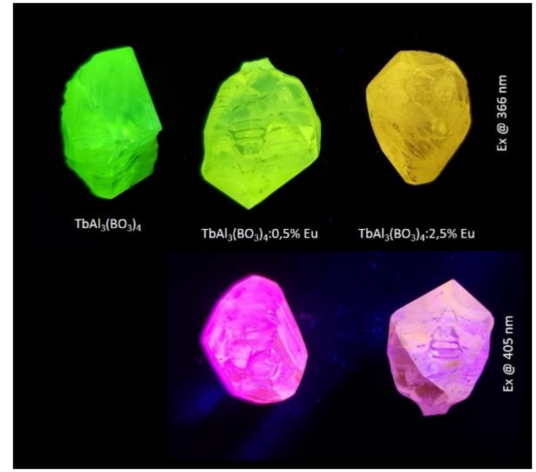
Functional Materials

Content

He, who wants to see something new, needs to invent it!



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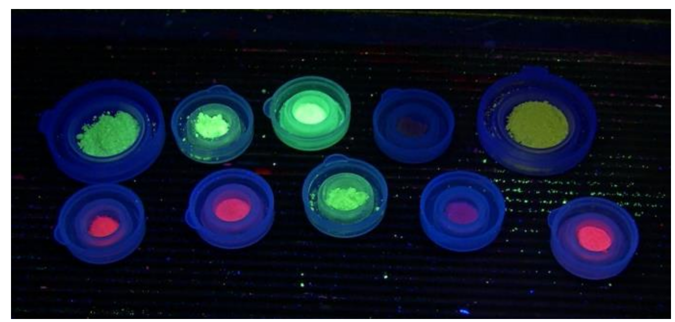


Literature

1. U. Müller: Anorganische StrukturchemieTeubner Studienbücher 1991

2. A.R. West, Grundlagen der Festkörperchemie, VCH Verlagsgesellschaft, Weinheim 1992

3. H. Briehl, Chemie der Werkstoffe, B.G. Teubner Verlagsgesellschaft, Stuttgart 1995

4. D.R. Askeland, Materialwissenschaften: Grundlagen, Übungen, Lösungen, Spektrum Akademischer Verlag, Heidelberg/Berlin/Oxford 1996

5. L. Smart, E. Moore: Einführung in die Festkörperchemie, Vieweg–Lehrbuch 1997

6. W. Göpel, C. Ziegler, Einführung in die Materialwissenschaften: Physikalisch-chemische Grundlagen und Anwendungen, B.G. Teubner Verlagsgesellschaft, Stuttgart/Leipzig 1996

7. E. Roos, K. Maile, Werkstoffkunde für Ingenieure, Springer-Verlag, Berlin/Heidelberg 2002

8. M. Merkel, K.-H. Thomas, Taschenbuch der Werkstoffe, Fachbuchverlag Leipzig 2003

1.1. About Applications of Functional Materials

Some Considerations Previous to the Selection of a Material

1. **Is the material generally suitable for the destined application?**

   ⇒ Stability against changes in temperature, moisture, oxygen, other gases such as N_2, CO_2, Hg, chemicals, mechanical stress, electrical fields, magnetic fields, plasmas, etc.

2. **Are there suitable technologies available to shape the material into its dedicated outer form?**

   ⇒ Preparation of thin or thick coatings, processing of extremely hard, moisture-sensitive, temperature-sensitive or brittle materials

3. **Do material properties change during processing?**

   ⇒ Dependence of material properties on layer thickness or on temperature treatment

4. **Is the material environmentally safe? Does it emit pollutants?**

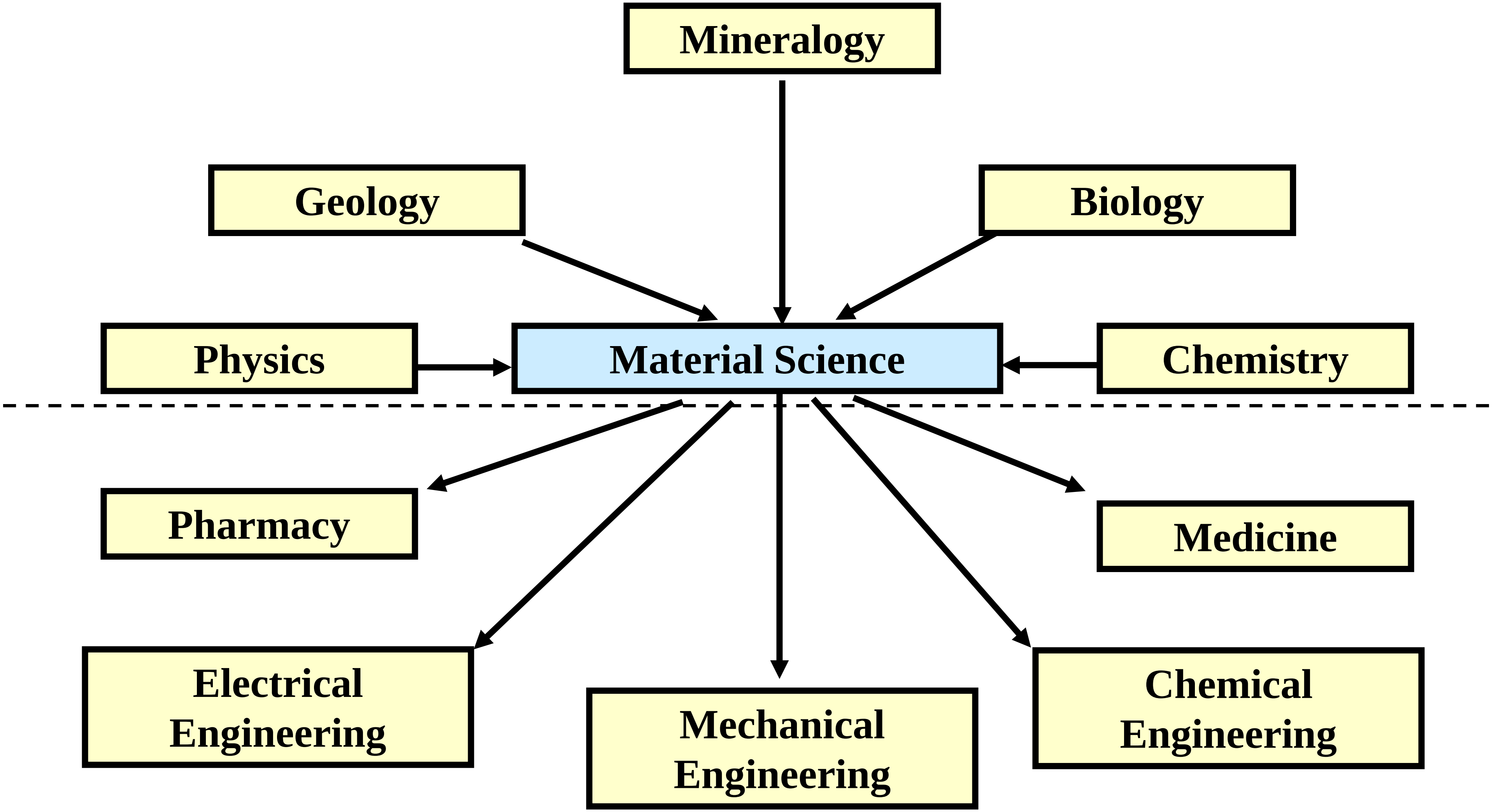
5. **Is it possible to recycle or dispose of the material in a environmentally sound way, after usage?**

Prerequisites to Answer these Questions

⇒ Broad (cross-sectional) knowledge about chemical (catalytic), mechanical, thermal, electrical, magnetic, and optical properties of numerous materials

1.2 Importance of Material Science

Link to Other Sciences and Engineering Branches



1.2 Importance of Material Science

Aim of Material Science

Exact atomic construction of materials $\Rightarrow$ prediction of all macroscopic properties

The Problem is:

- **the exact structure is never known, since every material exhibits impurities, defects and broad particle size distributions**
- **there is no physical theory that can predict macroscopic properties, such as electrical conductivity, magnetism, absorption spectrum, luminescence, quantum efficiency, etc., to one hundred percent**

Therefore Material Science contents oneself with the:

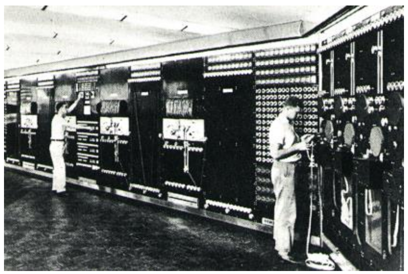
- **description of material properties**
- **investigation of the cause for the properties**
- **material selection**
- **material synthesis and optimisation**
- **analysis of materials**

1.2 Importance of Material Science

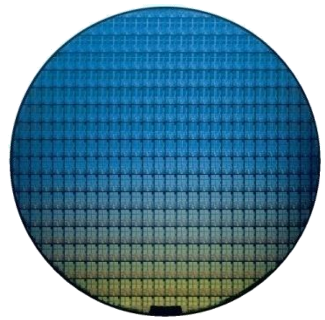
Importance of Functional Materials

Material development (hardware) is crucial for the speed of technical progress

1. **Example: Micro electronics**



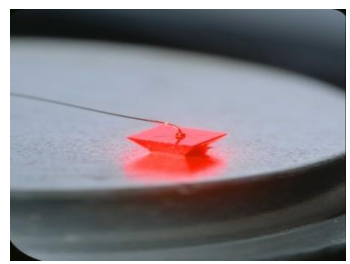
Mainframes with vacuum tubes (1950)



Si-wafer for micro electronics (2000)

2. **Example: Light sources**

Fluorescent tubes since ca. 1940



(Al,In,Ga)P chip for red LEDs (2000)

Software and drivers can be developed relatively easy and fast in comparison...

1.3 History

Development of Material's Chemistry/Phyics

Material research
„Trial & error"
Oral transmission

Chemistry
Solid state chemistry
High pressure chemistry
Polymer chemistry

Physics
Electromagnetism
Solid state physics
Quantum mechanics
Statistical thermodynamic

Material Science
Selective synthesis
Theoretical understanding of structure and function

Example: Egyptian blue

1.3 History

Progress in Material Handling

100000 B.C.	Wood, bones, stone	600 A.D.	Chinaware
9000 B.C.	Fibres	1500 A.D.	Steel, cast iron
7000 B.C.	Mud brick	1700 A.D.	Böttger porcelain
6000 B.C.	Ceramics	1820 A.D.	Plastics, rubber
5000 B.C.	Hemp	1850 A.D.	Concrete
3500 B.C.	Potter's wheel	1900 A.D.	Flat glass
3000 B.C.	Glaze, bronze	1919 A.D.	Stainless steel
2500 B.C.	Silk	1930 A.D.	Al-alloys
2000 B.C.	Glass	1950 A.D.	Semiconductor(diodes)
1500 B.C.	Iron	1960 A.D.	Ti-alloys
1000 B.C.	Hypothesis of atoms	1986 A.D.	High temperature super conductor
500 B.C.	Glazed bricks	1993 A.D.	Blue InGaN LEDs
25 B.C.	Cement	2000 A.D.	Composites, Super alloys
Around 0	Glass blowing	2007 A.D.	UV-C AlGaN LEDs

1.4 Principals to Classify and Order

Categorisation According to Phase State

Solid | **Liquid** | **Gaseous** | **Plasma**

- **Solid** →
  - **Metals**
    Fe, Cu, Ag, Au
    Ta, Nb, W, Mo,
    Ti, Mg, Al, Ga
    Na, K, Ba, Sr
    Pd, Pt, Rh, Ir
  - **Non-metals**
    Glass, porcelain,
    plastics, graphite
    ceramics
    (ZrO_2, Al_2O_3)
  - **Natural substances**
    Wood, coke,
    rubber, asbestos,
    chalk, marble,
    gemstones

→ **Composites**
(Concrete, glass ceramics, milk carton...)

1.4 Principals to Classify and Order

Structural Materials (Classical Materials)

⇒ Mechanic properties are most important

• Construction materials	Cement, mortar lime, gypsum
• Ceramics	Construction ceramics vessel ceramics technical ceramics (engine parts)
• Glass and glass ceramic	

Functional Materials (Modern Materials)

⇒ Materials, that belong to a certain functional group

• Ceramics	Bio-ceramics Electro-ceramics Magneto-ceramics Catalysts Opto-ceramics
• Single crystals	Laser-crystals, frequency-doubler (NLO-crystals)

1.4 Principals to Classify and Order

Properties of Materials

Metals: **High electrical and thermal conductivity, high strength and plasticity**
***Exp.*: Cu as conductive material, hardened steel for tools**

Semiconductors: **Simple adjustability of electrical conductivity by dopants, very brittle**
***Exp.*: Si, Ge, GaAs, $(Ga_{1-x}In_x)N$ as materials for diodes and solar cells**

Ceramics: **Poor electrical and thermal conductivity, suitable for insulating components, high temperature stability, extremely hard, very brittle**
***Exp.*: Capacitors, Al_2O_3 and MgO as fire-resistant vessels, porcelain**

Polymers: **Normally, poor electrical and thermal conductivity, high mechanical flexibility, low temperature stability**
***Exp.:* Polyethylene as packaging material, epoxy resin for the casing of electrical components**

Composites: **High strength, relatively low density**
***Exp.:* Concrete, graphite-epoxy as components for airplanes**

1.4 Principals to Classify and Order

Properties and Applications

"Electrical" materials

Material type (property)	Compound	Application(s)
Metallic conductor	Cu, Ag, Au	Electrical engineering
Low-dimensional metallic conductor	$K_2[Pt(CN)_4]$	
	Hexagonal C_x (graphite)	Electrodes
Semi-conductor	Si, Ge, GaAs,	Diodes, transistors, IC's
	Si, $CuInSe_2$	Solar cells
	GaAs, AlInGaP, AlInGaN	LEDs, laser diodes, photo diodes
	$Li_{0.05}Ni_{0..95}O$	Thermistors
	Se	Photo conductors
	SnO_2:In	Transparent electrodes
Thermo-electrical materials	Bi_2Te_3, PbTe	Thermo-electrical cooler
Superconductors	Nb_3Sn	High-field magnets
	$YBaCu_3O_7$	Resistance-free transport of electricity
Ionic conductors	$NaAl_{11}O_{17}$ (ß-alumina)	Long-lasting batteries, accumulators
	ZrO_2:Y	O_2-sensors (Lambda-probe)

1.4 Principals to Classify and Order

Properties and Applications

“Dielectrical”, “magnetic”, and “optical” materials

Material type (property)	Compound	Application(s)
Piezo-electrics	$Pb(Ti_{1-x}Zr_x)O_3$ (PZT)	Electro-acoustics: microphone, speaker
Pyro-electrics	ZnO	IR-detectors
Ferro-electrics	$BaTiO_3$, $PbTiO_3$	Capacitors, sensors
Ferro- and Ferri-magnets	$Nd_2Fe_{14}B$, $BaFe_{12}O_{19}$, $SmCo_5$	Permanent magnets
	Fe, γ-Fe_2O_3, CrO_2	Audio- and video tapes
	MFe_2O_4 (Ferrite), $ZnFe_2O_4$	Engines, transformers
	$Y_3Fe_5O_{12}$ (YIG)	Information storage
	$FeBO_3$	Magneto-optics: modulation of light
Colour	$CoAl_2O_4$, CdS, Fe_2O_3, TiO_2	Colour filter, dispersion paint
Photoluminescence	$BaMgAl_{10}O_{17}$:Eu, Y_2O_3:Eu	Fluorescent tubes
	$Y_3Al_5O_{12}$:Ce, $Sr_2Si_5N_8$:Eu	white LEDs
Cathodoluminescence	ZnS:Ag, ZnS:Cu, Y_2O_2S:Eu	Cathode ray tube
X-ray luminescence	$Bi_4Ge_3O_{12}$, Lu_2SiO_5:Ce	PET
Stimulated emission of light	Al_2O_3:Cr, Al_2O_3:Ti, $Y_3Al_5O_{12}$:Nd	Solid state laser

1.5 Structure-Property-Correlations

Electronic Structure

- Free electrons lead to high electrical and thermal conductivity, and to strong absorption
- Unpaired electrons lead to para , and thus to ferro- or anti-ferromagnetic behaviour
- Weakly bound electrons can easily be influenced by electro-magnetic radiation, resulting in altered optical behaviour

Atomic Structure

- The crystal structure strongly influences the mechanical, electrical, thermal, catalytic and optical properties

  Graphite (layered structure) $\leftrightarrow$ diamond (network structure)
- Amorphous materials possess exceptional physical properties, e.g. glass is transparent, but after crystallisation it often becomes impermeable to light

1.5 Structure-Property-Correlations

Nanostructure

- By nanoscale structuring a large number of boundary surfaces is created, i.e. most atoms are located at boundary layers und thus have different physical properties than atoms within the bulk material
- Quantum size effects

Microstructure (texture)

- Mixture and separation on micrometre scale in glasses and alloys
- Primarily influences mechanical and optical properties
- Micro-crystalline materials: sintered micro-crystallites
- Glass ceramics: micro-crystallites in glass matrix
- Composites: Different phases

1.6 Phases and Crystals

Phases and Phase Transitions

Phase: Homogenous material system in a well defined thermodynamic state

Independent state variables: T, p, chemical composition x, magnetic field strength

Dependent state variables (functions): V, U, H, S, F, G, polarisation, magnetisation, electrical resistance

Phase transition: Upon alteration of independent state variables, a non-differentiable point occurs in at least one state function, e.g. G(p,T):

Discontinuity in 1. derivation: Phase transition of 1st order, e.g. melting of Hg at –39 °C
Discontinuity in 2. derivation: Phase transition of 2nd order, e.g. glass transition of poly-styrene at about 100 °C

Polymorphism: Phenomenon, that a homogenous material system crystallises in different lattice types, depending on independent state variables

Crystals and Mixed Crystals

Ideal crystal: Mathematical, spatially periodical abstraction of real crystals

Substitutional mixed crystals: Atoms are isotypically substituted by "impurity" atoms

Intercalation mixed crystals: "Impurity" atoms are incorporated on interstitials

Real crystal: Ideal crystal + defects + impurities (dopants)

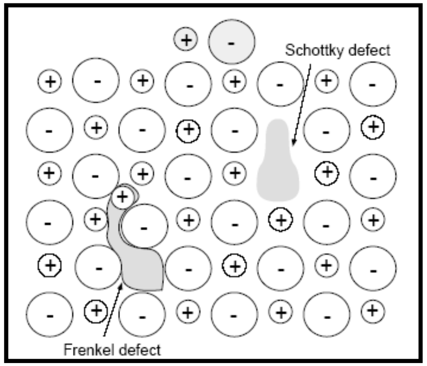
<u>Defects of different dimensions</u>

0-dim. (point defects): Schottky-defects (cation and anion vacancies)
Frenkel-defects (ion → interstitials)

1-dim. (line defects): Dislocations (steps, screws)

2-dim. (area defects): Stacking faults, boundary surface, (surfaces, phase boundary, twin boundary, …)

3-dim. (spatial defects): Cavities, pores, inclusions, …



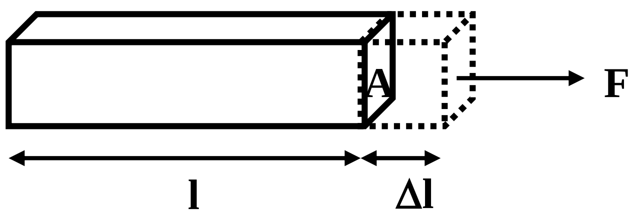
2.1 Mechanical Properties

Important Mechanical Quantities

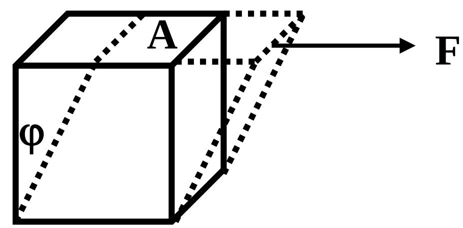
⇒ Elasticity, plasticity, breaking strength, ductility, hardness (Mohs, Brinell, Vickers, Knoop, Rockwell, Shore, … → scales of hardness)

⇒ Different ways of mechanical deformation

One dimensional test



Shear experiment

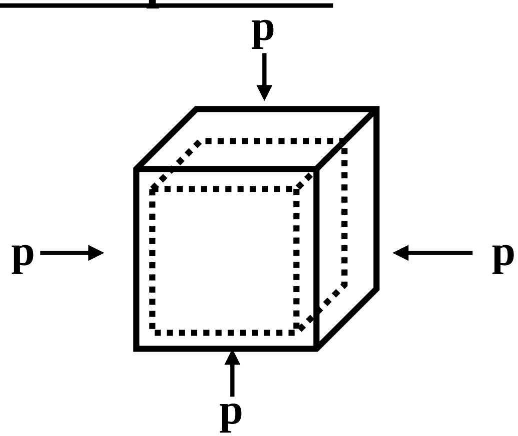


Tensional stress	$\sigma = F/A$	Shear stress	$\tau = F/A$
Elongation	$\varepsilon = l/\Delta l$	Shearing angle	φ
Elastic modulus	$E = \sigma/\varepsilon$	Shear modulus	$G = \tau/\varphi$

2.1 Mechanical Properties

Important Mechanical Quantities

Compression experiment



Pressure	p
Relative change in volume	$\Delta V/V$
Compressive modulus	$\kappa = p/(\Delta V/V)$

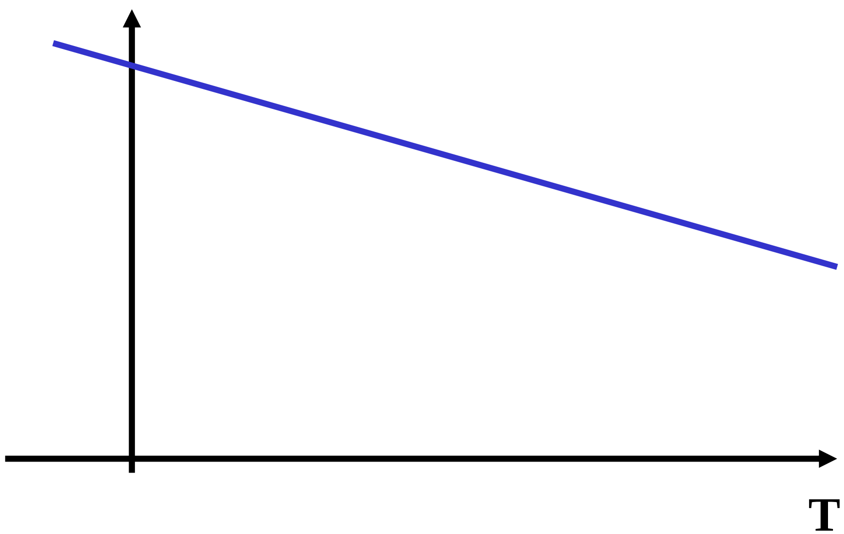
The moduli κ, G and E are not independent from one another but linked

Material	Young's modulus E
Natural rubber	0.1 GPa
Polyethylene	2 GPa
Polystyrene	3 GPa
Pb	18 GPa
ß-Sn	54 GPa
Al	69 GPa
Window glass	70 GPa
SiO_2 (quartz)	74 GPa
Au	80 GPa
Cu	110 GPa
Steel	207 GPa
$Y_3Al_5O_{12}$	283 GPa
W	355 GPa
Al_2O_3	373 GPa
SiC	470 GPa

2.1 Mechanical Properties

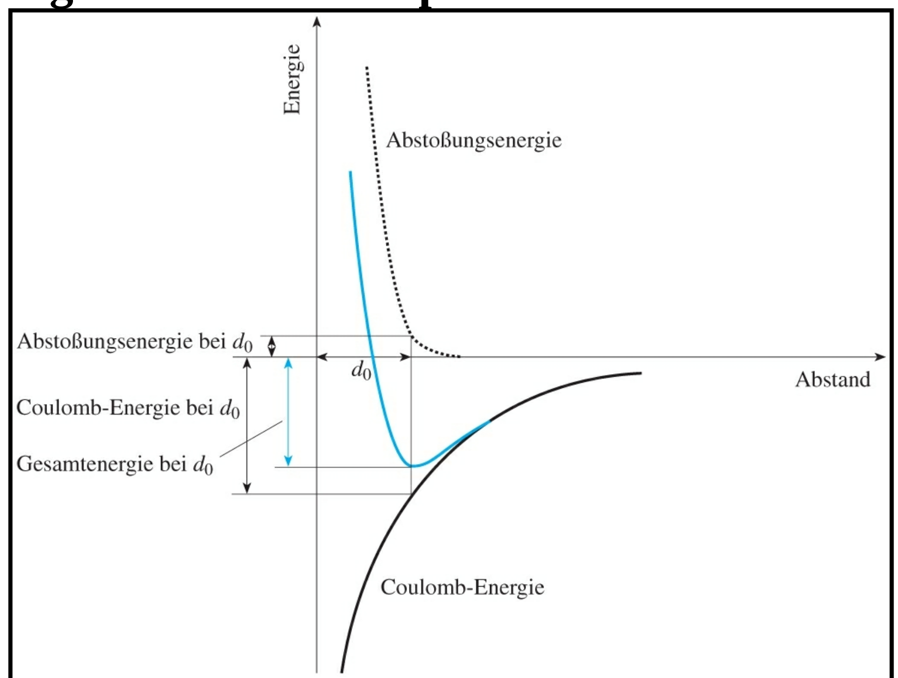
Influence of Temperature on Moduli

Typical dependence
κ, G, E



Polymers, highly elastic ⇒ v. d. W. forces
Metals, elastic ⇒ metallic interactions
Ceramics, brittle ⇒ ionic interactions

Cause: Potential shape,
e.g. Lennard-Jones potential



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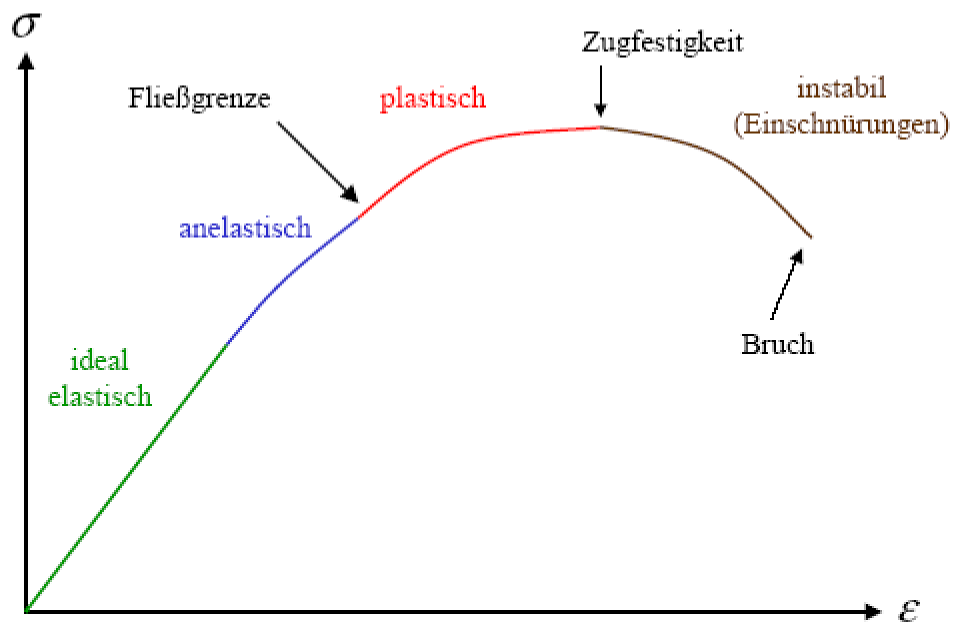
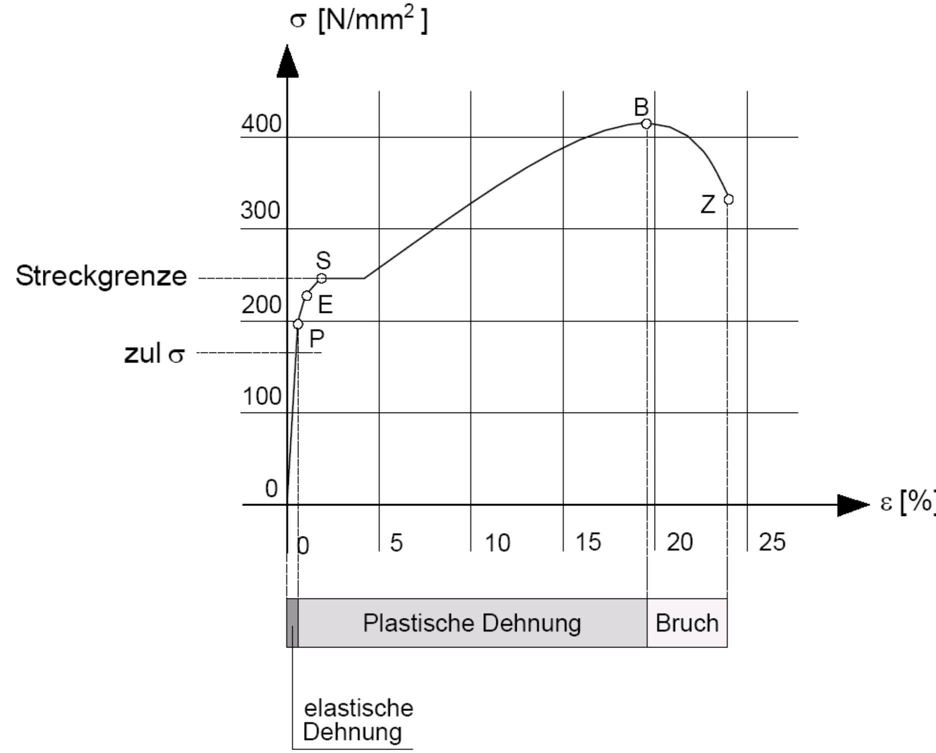
Elastic shape formations by deflection of the atoms from their equilibrium position

2.1 Mechanical Properties

Elasticity and Plasticity

Tension-Strain-Diagram (typically) **(for construction steel S235)**





Elastic deformation: **σ = ε · E (Hook's law)**

Inelastic deformation: **Hooke's law is not valid, anymore (hysteresis)**

Plastic deformation: **permanent deformation ⇒ ductility**

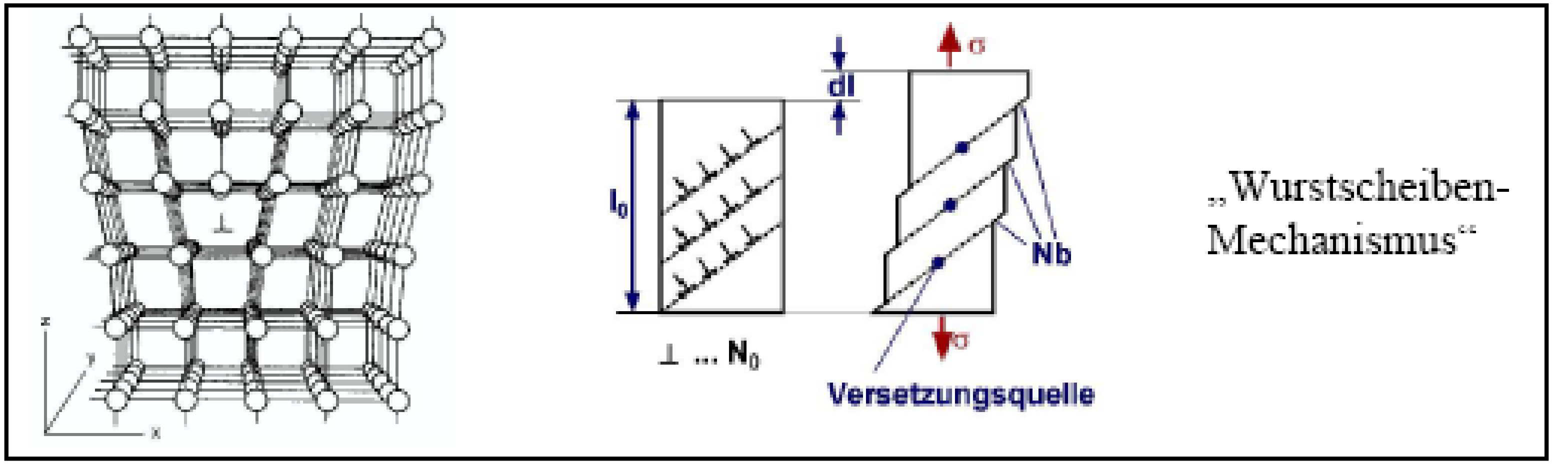
2.1 Mechanical Properties

Ductility Describes the Capability of a Material to Be Plastically Deformed without Breaking

$D = (L_b - L_0)/L_0$ with L_0 = length of sample without strain
L_b = length of sample after breaking

Materials are ductile, if D > 0.5 ⇒ most metals

Plastic deformations rely on translational motions of slippery dislocations!



2.1 Mechanical Properties

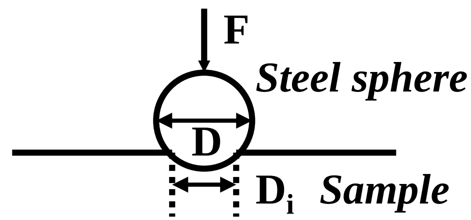
Hardness Describes the Resistance of Materials against the Intrusion of Objects into their Surface

Mohs-Hardness (scratch-test)

Empirical scale of comparison

Mohs-Hardness	Material for comparison
1	Talcum $Mg_3[Si_4O_{10}(OH)_2]$
2	Gypsum $CaSO_4 \cdot 2H_2O$
3	Calcite $CaCO_3$
4	Fluorite CaF_2
5	Apatite $Ca_5(PO_4)_3(F,Cl)$
6	Orthoklas $K[AlSi_3O_8]$
7	Quartz SiO_2
8	Topaz $Al_2SiO_4(F,OH)_2$
9	Corundum Al_2O_3 (~ Cr, W, Ir)
10	Diamond C_{cubic}

Brinell-Hardness HB (pressure-test)



$$HB = \frac{F}{(\pi/2)D\left(D - \sqrt{D^2 - D_i^2}\right)}$$

Material	HB
Polymers	10 - 20
Brass (Cu-Zn)	50
Mundane steel	200
Annealed steel	500 – 1000
Diamond	7500

2.2 Thermal Properties

Thermal Properties of Solids Depend Strongly on Bonding Energies of the Atomic Components

Type of bonding	Bonding energy [kJ/mol]
Ionic	600 – 1500
Covalent	500 – 1250
Metallic	100 – 800
H-bonds	< 170
Van der Waals	< 50

Covalent part of ionic compounds

$$KO = \exp^{-0.25(\Delta X)^2}$$

The bonding strength influences the phonon frequencies (lattice vibrations) and thus the following temperature-dependant properties:

- **Molar heat capacity and specific heat capacity**
- **Thermal conductivity**
- **Thermal expansion coefficient**

2.2 Thermal Properties

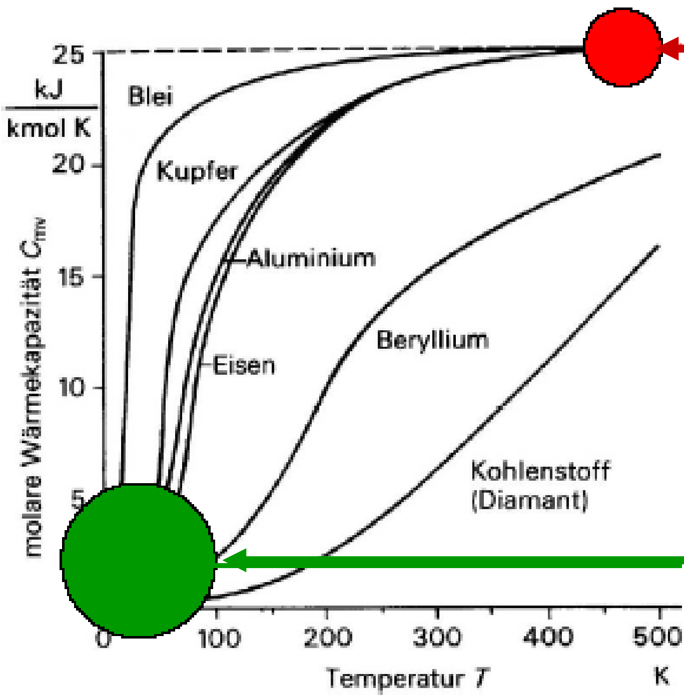
Molar Heat Capacity

$$c_{vm} = \left(\frac{\delta U_m}{\delta T}\right)_{V,N}$$

$$c_{pm} = \left(\frac{\delta H_m}{\delta T}\right)_{p,N}$$

In solids: $c_{vm} \approx c_{pm}$

Temperature-dependence of heat capacity



At high temperatures: c_{vm} = 3R ≅ 25 J/K·mol
(Dulong-Petit's rule)
Metals ~ above 100 °C
Ceramics ~ above 1000 °C

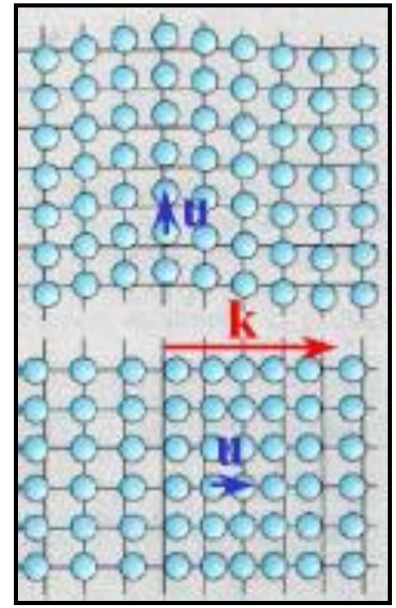
At low temperatures: $c_{vm} \sim T^3$

At 0 K: $c_{vm} = 0$

2.2 Thermal Properties

Molar Heat Capacity

Lattice vibrations in solids
(k = wave vector, u = deflection)



<u>Debye-Theory: Assumptions</u>

- **Atoms vibrate as couples (phonons)**
- **The distribution of frequencies is discrete**
- **Maximal wavelength depends on the size of the crystal = 2 * length**
- **Minimal wavelength is given by the lattice spacing**
- **For every wavelength there is a longitudinal and two transversal modes, thus 3N modes for N atoms**
- **The energy of every vibration is given by E = hν**
- **The excitation into a higher vibrational state is subject to Boltzmann-statistics, i.e. exp(-ΔE/kT) = exp(-hΔν/kT)**

2.2 Thermal Properties

Molar Heat Capacity

<u>**Debye-Theory – Results**</u>

At low temperatures:

$$c_{vm} = \left(\frac{T}{\Theta_D}\right)^3$$

with $\Theta_D = h\nu_D/k$ **= Debye-temprature**
and ν_D **= Debye-frequency**

Material	Θ_D [K]
Ag	225
C (diamond)	1800
Fe	465
Pb	94.5
NaCl	281
CaF_2	474
FeS_2	645

Explanation: At low temperatures, according to Boltzmann-statistics, only lo-lying frequencies are excited. With increasing temperature, more and more frequencies can be excited.

