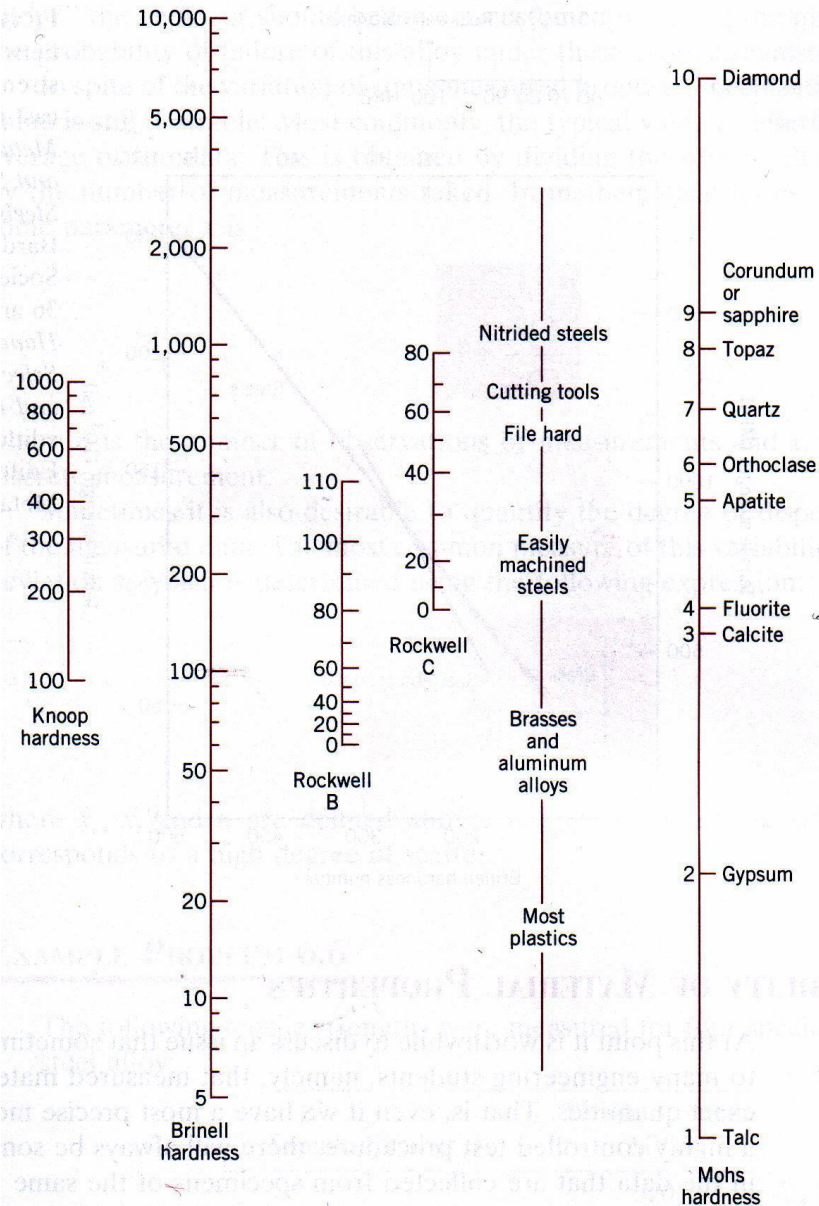


TABLE 6-5 ■ Comparison of typical hardness tests

Test	Indenter	Load	Application
Brinell	10-mm ball	3000 kg	Cast iron and steel
Brinell	10-mm ball	500 kg	Nonferrous alloys
Rockwell A	Brale	60 kg	Very hard materials
Rockwell B	1/16-in. ball	100 kg	Brass, low-strength steel
Rockwell C	Brale		High-strength steel
Rockwell D	Brale		High-strength steel
Rockwell E	1/8-in. ball		Very soft materials
Rockwell F	1/16-in. ball	60 kg	Aluminum, soft materials
Vickers	Diamond pyramid	10 kg	All materials
Knoop	Diamond pyramid	500 g	All materials



conversion of Vickers hardness (HV) to value in rearranged H_{15} hardness scale:
 $H_{15} = 0,67 \text{ HV}^{-1/3}$

W.D. Callister, Jr.: Materials Science and Engineering, An Introduction (5th Edition, John Wiley & Sons, Inc., 2000.

Askeland D. R., Phulé P. P.: The Science and Engineering of Materials (4th Edition). Thomson Brooks/Cole 2003.