Materials with weak bonds: low Debye-frequencies
Materials with strong bonds: high Debye-frequencies

$$\nu = \frac{1}{2\pi} \cdot \sqrt{\frac{D}{m}}$$

D = force constant
m = mass

At high temperatures:

$c_{vm} = 3R \cong 25$ **J/K·mol**

Explanation: All 3 N vibrational modes are excited. Every vibrational mode contributes the amount of k (1/2 k from potential energy and 1/2 k from kinetic energy) to the heat capacity.

2.2 Thermal Properties

Molar Heat Capacity

<u>Exceptions in solids</u>

Metals (with electron gas)

At extremely low temperatures, free electrons contribute extensively to the heat capacity, because of $c_{el} \sim T$

Formation of point defects in crystals (e.g. Frenkel- or Schottky-defects) lead to a increase in heat capacity

Disorder in amorphous materials, s.a. glasses, leads to differences in the vibrational spectra and thus to a alteration of the heat capacity, especially at temperatures above 50 K

Phase transitions (structural, magnetic) lead to anomalies of the heat capacity close to the transformation temperature

2.2 Thermal Properties

Molar Heat Capacity and specific Heat

Specific heat c = heat capacity/molar mass [J/K·g]

Material	Heat capacity [J/K·g]	Material	Heat capacity [J/K·g]
Al	0.90	Al_2O_3	0.84
Cu	0.39	C (diamond)	0.52
B	1.03	SiC	1.05
Fe	0.44	Si_3N_4	0.71
Pb	0.16	SiO_2 (quartz)	1.11
Mg	1.02	Polyethylene, high density	1.84
Ni	0.44	Polyethylene, low density	2.30
Si	0.70	Polystyrene	1.17
Ti	0.53	Nylon-6,6	1.67
W	0.13	H_2O	4.18
Zn	0.39	N_2	1.04

2.2 Thermal Properties

Heat Transfer

1. Thermal Radiation

- Electromagnetic radiation (microwaves, IR, VIS, UV, etc.)
- Heat flux in all phases, even in vacuum

$$\dot{Q} = \varepsilon\sigma A T^4$$

with A = area, ε = emission intensity, σ = Boltzmann-constant
i.e. ~ T^4

2. Convection

- Transport of particles
- Heat flux in liquids and gases but not in solids or vacuum

$$\dot{Q} = \alpha A(T_1 - T_2)$$

with A = area, α = thermal transfer coefficient [$Wm^{-2}K^{-1}$]
(describes the flow conditions around a body)

3. Thermal conduction

- No macroscopic material flow
- Heat flux in all phase but not in vacuum

2.2 Thermal Properties

Heat Conductivity

<u>Thermal transport in solids</u>

- **Phonons**
- **free electrons**
- **At extremely high temperatures: IR-radiation (→ incandescent bulb) ~ T^4**

Temperature gradient $\frac{dT}{dz}$

Heat flux $J_Q = \frac{1}{A} \cdot \frac{dQ}{dt}$

$$J_Q = \frac{1}{A} \cdot \frac{dQ}{dt} = -\lambda \frac{dT}{dz}$$

λ = heat conductivity coefficient

<u>Non-metallic solids (ceramics)</u>

- **Phonons are responsible for heat conductivity**
- **Heat conductivity of almost perfect single crystals is much higher than of poly-crystalline materials (spreading of phonons at grain boundaries), materials with a lot of defects or impurities and glasses (spreading of phonons through disorder)**
- **Often, the heat conductivity decreases with increasing temperature, since ever more defects are generated**

2.2 Thermal Properties

Heat Conductivity

Metallic solids

- **Heat conductivity is dominated by free electrons and is thus significantly higher than for non-metals**
- **As first approximation, heat conductivity is proportional to electric conductivity:**
  $\lambda = L \cdot \sigma \cdot T$ (Wiedemann-Franz-law) with $L = 2.3 \cdot 10^{-8}$ JΩ/s$\cdot K^2$ (Lorentz constant)

Semi-conductors

- **Heat transport by electrons and phonons**
- **At low temperatures, phonons dominate heat transport**
- **With increasing temperature, more and more electrons are promoted into the conduction band, which leads to a considerable increase in thermal conductivity**

Polymers

- **Poor heat conductors, since, in general, no free electrons are available and a significant amount of energy is stored in local movements of chain segments, so that the transport of heat is severely hindered**

High thermal conductivity is of importance for the cooling of light and radiation sources, LEDs, displays, micro processors, etc.

2.2 Thermal Properties

Thermal Conductivity λ [$Js^{-1}m^{-1}K^{-1}$] = [$Wm^{-1}K^{-1}$]

Material	Thermal conductivity [J/m·s·K]	Material	Thermal conductivity [J/m·s·K]
Al	238	Al_2O_3	16
Cu	402	C (diamond)	23
Fe	79	C (graphite)	335
Mg	100	Clay (oven)	0,27
Pb	35	SiC	88
Si	150	Si_3N_4	14,6
Ti	22	Na-lime glass	0,96
W	172	Quartz glass	1,34
Zn	117	Vycor glass	1,26
Zr	23	ZrO_2	5
Ag	428		
		Nylon-6,6	0,25
Cu-Ni(30%)	50	Polyethylene	0,33
Ferrite	75	Polyimide	0,21
Gold brass	222	Polystyrene foam	0,03

2.2 Thermal Properties

Thermal Expansion

Linear thermal extension coefficient α

$$\alpha = \frac{1}{L_0} \cdot \left(\frac{\delta L}{\delta T}\right)_p$$

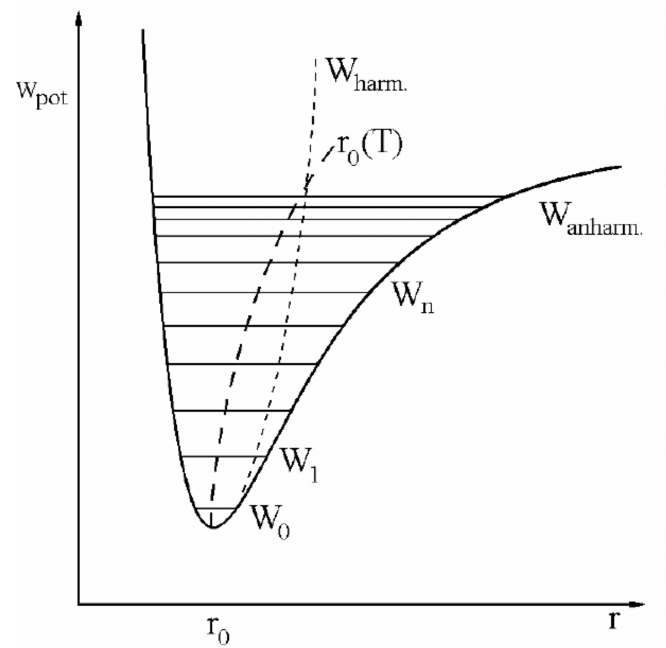
$$\Delta L = \alpha \cdot L_0 \cdot \Delta T$$

Volume-expansion coefficient γ = 3α

$$\gamma = \frac{1}{V_0} \cdot \left(\frac{\delta V}{\delta T}\right)_p$$

$$\Delta V = \alpha \cdot V_0 \cdot \Delta T$$

Thermal expansion, explained utilizing the model of a diatomic anharmonic oscillator, described by the so-called Morse-potential



The equilibrium distance increases with temperature, because evermore vibrational states are occupied

2.2 Thermal Properties

Thermal Expansion Coefficient of Different Materials

Ceramics

Low expansion coefficient, due to highly ionic or covalent bonding

Al_2O_3	α = 8.8 ppm/K
Quartz glass	α = 0.5 ppm/K

Metals

High expansion coefficient, since metallic bonds are weaker than covalent or ionic bonds

Ag	α = 19 ppm/K
Al	α = 24 ppm/K

Polymers

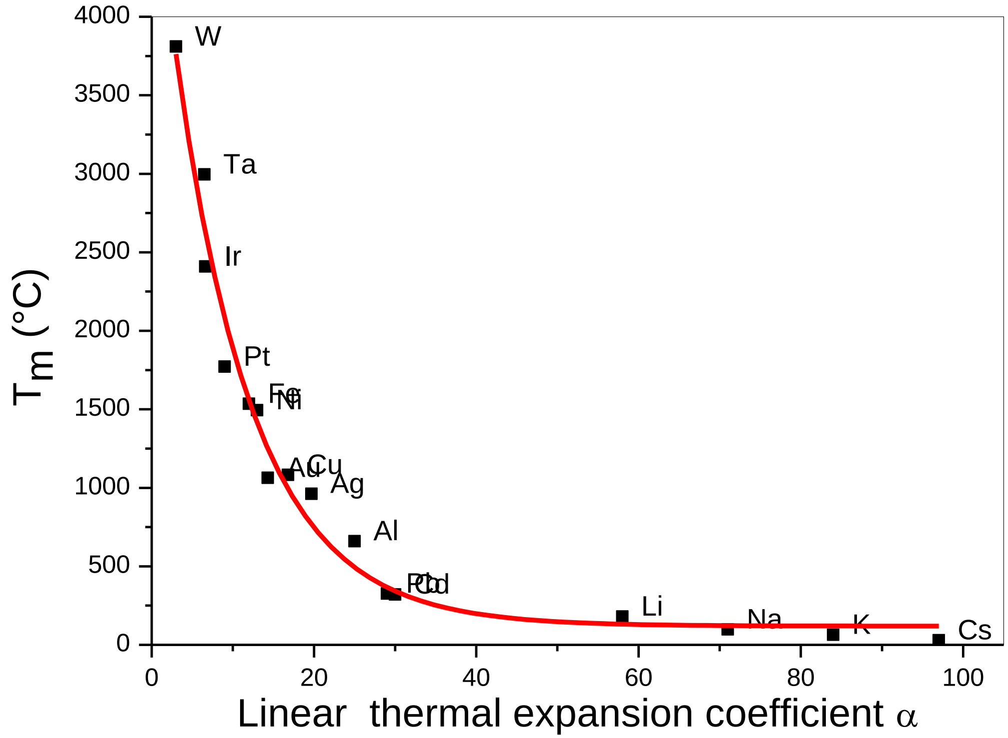
Very high expansion coefficients, due to only weak bonding interactions (van-der-Waals, H-bonds) between the individual polymer chains

Teflon	α = 150 ppm/K
Nylon-6,6	α = 80 ppm/K

2.2 Thermal Properties

Thermal Expansion Coefficient and Melting Point

Metal	T_m [°C]	α [ppm/K]
W	3810	3.0
Ta	2996	6.5
Ir	2410	6.6
Pt	1772	9.0
Fe	1535	12.0
Ni	1495	13.0
Au	1064	14.3
Cu	1083	16.8
Ag	962	19.7
Al	660	25
Pb	327	29
Cd	321	30
Li	180	58
Na	98	71
K	64	84
Cs	29	97



2.2 Thermal Properties

Thermal Expansion Coefficient – Challenges for Materials Sciences

Composites

- Expansion coefficients of the individual components must be adjusted properly, so that the material does not break upon temperature changes

Development of materials with extremely low expansion coefficients

- *Example:* Zerodur made by Schott

  Glass ceramics based on $Li_2O \cdot Al_2O_3 \cdot SiO_2$ (Zerodur):

  Glass possess a positive expansion coefficient,
  crystals exhibit negative expansion coefficients
  $\Rightarrow \alpha$(Zerodur) = 0.02 ppm/K
  Application: Ceran hobs

Examples for substances with negative thermal expansion

- $H_2O(l)$ 0 – 4 °C
- $H_2O(s)$ < 0 °C
- Silicon
- Some zeolites
- Some tungstates and molybdates

2.2 Thermal Properties

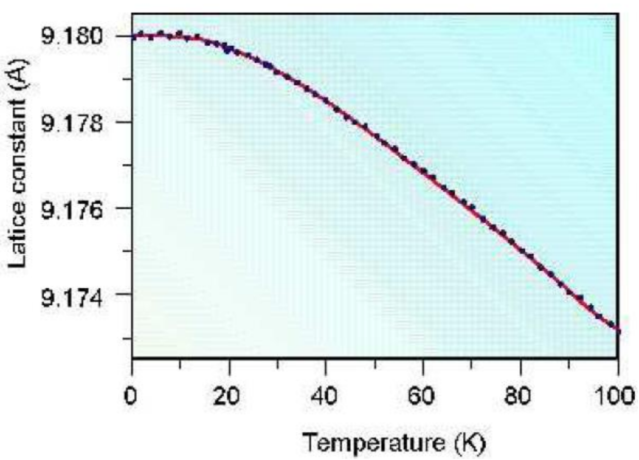
Negative Thermal Expansion Occurs in Crystals with Highly Open Structure

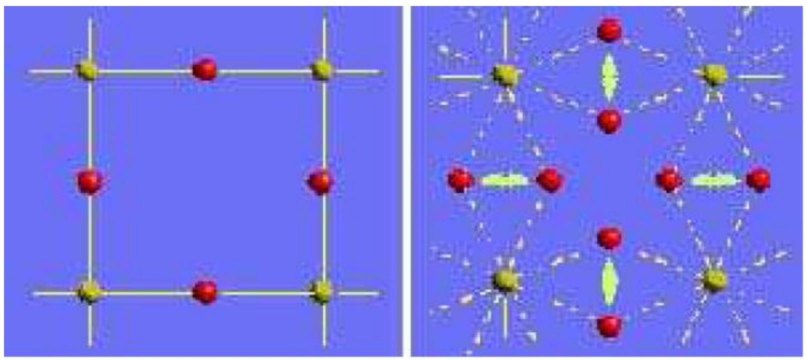
Cause

Cooperative vibrational modes or so-called liberation movements of adjacent polyhedra

Example: **ZrW_2O_8 discovered by A. Sleight in 1998 (Inorg. Chem. 37 (1998) 2854)**

- **negative thermal expansion from T = 0 K until decomposition at 1050 K**
- **Liberation movements of ZrO_6-octahedra and WO_4-tetrahedra**
- **Liberation overcompensates normal thermal expansion**
- **Numerous technical applications, e.g. electronics, optics, fuel cells, oxygen sensors, shock absorbers, thermostats, dentures**



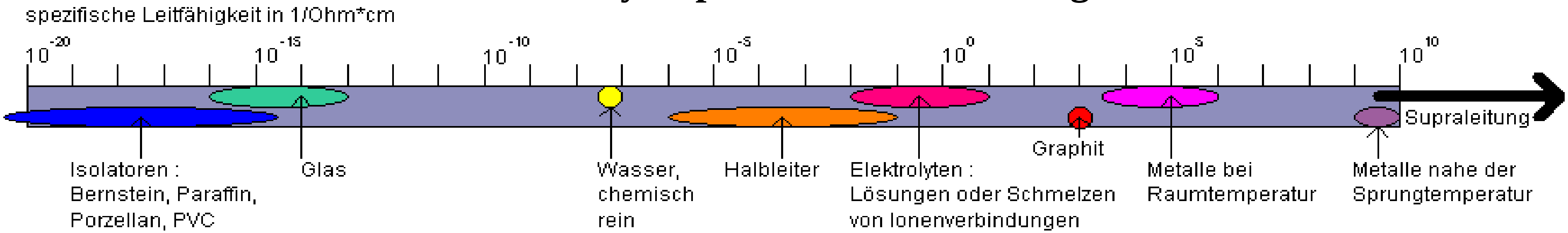


2.3 Electrical and Dielectrical Properties

Relevance

1. **Minimisation of thermal loss in power lines**
   ⇒ **as high electrical conductivity as possible of the cable materials**

2. **Prevention of disruptive discharges or generation of light arcs**
   ⇒ **as low electrical conductivity as possible of the isolating materials**



3. **Enhancement of the efficiency of solar cells as alternative energy sources**
   ⇒ **as high efficiency as possible of the formation of electron/hole pairs and their consecutive separation**

4. **Miniaturisation in electronics**
   ⇒ **selective fine-tuning of electrical conductivity**

2.3 Electrical and Dielectrical Properties

Ohm's Law and Electrical Conductivity

Ohm's law $R = U/I$

Resistance R depends on
- **Properties of conductive material**
- **Dimensions of conductor**

$$R = \rho \cdot \frac{l}{A} = \frac{1}{\sigma} \cdot \frac{l}{A}$$

R = resistance[Ω]
U = voltage[V]
I = current [A]
ρ = specific resistance [Ω·m]
A = cross-sectional area [m^2]
l = length of conductor [m]
P = power [W]
σ = specific conductivity [$\Omega^{-1} \cdot m^{-1}$]

According to the above equation, the dimensions of resistors can be adjusted for a particular application. Furthermore, the thermal loss should be as small as possible in order to minimize energy loss and unnecessary heating of the conductor.

Thermal loss $P = U \cdot I = I^2 \cdot R$

2.3 Electrical and Dielectrical Properties

Specific Resistance and Specific Conductivity

⇒ Specific material properties

<u>Type of charge carrier</u>

- Electrons
- Ions (cations > anions)

The specific conductivity/resistance of a material depends on charge, number density and the mobility of the charge carriers.

$$\sigma = N_V \cdot q \cdot \mu$$

N_V = number of charge carriers per volume [m^{-3}]
q = electrical charge [C]
μ = electronic mobility [$m^2 \cdot V^{-1} \cdot s^{-1}$]

<u>Electrical conduction in</u>

- Semi-conductors and insulators number of charge carriers crucial
- Metals mobility of charge carriers crucial

2.3 Electrical and Dielectrical Properties

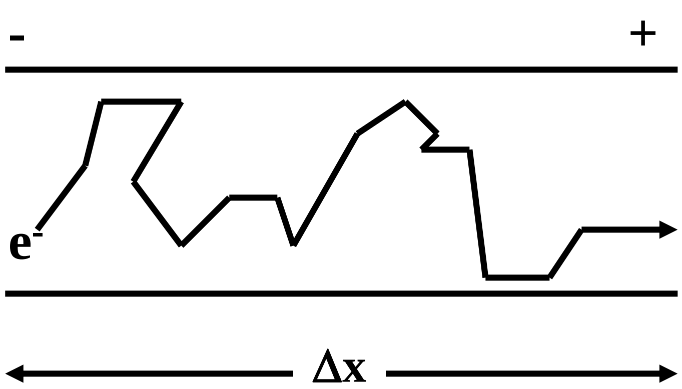
Definition of Electrical mobility μ

⇒ The electronic mobility μ is defined as the drift velocity of the charge carriers with regard to the applied electrical field strength

$$\mu = v/E$$

v = drift velocity [m/s]
E = electrical field strength [V/m]

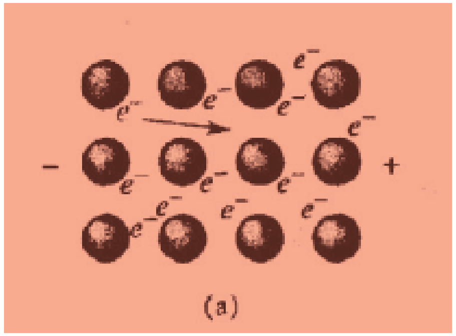
The drift velocity $v = \Delta x/\Delta t$ is the average velocity of the charge carriers along the direction of the applied field

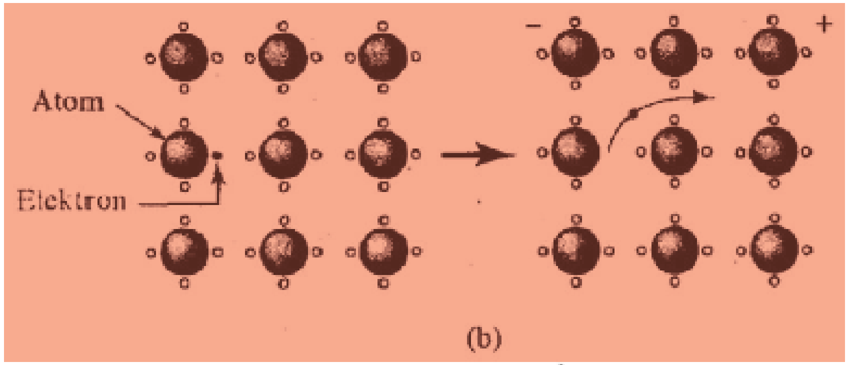


Coincidental movements of charge carriers in a conductor due to scattering at atoms and lattice perturbations (impurities)

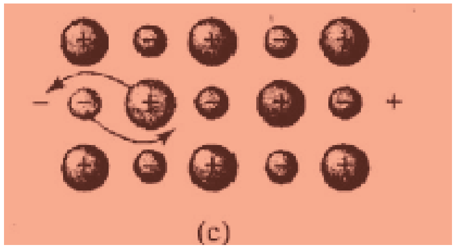
Charge Carriers in Different Materials

a)	Metals	mobile valence electrons
b)	Semi-metals/insulators	promotion of electrons from valence into conduction band by breaking of covalent bonds
c)	Ionic solids	Diffusion of ions



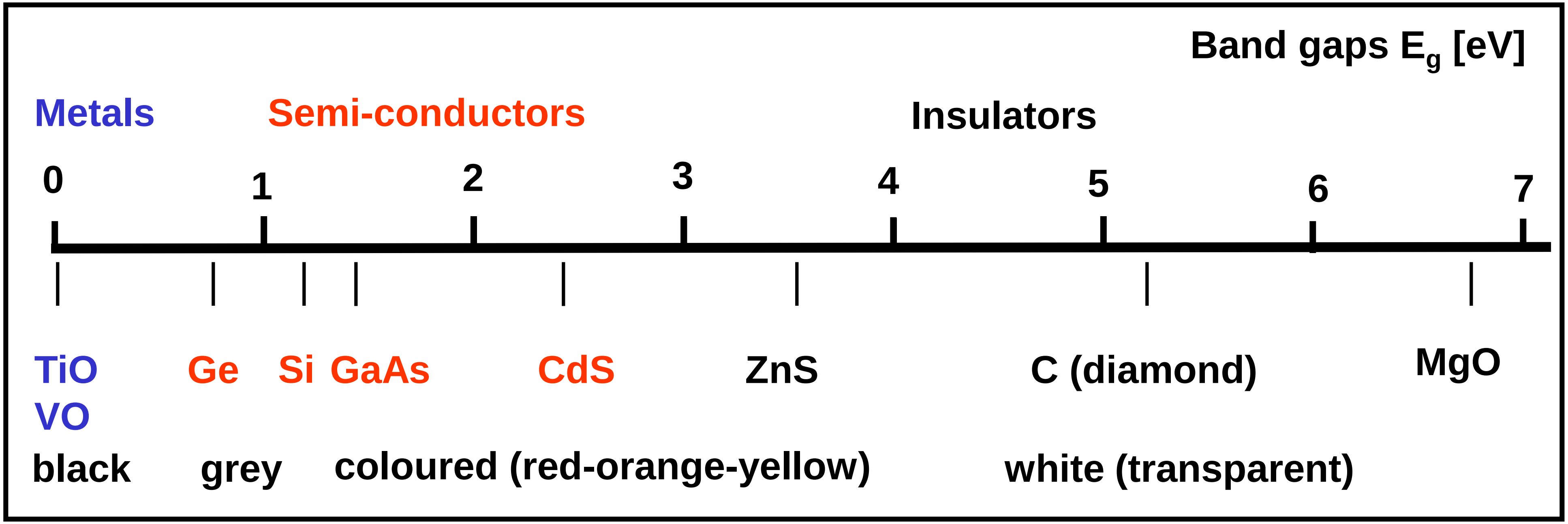


according to D.R. Askeland
Materialwissenschaften
Spektrum-Verlag 1996



2.3 Electrical and Dielectrical Properties

Band Gaps of Materials



Metals are black and intransparent, because visible light of each wavelength is absorbed

Semi-conductors are coloured, because light of a particular colour (energy) is absorbed (valence electrons are excited via band gap)

In insulators, the band gap is too high for visible light to excite the valence electrons. Thus, most insulators are colourless or transparent

2.3 Electrical and Dielectrical Properties

Specific Electrical Conductivity of Selected Materials

Material	Electronic configuration	Specific conductivity [$\Omega^{-1} \cdot m^{-1}$]
Na	$[Ne]3s^1$	$2.13 \cdot 10^5$
K	$[Ar]4s^1$	$1.64 \cdot 10^5$
Mg	$[Ne]3s^2$	$2.25 \cdot 10^5$
Ca	$[Ar]4s^2$	$3.16 \cdot 10^5$
Al	$[Ne]3s^2 3p^1$	$3.77 \cdot 10^5$
Ga	$[Ar]4s^2 3d^{10} 4p^1$	$0.66 \cdot 10^5$
Fe	$[Ar]4s^2 3d^6$	$1.00 \cdot 10^5$
Ni	$[Ar]4s^2 3d^8$	$1.46 \cdot 10^5$
Cu	$[Ar]4s^1 3d^{10}$	$5.98 \cdot 10^5$
Ag	$[Kr]5s^1 4d^{10}$	$6.80 \cdot 10^5$
Au	$[Xe]6s^1 5d^{10}$	$4.26 \cdot 10^5$
C_{cubic} (diamond)	$[He]2s^2 2p^2$	$< 1 \cdot 10^{-18}$
Si	$[Ne]3s^2 3p^2$	$5.0 \cdot 10^{-6}$
Ge	$[Ar]4s^2 4p^2$	0.02
Sn	$[Kr]5s^2 5p^2$	$0.9 \cdot 10^5$
Polyethylene	-	$1 \cdot 10^{-15}$
Polytetrafluoroethylene	-	$1 \cdot 10^{-18}$
Al_2O_3	-	$1 \cdot 10^{-14}$
SiO_2 (quartz glass)	-	$1 \cdot 10^{-17}$

Methods to Engineer Electrical Conductivity

In pure, defect-free metals, the conductivity depends solely on the mobility of the charge carriers:

- **Mobility is proportional to drift velocity**
- **Which depends on the average free path length**
- **The higher the average free path length the higher is the mobility and thus the electrical conductivity**
- **The average free path length is defined as the average distance which can be covered by the electrons between two impacts ⇒ temperature-dependant resistance ρ_T**

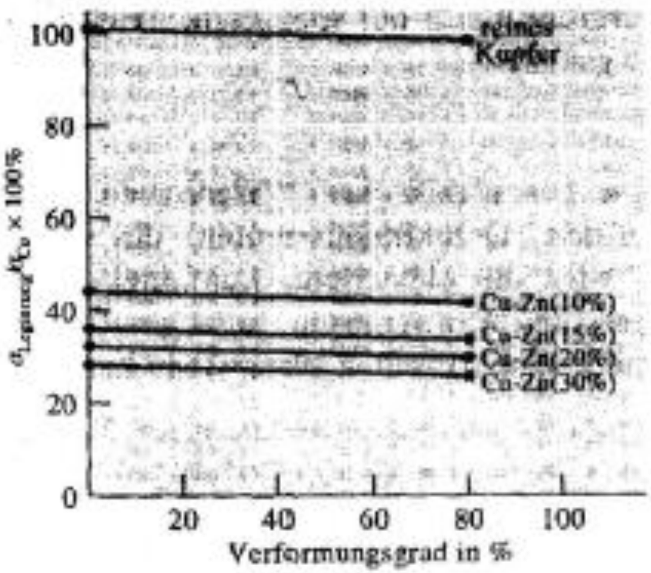
Influence of lattice perturbations (voids, interstitials, grain boundaries, alien atoms)

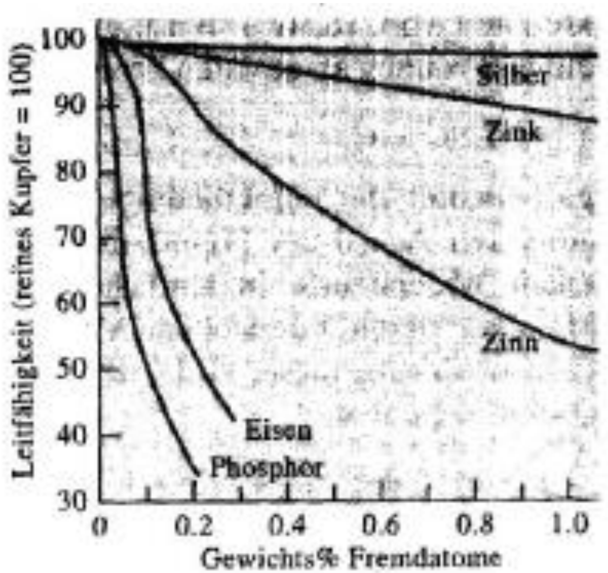
- **By scattering of electrons at lattice perturbations the mobility and thus the conductivity is reduced**
- **Scattering at lattice vibrations yields a temperature-dependant term to the resistance**
  $\rho_d = b \cdot (1-x) \cdot x$ **with x = 0.0 – 1.0 = relative amount of alien atoms**
- **The total resistance ρ is given by the addition of the temperature-dependant resistance and the resistance resulting from lattice perturbations**
  $\rho = \rho_d + \rho_T$

2.3 Electrical and Dielectrical Properties

Methods to Engineer the Electrical Conductivity

Influence of fabrication and annealing





according to D.R. Askeland Materialwissenschaften Spektrum-Verlag 1996

Formation of mixed crystals + cold forming

Influence of alien atoms

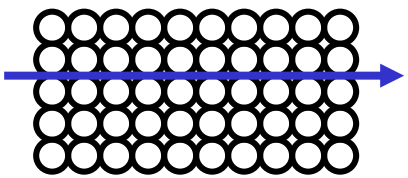
- Cold forming is a effective method to harden materials, whilst the electrical properties remain almost unchanged
- Tempering leads to a reduction of defects and thus to a higher electrical conductivity (Exp.: Annealing of Cu)

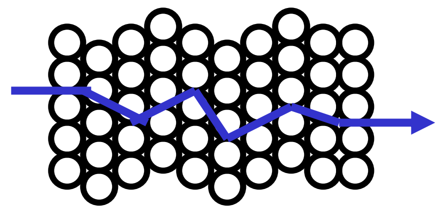
Influence of Temperature (Metals)

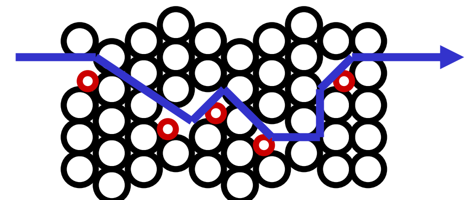
In metals, a high density of charge carriers is present, independent of the temperature. The movement of the conductive electrons accelerated by a applied voltage is hindered by impacts with the thermally excited lattice.

Electron movement in

ideal crystals (at rest)   **Ideal crystals (thermally excited)**   **real crystals (thermally excited)**



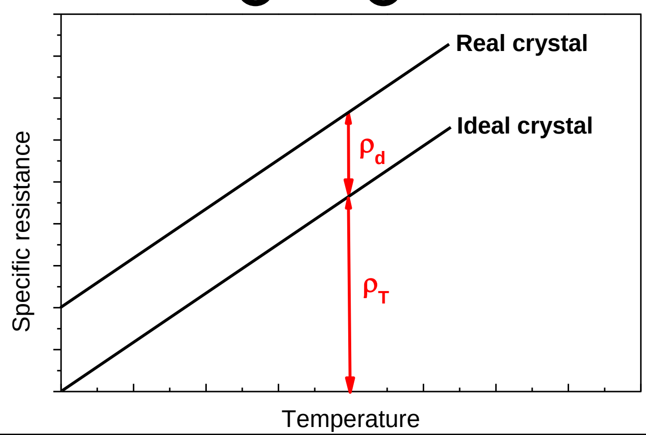




$$\rho_T = \rho_r \cdot (1 + \alpha \Delta T)$$

$$\rho = \rho_d + \rho_T$$

$$\Rightarrow \quad \rho = \rho_d + \rho_r \cdot (1 + \alpha \Delta T)$$



with α = temperature coefficient [Ωcm/K]

ρ_T = T-dependant resistance

ρ_d = defect-dependant resistance

2.3 Electrical and Dielectrical Properties

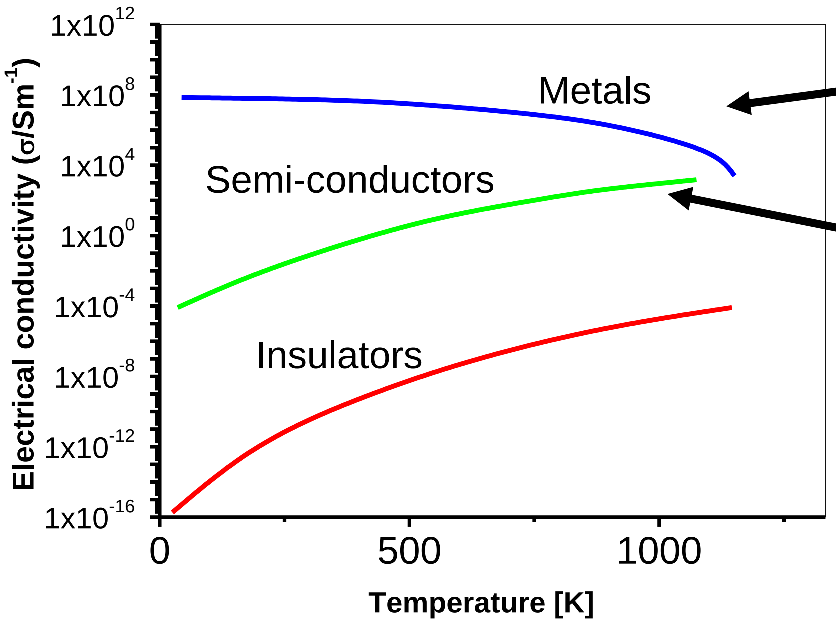
Influence of Temperature (Metals)

Mobility and electrical conductivity are reduced by scattering, leading to a almost linear increase of the resistance with regard to the temperature (rule of Mathiesen)

Metal	Specific resistance ρ_r at room temp. [10^{-6} Ωcm]	Temperature coefficient α [K^{-1}]
Be	4.0	0.0250
Mg	4.45	0.0165
Ca	3.91	0.0042
Al	2.65	0.0043
Cr	12.90	0.0030
Fe	9.71	0.0065
Co	6.24	0.0060
Ni	6.84	0.0069
Cu	1.67	0.0068
Ag	1.59	0.0041

2.3 Electrical and Dielectrical Properties

Influence of Temperature (Metals - Semi-Conductors - Insulators)



~10^{22} free electrons per cm^3

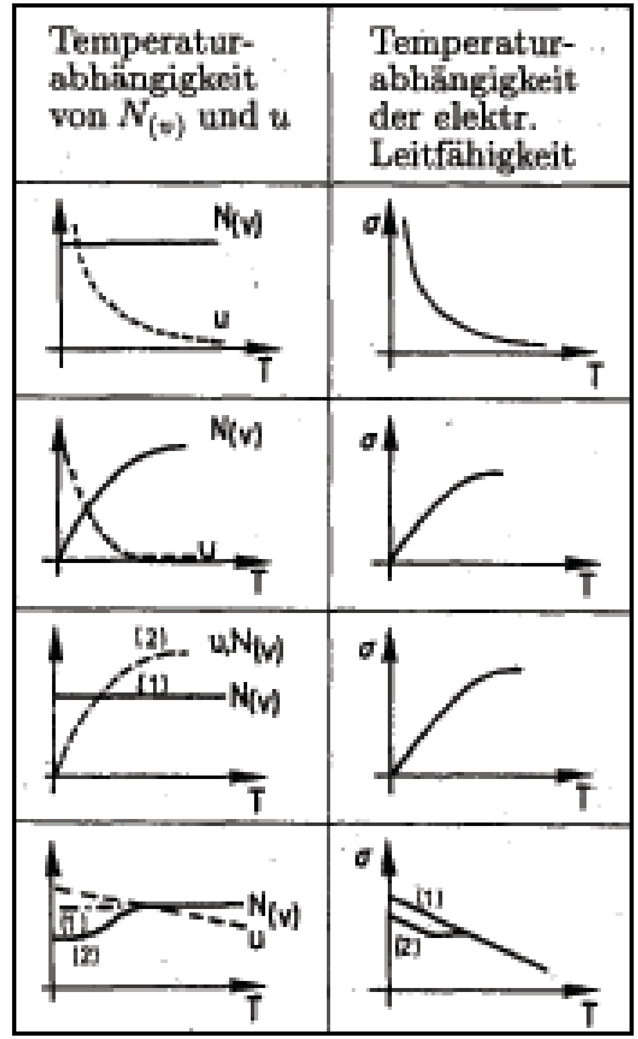
10^{13}-10^{17} free electrons per cm^3

Metals: Electrical conductivity decreases with increasing temperature

Semi-conductors + insulators: Electrical conductivity increases with temperature

Influence of the Temperature on Different Types of Electrical Conductors

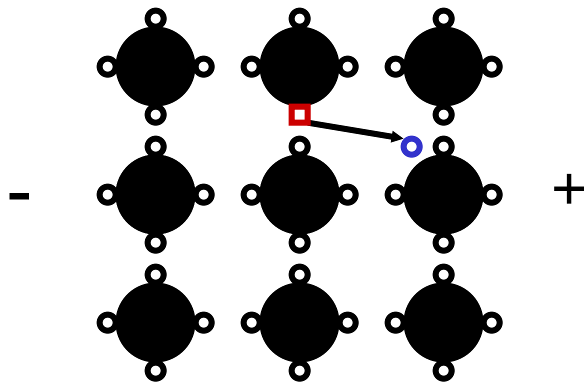
Type	charge carrier density N_V	mobility μ
Metals	const.	$\sim T^{-1}$
Intrinsic semi-conductors	$\sim \exp(-\Delta E/kT)$	$\sim T^{-3/2}$
Solid electrolytes	const. (1) $\sim \exp(-\Delta E/kT)$ (2)	$\sim \exp(-\Delta E/kT)$
Liquid electrolytes	const. (1) $\sim \alpha_T$ (2)	decreasing

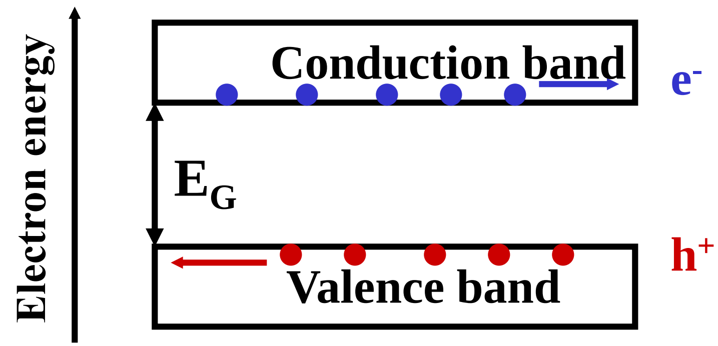


2.3 Electrical and Dielectrical Properties

Influence of Temperature (Intrinsic Semi-conductors)

Semi-conductors and intrinsic semi-conductors need electrons in the conduction band to become electrically conductive





- **The number of electrons and holes in intrinsic semi-conductors is equal**
  - ⇒ **Formation of electron-hole pairs**
  - ⇒ $N_V = N_{V,e} = N_{V,h}$
- **The number of electron-hole pairs limits the specific conductivity**
  - ⇒ $\sigma = N_{V,e} \cdot q \cdot \mu_e + N_{V,h} \cdot q \cdot \mu_h$

    μ_e = **mobility of electrons**

    μ_h = **mobility of holes**
  - ⇒ $\sigma = N_V \cdot q \cdot (\mu_e + \mu_h)$

2.3 Electrical and Dielectrical Properties

Influence of Temperature (Intrinsic Semi-conductors)

The number of electron-hole pairs N_V (excitons) strongly depends on temperature!

T = 0 K

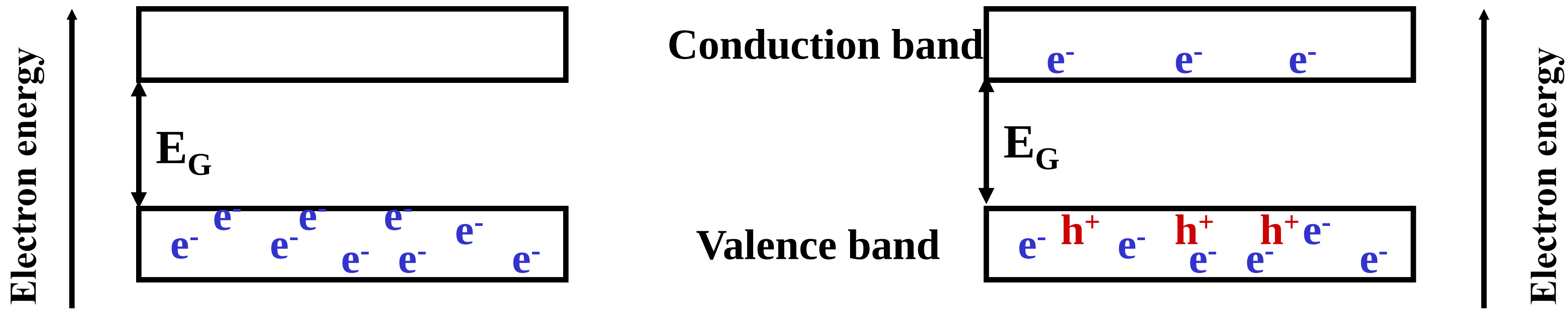
⇒ all electrons in valence band

$N_V = 0$

T > 0 K

⇒ probability for the transition of a electron into the conduction band increases with increasing temperature

$N_V = N_{V,e} = N_{V,h} = N_{V,\infty} \cdot \exp(-E_G/2kT)$
($k = 1.38 \cdot 10^{-23}$ J/K)



2.3 Electrical and Dielectrical Properties

Influence of Temperature (Intrinsic Semi-conductors)

The electrical conductivity σ of a intrinsic semi-conductor is given by:

$\sigma = N_V \cdot q \cdot (\mu_e + \mu_h)$ and $N_V = N_{V,e} = N_{V,h} = N_{V,\infty} . \exp(-E_G/2kT)$ combined to:

$\sigma = q \cdot (\mu_e + \mu_h) \cdot N_{V,\infty} . \exp(-E_G/2kT)$

Material	Electronic mobility[$cm^2/V \cdot s$]	Mobility of holes [$cm^2/V \cdot s$]
Csp^3	1800	1400
Si	1900	500
Ge	3800	1820
Sn	2500	2400
GaP	300	100
GaAs	8800	400

- The mobility of the electrons and holes is proportional to $T^{-3/2}$, thus decrease with increasing temperature
- But the temperature dependence of the number density is so dominating that the conductivity still increases with temperature

2.3 Electrical and Dielectrical Properties

The Size of the Band Gap E_G Depends on the Chemical Composition, the Difference in Electronegativity and on the Structure

Substance	Structure type	Band gap E_G [eV]	EN-difference
MgF_2	Rutile	12.0	2.9
MgO	Rock salt	7.8	2.3
AlN	Wurtzite	6.2	1.4
Csp^3	Diamond	5.3	0.0
GaN	Wurtzite	3.5	1.2
AlP	Zinc blende	3.0	0.6
GaP	Zinc blende	2.2	0.4
Si (crystalline)	Diamond	1.1	0.0
ZnSe	Zinc blende	2.3	0.9
GaAs	Zinc blende	1.3	0.4
Ge	Diamond	0.7	0.0
InSb	Zinc blende	0.18	0.2
α-Sn (grey)	Diamond	0.08	0.0

2.3 Electrical and Dielectrical Properties

Influence of Temperature (Doped Semi-conductors)

- **In doped semi-conductors (impurity semi-conductors) foreign atoms (dopants) are added**
- **The type of the atom is responsible for the type of conduction possible, the number of foreign atoms defines the conductivity**

One differentiates between:

n-semi-conductors, which are created by adding elements with more valence electrons (electronic conductions dominates: n-(negative)-semi-conductor)

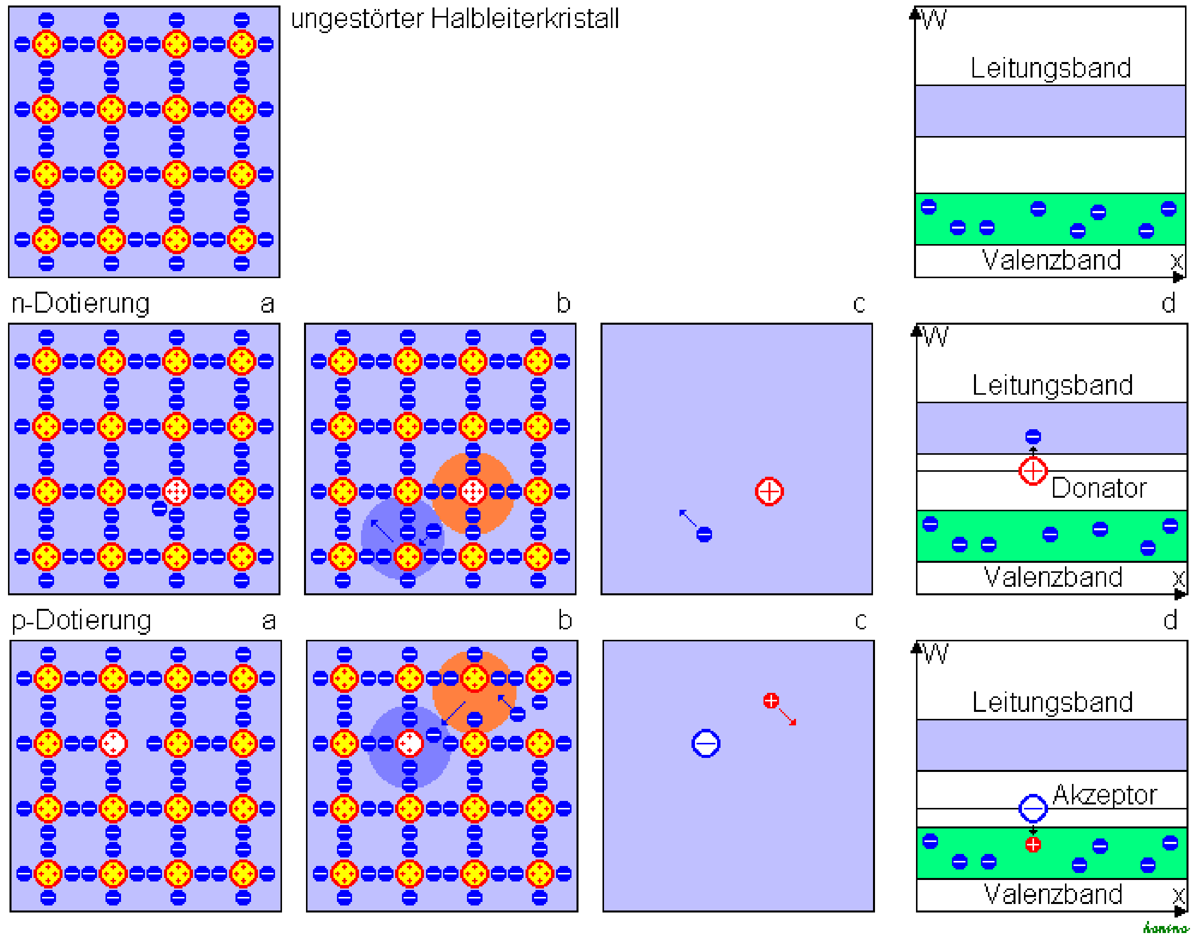
and

p-semi-conductor, which are created by the addition of elements with less valence electrons (conduction via holes dominates: p-(positive)-semi-conductors)

2.3 Electrical and Dielectrical Properties

Impurity Semi-conductors = Intrinsic Semi-conductors + Dopants

<u>**Example: Doping of Silicon**</u>
By doping pure silicon ($\sigma = 5{\cdot}10^{-6}\ \Omega^{-1}cm^{-1}$) its conductivity can be enhanced



n-Si donors:
P, As, Sb "electron conductors"
1 ppm P $\Rightarrow \sigma = 10\ \Omega^{-1}cm^{-1}$

p-Si acceptors:
B, Al, Ga, In „Lochleiter"
1 ppm B $\Rightarrow \sigma = 4\ \Omega^{-1}cm^{-1}$

Typical concentration of dopants: 10^{21} m^{-3} (lattice atoms ~ 10^{28} m^{-3}) $\Rightarrow$ ~10^{-5}%

2.3 Electrical and Dielectrical Properties

Silicon-based Semi-Conductor Materials

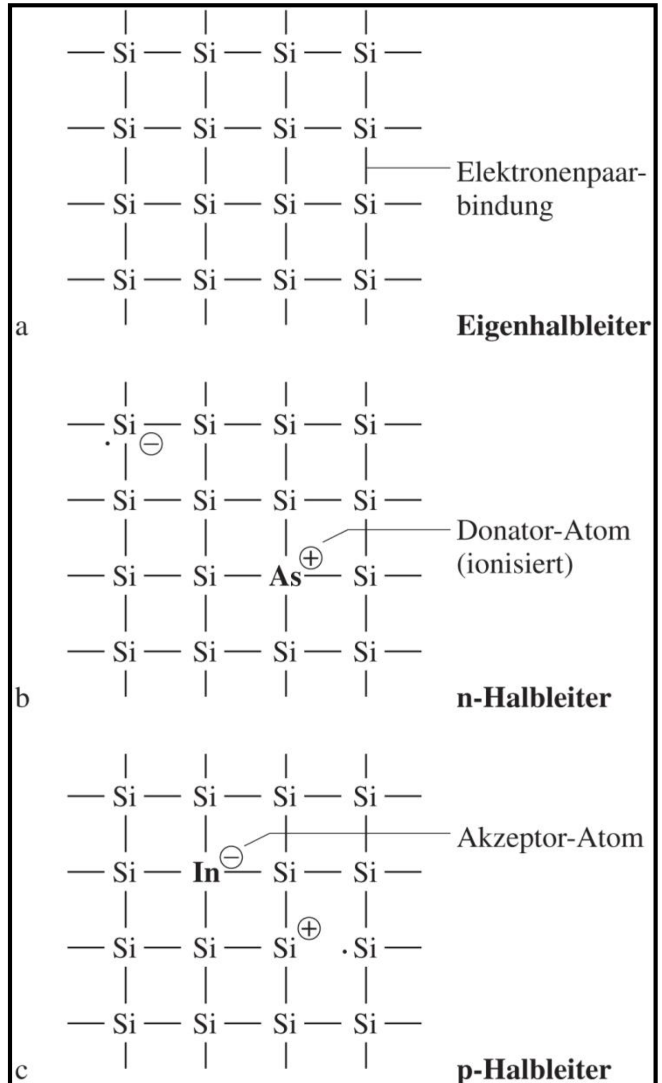
n-semi-conductor Electron excess

P, As, Sb	5 valence electrons
Si	4 valence electrons

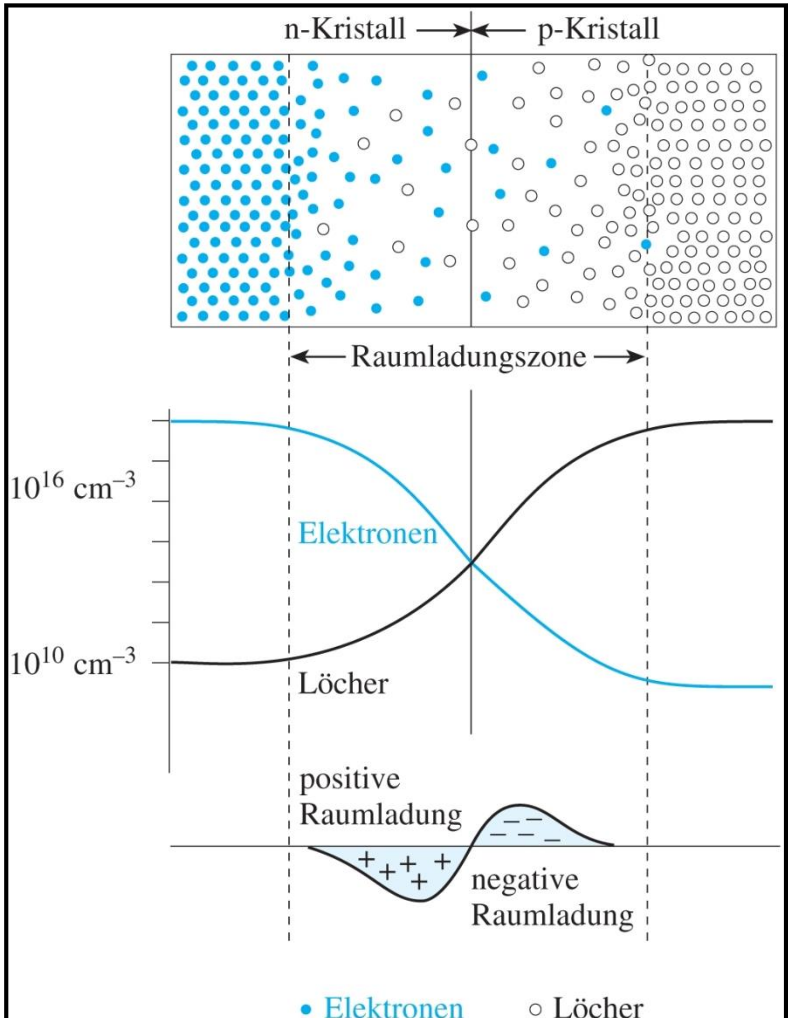
p-semi-conductor Electron deficit

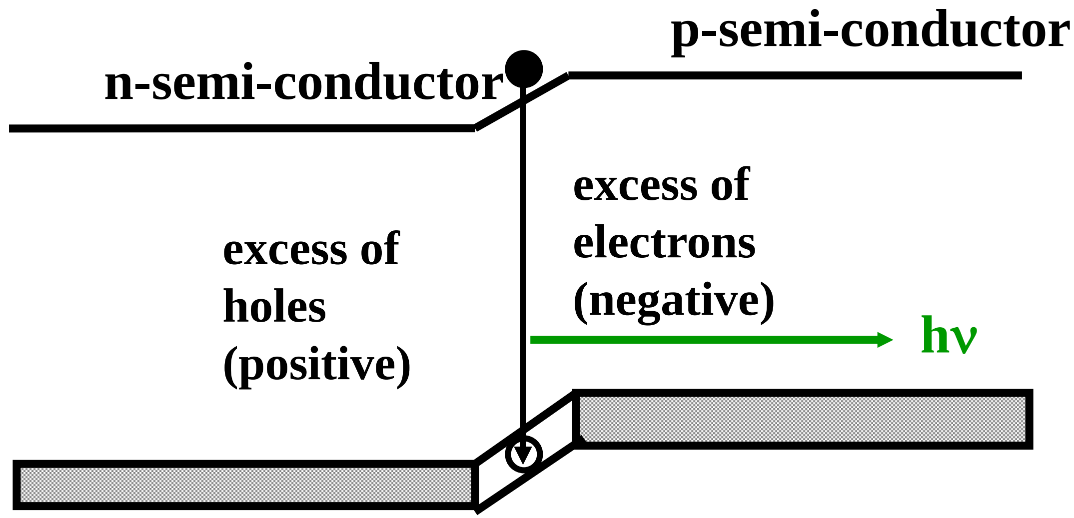
B, Al, Ga, In	3 valence electrons
Si	4 valence electrons

	Si		Ge	
Dopant	E_d [eV]	E_a [eV]	E_d [eV]	E_a [eV]
P	0.045		0.0120	
As	0.049		0.0127	
Sb	0.039		0.0096	
B		0.045		0.0104
Al		0.057		0.0102
Ga		0.065		0.0108
In		0.160		0.0112



Excursion: p/n-Diode (Borderline between n- and p-doped Semi-conductor Crystal)





+ pole **- pole**

broadening of barrier layer ⇒ no current

- pole **+ pole**

termination of barrier layer ⇒ current

2.3 Electrical and Dielectrical Properties

Influence of Temperature (Doped Semi-conductor)

Besides impurities, i.e. the donor, there is intrinsic conductivity as well

The total number density of charge carriers sums up to:

$N_{V,tot} = N_{V,e,\ donor} + N_{V,e,intrinsic} + N_{V,h,intrinsic}$ **for n-semi-conductor**

$N_{V,tot} = N_{V,h,acceptor} + N_{V,e,intrinsic} + N_{V,h,intrinsic}$ **for p-semi-conductor**

contribution of dopants — **contribution of intrinsic conductivity**

$$N_{V,tot} = N_{V,\infty,donor} \cdot \exp(-E_d/kT) + 2N_{V,\infty,intrinsic} \cdot \exp(-E_G/2kT)$$

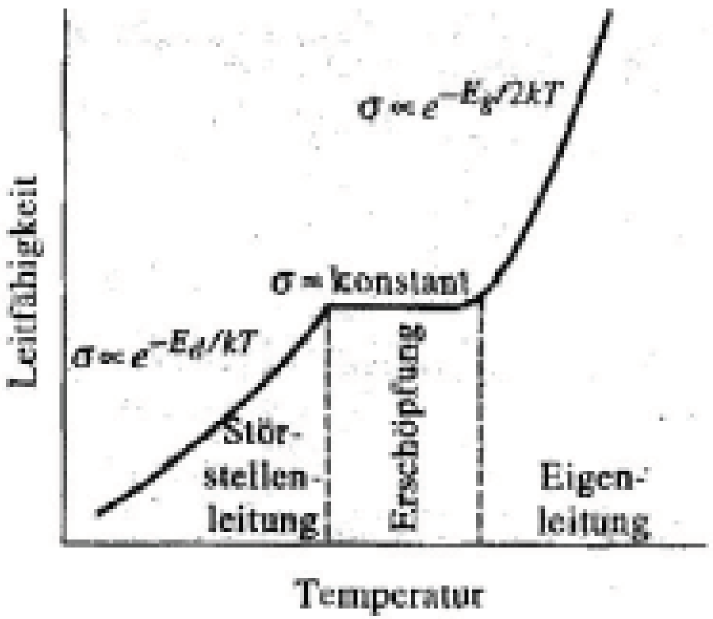
- **At low temperatures, intrinsic conductivity is neglectable, but at high temperatures, becomes the dominating factor**
- **In between, there is a plateau-like area, where conductivity is temperature-independant (donor-depletion)**

2.3 Electrical and Dielectrical Properties

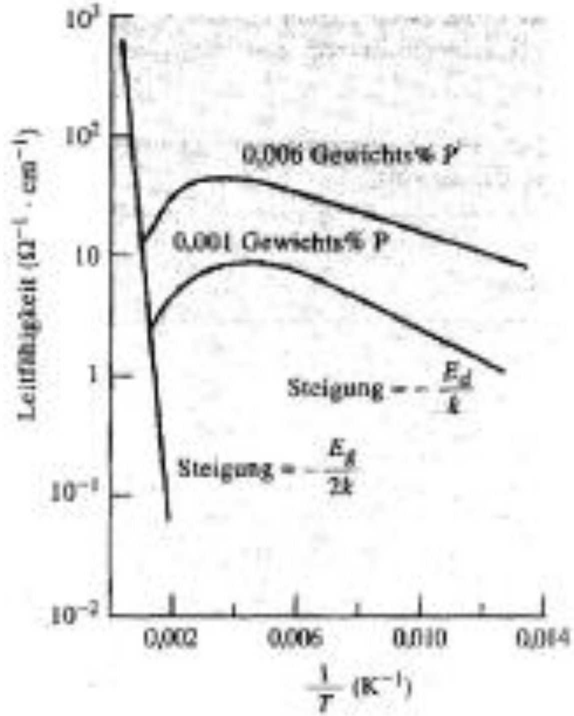
Influence of Temperature (Doped Semi-conductor)

Si:P (n-semi-conductor)

Linear depiction



Arrhenius depiction (lnσ over 1/T)



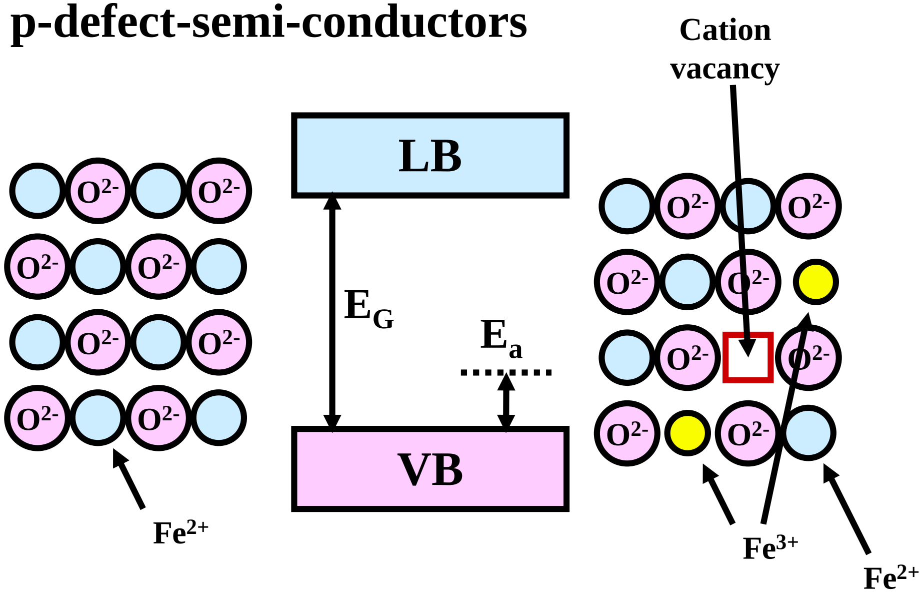
Source: ***D.R. Askeland, Materialwissenschaften, Spektrum-Verlag 1996***

2.3 Electrical and Dielectrical Properties

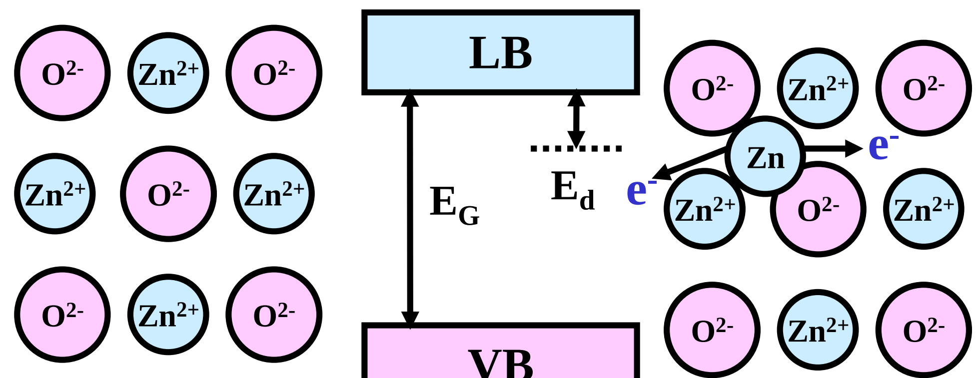
Influence of Temperature (Defect Semi-conductor)

Defect semi-conductors or non-stoichiometric semi-conductors are ionic compounds, which comprise either a excess of anions (p-conduction) or cations (n-conduction)

$Fe_{1-x}O$
p-defect-semi-conductors



ZnO_{1-x} (ZnO:Zn)
n-defect-semi-conductor



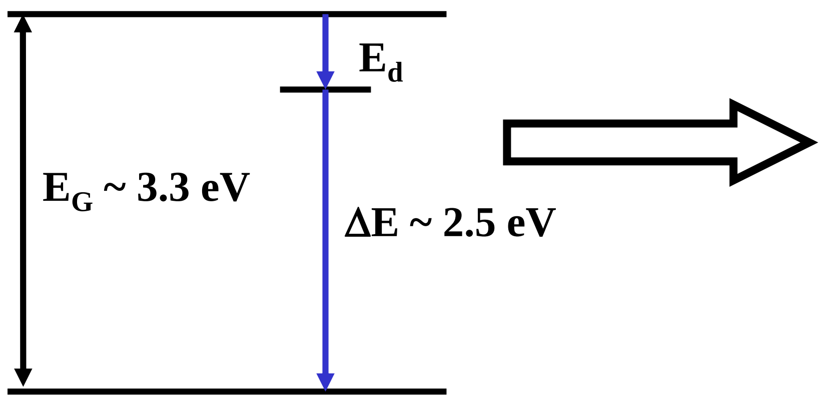
- **Exists for compounds, where the cation tends to interchange valences!**
- **Defects in optical materials lead to greying (phosphors, pigments)**

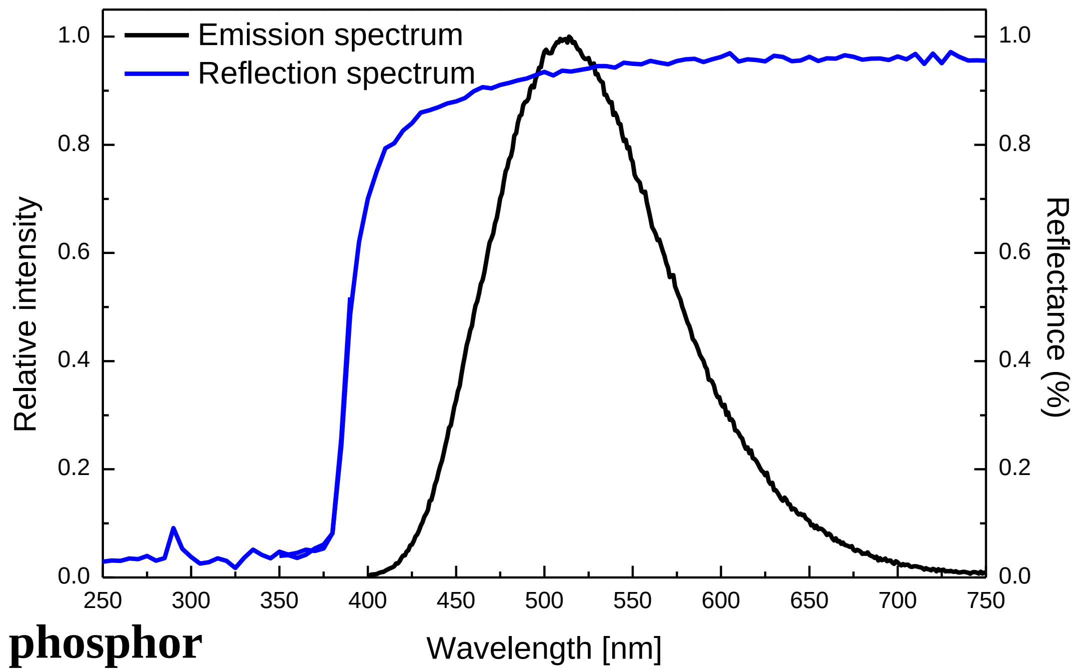
Defect-semi-conductors Show Luminescence

Example: ZnO:Zn,$V^{\cdot\cdot}_O$

$$Zn^x_{Zn} + O^x_O \xrightarrow{ZnO} Zn^x_i + 0.5\ O_2 \quad \text{sowie} \quad Zn^x_{Zn} + O^x_O \xrightarrow{ZnO} Zn^x_{Zn} + V^{\cdot\cdot}_O + 0.5\ O_2$$

Sauerstoffdefekte = Donatoren, n-Halbleiter **Emissions- und Reflexionsspektrum**

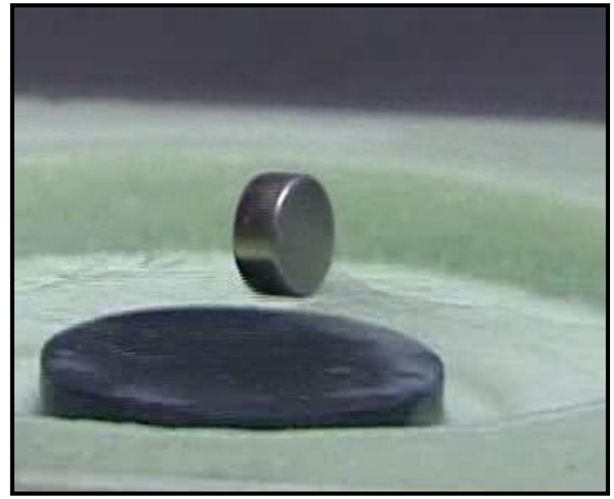




⇒ Application as an electroluminescence phosphor

2.3 Electrical and Dielectrical Properties

Influence of Temperature: Superconductor



Floating high-temperature superconductor in a magnetic field

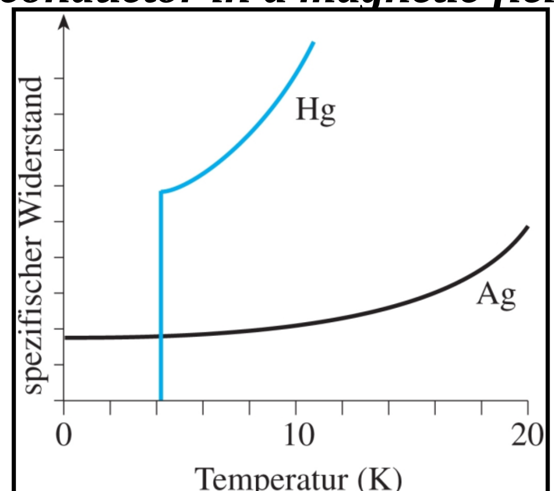
Definition

Superconductors are materials that loose any electrical resistance at a certain temperature (transition temperature), and then suppress subcritical magnetic fields from their inside (Meißner-Ochsenfeld-effect)

⇒ Already observed for more than 10000 materials

Normal conductors

Scattering of electrons at defects and interactions with lattice vibrations (electron-phonon-scattering) ⇒ fermions



Superconductors

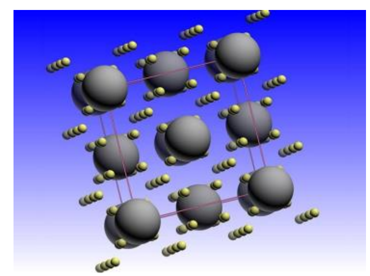
Coupling of conduction electrons by electron-phonon inter-actions ⇒ bosons (spin: 0, 1ħ, 2ħ)

2.3 Electrical and Dielectrical Properties

History of Superconductor Research

Year	Material	T_c [K]	Autor/Literatur
1911	Hg	4.2	*H.K. Onnes*
1930	Nb	9.3	
1933	Meißner-Ochsenfeld-effect		*W. Meißner, R. Ochsenfeld*
1950	Nb_3Sn	18.1	
1957	BCS-theory		*Bardeen, Cooper, Schrieffer*
1972	Nb_3Ge	23.3	
1986	$La_{1.8}Ba_{0.2}CuO_4$	35	*J.G. Bednorz, K.A. Müller*
1987	$YBa_2Cu_3O_{7-x}$	93	
1988	$Bi_2Sr_2Ca_{n-1}Cu_nO_x$	125	
1988	$Tl_2Ba_2Ca_2Cu_3O_{10}$	127	
1993	$HgBa_2Ca_2Cu_3O_{8+x}$	135	
1995	Pressure applications	164	
2019	LaH_{10} at 170 GPa	250	*Nature 569 (2019) 528*

Heike Kamerlingh Onnes 1911



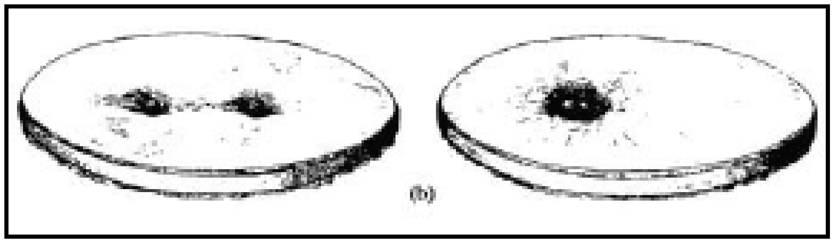
Known superconductors, today: metals, alloys, cuprates, organic compounds, fullerenes

BCS-Theory: Cooper-Pairs

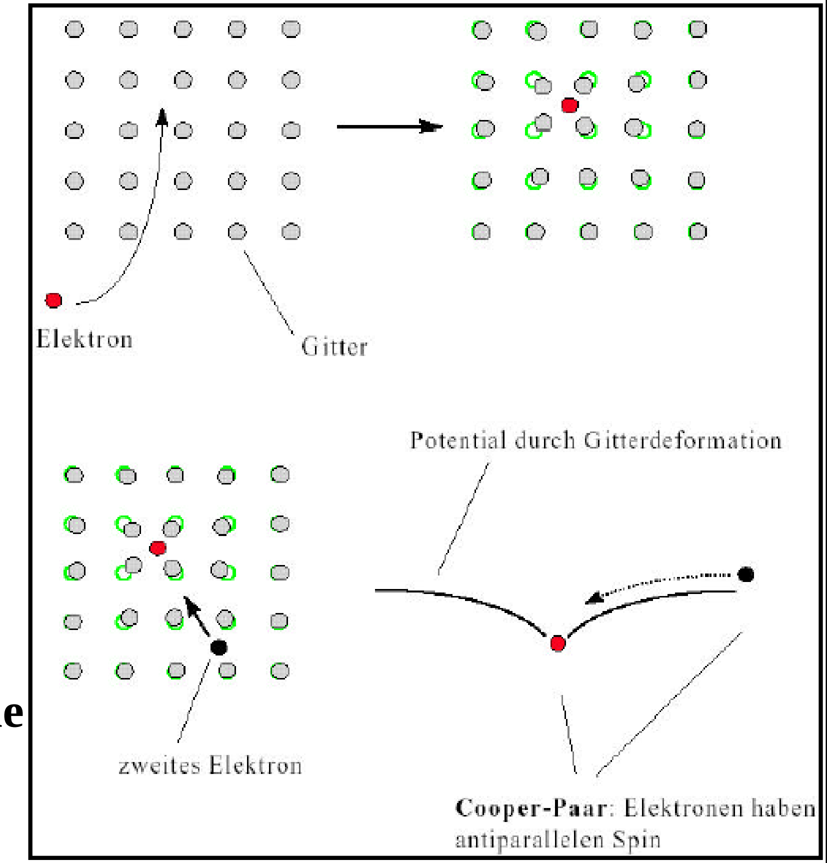
<u>Below T_c, electrons with anti-parallel spins form Cooper-pairs</u>

A electron induces a elastic perturbation of the lattice in its surrounding, due to its charge, i.e. dislocation of the atomic torso. If a electron moves through the lattice, the perturbation follows straight.

In Cooper-pairs, there is a 2nd electron coupled to the first electron via this perturbation.



e⁻-distance: 0.1 – 1 µm!



Cooper-pairs exist only at very low temperatures.

At high temperature, the interaction between the coupled electrons is cancelled and the electrons become Metallic in behaviour.

2.3 Electrical and Dielectrical Properties

High-temperature Superconductors

Prerequisites

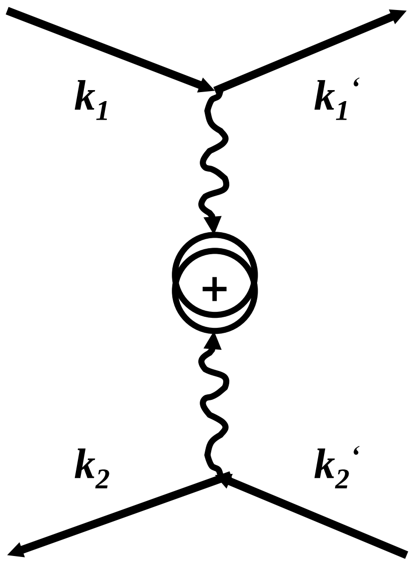
- Strong coupling of electron movement with lattice vibrations

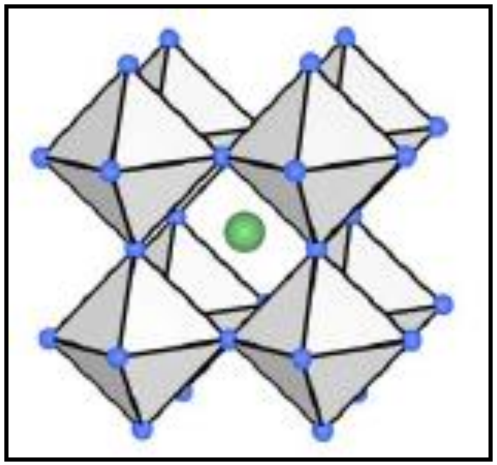
⇒ HT-superconductors should be poor conductors at room temp. (ceramic compounds)

⇒ Good metallic conductors (Cu, Ag) do not show transition into superconducting state

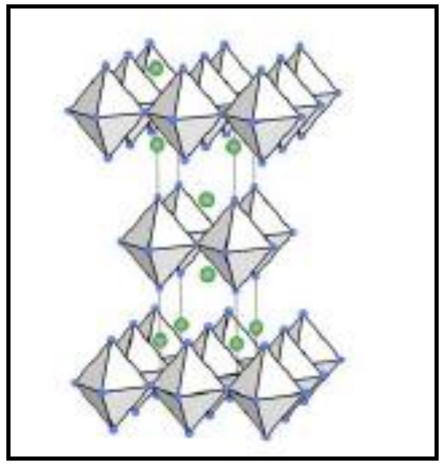
- Ready electrical polarisation of certain lattice elements

⇒ Small cations with high coordination number





$CaTiO_3$ (perowskit)

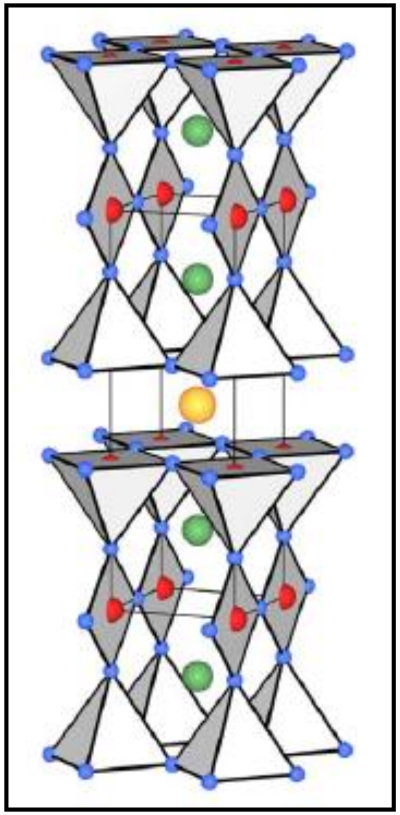


La_2CuO_4 (K_2NiF_4-type)
$La_{1.8}Sr_{0.2}CuO_4$

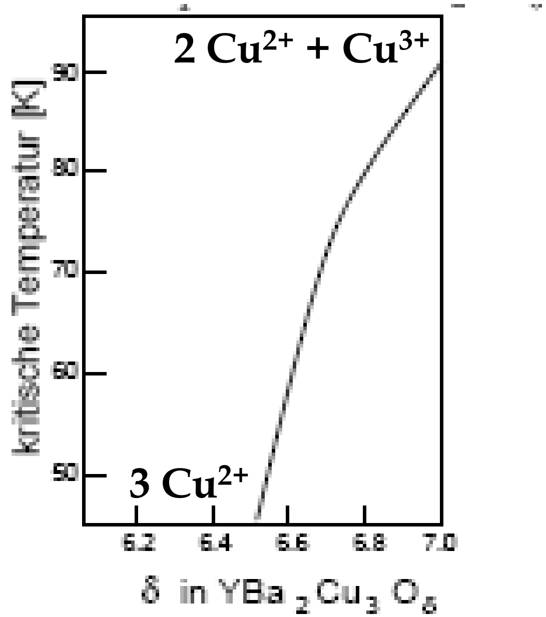
La_2CuO_4 is anti-ferro-magnetic and non-conducting, because Cu^{2+} ([Ar]d^9) shows super exchange
$La_{1.8}Sr_{0.2}CuO_4$ comprises mixed-valent $Cu^{2+/3+}$, destroying the coupling of the electrons and supressing the anti-ferromagnetism.

High-temperature Superconductors

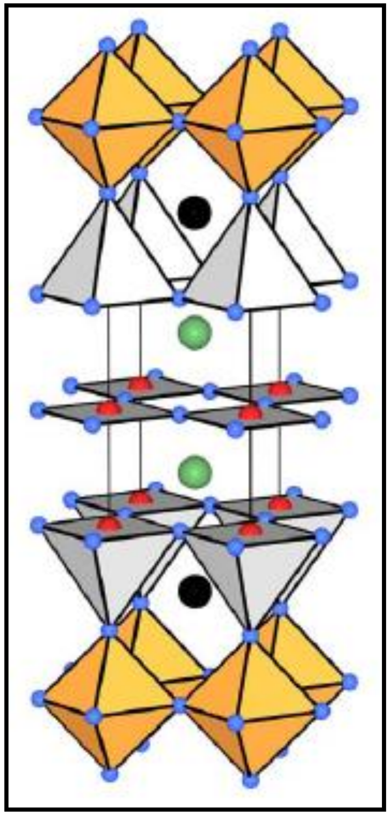
Structure of $YBa_2Cu_3O_{7-x}$



Influence of the oxygen content δ on the transition temperature



Structure of $TlBa_2Ca_2Cu_3O_{8+x}$



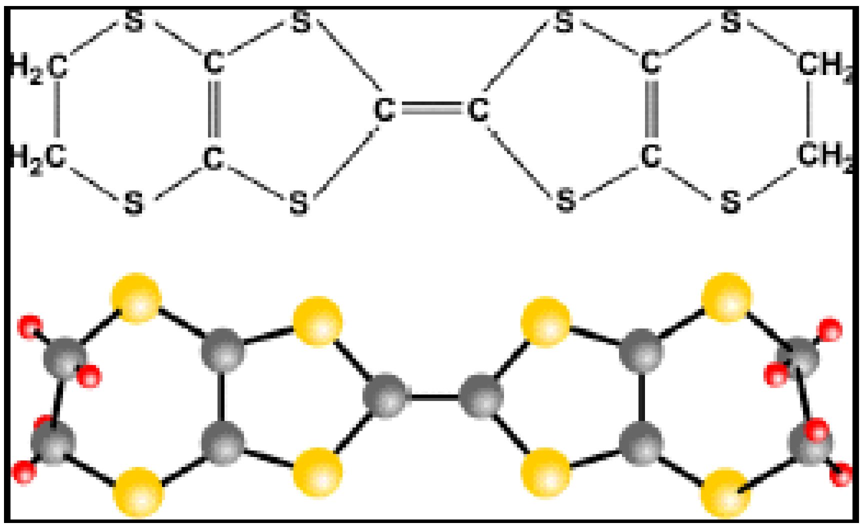
CuO_2-layers mediate the superconductivity, Y^{3+}-cations act as "spacer"

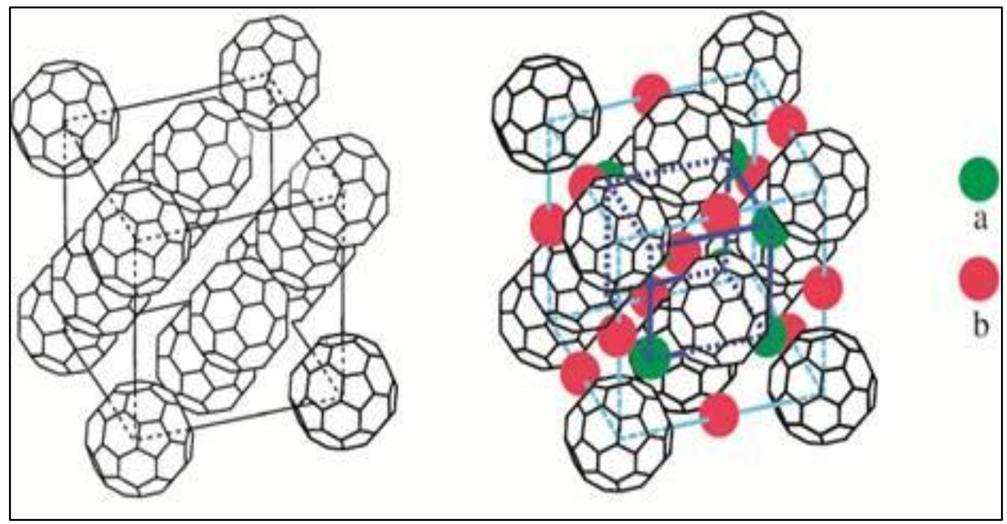
Organic High-temperature Superconductors

Organic compounds, e.g. polymers normally are insulators.
Even there formation of Cooper-pairs is possible (W.A. Little)

- **Theoretical $T_{trans.}$ up to 300 K**
- **High potential due to versatile synthetic routes**

⇒ **Fulleride-superconductor:** K_3C_{60}: T_c = 19 K, Rb_3C_{60}: T_c = 27 K, Cs_3C_{60}: T_c = 40 K
Complex-superconductors: $(BEDT\text{-}TTF)_2Cu(NCS)_2$: T_c = 11 K

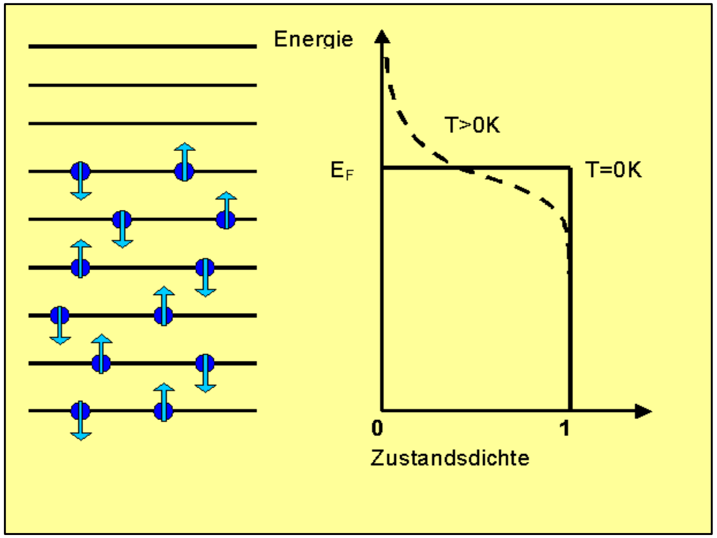




Bis-ethylenedi-thiotetra-thiafulvalene (BEDT-TTF) **C_{60} fullerene**

2.3 Electrical and Dielectrical Properties

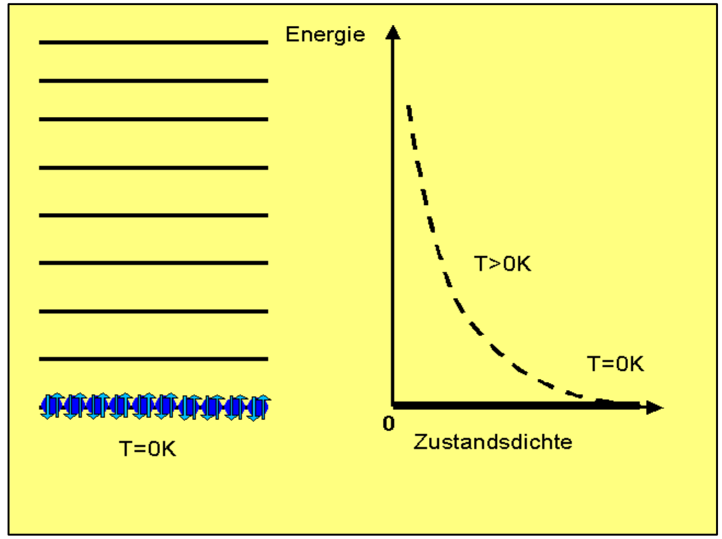
Fermi-Dirac-Statistics



Fermions are particles with half-integer spin, e.g. electrons, protons, neutrons, neutrinos, quarks

Pauli's rule states that every energy state can be occupied by a maximum of two electrons with opposing spins

Bose-Einstein-Statistics



Bosons are particles with integer spin, e.g. photons, deuterium cores, gluons, gravitons

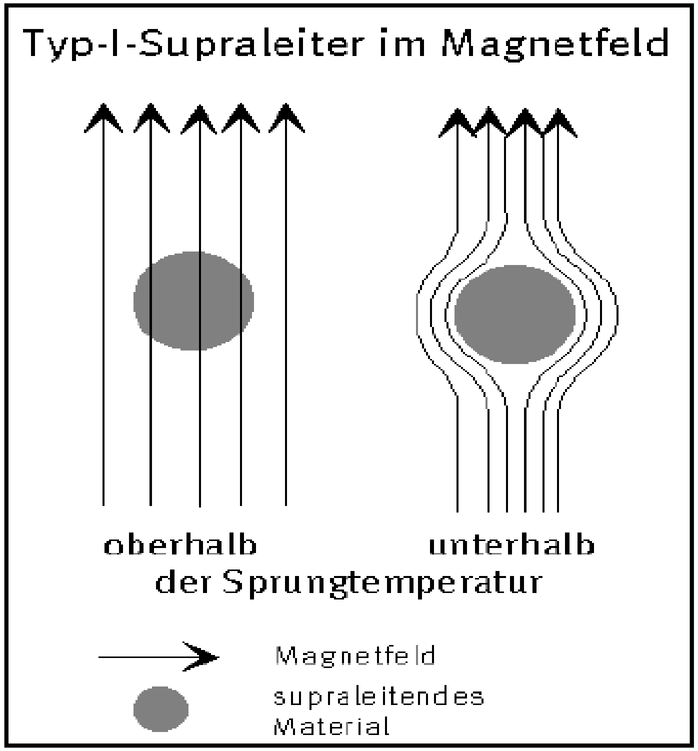
Cooper-pairs are formed by electrons with opposing spin, i.e. the total spin is zero. Cooper-pairs are bosons, too. Pauli's rule does not apply anymore. All Cooper-pairs can occupy the same quantum-mechanical sate of the same energy

2.3 Electrical and Dielectrical Properties

Meißner-Ochsenfeld-Effect

Walther Meißner and Robert Ochsenfeld 1933

A external magnetic field is supressed from the inner of a superconductor, i.e. the superconductor becomes a ideal diamagnet (all electrons paired)



<u>Explanation</u>

Below the transition temperature, eddy currents are formed within the superconductor, which create a Magnetic field of their own

Both magnetic fields compensate each other

⇒ the magnet floats

2.3 Electrical and Dielectrical Properties

Applications for High-temperature Superconductors

- NMR-Spectroscopy
- Magnetic resonance tomography
- Propulsion technology for trains (Mag-lev Transrapid)
- Electrical engines and generators
- Fusion reactors
- Power lines for direct and alternating current
- Particle accelerator
- Measurement of extremely small magnetic fields (*S*uperconducting *Q*uantum *I*nterference *D*evice, *SQUID*)

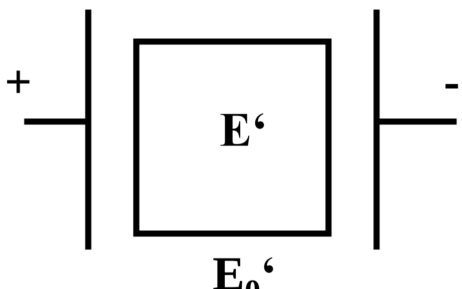
Insulators (Dielectrics)

- ⇒ **A very high electrical resistance is caused by a high energy gap between valence and conduction band**
- ⇒ **Ceramics and polymers**

Insulators can create (transmitter) or receive (antenna) information or they can store electrical charges in capacitors

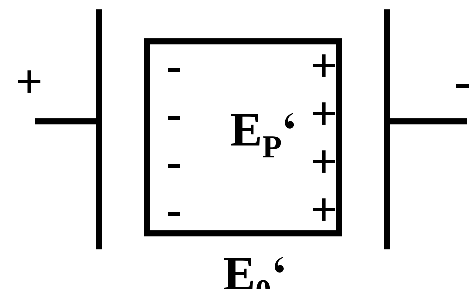
The term "dielectrics" already implies that a external electrical field can penetrate the material.

In metals or semi-conductors it is E‘ = 0



Free charge is rearranged until E‘ = 0

In Insulators (dielectrics)

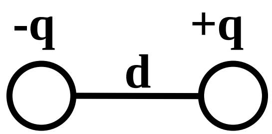


The external field is reduced by polarisation

2.3 Electrical and Dielectrical Properties

Dipoles and Polarisation

Electrical fields are capable to induce dipoles in materials or can align permanently existing dipoles along the field direction.



Elemental dipoles are atoms or groups of atoms, where positive and negative charges do not balance

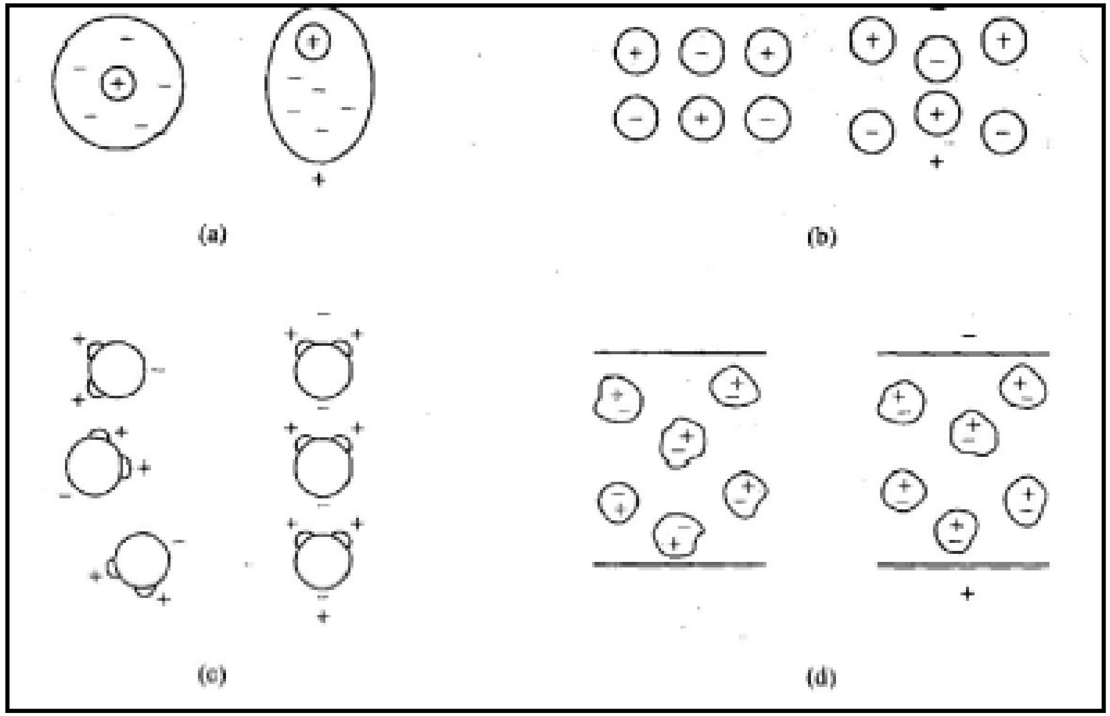
⇒ Angled molecules: H_2O, NH_3, SO_2, CH_2Cl_2, ...

The orientation of dipoles in a electrical field is called polarisation P :

In molecules	in solids
$P = q \cdot d$	$P = z \cdot q \cdot d$
$P = \varepsilon_0 \cdot (\varepsilon_r - 1) \cdot E_0$	z = number of shifted charge centres
	q = electrical charge
	ε_r-1 = electrical susceptibility χ_e
	d = distance between positive and negative charge
	ε_0 = Permittivity number of vacuum = $8.854 \cdot 10^{-12}$ C^2/Jm
$E_p = 1/(\varepsilon_0 \cdot \varepsilon_r) \cdot P$	ε_r = Permittivity number of the material

2.3 Electrical and Dielectrical Properties

Types of Polarisation



a) Electron polarisation

In a electrical field, electrons are slightly shifted in positive field direction. This effect can be observed for all substances.

The electron polarisation vanishes, when the field is switched off.

b) Ion polarisation

In a heteropolar-bound material a electrical field induces slight shifts of the charges. By these shifts the outer dimension of the material can be influenced. The ion polarisation vanishes, when the electrical field is switched off.

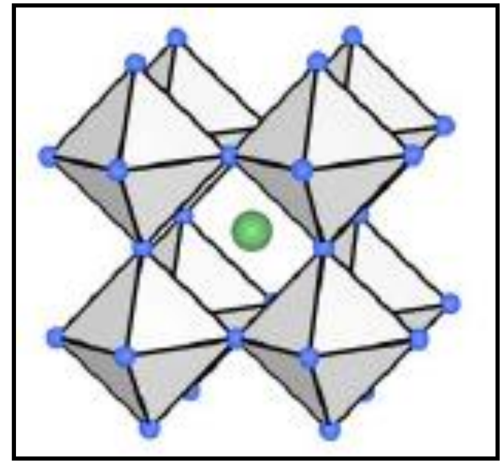
⇒ These two types are also called displacement polarisation!

2.3 Electrical and Dielectrical Properties

Types of Polarisation

c) Molecular polarisation

Permanent dipoles align preferably along the external field. In some compounds, e.g. $BaTiO_3$ dipoles remain in their alignment After the elctrical field is switched off (⇒ ferro electrics).
$BaTiO_3$ crystallises in a tetragonal structure with permanent polarisation



$BaTiO_3$ is a perowskit

d) Polarisation by space charge

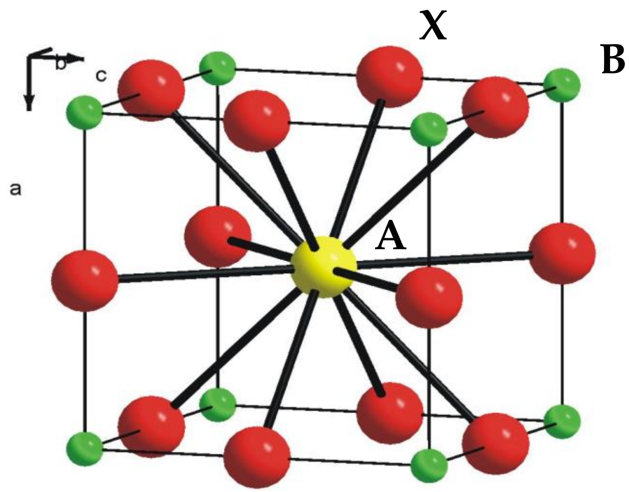
Alien atoms can cause accumulation of charges within inner phase boundaries of a material, which can migrate to the surface, if stimulated by a electrical field.
For most dielectrics this kind of polarisation is of no importance

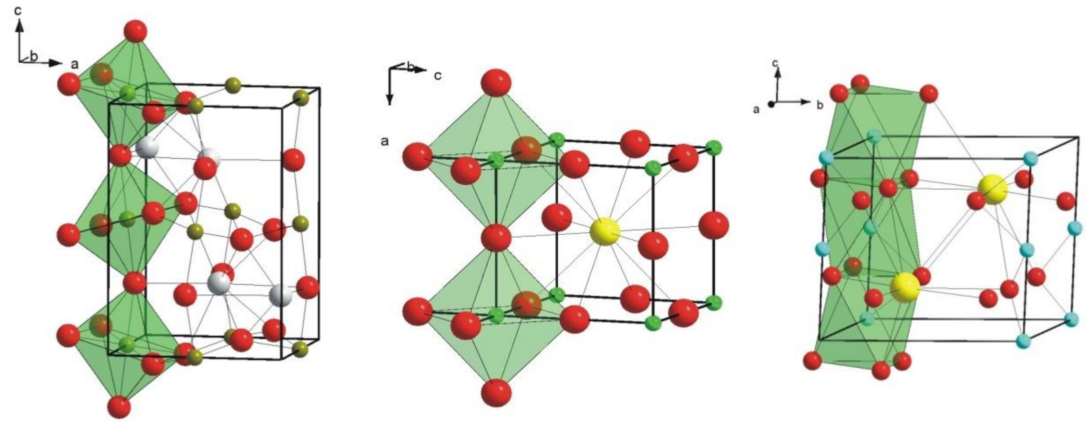
⇒ These two types are also called orientation polarisation!

2.3 Electrical and Dielectrical Properties

Perowskit ABX_3

$\Rightarrow$ **Jahn-Teller-Polarons (fermionic quasi particles)**





0.8 — **0.89** — **1.0** — **t**

orthorhombic ($GdFeO_3$)	cubic ($SrTiO_3$)	hexagonal ($BaNiO_3$)

$$a = 2(r_B + r_O) = \frac{2(r_A + r_O)}{\sqrt{2}}$$

$$t \equiv \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)} \qquad (\text{"}Tolerance - term\text{"})$$

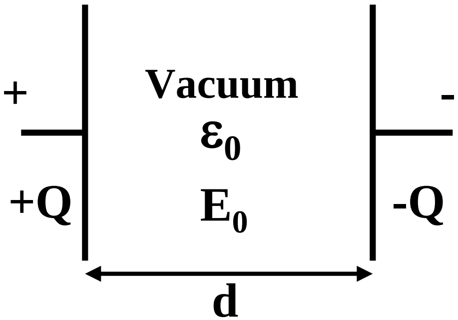
$X = O^{2-}, F^-, Cl^-$
A = Alkali, alkaline earth and RE metals
B = Transition metals and Si, Al, Ge, Ga, Bi, Pb

Perowskit is the name of a Russian mineralogist: Count Lev Aleksevich of Perovski.
The mineral $CaTiO_3$ was discovered by Gustav Rose in 1839 at Ural, Russia

2.3 Electrical and Dielectrical Properties

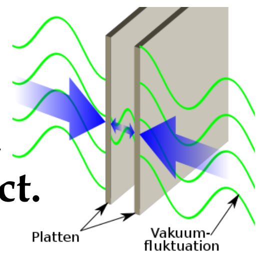
Matter as Mediator in Capacitors

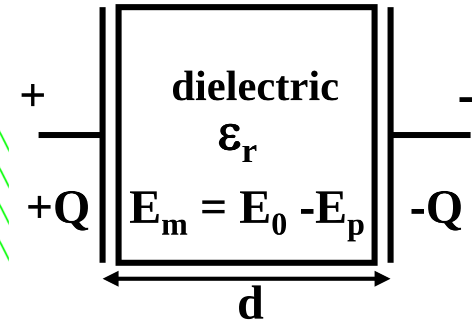
Within dielectrics, a external field E_0 is reduced by the factor ε_r



Vacuum polarisation/fluctuation
- **Lamb-shift**
- **Casimir-effect**
- **Spontaneous emission**
- **Van-der-Waals interacct.**
- **Hawking radiation**

$\Rightarrow \varepsilon_0 = 8.854 \cdot 10^{-12}\ AsV^{-1}m^{-1} \neq 0$!





If matter is introduced into the capacitor, U is reduced by ε_r, since E_0 is also reduced by ε_r, and $U = E \cdot d$.

Q remains unchanged, because the plates are not electrically connected!

Vacuum:	$Q = C_0 \cdot U$	$C_0 = \varepsilon_0 \cdot A/d$	**with C = capacity [C/V = F]**
With matter:	$Q = C_m \cdot U/\varepsilon_r$	$C_m = \varepsilon_r \cdot \varepsilon_0 \cdot A/d$	**thus $C_m/C_0 = \varepsilon_r$**

To obtain a high capacity capacitor, the area A must be as large as possible, d small and ε_r of the filling as large as possible!

2.3 Electrical and Dielectrical Properties

Capacitors

Capacitors are used to:

- **Store charge**
- **Smooth currents**
- **Couple frequency-dependant alternating and direct current circuits**

<u>Criteria for the application of dielectric materials for capacitors</u>

1. **High permittivity number $\varepsilon_r = \varepsilon/\varepsilon_0$**
2. **High dielectric strength: $E_{max} = (V/d)_{max}$**
   ⇒ limits the maximal field strength a dielectric may be exposed to

High electrical resistance

⇒ Prevents exchange of charges between the capacitor plates

⇒ Polymers and ceramic materials

4. **Low dielectric losses, thus a small loss factor = tanδ**
   (Movement of dipoles leads to heating of the material and thus to a reduction of the offset angle of the current to 90° - δ with δ = loss angle)

2.3 Electrical and Dielectrical Properties

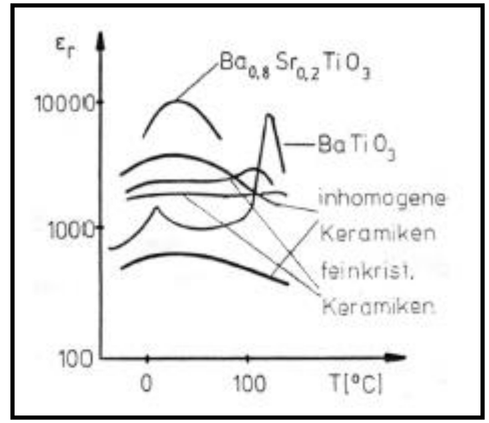
Properties of Dielectric Materials

Material	Permittivity number (at 10^6 Hz)	Dielectric strength (10^6 V/m)	tanδ (at 10^6 Hz)	Specific electrical resistance (Ω·cm)
Polyethylene	2.3	20	0.0001	> 10^{16}
Polytetrafluoroethylene	2.1	20	0.00007	10^{18}
Polystyrene	2.5	20	0.0002	10^{18}
Polyvinylchloride	3.5	40	0.05	10^{12}
Nylon	4.0	20	0.04	10^{15}
Rubber	4.0	24		
Phenol resin	7.0	12	0.05	10^{12}
SiO_2 (quartz glass)	3.8	10	0.00004	10^{11}– 10^{12}
Sodium-lime glass	7.0	10	0.009	10^{15}
Al_2O_3	6.5	6	0.001	10^{11}– 10^{13}
TiO_2	14 – 110	8	0.0002	10^{13}– 10^{18}
Mica	7.0	40		10^{13}
$Ba_{1-x}Ca_xTi_{1-y}Zr_yO_3$	3000	12		10^8 – 10^{15}
H_2O	78			10^{14}

2.3 Electrical and Dielectrical Properties

Properties of Dielectric Materials

High and highest permittivity numbers are observed for perowskites ($BaTiO_3$, $PbTiO_3$, $LiNbO_3$) and layered perowskites (Ba_2GdNbO_6)



<u>$BaTiO_3$</u>

- **ε_r = 7000 close to Curie-temperature T_c**
- **But highly T-dependant, ε_r decrease to 1000 – 2000 upon cooling**

⇒ Dependence of capacity on temperature

<u>Aim</u>

Dielectrics with ε_r = const. in the range of 218 K (-55 °C) till 398 K (+125 °C)

⇒ Ceramics from (doped) mixed crystals

⇒ $Ba_{1-x}Ca_xTi_{1-y}Zr_yO_3$:Nb

Material	T-dependence	ε_r
NP0	+/- zero	↓
X7R	moderate	
Z5U	strong	

(Electronic Industries Association EIA)

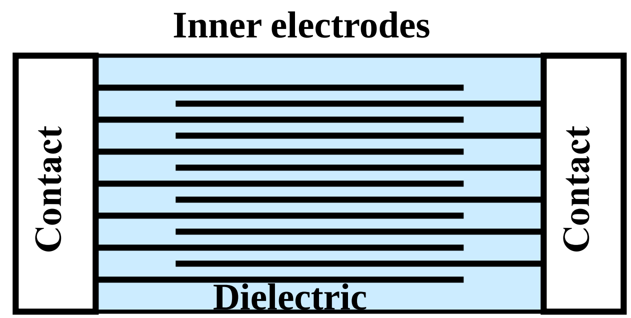
In addition, particle size and particle size distribution influence the permittivity!

2.3 Electrical and Dielectrical Properties

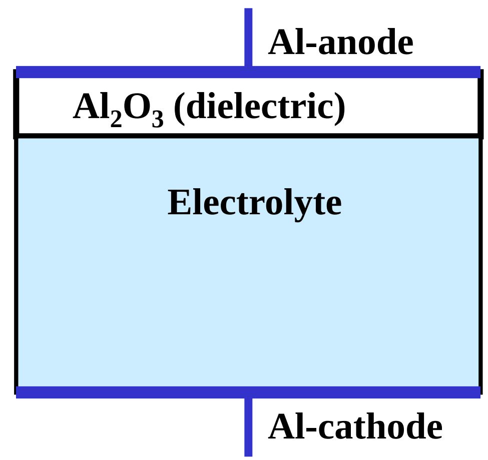
Designs of Capacitors

1. Disc capacitors

2. Multi-layer capacitors



3. Wound capacitor



4. Electrolyte capacitors
   Al-Elko: Al_2O_3 + electrolyte citric acid
   Ta-Elko: Ta_2O_5 + electrolyte sulphuric acid

2.3 Electrical and Dielectrical Properties

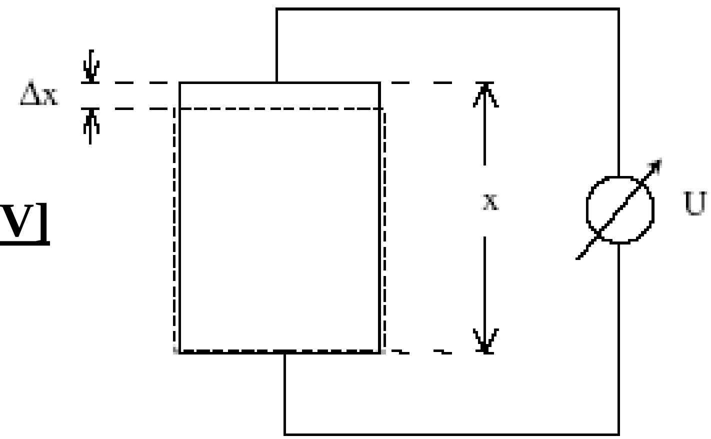
Piezoelectricity and Electrostriction

In a electrical field, the dimensions of a solid can change depending on the polarisation. This effect is called electrostriction

For certain piezoelectric substances a polarisation and the formation of a electrical voltage can be observed, if the dimensions of the material are changed by external forces

Piezoelectric substances

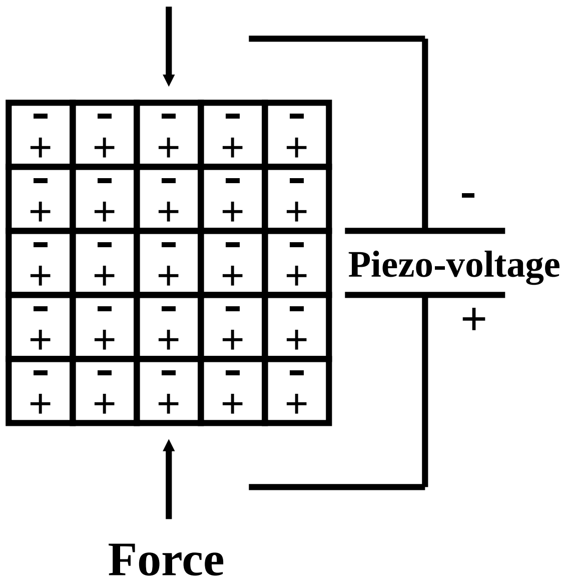
⇒ Unit cell without symmetry centre

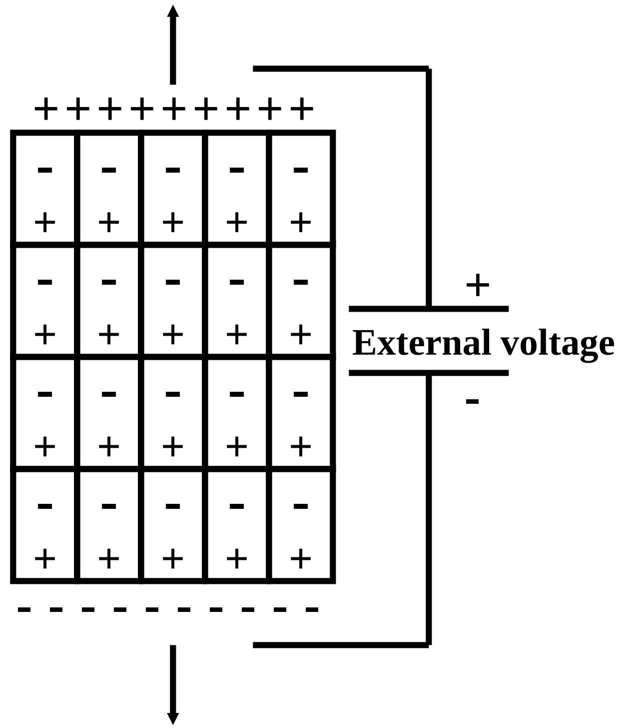


Material	Formula	Piezo-modulus d [m/V]
α-Quartz	SiO_2	$2.3 \cdot 10^{-12}$
Barium titanate	$BaTiO_3$	$100 \cdot 10^{-12}$
PZT	$PbZrO_3$-$PbTiO_3$	$250 \cdot 10^{-12}$
PLTZ	$(Pb,La)(Ti,Zr)O_3$	
	$PbNb_2O_6$	$80 \cdot 10^{-12}$

$$E = \frac{1}{d} \cdot \frac{\Delta x}{x} = \frac{1}{d} \cdot \varepsilon$$

The Piezoelectric Effect





By external compression the distances between the charges are reduced, so that a piezoelectric voltage is created

Application of a external field results in a change in length (elongation) of the crystal

2.3 Electrical and Dielectrical Properties

Application of the Piezoelectric Effect

1. **Electroacoustic transducer**

   Sound wave ↔ electrical signal

   ⇒ A impinging sound wave deforms the piezoelectric material by the frequency of the wave and creates a electrical alternating voltage

   (The alternating voltage can be retransformed into sound waves after sufficient amplification by a second transducer, e.g. in phono devices)

2. **Temperature sensors**

   ⇒ Changes in temperature can induce polarisation and electrical voltages in certain pyroelectric materials

3. **Stabilisation of resonant circuits in watches and electronic devices**

   ⇒ Quartz crystals are excited to vibrate by applying a external alternating field

   ⇒ As soon as the oscillation frequency of the quartz crystal coincides with the external electrical field resonance occurs and a stationary wave is created

2.3 Electrical and Dielectrical Properties

Ferroelectricity

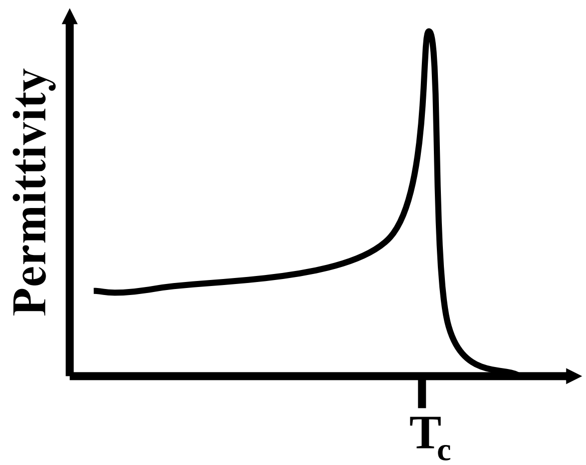
In $BaTiO_3$ and several other materials a certain polarisation remains after switching off the electrical field!

Cause for the ferroelectric behaviour is the interaction between permanent dipoles (domains ~ 10 µm), which is favoured by their uniform orientation

At Curie-temperature T_c ferroelectric behaviour vanishes

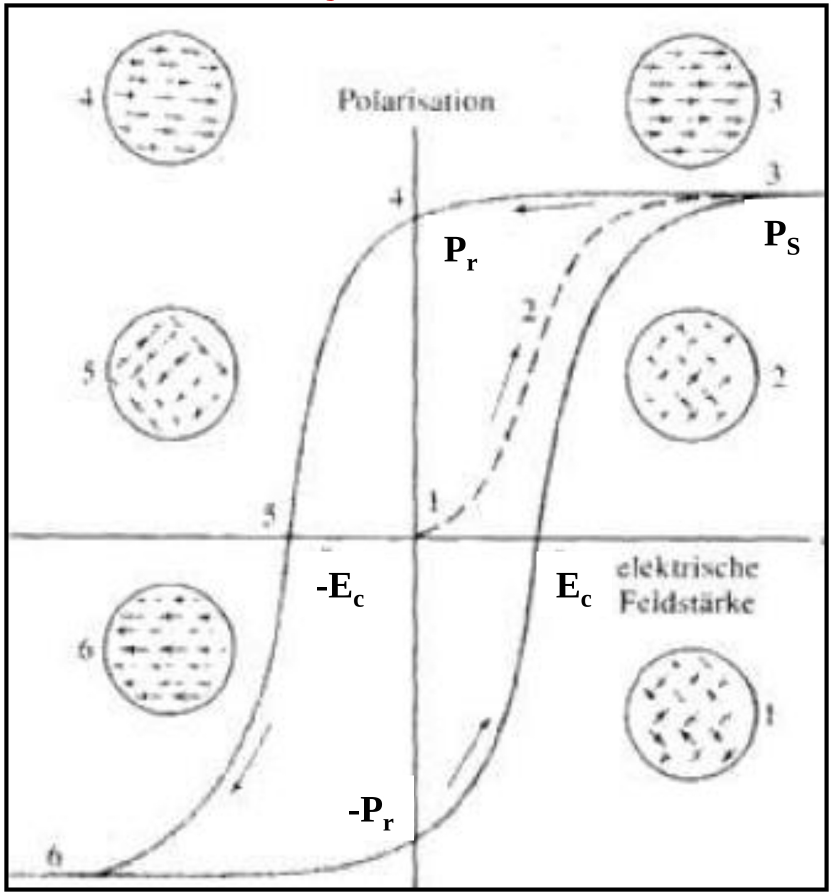
In $BaTiO_3$ at Curie-temperature, a

Phase transition from tetragonal – cubic occurs!



2.3 Electrical and Dielectrical Properties

Ferroelectricity



P_r = remanent polarisation
P_s = saturation polarisation
E_c = coercive field strength

The ability of ferroelectric materials to maintain a polarised state, offers the possibility to store information

2.4 Magnetic Properties

The Magnetic Behaviour of Matter Is Determined by Mobile Charge Carriers

<u>History</u>

600 v. Chr.	Thales of Milet	λιϑος μαγντiς = stone made of magnesia
100 v. Chr.	Chinese	Compass
1820	Oersted	Electrical currents move a magnetic needle
1830 - 1845	Faraday	Magnetic induction: generator, transformer, ...
1864	Maxwell	Electromagnetism (Maxwell-equations)
1896	Zeeman	Splitting of line spectra by magnetic field
1900	Curie	Temperature-dependence of magnetism
1907	Weiss	First quantum-mechanic interpretation of macroscopic magnetism

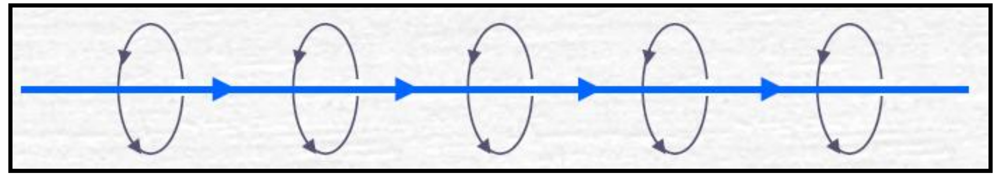
<u>Types of magnetism</u>

Diamagnetism	Molecules without unpaired electrons	
Paramagnetism	Molecules with at least one unpaired electron	
Ferromagnetism	Cooperative effect	→ in solids only
Ferrimagnetism	Cooperative effect	→ in solids only
Anti-ferromagnetism	Cooperative effect	→ in solids only

2.4 Magnetic Properties

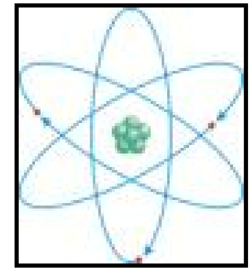
Manifestations of Magnetism

1. Moving charge carriers in conductor



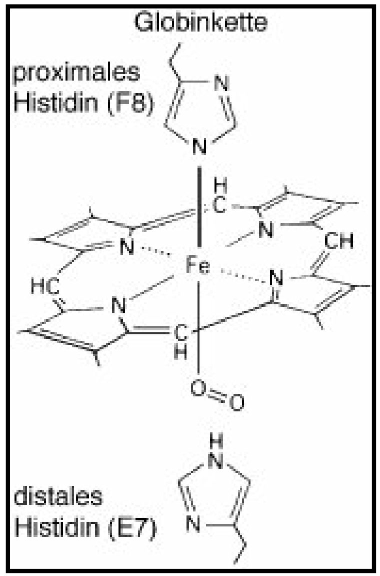
electrical conductor

2. Atomic magnetism, i.e. moving charge carriers (electrons) in atom

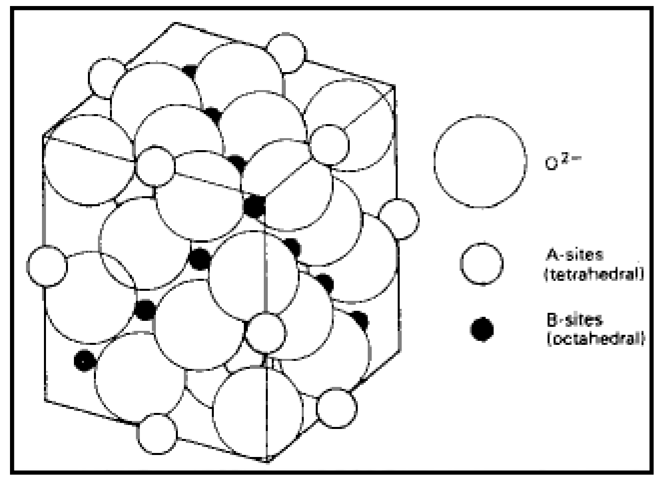


3. Molecular magnetism

4. Solid state magnetism



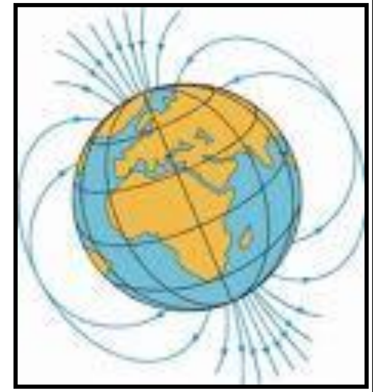
Haemoglobin



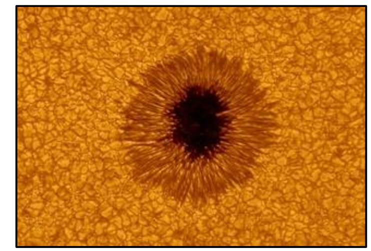
Magnetite Fe_3O_4 “a ferrimagnet“

2.4 Magnetic Properties

Importance of Magnetism



Terrestrial magnetic field	Deflection of solar wind (→ aurora borealis)
	Orientation of migrating birds, sharks, crayfish
	⇒ Fe_3O_4-nano-particles
Stellar magnetic field	Sunspots (magnetic tubes)
	Form of planetary nebula

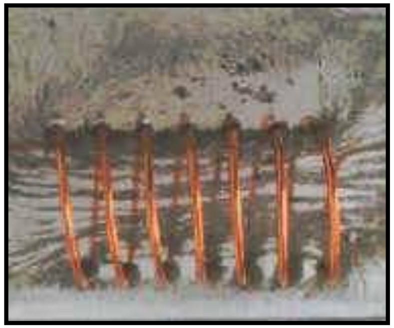


Technical Area	Examples
Analytics	NMR, EPR, optical spectroscopy
Data storage	Magnetic tapes, floppy drives, hard drives
Electronics	Coils, generators, transformers
High-energy physics	Ring accelerators
Medicine	MRTs, NMR-shift reagents
Optics	Magneto optic crystals
Navigation	Shipping
Sensors	Giant Magneto-Resistance (GMR)-sensors
	Superconducting Quantum interference devices (SQUID)-sensors

2.4 Magnetic Properties

Magnetic Field Strength H, Magnetic flux density B, and Magnetisation M

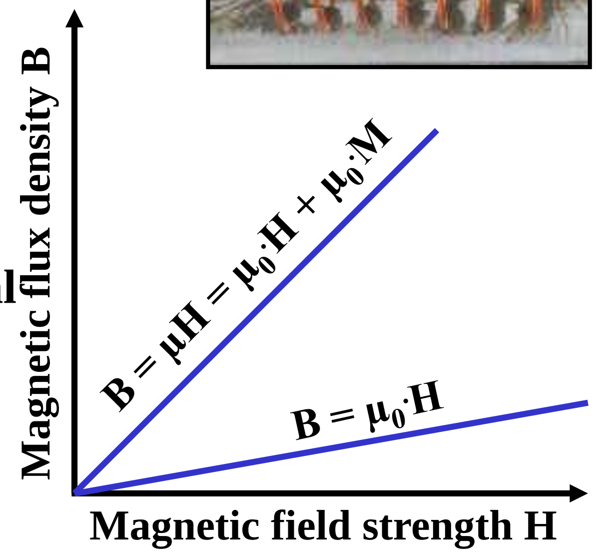
A magnetic field induces, in vacuum, a magnetic flux, which strength and direction can be visualised by flux lines. The number of these lines per area unit is called magnetic flux density B or magnetic induction and is proportional to the magnetic field strength H.



$$B = \mu_0 H$$

with μ_0 = permeability of vacuum [Vs/Am]
= $4\pi\cdot10^{-7}$ Vs/Am

The flux density is changed upon penetration of the Magnetic field into matter, which can be expressed by μ_r or M



$$B = \mu_0 \mu_r H$$

with μ_r = relative permeability of the material
M = magnetisation

$$B = \mu H = \mu_0 H + \mu_0 M$$

$\mu = \mu_r \cdot \mu_0$ = absolute permeability

2.4 Magnetic Properties

Typical magnetic Flux Densities B

Example	Magnetic flux density B [T]
Colliding neutron stars	10^{11}
Neutron star	10^{8}
White dwarf	10^{4}
Inner exchange fields in ferromagnets	10^{1} - 10^{3}
Superconductive magnets	10^{1} (world record: 30 T at HMI Berlin)
Coil with iron yoke	10^{0}
Surface of ferromagnets	10^{-1} - 10^{1}
Sunspots, planetary nebula	10^{-1}
Terrestrial magnetic field	10^{-4} (48 µT bei Frankfurt am Main)
Technical stray fields "urban noise“	10^{-12} - 10^{-5}
Field in galaxies	10^{-10}
Fields in galaxy clusters	10^{-10} - 10^{-13}
Intergalactic magnetic field	10^{-13}

1 T (Tesla) = 1 Vs/m^2 = 10^4 G (Gauß) unit of magnetic flux density

2.4 Magnetic Properties

Magnetic Susceptibility χ

Is a degree for the field enforcement caused by a material:

$$\chi_V = \frac{M}{H} = \frac{B_{inside} - B_{outside}}{B_{outside}}$$

"Volume susceptibility"

Therefore, magnetic flux density can be expressed as:

$$B = \mu H = \mu_0 H + \mu_0 M = \mu_0 (H + M) = \mu_0 (H + \chi H) = \mu_0 (1 + \chi) H$$

Also:

$\mu_r = 1 + \chi$ **with** $\chi_V \cdot V_m = \chi_g \cdot M = \chi_{mol}$ χ_{mol} **= molar susceptibility,** χ_V **= vol. suscept.**

Of great technical importance are magnetic materials where M is much higher than H

$$\Rightarrow \quad B \cong \mu_0 M$$

$\mu > 1$	and	$\chi > 0$	paramagnets
$\mu >> 1$	and	$\chi >> 0$	ferromagnets

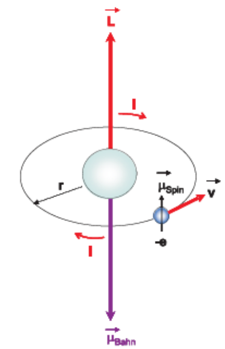
2.4 Magnetic Properties

Magnetic Dipoles and Magnetic Momentum μ

Magnetisation M is caused by orientation of induced or permanent magnetic dipoles in a external magnetic field with the field strength H

The strength of the magnetic field induced by the dipole is its magnetic momentum μ

$$M = \frac{\sum_i \mu_i}{V}$$

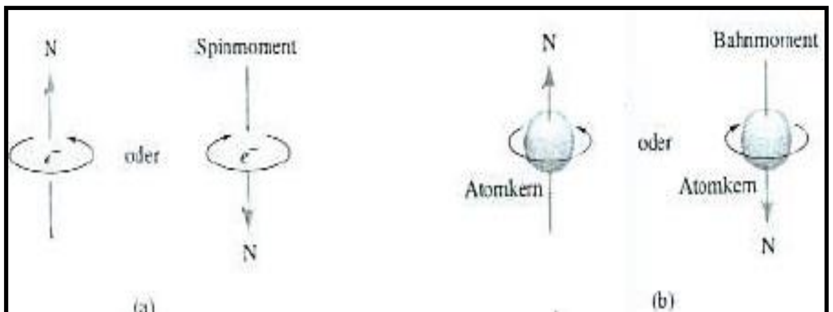


Every electron in atom causes a magnetic moment comprising to components:

a. Spin momentum: Angular momentum (spin) of an electron: $\mu_S = -g_s \cdot \mu_B \cdot S$ with $g_s = 2$

b. Orbital momentum: Results from movement of an electron: $\mu_l = -g_l \cdot \mu_B \cdot n$ with $g_l = 1$

c. Total momentum: Due to spin orbit coupling: $\mu_J = -g_j \cdot \mu_B \cdot J$ with $g_l < g_j < g_s$



Additionally, a nuclear spin momentum exists, which can be neglected for the macroscopically observable magnetism due to its small value (m_{proton} ~ 1836 m_e)

2.4 Magnetic Properties

Bohr‘s Magneton μ_B

The elemental magnetic moments can be expressed as multiples of **Bohr‘s magneton μ_B**, which is the base unit of the magnetic momentum

$$\mu_B = \frac{e \cdot h}{4\pi \cdot m_e} = 9.27 \cdot 10^{-24}\,\mathrm{Am}^2$$

$e = 1.602 \cdot 10^{-19}$ C unit charge
$h = 6.626 \cdot 10^{-34}$ Js Planck‘s constant
$m_e = 0.9109 \cdot 10^{-30}$ kg rest mass of electron

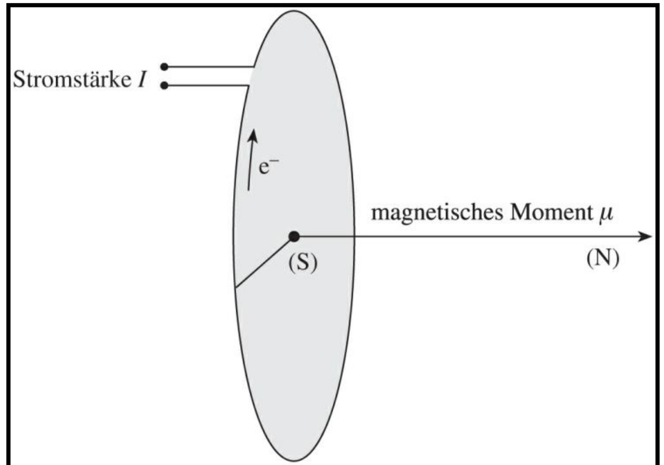
It equals a magnetic moment which is induced by a electron on a circular path with Bohr‘s radius (53 pm) around a proton

For light elements with n unpaired electrons the magnetic moment μ equals the “spin-only” value

$$\mu_{ber} = \sqrt{n(n+2)} \cdot \mu_B$$

$$\mu_{ber} = 2\sqrt{S(S+1)} \cdot \mu_B$$

total spin $S = \Sigma s$
with $s = ½$ d. h. $S = n/2$
and $n = 2S$



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2.4 Magnetic Properties

Magnetic Behaviour of 3d-Transition Metal Ions

Electronic configuration	Ion	Ground state	Number of unpaired electrons	$\mu_{calc.}$ [μ_B] *high-spin*	$\mu_{exp.}$ [μ_B]
$[Ar]3d^0$	Sc^{3+}	$^1S_0$	0	0	0
$[Ar]3d^1$	Ti^{3+}	$^2D_{3/2}$	1	1.73	1.7 – 1.8
$[Ar]3d^2$	V^{3+}	$^3F_2$	2	2.83	2.7 – 2.9
$[Ar]3d^3$	V^{2+}, Cr^{3+}, Mn^{4+}	$^4F_{3/2}$	3	3.87	3.7 – 3.9
$[Ar]3d^4$	Cr^{2+}, Mn^{3+}	$^5D_0$	4	4.90	4.8 – 4.9
$[Ar]3d^5$	Mn^{2+}, Fe^{3+}	$^6S_{5/2}$	5	5.92	5.7 – 6.0
$[Ar]3d^6$	Fe^{2+}, Co^{3+}	$^5D_4$	4	4.90	5.0 – 5.6
$[Ar]3d^7$	Co^{2+}, Ni^{3+}	$^4F_{9/2}$	3	3.87	4.3 – 5.2
$[Ar]3d^8$	Ni^{2+}	$^3F_4$	2	2.83	2.9 – 3.9
$[Ar]3d^9$	Cu^{2+}	$^2D_{5/2}$	1	1.73	1.9 – 2.1
$[Ar]3d^{10}$	Cu^+, Zn^{2+}	$^1S_0$	0	0	0

The electron spin is almost exclusively responsible for the magnetic behaviour of 3d-transition metal ions

2.4 Magnetic Properties

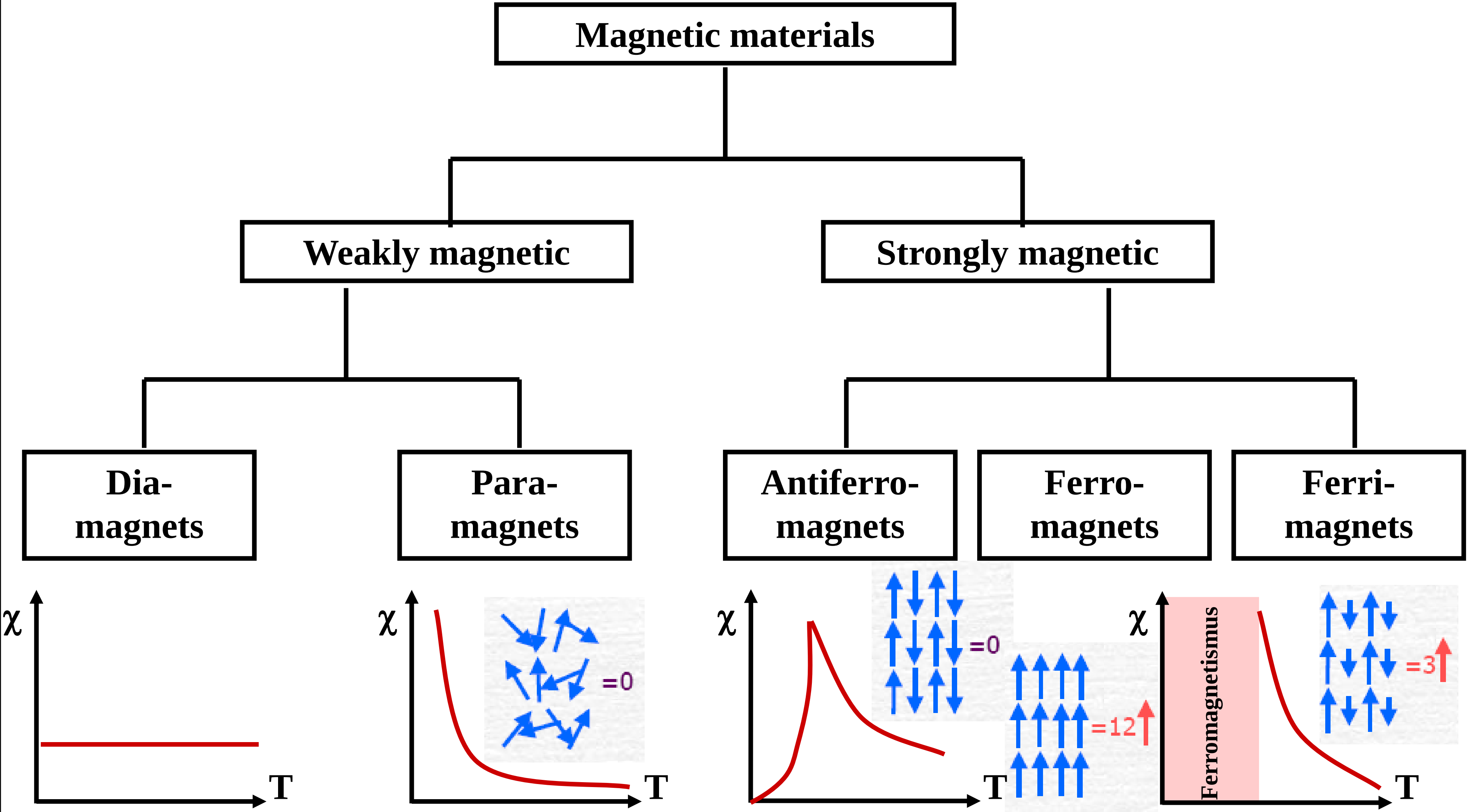
Excursion: Units of Electromagnetism

Electricity			Magnetism		
Electrical field strength	E	[V/m]	Magnetic field strength	H	[A/m]
Electrical flux density	D	[As/m^2]	Magnetic flux density	B	[Vs/m^2]
Permittivity of vacuum (electrical field constant)	ε_0	[As/Vm]	Permeability of vacuum (magnetic field constant)	μ_0	[Vs/Am]
Electrical resistance	R	[V/A]	Magnetic resistance	R_m	[A/V]

If electrical units shall be compared to analogous magnetics units, A and V have to be interchanged

2.4 Magnetic Properties

Classification of Magnetic Materials



2.4 Magnetic Properties

Diamagnetism

Diamagnetism is caused by the magnetic orbital momentums of the electrons and occurs in every material. Is a magnetic field switched on, it induces circular currents which according to Lenz's rule weaken the external magnetic field:

$\mu_r < 1$ and $\chi < 0$

- **Diamagnetism is weak and is superimposed by other types of magnetism**
- **Diamagnetism is independent of the field strength and almost temperature-independent**
- **Atoms, ions and molecules with filled shells or solids comprising such are diamagnetic**
- **Superconductors in not to strong fields are ideal diamagnets!**

Material	Susceptibility χ [10^{-6}]
N_2	-0.0003
Cu	-1.1
Pb	-1.8
$C_{sp}{}^3$	-2.1
Ag	-2.4
Hg	-2.9
$C_{sp}{}^2$	-2.1, -260
C_6H_6	-7.2
NaCl	-13.9
Bi	-16.6
H_2O	-90

2.4 Magnetic Properties

Paramagnetism

Paramagnetism occurs, if a permanent magnetic momentum exists, for which unpaired electrons (spin magnetism) or unfilled electron shells (orbital magnetism) can be responsible.

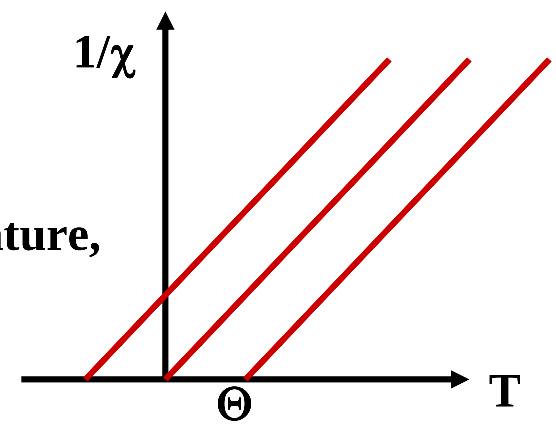
Without a magnetic field the momentums are statistically distributed.
In a magnetic field, they are oriented in such a way that they enforce the external field, i.e.
$\mu_r > 1$ and $\chi > 0$

<u>Temperature-dependence of paramagnetic materials</u>

Curie-Weiß-law

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

with Θ = paramagnetic Curie-temperature
C = Curie-constant



The paramagnetic susceptibility decreases with increasing temperature, because thermal movement contradicts magnetic ordering

Cooperative Magnetism (Bi-nuclear Metal Complexes as a Example)

Ferromagnetism

Parallel orientation of spins at low temperatures with high total spin

⇒ $Cr^{4+}(d^2)$-O-$Cr^{4+}(d^2)$ S = 4/2

Anti-ferromagnetism

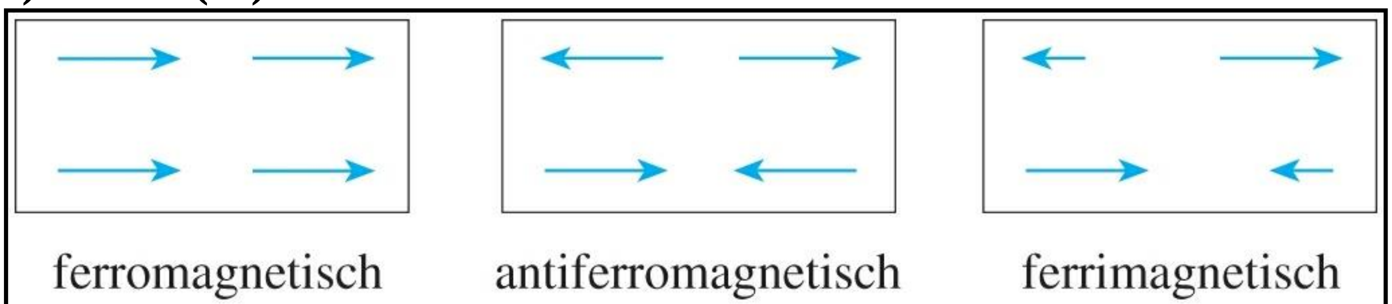
Antiparallel orientation of spins at low temperatures, total spin is zero

⇒ $Mn^{2+}(d^5)$-O-$Mn^{2+}(d^5)$ S = 0

Ferrimagnetism

Antiparallel orientation of spins at low temperatures, but total spin is not zero

⇒ $Fe^{2+}(d^6)$-O-$Fe^{3+}(d^5)$ S = 1/2

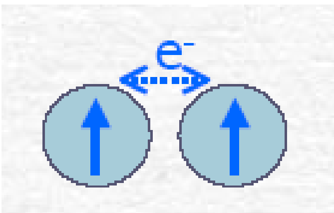


2.4 Magnetic Properties

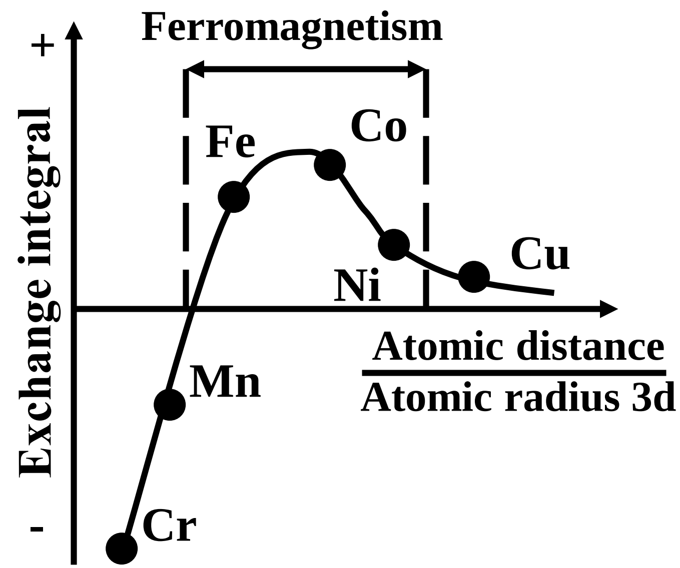
Distance-dependence of Exchange Interactions

<u>Positive (ferromagnetic) exchange interactions (+)</u>

Delocalised s- and d-electrons (band magnetism)

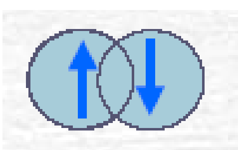


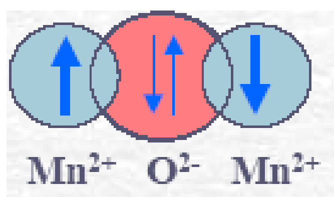
Examples: Fe, Co, Ni, Gd



<u>Negative (antiferromagnetic) exchange interactions (–)</u>

Overlap of 3d-orbitals (super-exchange)





Examples: Cr, Mn, MnO

$$\psi(r_1, r_2) = \psi_a(r_1)\psi_b(r_2)$$
$$\psi(r_1, r_2) = \psi_a(r_2)\psi_b(r_1)$$
$$\psi(r_1, r_2) = \psi_a(r_1)\psi_b(r_2) + \psi_a(r_2)\psi_b(r_1)$$
$$\psi(r_1, r_2) = \psi_a(r_1)\psi_b(r_2) - \psi_a(r_2)\psi_b(r_1)$$

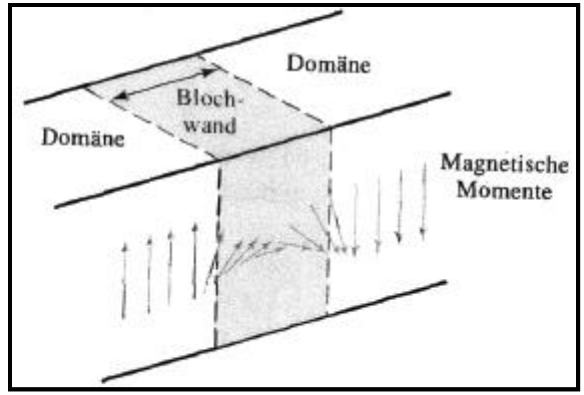
2.4 Magnetic Properties

Ferromagnetism

Below a certain temperature T_C a spontaneous orientation of elemental magnets is observed

⇒ Even without external field domains exist (Weiß areas), where neighbouring magnetic momentums are oriented in parallel

⇒ These domains have a length of about 50 µm and are separated by about 100 nm thick Bloch walls →



<u>Properties of prominent ferromagnetic materials</u>

Material	T_C (K)	magnetic momentum [μ_B]
Co	1394	1.715
Fe	1043	2.22
Ni	631	0.605
MnSb	587	3.5
CrO_2	386	2,03
Gd	289	7.5
Dy	88	10,2
EuO	70	6.9
EuS	16.5	6.9

$$\frac{\mu}{\mu_B} = g_J\sqrt{J(J+1)}$$

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

10,2 → Spin-Bahn-Kopplung → J

$$\chi_m = \frac{N_A {\mu_B}^2 g^2}{kT} \cdot \frac{\left[2 \cdot \exp\left(\frac{2J}{kT}\right)\right]}{1 + 3 \cdot \exp\left(\frac{2J}{kT}\right)}$$

Bleaney-Bowers-Gleichungen

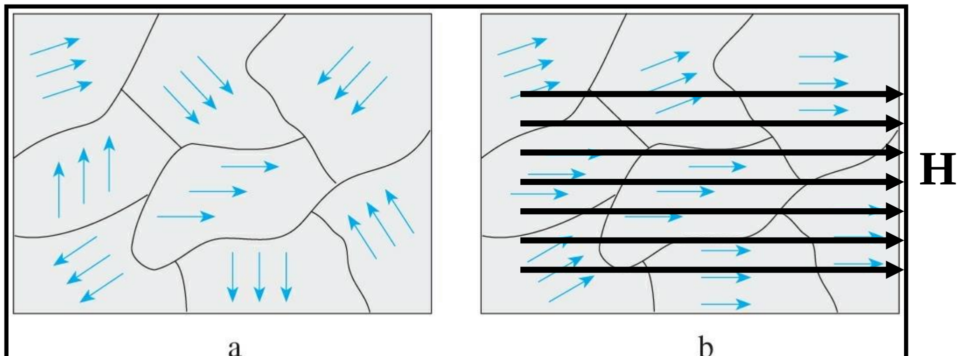
2.4 Magnetic Properties

Ferromagnetism

Upon application of a external magnetic field the domains that are oriented parallel to the external field expand. The other domains shrink.

Above Curie-temperature T_C ferromagnets become paramagnetic

$H = 0, M = 0$ $\qquad$ $H > 0, M < M_s$



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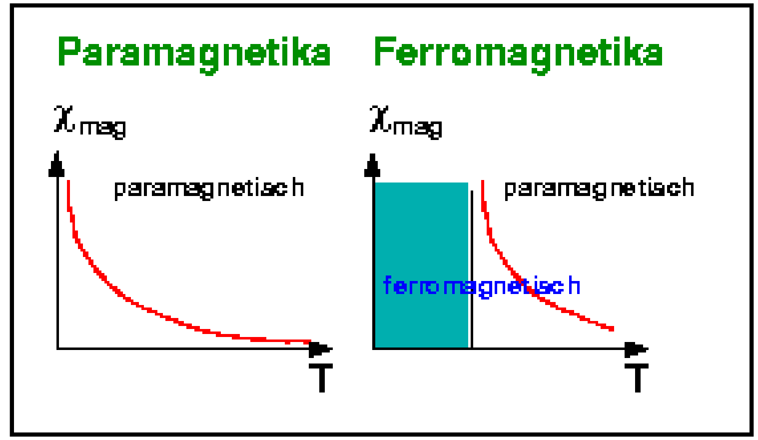
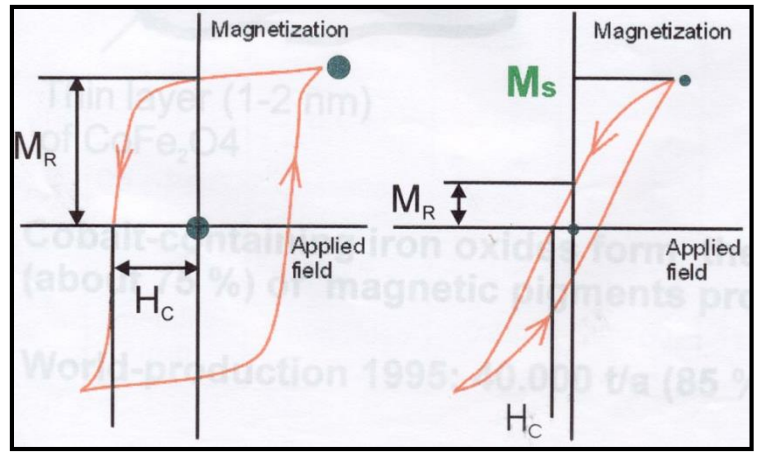
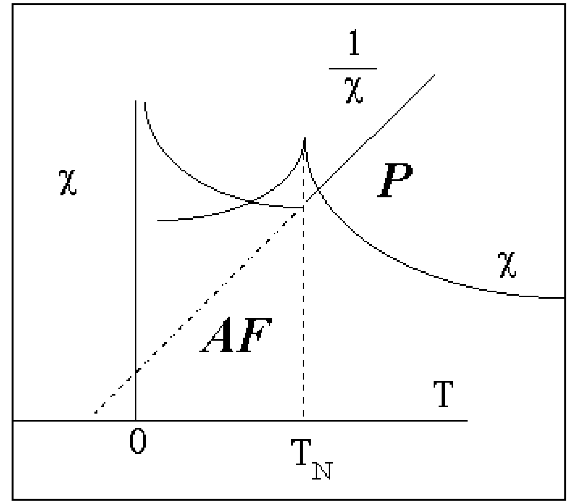




Magnetic remanence M_R
Saturation magnetisation M_s
Coercive field strength H_c

2.4 Magnetic Properties

Antiferromagnetism

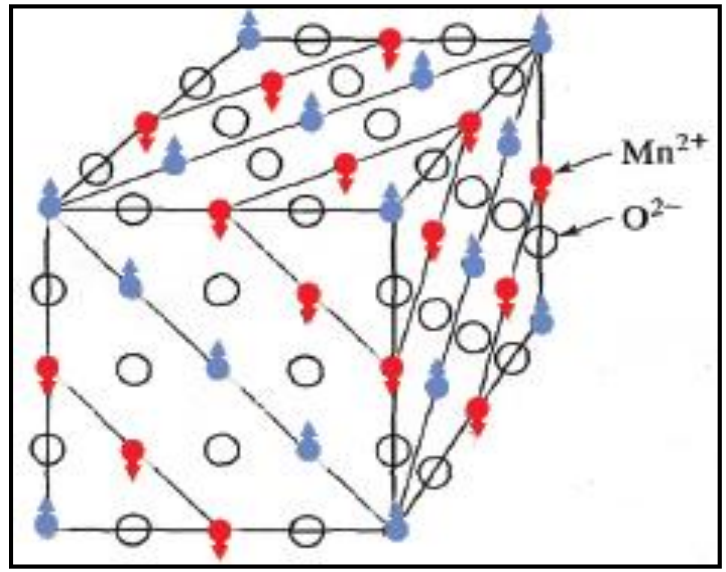


Below a certain temperature T_N (Néel-temperature) neighbouring magnetic momentums are oriented in anti-parallel and compensate each other

Then, the following is valid: $\mu_r = 1$ und $\chi = 0$

<u>Example: MnO</u>

Magnetic momentums of Mn^{2+}-ions in different levels compensate each other



Above Néel-temperature T_N anti-ferromagnets become paramagnetic

<u>Further examples</u>

EuTe, Rb_2MnCl_4

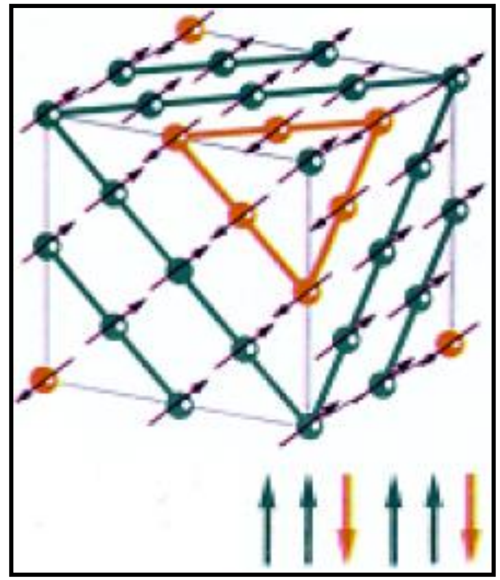
2.4 Magnetic Properties

Ferrimagnetism

Adjacent magnetic momentums are oriented in anti-parallel but do not compensate each other totally. Ferrimagnetism occurs in materials where different types of ion exhibit strongly deviating magnetic momentums:

Ferrites	MFe_2O_4	**with M = Zn^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}**
Garnets	$M_3Fe_2Fe_3O_{12}$	**with M = Ln^{3+}**

In a magnetic field, the magnetic momentums of the different types of ions are oriented in anti-parallel, resulting in a net magnetisation

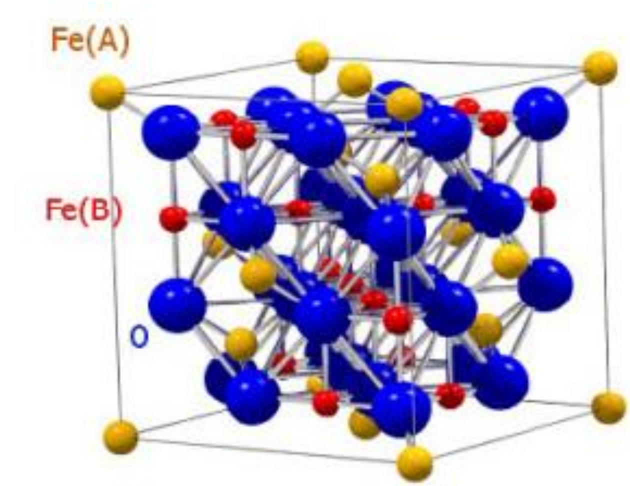


Remark

Anti-ferromagnetism is, strictly speaking, a special case of the more general ferrimagnetism, where both sub-layers can be regarded as equivalent

2.4 Magnetic Properties

Ferrimagnetism in Inverse Iron Oxide Spinels Fe_3O_4 (Magnetite), cubic



Natural magnets are crystalline materials frozen in the terrestrial magnetic field ⇒ permanent magnetisation

$$Fe_3O_4 = FeFe_2O_4 = [Fe^{3+}]^{tet}[Fe^{2+}Fe^{3+}]^{oct}O_4$$

$[Fe^{3+}]^{tet}$ ↑	$[Ar]3d^5$ h.s.	↑ ↑ ↑ ↑ ↑	$S = 0$ $[Fe^{3+}]^{tet}$-O-$[Fe^{3+}]^{oct}$
$[Fe^{3+}]^{oct}$ ↓	$[Ar]3d^5$ h.s.	↓ ↓ ↓ ↓ ↓	
$[Fe^{2+}]^{oct}$ ↑	$[Ar]3d^6$ h.s.	↑↓ ↑ ↑ ↑ ↑	$S = 4/2$ → Magnetisation!

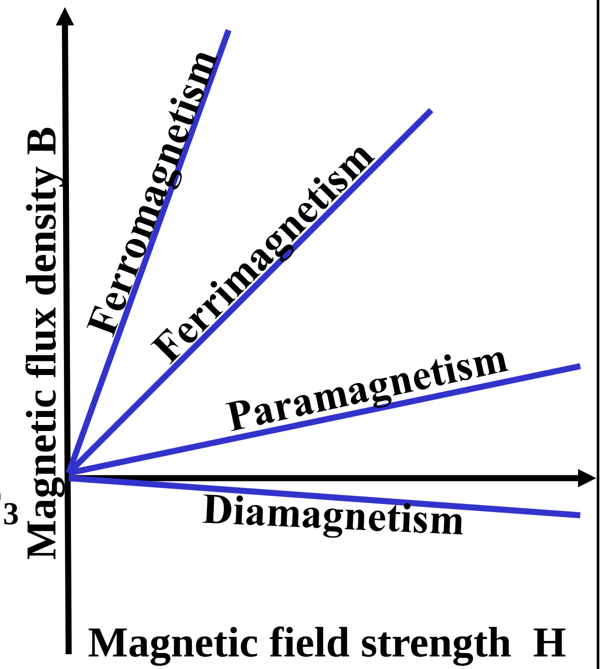
For $T < T_c$: Parallel orientation of spins in single domain

2.4 Magnetic Properties

Behaviour of Matter in a Magnetic Field: Summary and Examples

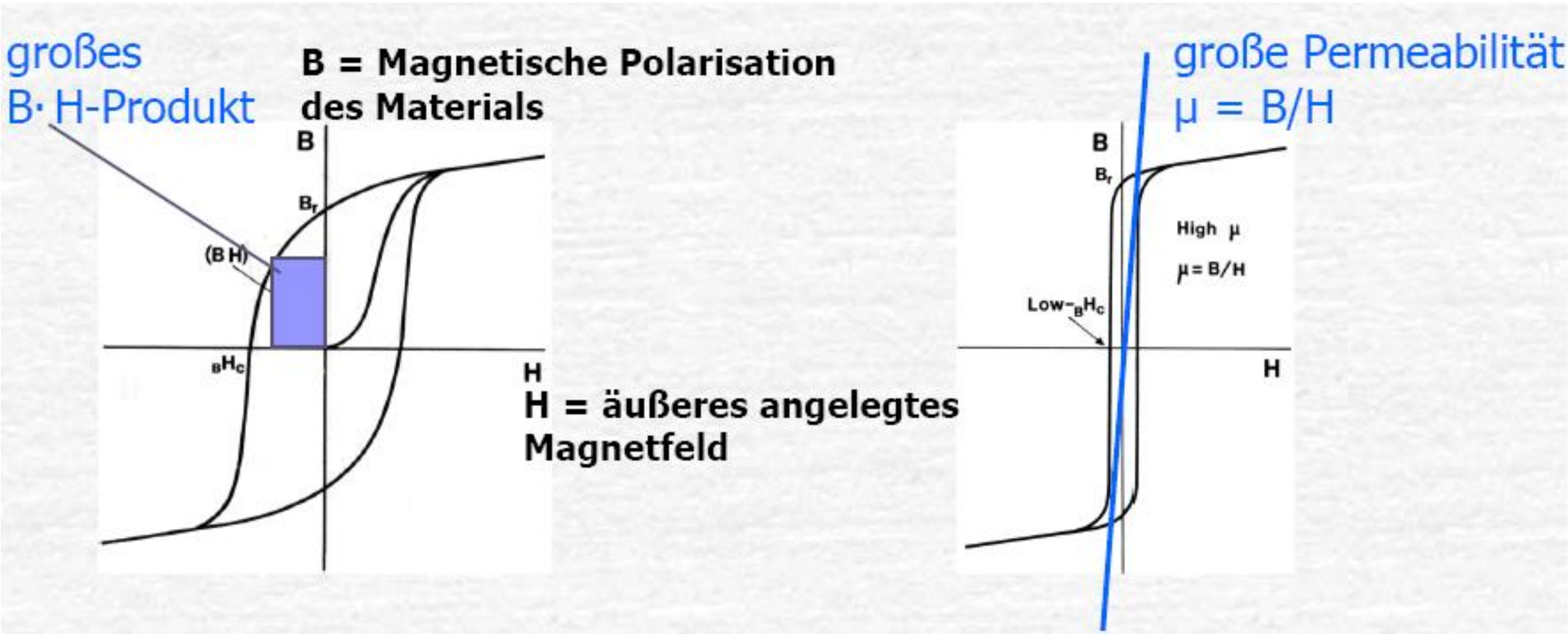
Types of magnetisation

• Diamagnetism	Bi, Cu, Ag, Au, Al_2O_3
• Paramagnetism	Al, Ti, Cu alloys
• Ferromagnetism	Fe, Co, Ni, Gd, γ-Fe_2O_3
• Antiferromagnetism	Mn, Cr, MnO, NiO, α-Fe_2O_3
• Ferrimagnetism	Ferrites, garnets , Fe_3O_4



Application of Magnetisation Curve

Size and shape of the hysteresis loop determine the behaviour of materials in a magnetic field And thus their range of application



Hard magnets: Energy storage, power source

Soft magnets: sensors, transformer sheets

2.4 Magnetic Properties

Application and Properties of Soft-magnetic Materials

⇒ Coil slugs of electromagnets, electric engines, transformers, generators, ...

The hysteresis loop must be run repeatedly, because, here, alternating current is used

⇒ Soft-magnetic materials are preferably used

Soft-magnetic materials exhibit the following properties

- High saturation magnetisation
  ⇒ Magnets show high flux densities
- High permeability
  ⇒ weak magnetic fields suffice to achieve saturation
- Small coercive field strength
  ⇒ Re-orientation of domains happens for small field strengths
- Small remanence
  ⇒ without external field, only small residual magnetisation remains
- Rapid reaction to high-frequency alternating fields
  ⇒ small energy losses du to friction of dipoles
- Small electric conductivity (ceramics with high resistance)
  ⇒ small Joule loss due to eddy currents

2.4 Magnetic Properties

Magnetic Storage Materials for Data Storage in Magnetic and Audio Tapes and Floppy Disks or Disk Storages

Operation scheme of magnetic storage materials

- **Magnetisation remains even without magnetic field**
- **The opposing magnetisation directions correspond to the binary values 0 and 1**
- **Write and erase of information is achieved by ready re-magnetisation**

Which conditions must be met by magnetic pigments?

1. **High remanence**
   ⇒ residual magnetisation after switching off the magnetic field
2. **Needle-shaped particles**
   ⇒ ready orientation in magnetic field
3. **No loss of magnetisation M through heating of magnetic band**
   ⇒ High Curie- or Néel-temperatures
4. **High signal/noise-ratio (dynamic)**
   ⇒ Pigments with as small particles as possible (uniform domains/particle)
5. **Possibility to fully erase magnetisation**
   ⇒ Intermediate coercive field strength H_c (needed field strength to de-magnetise)

2.4 Magnetic Properties

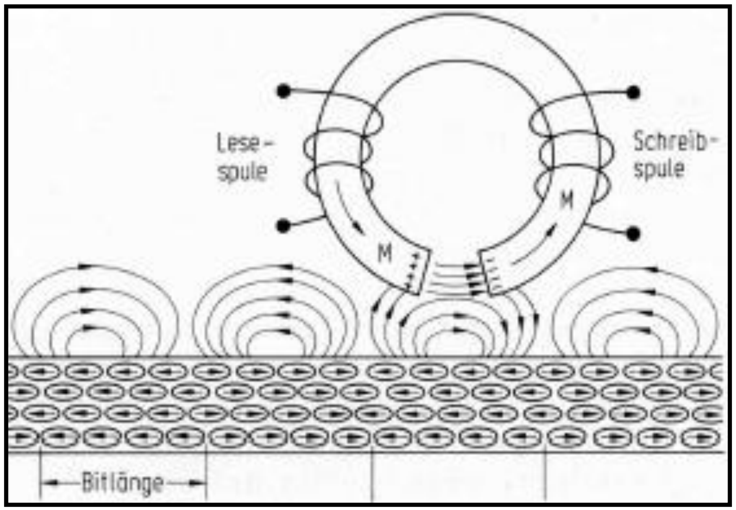
Magnetic Pigments for Magnetic Tapes

Pigment	Application	Particle Size [µm]	Specific surface [m^2/g]	Coercive field strength [kA/m]	Saturation magnetisation MS/δ [$\mu Tm^3/kg$]	M_R/M_S
γ-Fe_2O_3	Studio radio tapes	0.40	17 – 20	23 – 27	85 – 92	0.80 – 0.85
γ-Fe_2O_3	Cassettes IEC I	0.35	20 – 25	27 – 30	87 - 92	0.80 – 0.90
γ-Fe_2O_3 (Co-coated)	Cassettes IEC II	0.30	30 – 40	52 – 57	94 - 98	0.85 – 0.92
Fe (metallic)	8 mm video	0.25	50 - 60	115 - 127	130 - 160	0.85 – 0.90

2.4 Magnetic Properties

Audio Tape

Functional principle: presented by Valdemar Poulsen during world exhibition in Paris (1900)



AEG Magnetophon (1936)

Compact cassette (around 1960)

2.4 Magnetic Properties

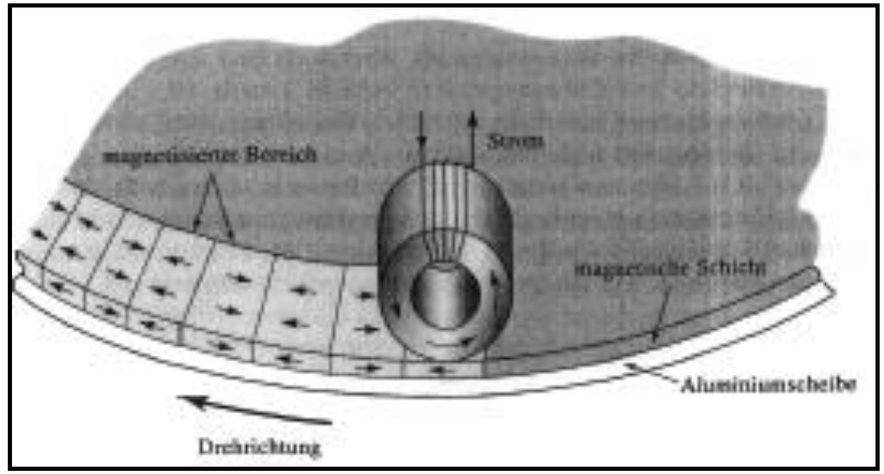
Floppy Disks

Construction of a storage medium

A Al-plate carrying a polymer film with magnetic pigments was used for floppy disks as well as for disk storages

Working scheme

During "writing", the current circulating through Coil of the head creates a magnetisation pattern within the magnetic layer



According to D.R. Askeland, Materialwissen-schaften, Spektrum-Verlag 1996

During "reading", the magnetisation pattern induces a current in the coil of the head

For the writing head a soft magnet is used, e.g. a Fe/Ni-alloys (Permalloy)

2.4 Magnetic Properties

Application and Properties of Hard-magnetic Materials

Hard-magnetic materials are used for permanent magnets and must possess the following properties:

- **High remanence**
- **High permeability**
- **High coercive field strength**
- **Broad hysteresis loop ⇒ high energy density**

Energy density $(BH)_{max} = B \cdot H$ $[VAs/m^3 = J/m^3]$

B = magnetic flux density $[T = Vs/m^2]$

H = magnetic field strength $[A/m]$

Meaning that the strength of a permanent magnet increases with the size of the hysteresis loop and thus with the maximal energy density

2.4 Magnetic Properties

Materials for Permanent Magnets

- The structure of cutting-edge permanent magnets is extremely fine
  ⇒ every crystallite contains only one domain, with grain boundaries and not Bloch walls separating them
- The orientation of these domains by rotation needs more energy than growth of domains in combination with a shift of Bloch walls
  ⇒ Magnets are difficult to demagnetize

Alloy	Coercive field strength H_c [kA/m]	Typical energy density $(BH)_{max}$ [kJ/m^3]
Steel (0.9% C, 1.0% Mn)	4	1.6
Martensitic steel (9% Co)	11	3.3
AlNiCo (21% Ni, 12% Al, 5% Co, Fe)	35	11
CuNiFe (60% Cu, 20% Fe, 20% Ni)	44	12
$SrFe_{12}O_{19}$	260	29
$SmCo_5$	760	200
Sm_2Co_{17}	720	250
$Nd_2Fe_{14}B$:Dy,Pr	880	360

2.4 Magnetic Properties

Electronic Configuration of Lanthanides and their Cations

Metals

[Xe]	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
5d	1	1	0	0	0	0	0	1	0	0	0	0	0	0	1
4f	0	1	3	4	5	6	7	7	9	10	11	12	13	14	14

Cations

[Xe]	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
		Ce^{4+}	Pr^{4+}	Nd^{4+}			Sm^{2+}	Eu^{2+}	Dy^{4+}					Tm^{2+}	Yb^{2+}
								Tb^{4+}							
4f	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

Electronic configuration

e.g. $Gd^{3+}/Eu^{2+}/Tb^{4+}$

m_l	-3	-2	-1	0	1	2	3	-2	-1	0	1	2	0	-1	0	1
[Xe]	↑	↑	↑	↑	↑	↑	↑									
	4f							5d					6s	6p		

Ce^{3+} - Yb^{3+}, Pr^{4+}, Nd^{4+}, Tb^{4+}, Dy^{4+}, Sm^{2+}, Eu^{2+}, Tm^{2+} → paramagnetic ions

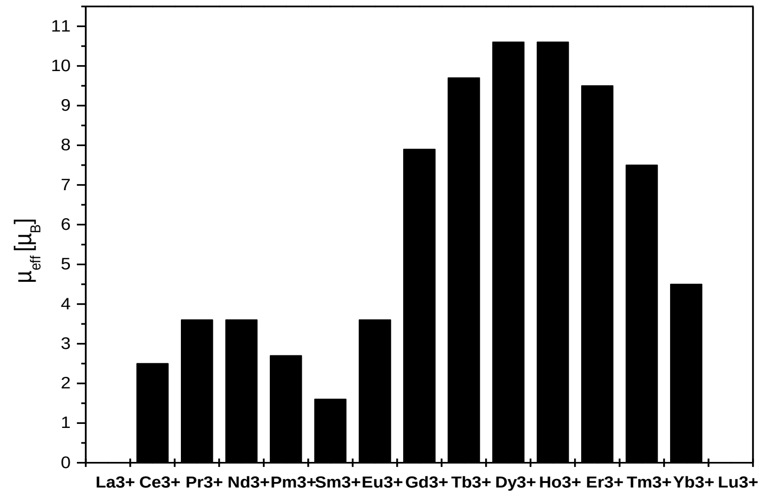
Gd^0, Tb^0, Dy^0 → ferromagnetic ordering (T_C < RT)

2.4 Magnetic Properties

Materials for Permanent Magnets – Advantages of Lanthanides

Highly paramagnetic as cations

- Gd^{3+} ⇒ magnetic contras agent [Gd^{3+}(dota)]
- Dy^{3+}/Ho^{3+} ⇒ maximal magnetic moment of all elemental cations ~ 10.6 μ_B
- For comparison: Fe^{3+}/Mn^{2+} $\mu_{eff} = 5.9\ \mu_B$

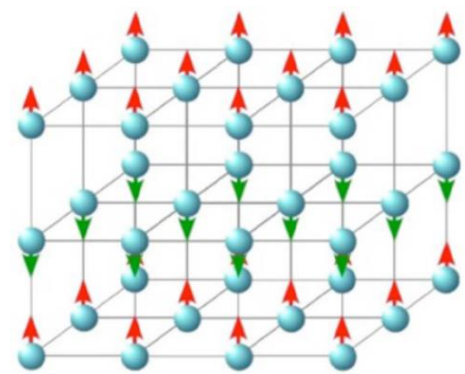


Ferromagnetic as metal or alloy

- Gd/Tb/Dy
- $Nd_2Fe_{14}B$
- $SmCo_5$ and Sm_2Co_{17}

As building block in ferromagnetic materials

- $Y_3Fe_5O_{12}$ „YIG“
- $Gd_3Fe_5O_{12}$ „GdIG“



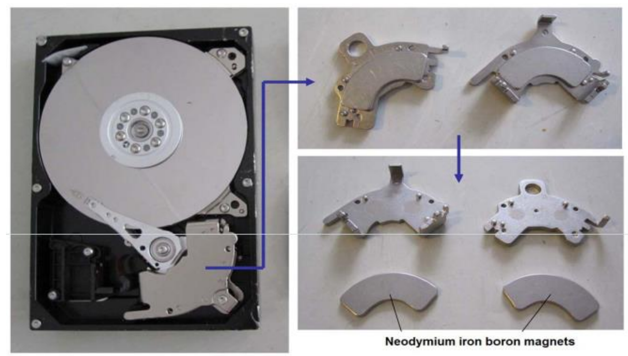
Ferromagnetic ordering in 4f ferromagnets

2.4 Magnetic Properties

Application Areas of $Nd_2Fe_{14}B$, $SmCo_5$, and Sm_2Co_{17}

- Application in electric engines in automotive industry
  > 25 actuating motors per car
  electric drive & brake

- Hard drives (HDDs)
  Magnets: 2 wt-% of HDD
  Rare earths: 0.6 wt-% of HDD



- Wind power stations
  Off-shore: 650 kg Nd/station
  ~ 100 kg/MW power output

2.4 Magnetic Properties

Alternatives for $Nd_2Fe_{14}B$, $SmCo_5$ and Sm_2Co_{17}

- **Permanent magnets on basis of iron oxide with addition of other oxides**

  Problem: energy product $(BH)_{max}$ is by a factor of ten smaller than for rare earth magnets

  ⇒ Not-applicable in many engines and generators!

- **Nano-scale Fe/Co-compounds**

  Nano-rods that order magnetically and can be stabilized as ferromagnetic domains in a matrix

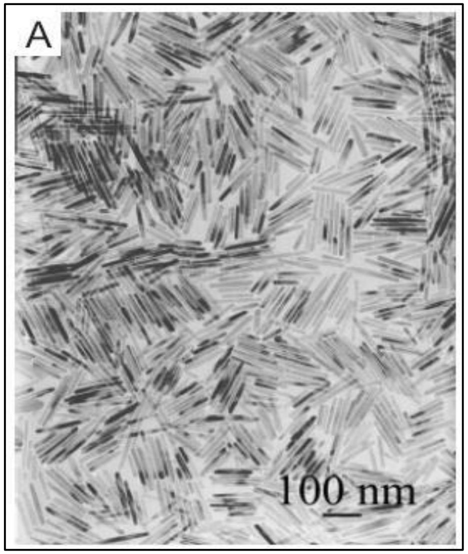
  ⇒ Technologically demanding

- **Novel molecular magnets**

  Exp.: $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$

  “Mn_{12}ac“

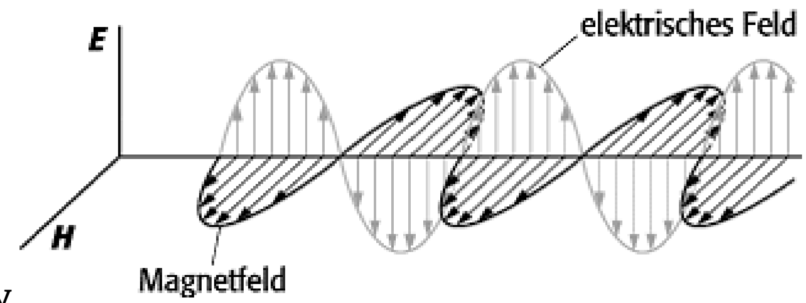
  ⇒ long-term research goal



2.5 Optical Properties

Wave Theory of Light: Huygens, Fresnel, Hertz, Maxwell

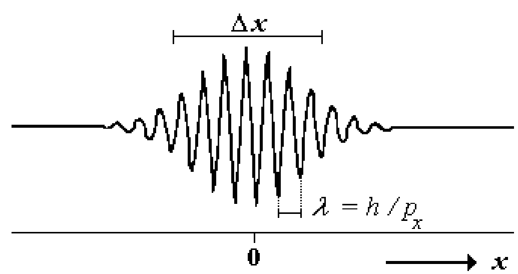
→ The light field consists of a an electric and a magnetic field component



But: The light field can take up or transfer energy only in packages (light quantums = photons)
→ "Wave-particle-dualism"

Proof for above hypothesis:

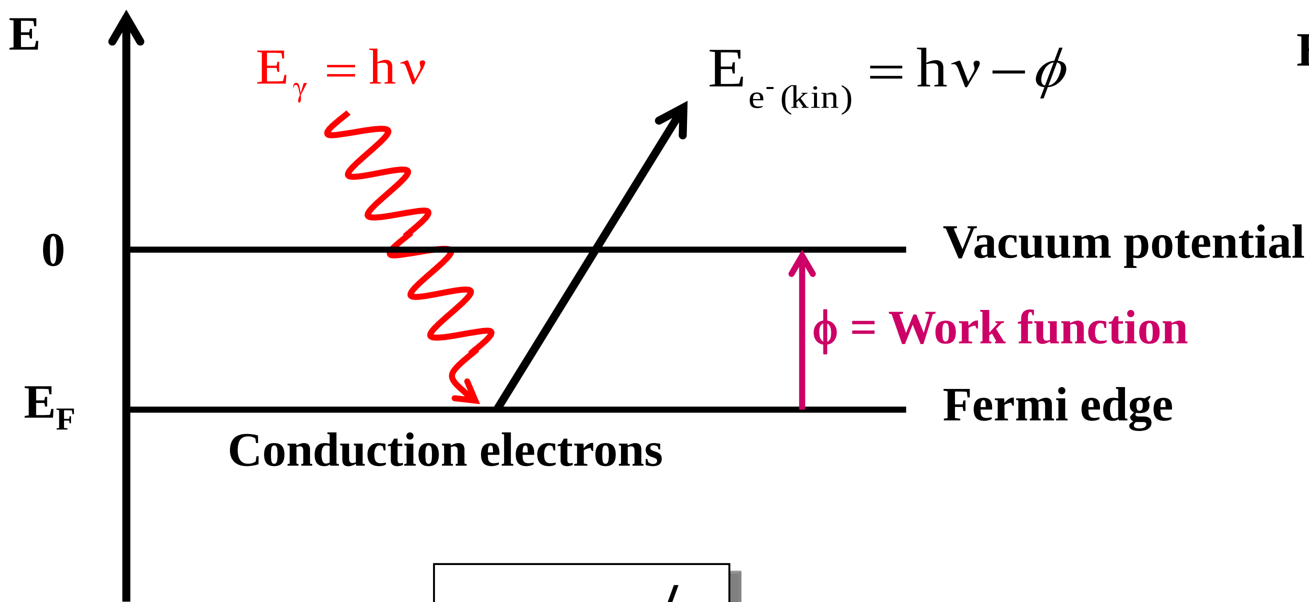
- Photons liberate electrons from an electrode, if their frequency $\upsilon > E/h$ (critical frequency)
- Derivation of Planck's radiation law for cavity radiation is based on the quantization of the energy of the light field (Planck, 1900)



→ Electromagnetic radiation consists of wave packages (photons) with discrete energy E and momentum p

Photoelectric Effect: Einstein 1905 → Nobel Price 1912

Light is quantized into photons of the energy hν. This quantization is fundamental and does not correlate with the quantization of harmonic oscillators as in Planck‘s explanation of the cavitation radiation.



Einstein-equation

$$E_{kin} = h\nu - \phi$$

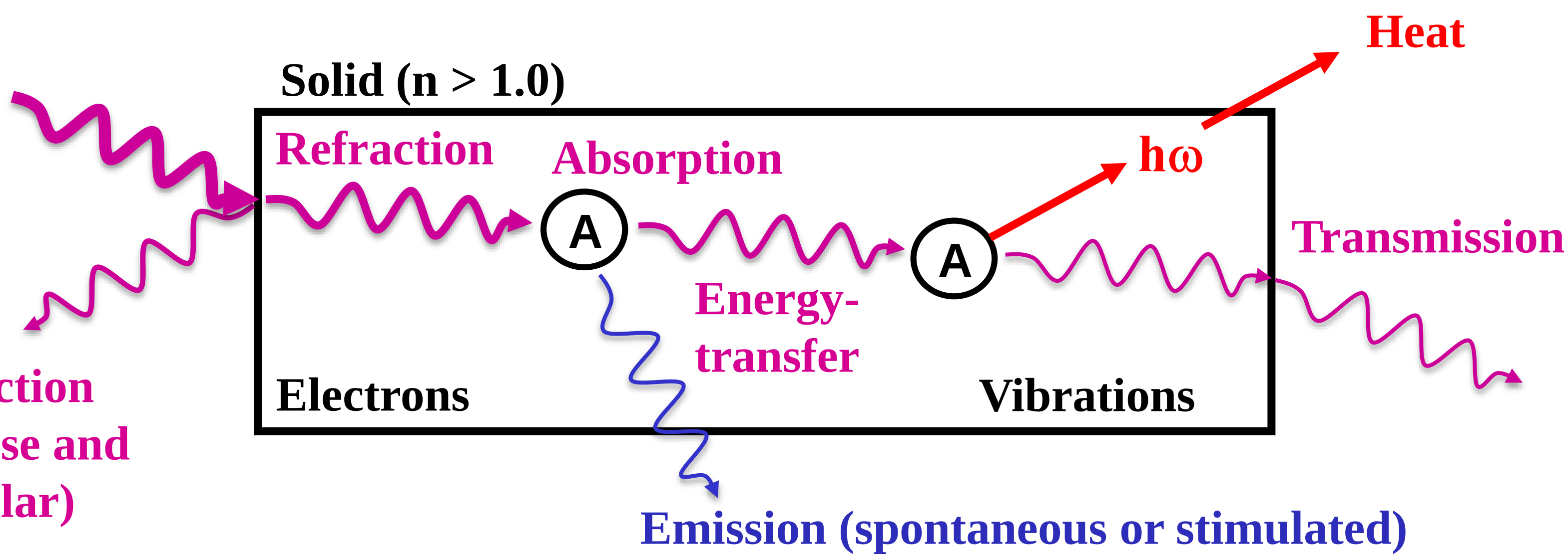
Critical frequency: $$\nu_g = \frac{\phi}{h}$$

Critical wavelength: $$\lambda_g = \frac{hc}{\phi}$$

The Optical Properties of a Substance Are Defined by its Interaction with Electromagnetic Radiation

Macroscopic phenomena

• Absorption	→ Luminescence, heat, charge separation or -storage
• Transmission	including refraction
• Reflection	diffuse and specular
• Spontaneous emission	by virtual photons
• Stimulated emission	by irradiated photons



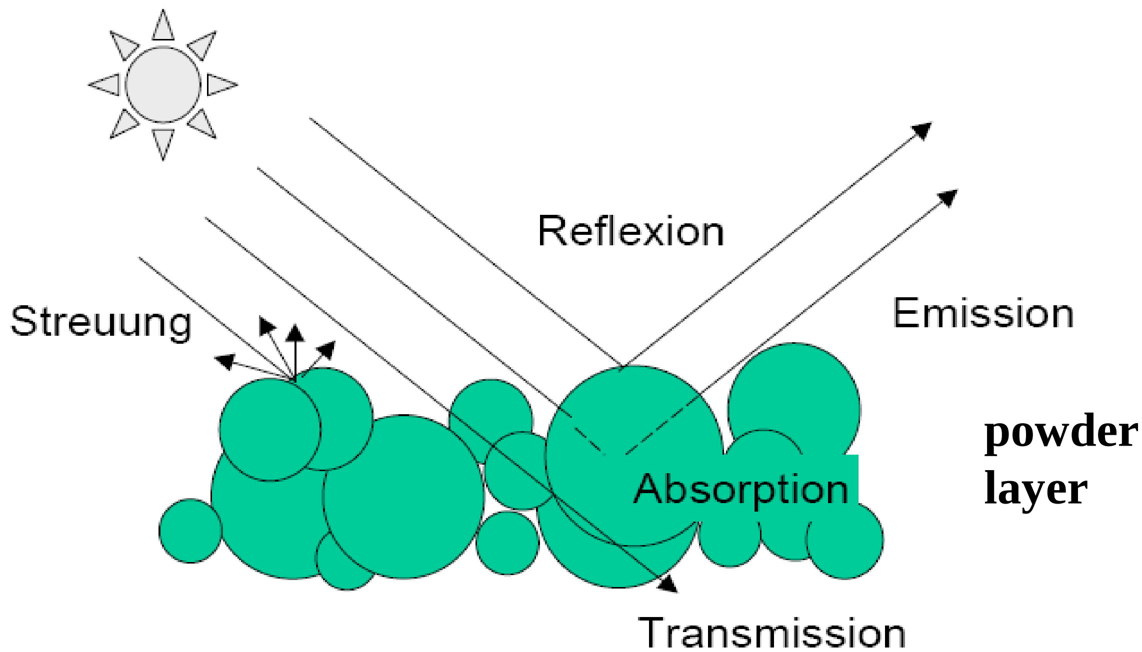
2.5 Optical Properties

Interactions between Electromagnetic Radiation and Matter

Absorption A
Uptake of electromagnetic energy by a medium

Reflection (refraction) R
Incident radiation is reflected, obeying the law of refraction

Transmission T
Passage of radiation
A + T + R = 1



Degree of absorption A: ratio of absorbed to total received radiation
Degree of transmission T: part of the radiation that passes an object
Degree of reflection R: ratio of reflected radiation (diffuse and specular) to total received radiation

2.5 Optical Properties

Interaction between Electromagnetic Radiation and Matter

Physical processes and types of radiation

Core excitation	**Gamma-rays**	**Mößbauer effect** **Fission, fusion**
Excitation of inner electrons	**X-rays**	**X-ray fluorescence (XRF)** **X-ray diffraction (XRD)**
Excitation of pouter electrons	**UV/Vis-radiation**	**Luminescence processes** **Refraction, diffraction**
Excitation of vibrations	**IR-radiation**	**Vibrations of molecules** **Solid state phonons**
Excitation of rotations	**Micro waves**	**Rotation of molecules**
Excitation of core spin	**Radio waves**	**EPR and NMR**

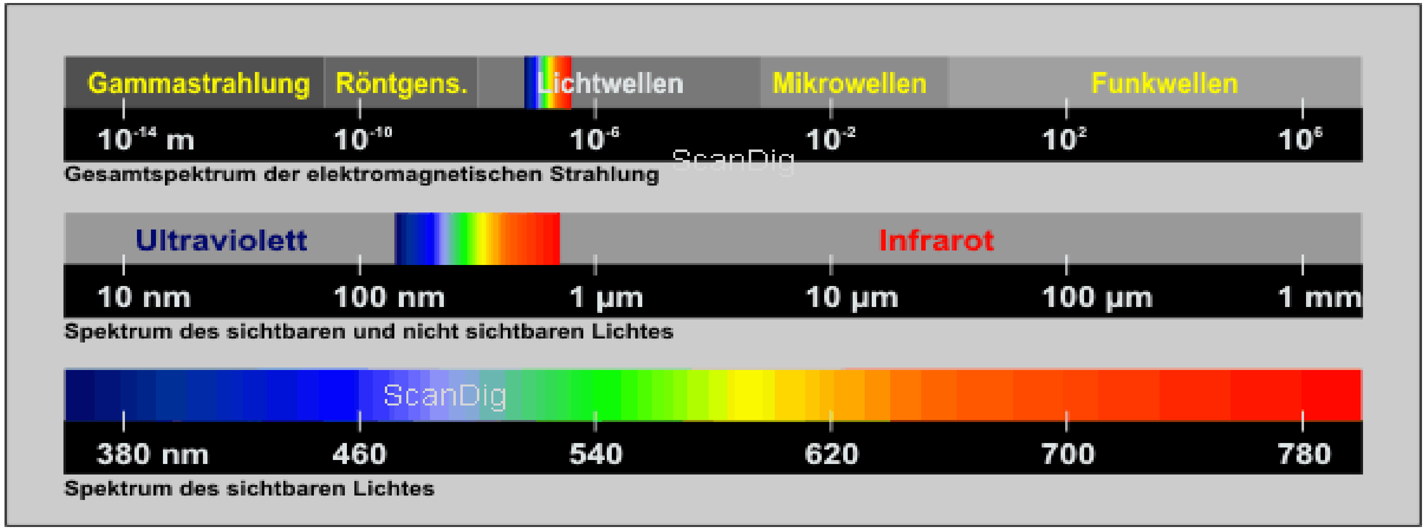
2.5 Optical Properties

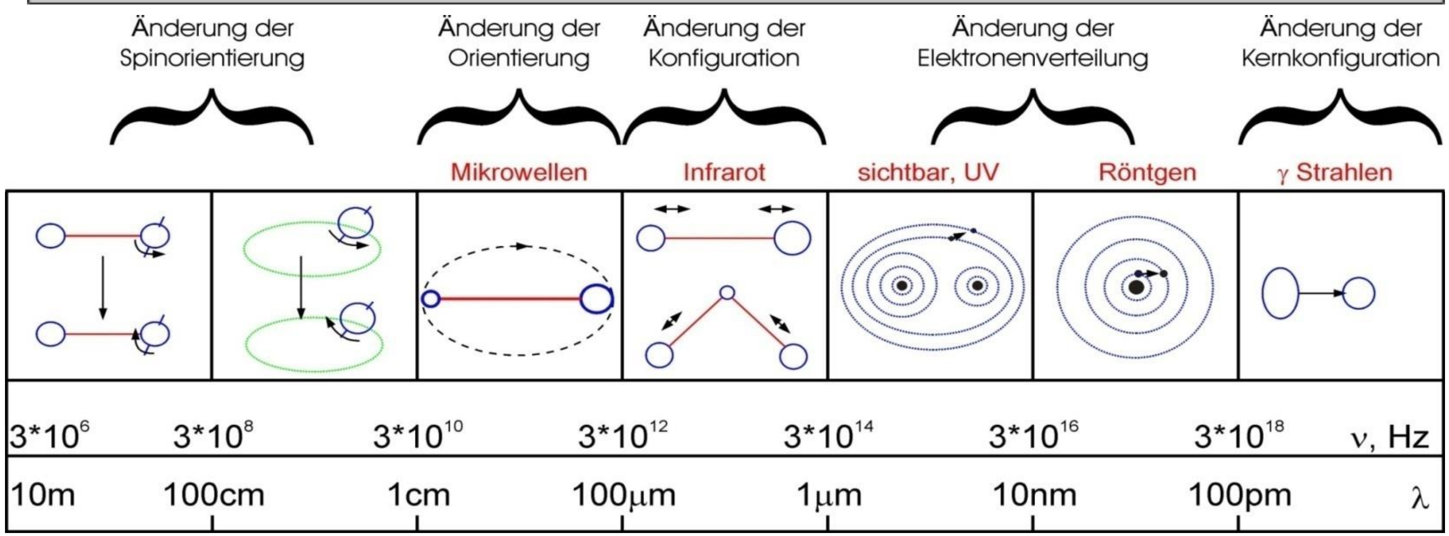
Types of Radiation and Physical Prozesses

Radiation

Optical radiation (10 nm – 1 mm)

Visible Light (380 – 780 nm)

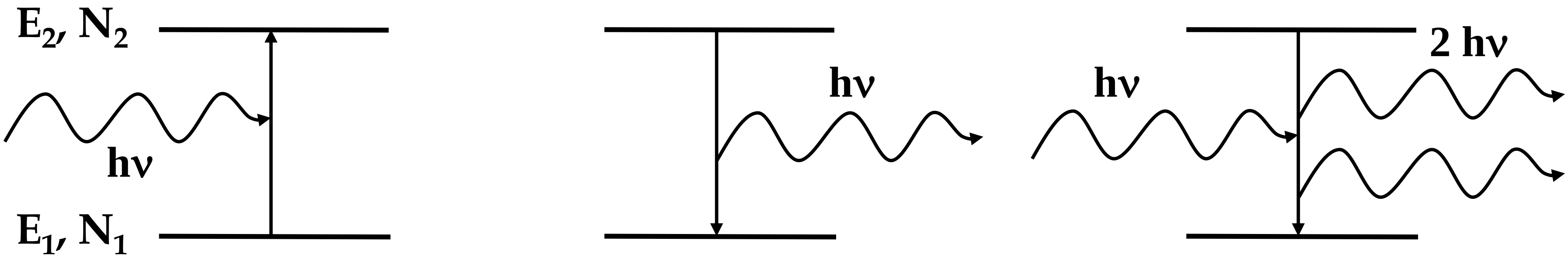




2.5 Optical Properties

Mikrosk. Wechselwirkungen zwischen elektromagnetischer Strahlung und Materie

Absorption (induced) | **Spontaneous Emission** | **Stimulated Emission**



$(dN_1/dt)_{ind.} = -B_{12}*N_1*u(\nu)$

$(dN_2/dt)_{spont.} = -A_{21}*N_2*u(\nu)$

$(dN_2/dt)_{ind.} = -B_{21}*N_2*u(\nu)$

mit A_{21}, B_{12}, B_{21} = Einstein-Koeffizienten and $u(\nu)$ = energy

$g_1B_{12} = g_2B_{21}$ mit g_1, g_2 = degeneration
$B_{21} = A_{21} \cdot \lambda^3/8\pi h$ d.h. Abklingzeit $\tau \sim \lambda^3$

<u>Erhaltungssätze</u>

1. Energieerhaltung: $h\nu = E_2 - E_1 = \Delta E$
2. Impulserhaltung: $h/\lambda = \pm 1 = \Delta l$

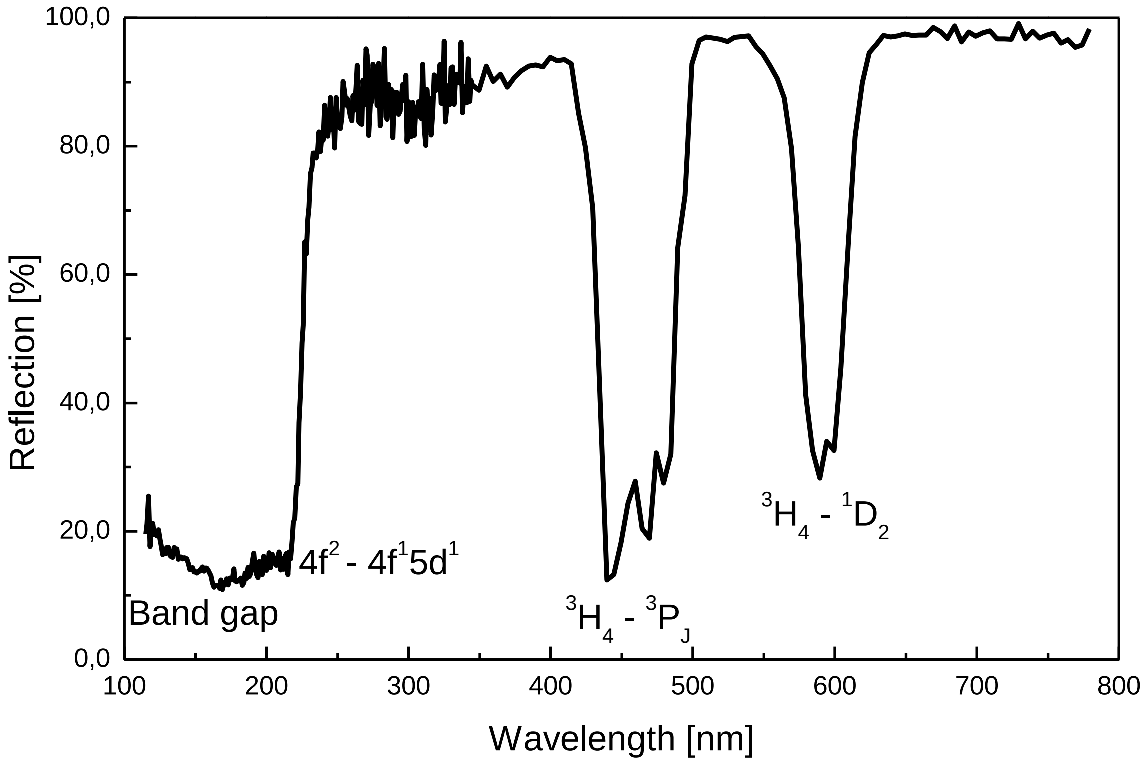
ns → np sowie nf → (n+1)d Übergänge sind erlaubt
nd → nd sowie nf → nf Übergänge sind verboten

2.5 Optical Properties

Absorption: Electronic Transitions

Example: $PrPO_4$ (powder)

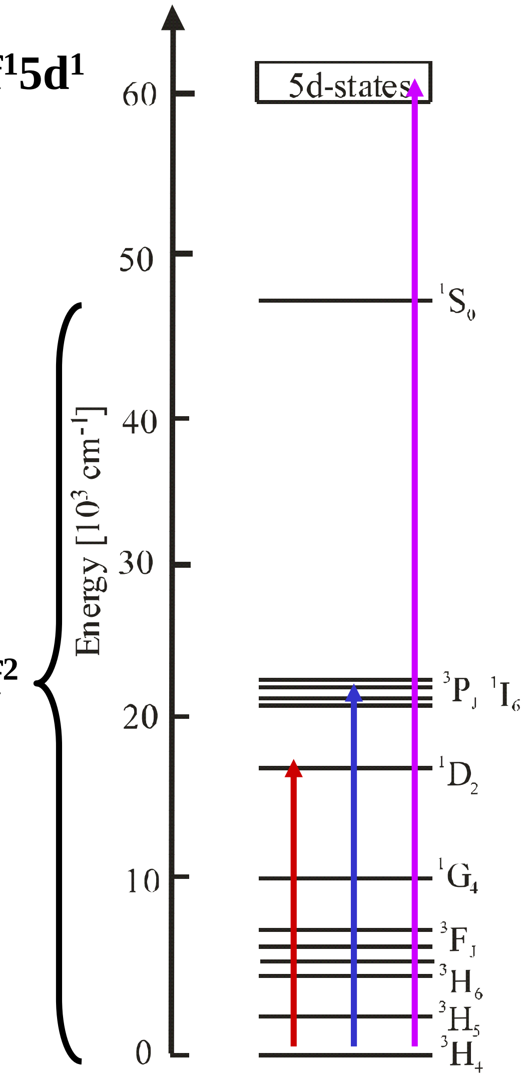
1. $4f^2$ - $4f^2$ transitions (450 and 580 nm)
2. $[Xe]4f^2$ – $[Xe]4f^15d^1$ transitions (210 nm)
3. VB - CB transition (~150 nm)



Pr^{3+}

$[Xe]4f^15d^1$

$[Xe]4f^2$

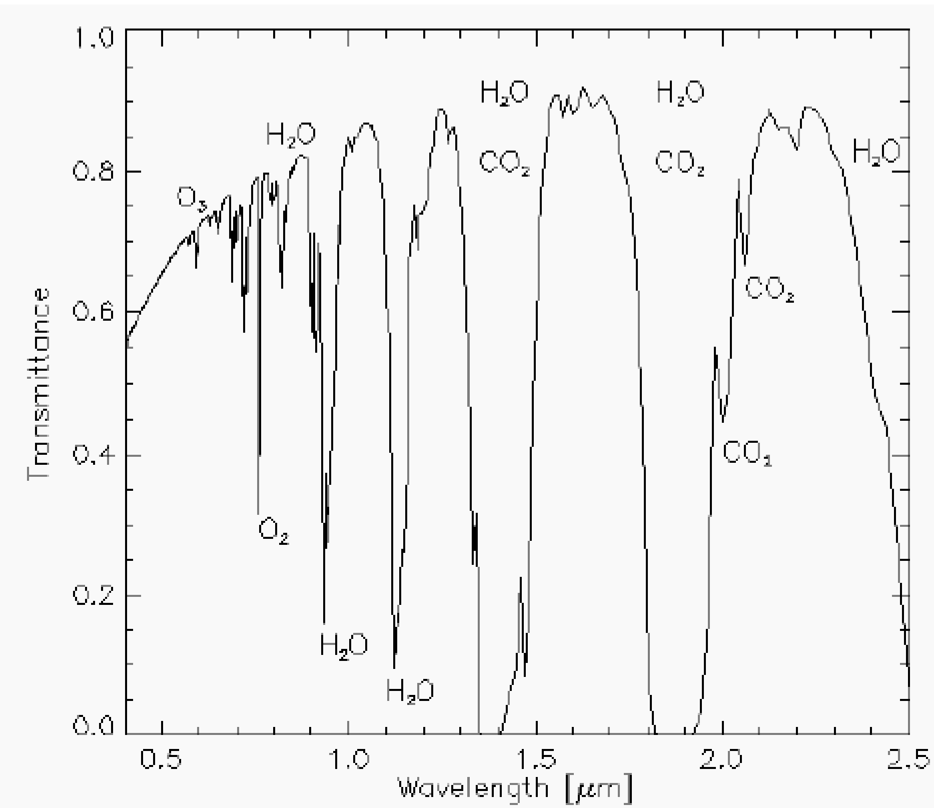


2.5 Optical Properties

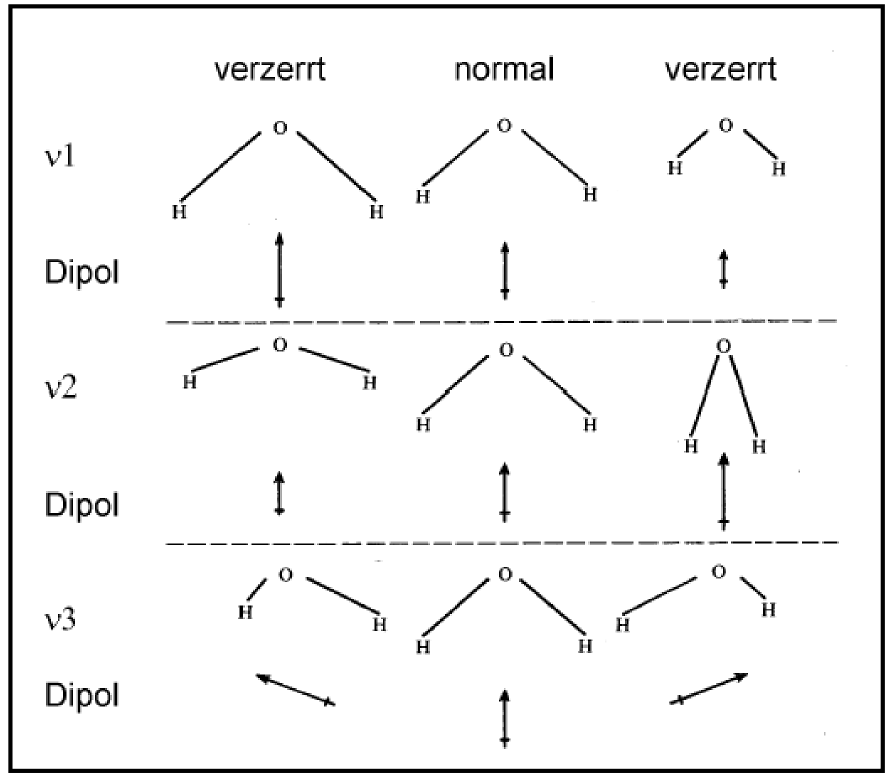
Absorption: Vibronic Transitions

Example: Absorption of light by atmosphere (absorbing gases: CO_2, H_2O, O_3)

IR-Spectrum



Normal vibrations of H_2O



2.5 Optical Properties

Conversion of the absorbed energy

• Solar thermal	Radiation → Thermal energy	Colour pigments Solar panels
• Luminescence	Radiation → Light	Light sources Laser Scintillators Diagnostics
• Photo voltaics	Radiation → Electricel energy	Solar cells
• Photo synthesis	Radiation → Chemical energy	Autotrophe organisms Photochemistry
• Storage	Radiation → Charge carrier	Afterglow pigments Detectors Optical Storage

2.5 Optical Properties

Transmission: Classification of Materials

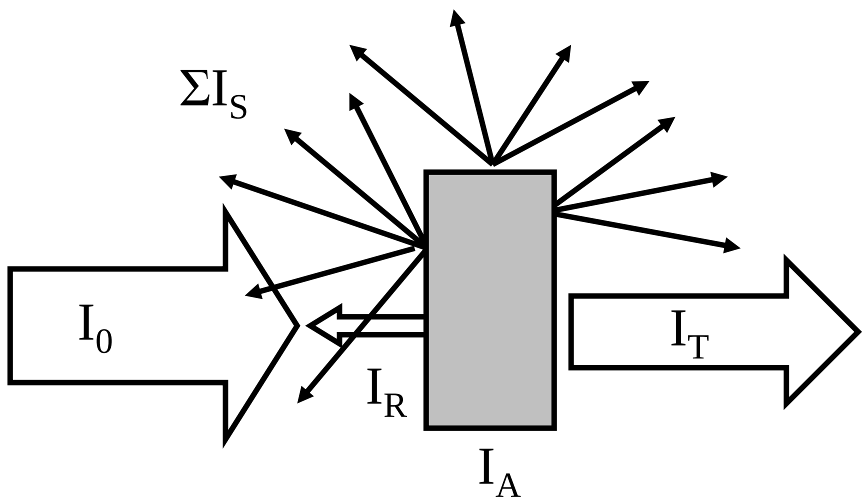
1. **Transparent (plain) materials** — **Single crystals, transparent ceramic**
- **high transmission**
- **negligible reflection and absorption**

2. **Translucent (dull) materials** — **Frosted glass, nano-powder layers**
- **high transmission, but strong refraction**
- **Light is transmitted hazily**

3. **Opaque (intransparent) materials** — **Ceramic, thick powder layers**
- **high reflection and absorption**
- **Negligible transmission**

Degree of transmission $T = I/I_0$ **with** $I = I_0 \cdot e^{-\mu \cdot d}$

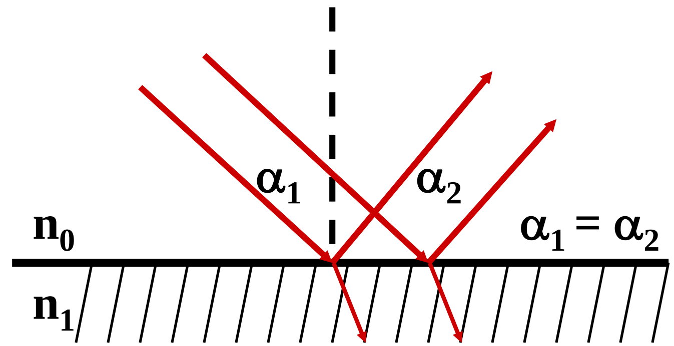
Extinction $E = -\lg(I/I_0) = \lg(I_0/I) = \lg O$
with O = Opacity



2.5 Optical Properties

Reflection: Specular (Regular)

Reflection at polished surface in one direction (reflective surface)



1. Case: Non-absorbing materials

$$R_{reg} = \frac{(n_1 - n_0)^2}{(n_1 + n_0)^2}$$

Substance	refractive index n_D
Vacuum	1,000
Air	1,0003
H_2O(s)	1,309
H_2O(l)	1,333
CaF_2 (Flussspat)	1,434
SiO_2 (Glass)	1,46
SiO_2 (Quartz)	1,55
Al_2O_3 (Sapphire)	1,76
$Y_3Al_5O_{12}$ (YAG)	1,83
Y_2O_3 (Bixbyite)	1,90
$ZrSiO_4$ (Zirconia)	1,923
Diamond	2,417
Lead glass	2,50

2. Case: Absorbing materials

$$R_{reg} = \frac{(n_1 - n_0)^2 + (n_1 k_1)^2}{(n_1 + n_0)^2 + (n_1 k_1)^2}$$

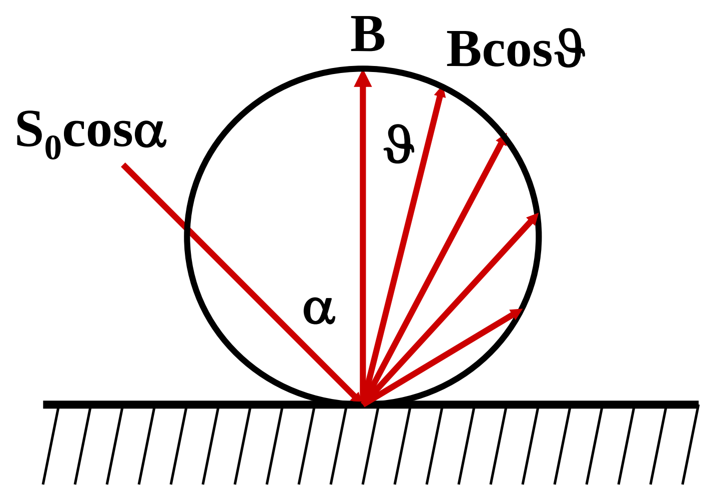
with n = refractive index
k = absorption index

Result

Based on a (specular) reflection spectrum, a absorption spectrum can be calculated, if the reflection spectrum is known over the whole range of the electromagnetic spectrum (Kramers-Kronig-Transformation)

2.5 Optical Properties

Reflection: Diffuse (Irregular)



Reflection at a non-polished surface in all directions of the half space (dull surface)

<u>Description by Kubelka-Munk-Theory</u>

- **requires optically infinitely thick powder**
- **holds for diffuse irradiation and diffuse remission, i.e. directional reflection must be eliminated**
- **Assumption: The sample consists of infinitesimal thin layers that are irradiated above and from below and weaken the light through absorption**

$$f(R) = \frac{(1-R)^2}{2R} = \frac{1}{s}\varepsilon c$$

with
R = degree of diffuse reflection
s = refractive coefficient
c = concentration of absorber
ε = absorption coefficient

Frequency-dependence of Optical Properties

The tendency to refract, transmit and reflect in a material is to a greater or lesser extent dependent on the frequency

This is macroscopically described by the refractive index n(ν) (index 0 = vacuum)

$$\mathrm{n}(\nu) = \frac{\mathrm{c}_0}{\mathrm{c}_1(\nu)} = \frac{\lambda_1(\nu)}{\lambda_0}$$

In a medium, electromagnetic waves spread with lower velocity than in vacuum due to polarisation of electrons

$$\mathrm{c}_1(\nu) = \frac{1}{\sqrt{\mu(\nu)\varepsilon(\nu)}}$$

thus, for non-magnetic materials

$$\mathrm{c}_1(\nu) = \frac{1}{\sqrt{\varepsilon(\nu)}}$$

The correlation between permittivity and refractive index is given by

$$\mathrm{n}(\nu) = \frac{\mathrm{c}_0}{\mathrm{c}_1(\nu)} = \sqrt{\frac{\mu(\nu)\varepsilon(\nu)}{\mu_0(\nu)\varepsilon_0(\nu)}} = \mu_r(\nu)\varepsilon_r(\nu)$$

and for non-magnetic materials

$$\mathrm{n}(\nu) = \sqrt{\varepsilon_r(\nu)}$$

2.5 Optical Properties

Frequency-dependence of Optical Properties

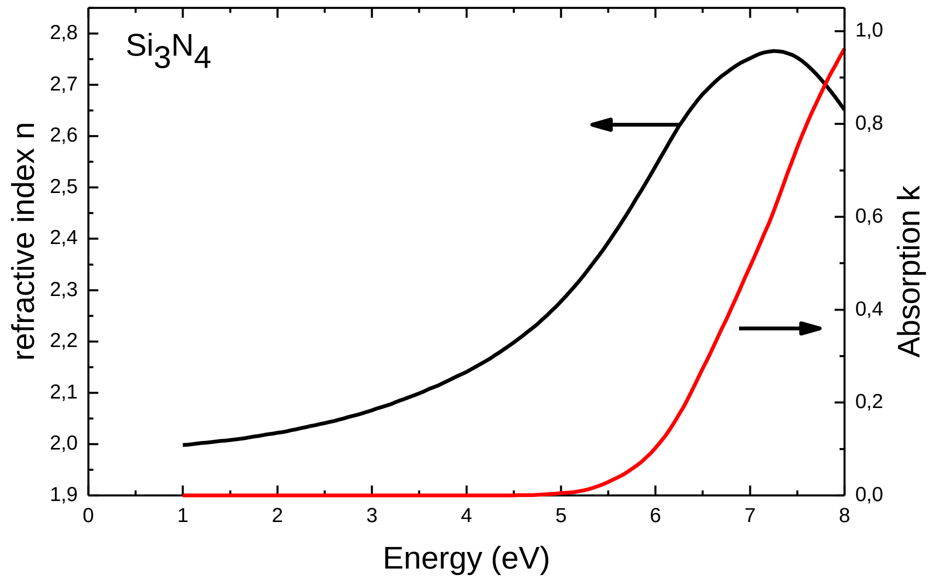
Thus, the refractive index of a material must always be given for a certain frequency

⇒ often, the frequency of sodium-D-line is chosen (589 nm)

The electromagnetic wave polarises the electrons of the medium

⇒ electronic polarisation

(Example: Silicon nitride Si_3N_4)



The strength of the interaction between photons and electrons thus depends on the polarizability of the electrons

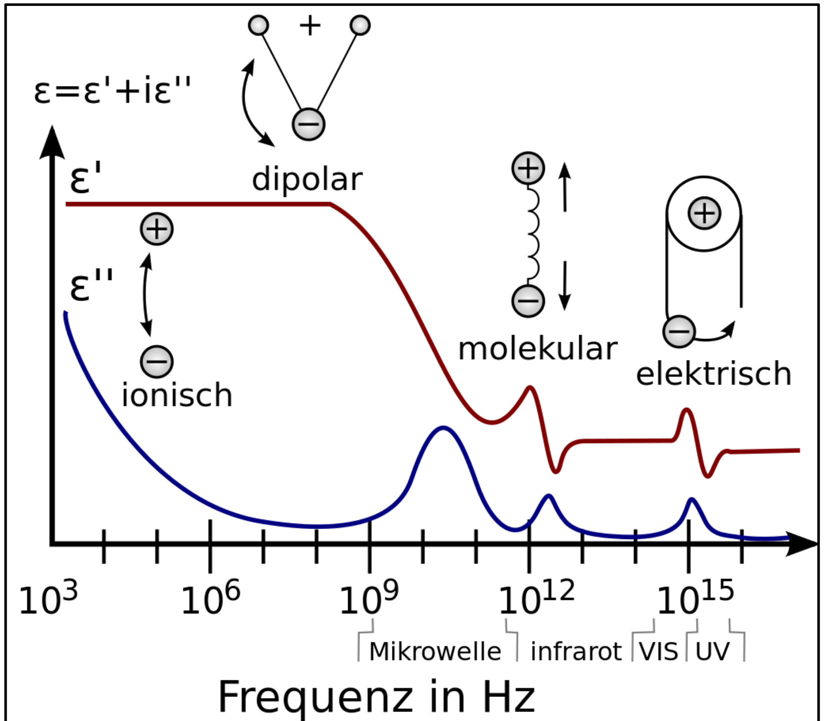
⇒ Materials with high (electron)density have a high refractive index (lead glass)

⇒ Materials with a low band gap have a high refractive index (TiO_2, ZnS)

2.5 Optical Properties

Frequency-dependence of Optical Properties

At low frequencies (IR-region) ionic polarisation (vibrations) dominates the interaction between solids and photons



At very high frequencies the interaction between photons and electrons becomes weaker more and more, so that the refractive index approaches 1

⇒ n = 1 for x-ray and gamma radiation

2.5 Optical Properties

Frequency-dependence of Optical Properties

Microwave region (radar radiation)

- **Absorption: Materials with the possibility for orientation polarisation or easily polarizable electrons**
  - **Conducting polymers**
  - **Ferrimagnets**
- **Transmission and reflection**
  - **Ceramics**
  - **Polymers**

Infrared region (thermal radiation)

- **Absorption: Molecular vibrations or ionic polarisation**
- **Transmission and reflection**
  - **Materials with low phonon frequencies, e.g. halides**

Visible spectral region (optical radiation)

- **Absorption: Electronic polarisation and electronic transitions**

Anisotropy of Refractive Index

The refractive index, n, can be dependent on spatial direction, thus being anisotropic
⇒ Crystals with low symmetry ($CaCO_3$, calcite)

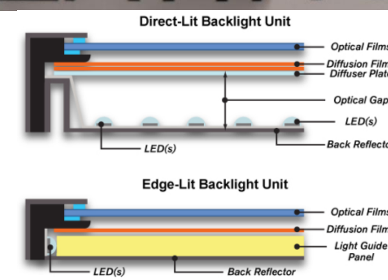
By variation of n depending on the direction of the polarisation of the electrical field, birefringence can occur

Optical Properties of substances with anisotropic refractive indices can be influenced by applying (high) voltages

<u>Applications</u>

- **In Pockels cell: electro-optical modulator, which changes the polarisation of light during passage, if voltage is applied (optical switches) $LiNbO_3$, KH_2PO_4, ß-BaB_2O_4**
- **LCD panels: control of light flux through polarisation via liquid crystals**

Calcite-crystal (above)
Demonstration of birefringence (below)

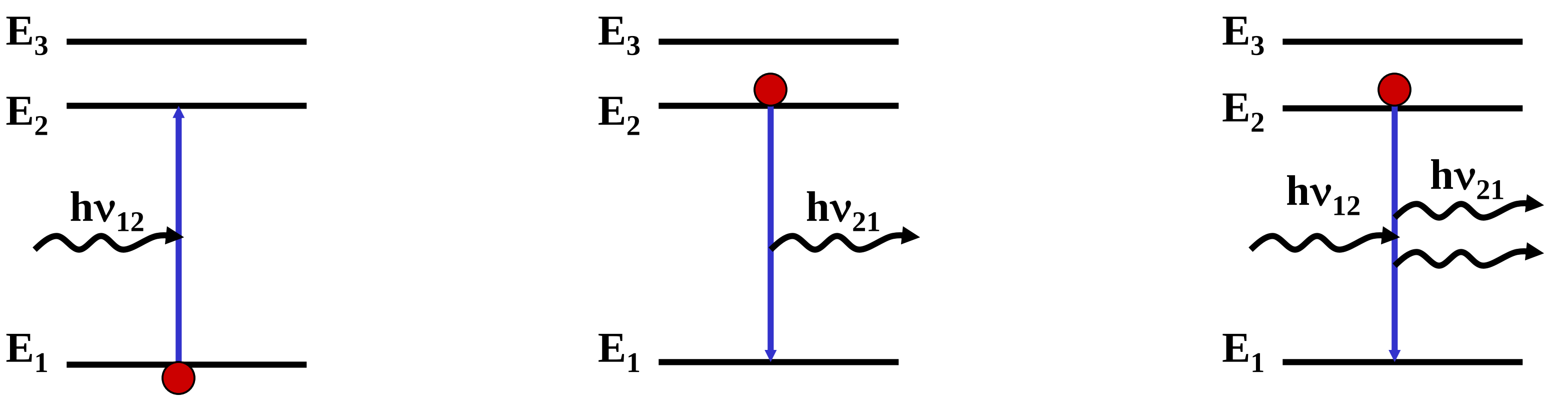


2.5 Optical Properties

Absorption and Emission

Light interacts with electrons of the atoms. Through interaction of a light quantum with a electron the quantum can be absorbed or reinforced. Crucial is the energy state of the electron.

Absorption | **spontaneous emission (luminescence)** | **stimulated emission (reinforced luminescence)**



Transformation of radiation or other forms of energy into visible light or UV-radiation is called luminescence

2.5 Optical Properties

Light Amplification by Stimulated Emission of Radiation (Laser)

Short introduction into history of Laser technology

1917	theoretical foundation (A. Einstein, D)
1954	first microwave Laser demonstrated: Maser
1960	first pulsed lasing processes in ruby-solid-state Laser demonstrated (Theodore H. Maiman, CA, USA)
1961	first Nd-glass-Laser
1964	first cw CO_2-Laser
1965	first application of a Laser to process diamond (Herziger, D)
1966	first tunable dye laser pumped by a ruby laser
1969	first factory to drill watch stones (Herziger, D)
1978	first Laser cutting system in a company
1995	first high-power diode-Laser for hardening
2002	first high-power fibre-Laser for welding
2016	13.5 nm (EUV) radiation generated by a CO_2-Laser irradiated molten Sn droplet

Laser radiation is the form of energy with the highest possible degree of order or minimal entropy and highest coherence

2.5 Optical Properties

Materials for Solid-State Laser

1. Active medium

- Single crystals or transparent ceramics
  Oxides: Al_2O_3, $Y_3Al_5O_{12}$, $Lu_3Al_5O_{12}$, $BeAl_2O_4$, $YAlO_3$, $CaWO_4$, YVO_4, $GdVO_4$, KYW_2O_8
  Fluorides: MgF_2, CaF_2, BaY_2F_8, $LiCaAlF_6$, $LiYF_4$, KY_3F_{10}
- Glasses: phosphates and silicates
- The host material must possess extremely good optical, mechanical and thermal properties

2. Dopants

- Transition metal ions
  Cr^{3+} (e.g. in ruby-Laser), Ti^{3+} (e.g. in sapphire Laser), U^{3+}
- Ions of rare earth elements (lanthanide ions)
  Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}
- Density of Laser-active dopants: 10^{19} cm^{-3} (higher as for gas-Laser: $10^{15} – 10^{17}$ cm^{-3})

2.5 Optical Properties

Ruby-Laser ($Al_2O_3:Cr$)

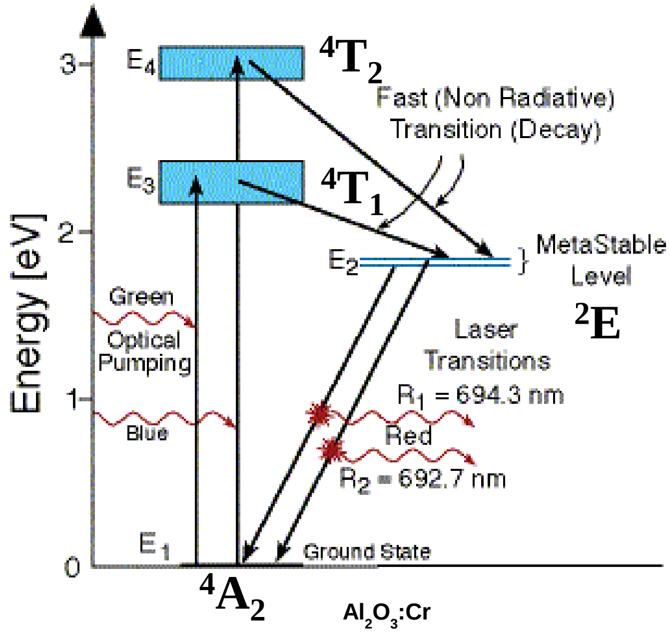
Excitation by a flash lamp in the blue and green spectral region leads to excitation of Cr^{3+} [Ar]$3d^3$ (pumping)

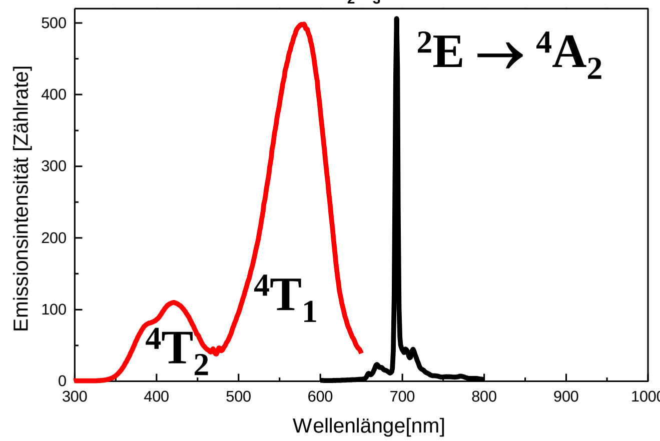
The lifetime of the ^4F_J states is very short and relaxation into metastable E-levels occurs (ISC)

Population of the E-levels increases until so-called population inversion is reached

Further irradiation by photons leads to stimulated emission and total depletion of the E-level

3-level-Laser: More than 50% of the atoms must be excited to achieve population inversion and light amplification





2.5 Optical Properties

YAG:Nd Laser ($Y_3Al_5O_{12}$:Nd)

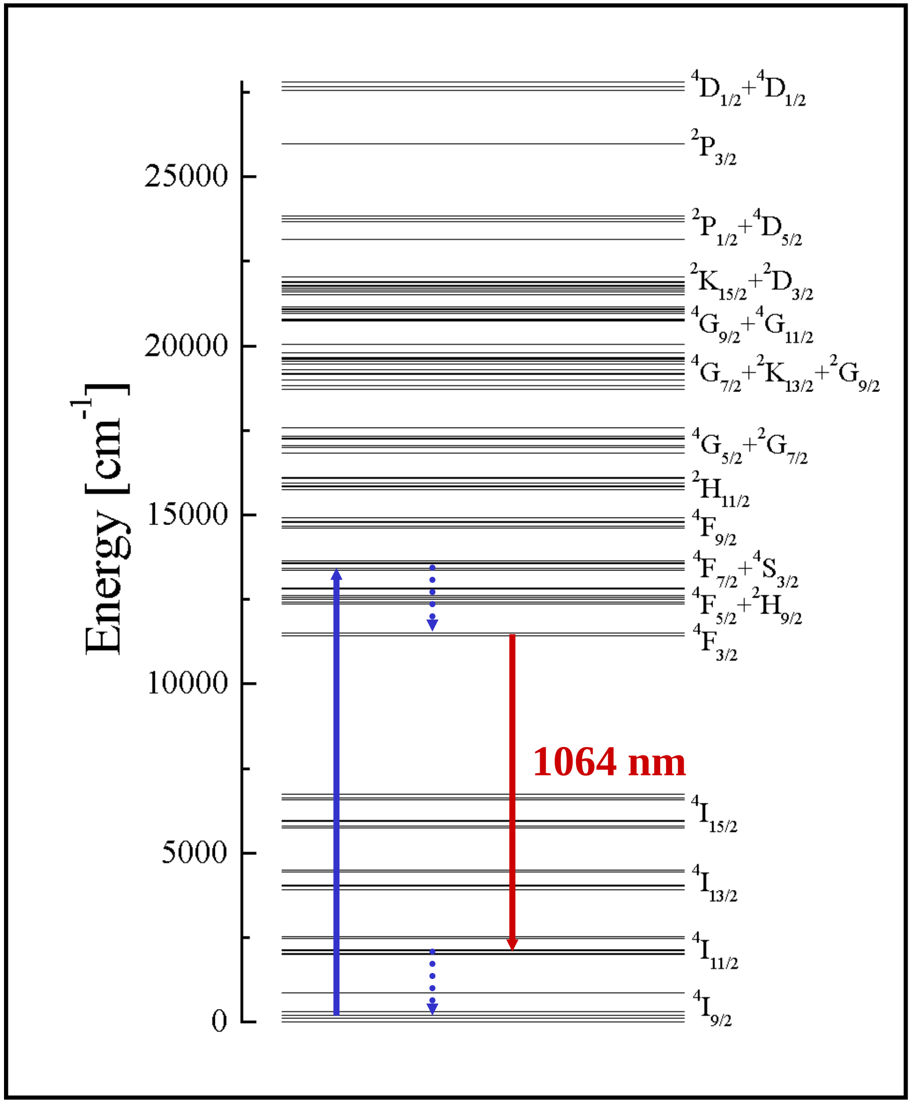
Most important commercial solid-state Laser

Excitation by diodes or flash lamps

4-level-Laser

Splitting of $^{2S+1}L_J$ multiplets into Stark-Levels by strong crystal field in YAG

But the splitting is relatively small, because the 4f-electrons are shielded by the outer completely occupied shells ($5s^2$ and $5p^6$)
~ 200 - 240 cm^{-1}



2.5 Optical Properties

YAG:Nd Laser ($Y_3Al_5O_{12}$:Nd)

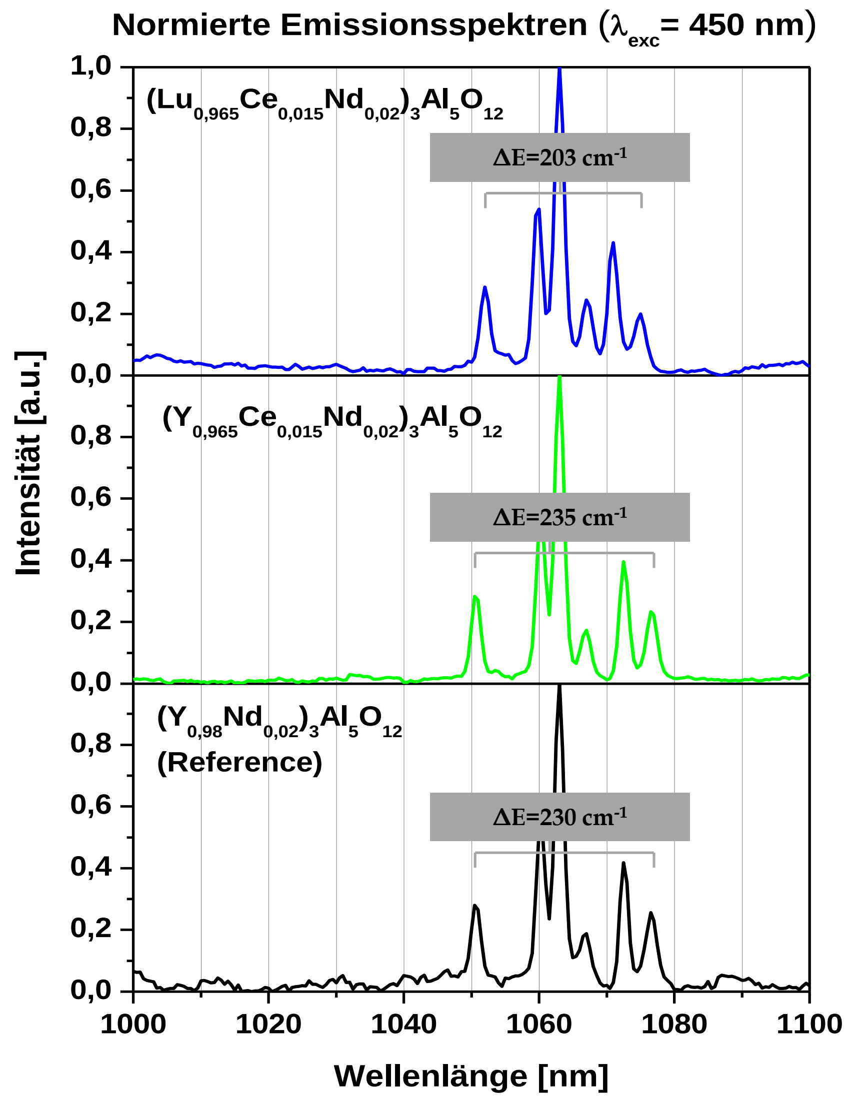
Strong splitting of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd^{3+} in garnets of the LnAG-type. Tuneable by type of occupation of the dodecahedral site

LuAG:Ce,Nd	YAG:Nd	YAG:Ce,Nd
203 cm^{-1}	230 cm^{-1}	235 cm^{-1}

Physical effect

Crystal field splitting
= f(coordination number, symmetry,
Ionic charge density, ...)

$Lu^{3+} < Y^{3+} < Nd^{3+} < Ce^{3+}$

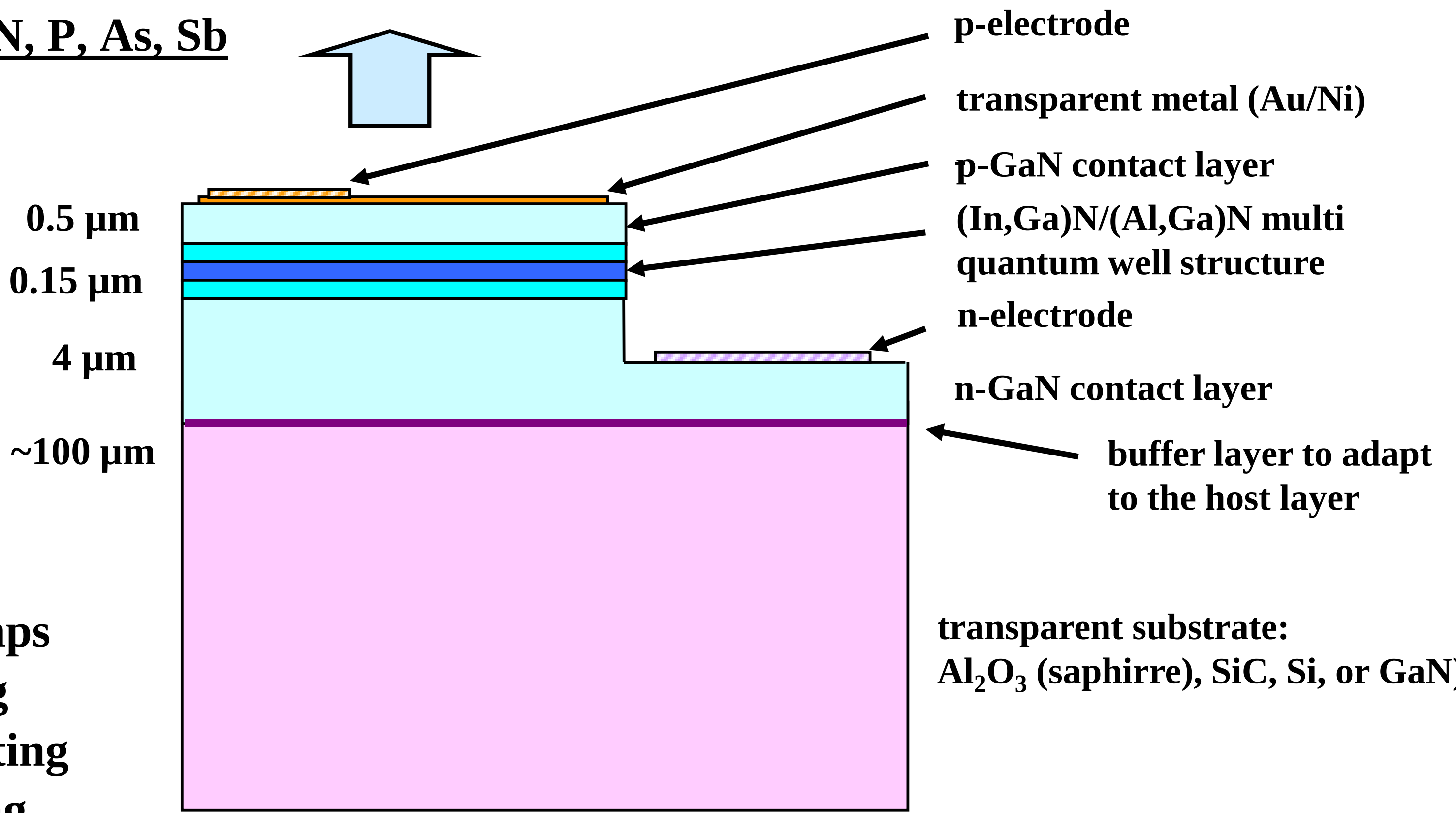


Light Emitting Diodes (LEDs)

LEDs are opto-electronic components with pn-transitions, composed of materials with band gap energies equivalent to visible radiation ⇒ III/V-semiconductors

Al, Ga, In + N, P, As, Sb

(Al,Ga)N
(Ga,In)N
(Al,Ga)P
(Al,Ga,In)P
(Al,Ga)As
GaAs

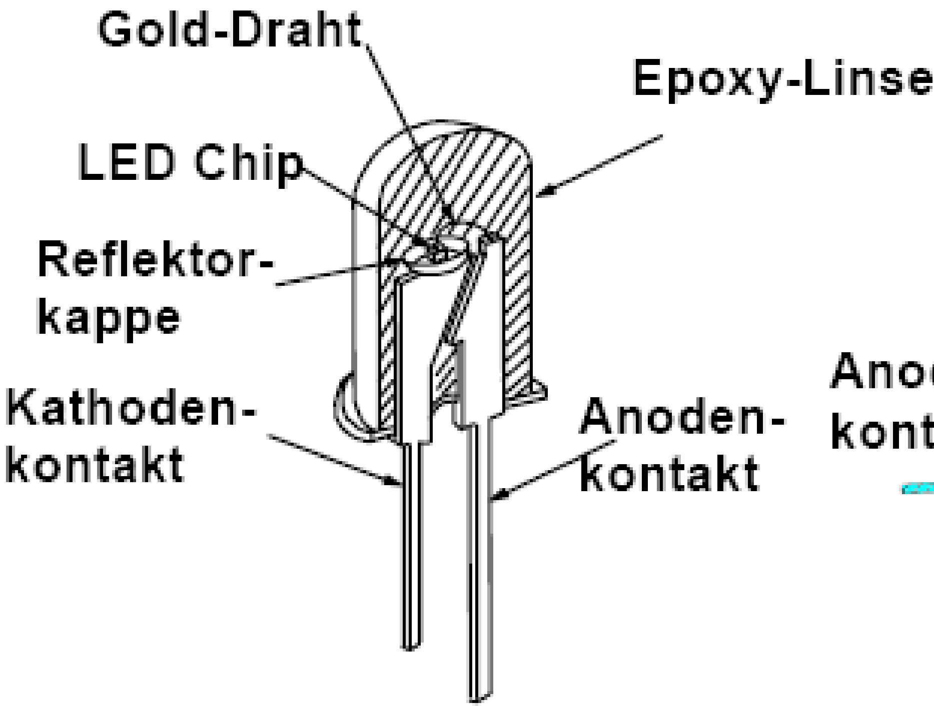


Applications
Signal lamps
Designer lamps
Back lighting
General lighting
Street lighting

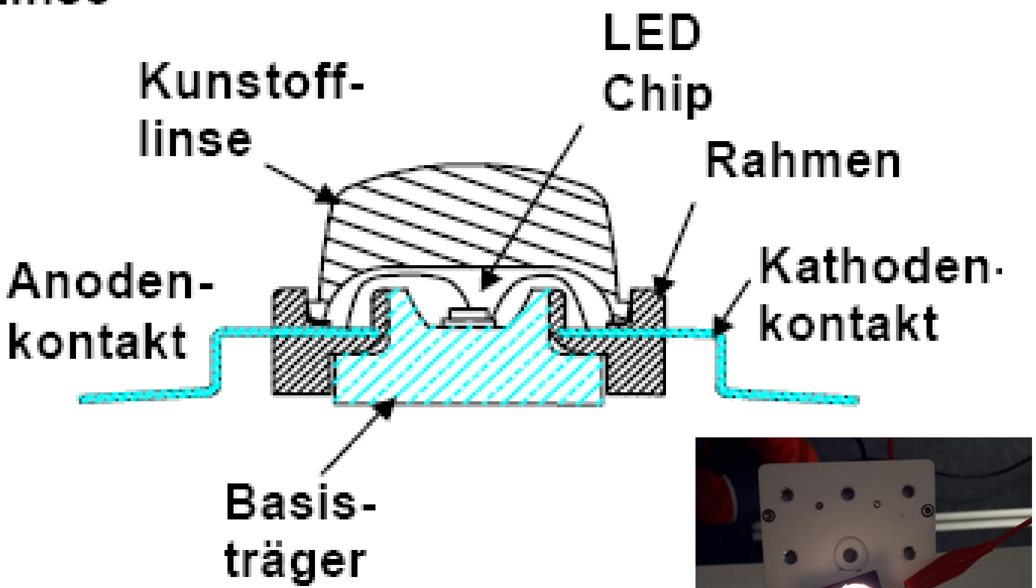
2.5 Optical Properties

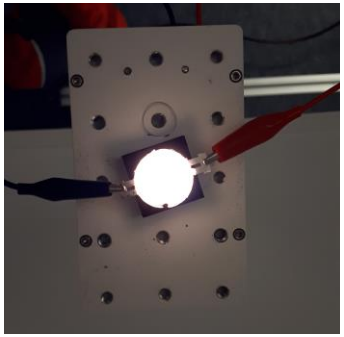
Light Emitting Diodes (LEDs)

Standard 5 mm LED



High-performance-LED

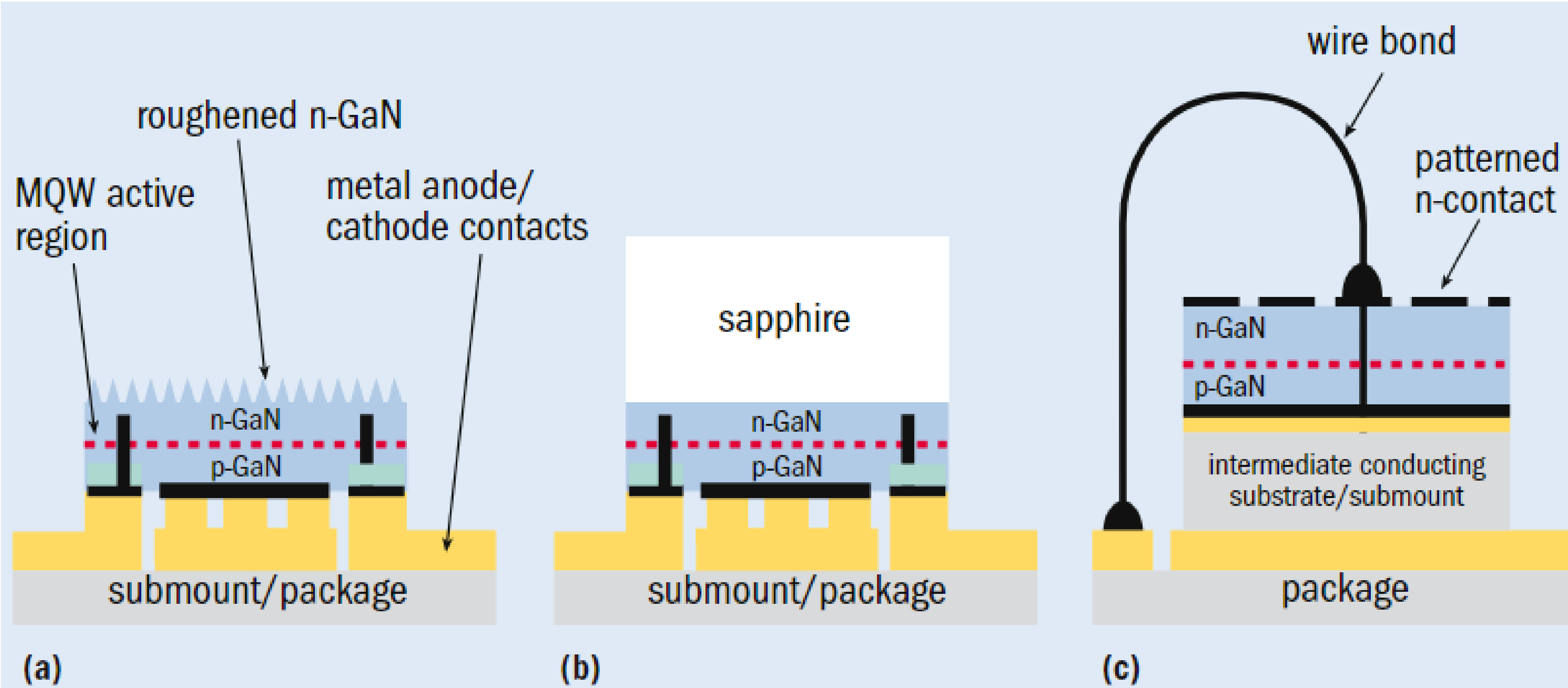




2.5 Optical Properties

Light Emitting Diodes (LEDs)

Thin Film Flip Chip **Flip Chip** **Vertical Thin Film Chip**

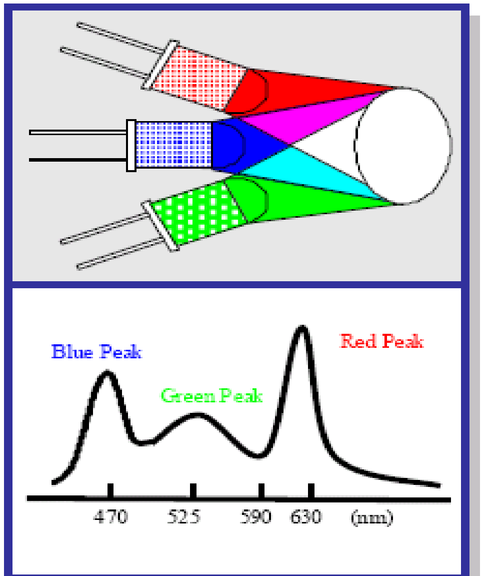


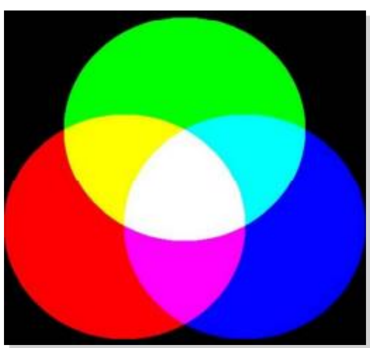
Source: https://www.lumileds.com/uploads/52/NA0307_01-pdf (06.11.2019)

2.5 Optical Properties

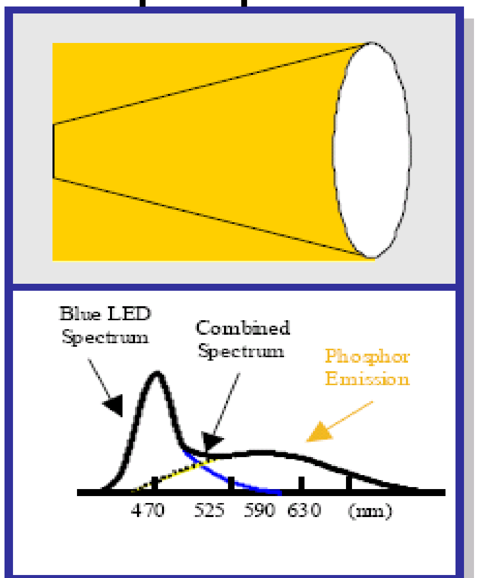
White emitting LEDs (Phosphor Converted Light Emitting Diodes pc LEDs)

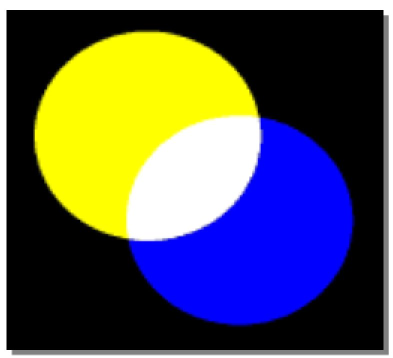
Red + Green + Blue LEDs



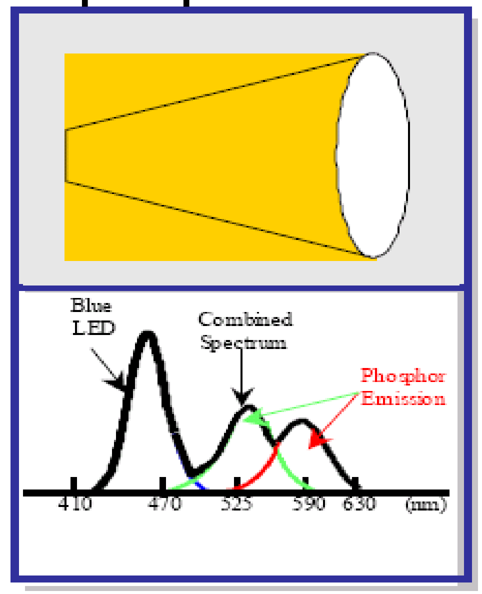


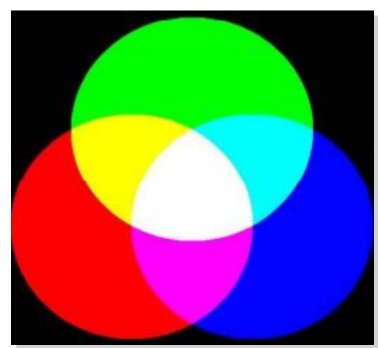
Blue LED + yellow phosphor



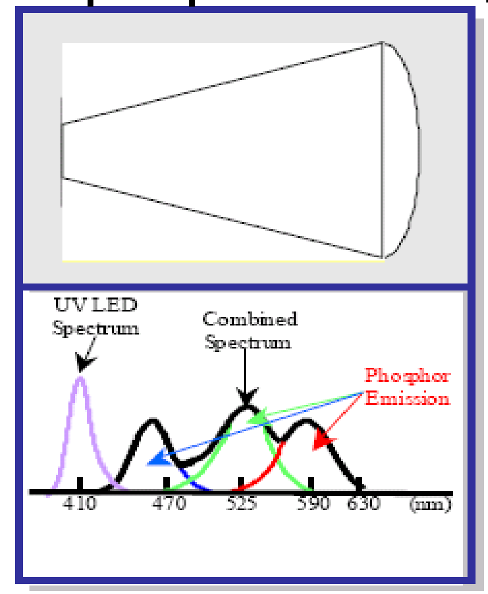


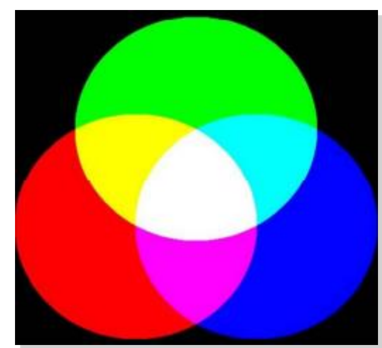
Blue LED + RG phosphor blend





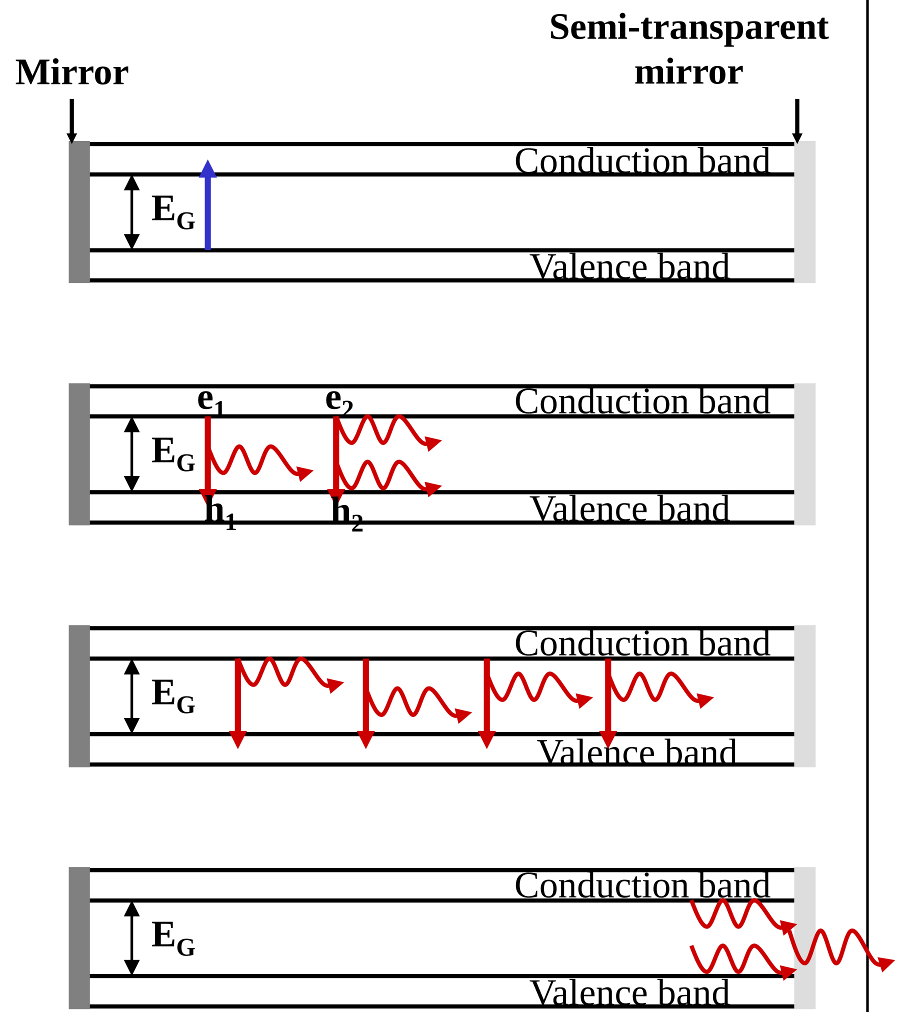
UV LED + RGB phosphor blend





2.5 Optical Properties

Semi-conductor Laser or Laser Diodes



1. Promotion of electrons from valence into conduction band by applying voltage

2. Electron e_1 recombines with hole h_1 and emits a photon which triggers the recombination of e_2 with hole h_2 under emission of a second photon

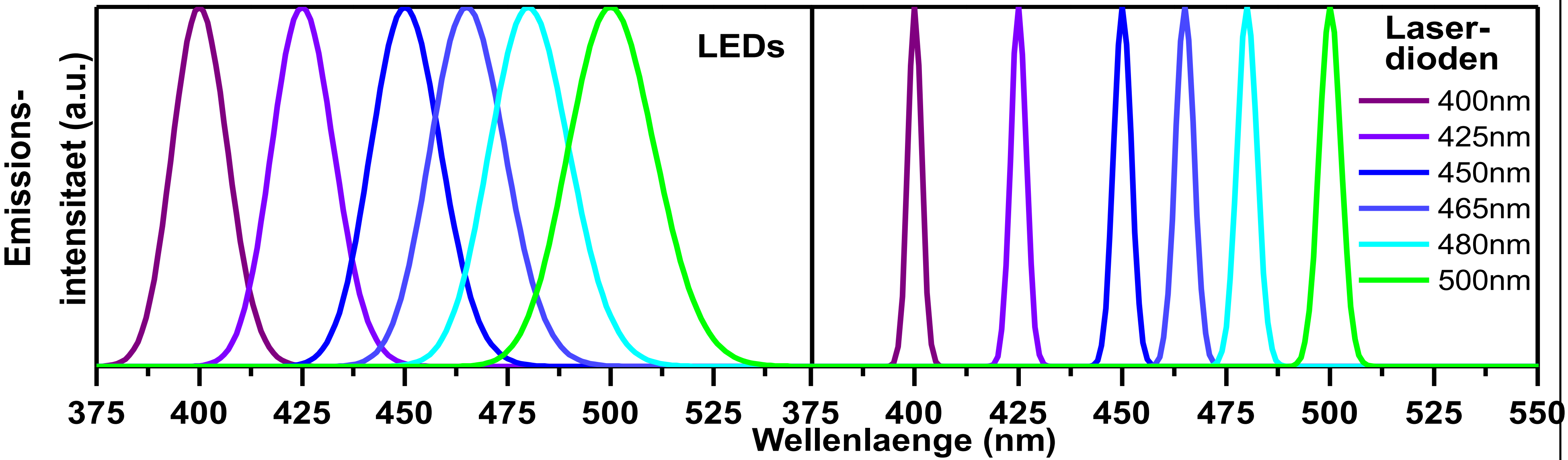
3. Continuous stimulation of further emission by reflected photons within the diode

4. At the semi-transparent mirror some photons are coupled out from the active area and leave the diode as laser beam

→ Resonator results in spectral focusing

2.5 Optical Properties

LEDs and Laser diodes



„LED platform“

465 nm LEDs — Illumination
410 nm LEDs — Full conversion
365 nm LEDs — Black light
265 nm LEDs — Disinfection

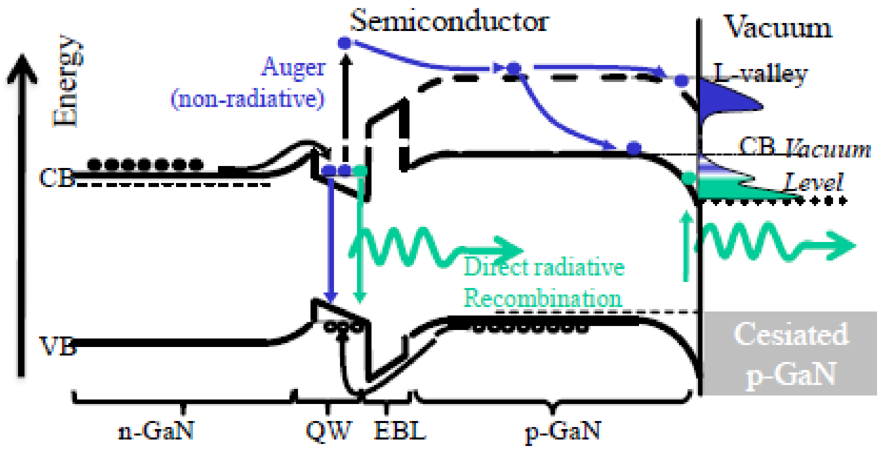
„Laser diode platform“

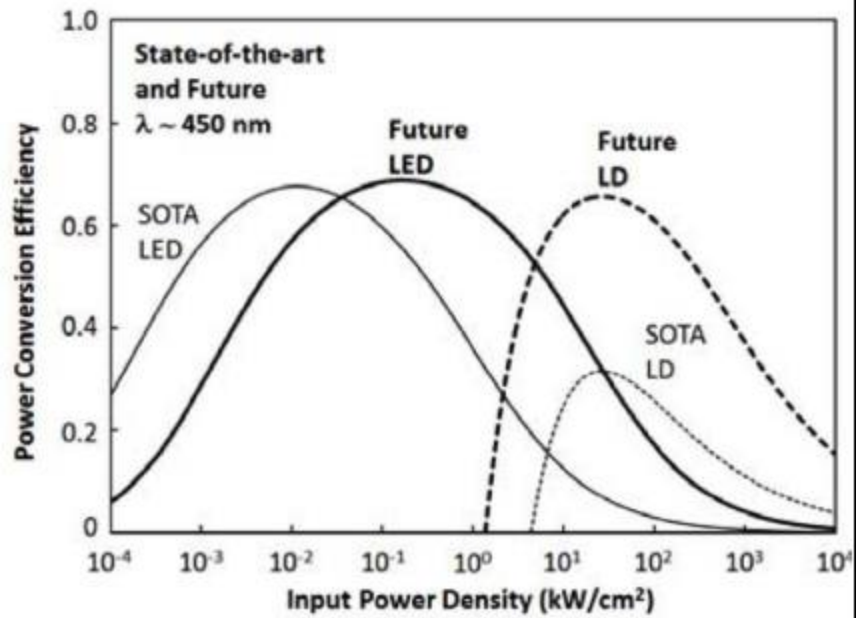
940 nm — Remote controls
785 nm — CD
655 nm — DVD
405 nm — Blue ray DVD

2.5 Optical Properties

LEDs and Laser diodes

At high current density one observes saturation of the electroluminescence due to the Auger effect





Due to stimulated emission in Laser diodes saturation will only observed for much higher current densities: Wall plug efficiency (WPE) up to 70%!)

Lit.: Phys. Rev. Lett. 110 (2013) 177406 , Phys. Stat. Solidi C 11 (2014) 674

2.5 Optical Properties

Fibre Optics for Transfer of Information

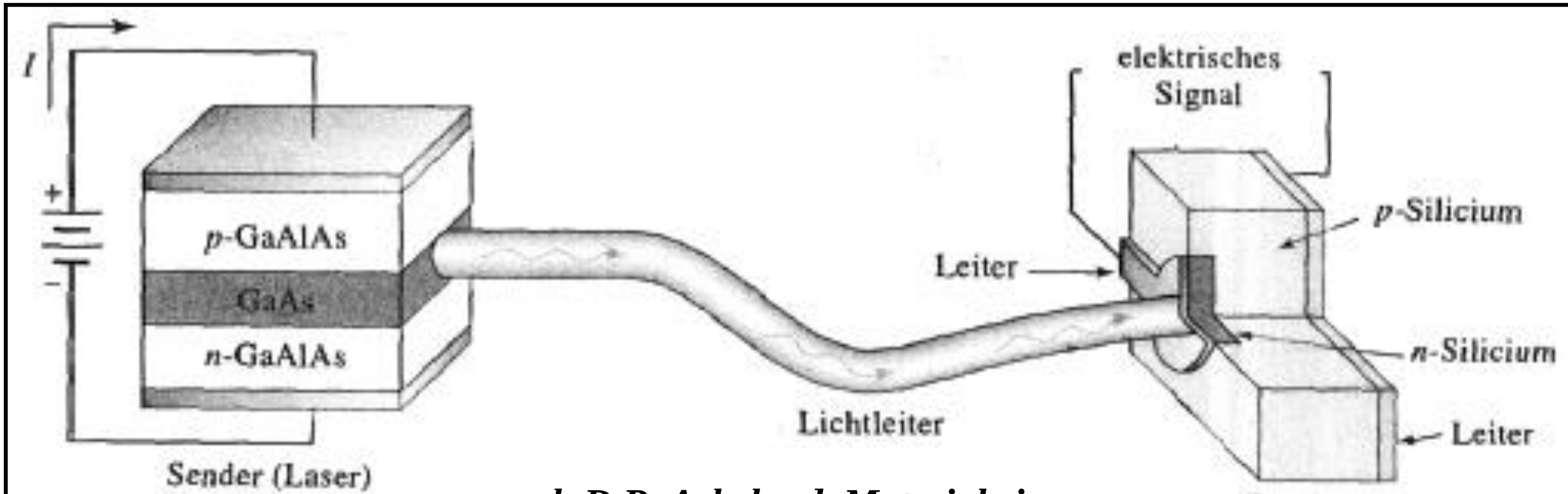
Signal generation

A Laser beam is loaded with information by modulating the beam intensity via the applied voltage.

The modulated Laser beam is guided to the receiver through a fibre optic.

Signal reception

Working principle is based on the photoelectric effect. During applied voltage, electrical current is measurable proportional to the incident beam intensity



nach D.R. Askeland, Materialwissen-schaften, Spektrum-Verlag 1996

2.5 Optical Properties

Fibre Optics for Transfer of Information

Light guidance in glasses is based on total reflection of light. A effect that is described by Snellius' equation:

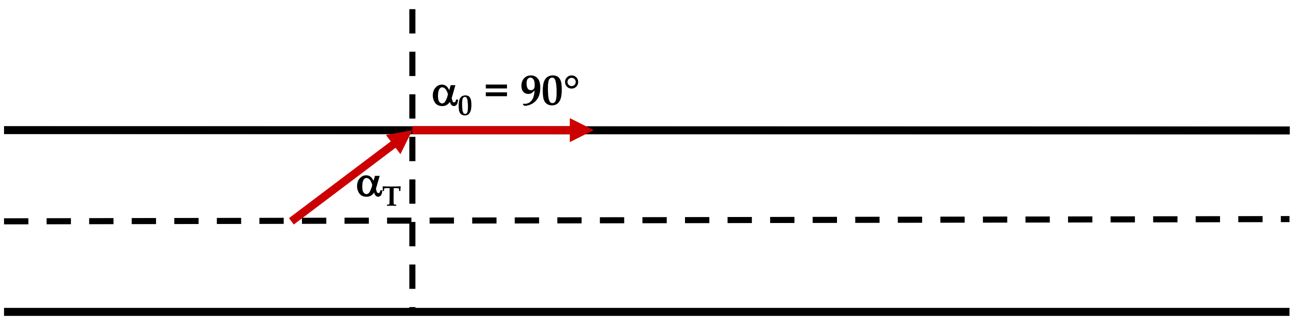
$$n_0 \cdot \sin\alpha_0 = n_1 \cdot \sin\alpha_1$$

Total reflection occurs upon transition from a optically more dense into a optically less dense medium, if the critical angle α_T is exceeded

Critical angle: $\alpha_1 = \arcsin(n_0/n_1)$ $n_0 \sim 1.0$ for air $n_1 \sim 1.5$ for normal glass

Air/glass: $\alpha_T = \arcsin(1/n_1) = \arcsin(1/1.5) = 41.8°$

Maximal entrance angle into fibre = 90° - α_T = 48.2°



90° - α_T increases with increasing refractive index of the fibre material!

2.5 Optical Properties

Materials for Fibre Optics

1. **Efficient light guidance over great distances requires little damping of the optical signals:**
- **no loss of intensity by lateral irradiation**
- **as high transparency as possible of the fibre material for the used wavelength**

2. **Small signal distortion is achieved by gradient fibres:**
- **fibre which refractive index continuously decreases from core to mantle**

Sodium silicate glass (Na_2O-SiO_2) is highly transparent for wavelengths important for optical transmissions, i.e. 0.8 and 1.8 µm but absorption due to impurities (ppm-range)
- **Fe, Co, Cr, Ni, V, Cu**
- **H_2O as OH-groups**

and refraction by defects
- **gas bubbles**
- **crystallites**

leads to damping of the optical signal

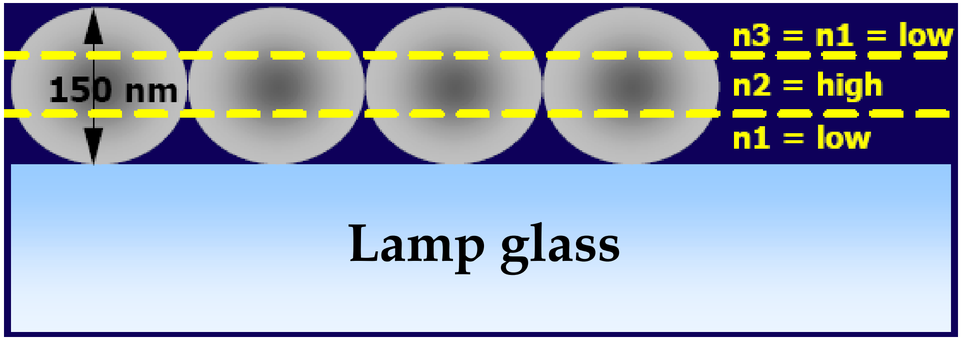
Reduction of refractive index by
addition of B_2O_3 or fluorides

Elevation of refractive index by
addition of P_2O_5, GeO_2 or PbO

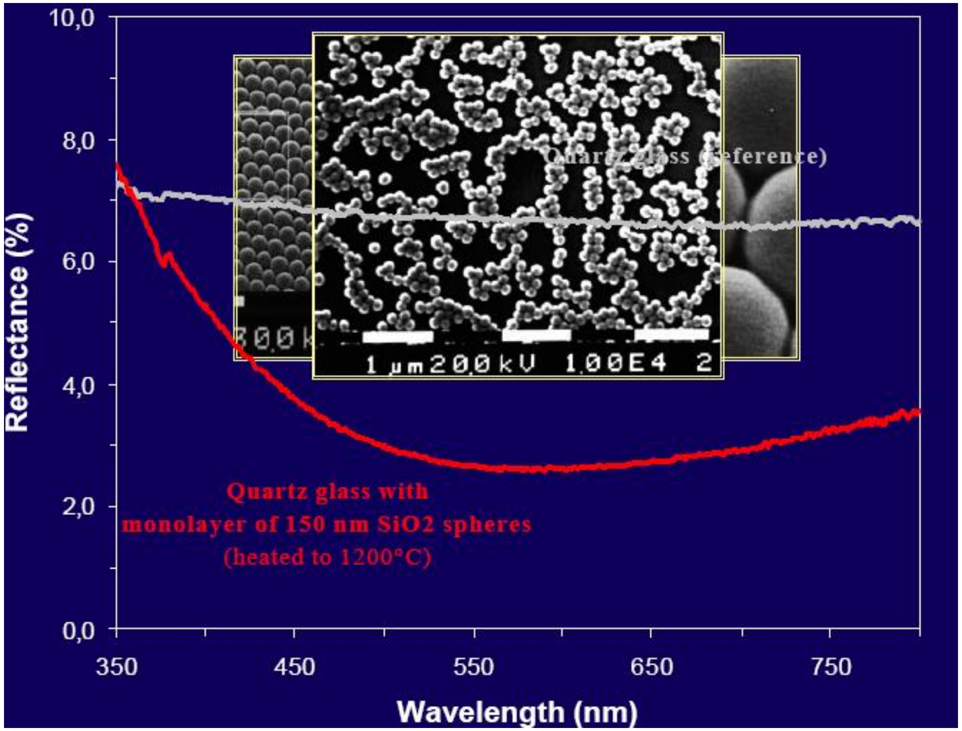
Interference Layers

⇒ Anti-reflection layers to enhance light in- and out-coupling

- Sequence of layers from highly refractive to low refractive materials, e.g. SiO_2 + TiO_2

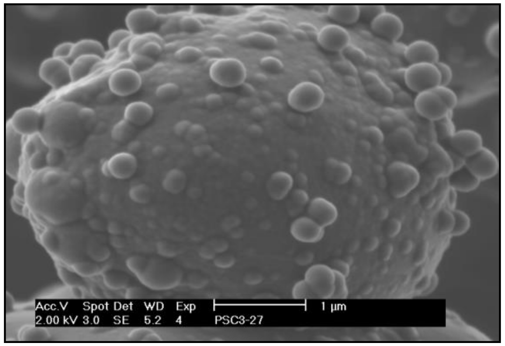


"Moth-eye-effect"



(Ca,Sr)S:Eu coated by SiO_2

n(SrS) ~ 2,1, n(SiO_2) ~ 1,5

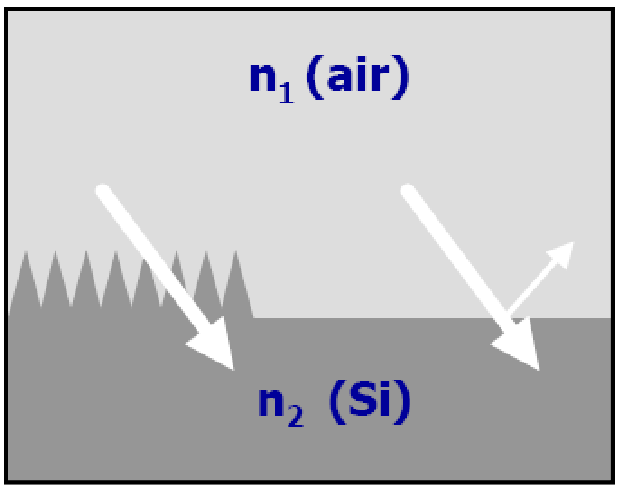


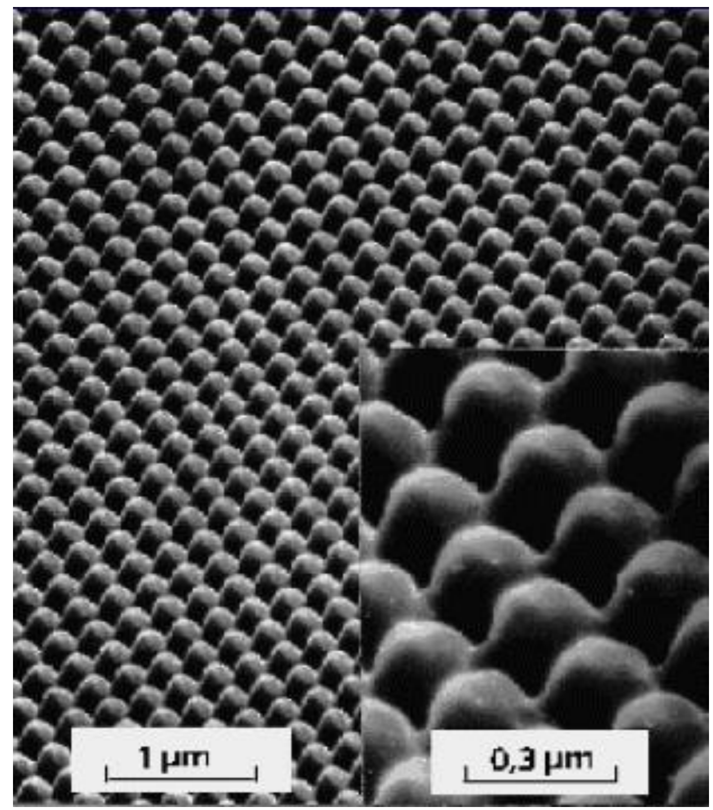
Interference Layers

⇒ Moth-eye-coating to enhance light in-coupling

⇒ Solar cells with higher efficiency

Fraunhofer Institutes Würzburg and Freiburg





Periodic surface structure

(Spektrum der Wissenschaft, August 1997, 20)

2.6 Catalytic Properties

Homogeneous and Heterogeneous Catalysis

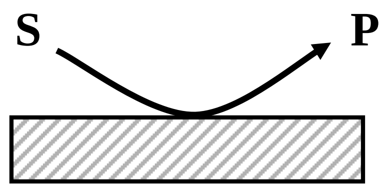
Homogeneous catalysis: reagents and catalysts are in the same phase

Heterogeneous catalysis: reagents and catalysts are in different phases

⇒ **Interaction at surfaces, e.g. reaction in gas phase or in solution**
Physisorption: 20 – 50 kJ/mol
Chemisorption: some 100 kJ/mol

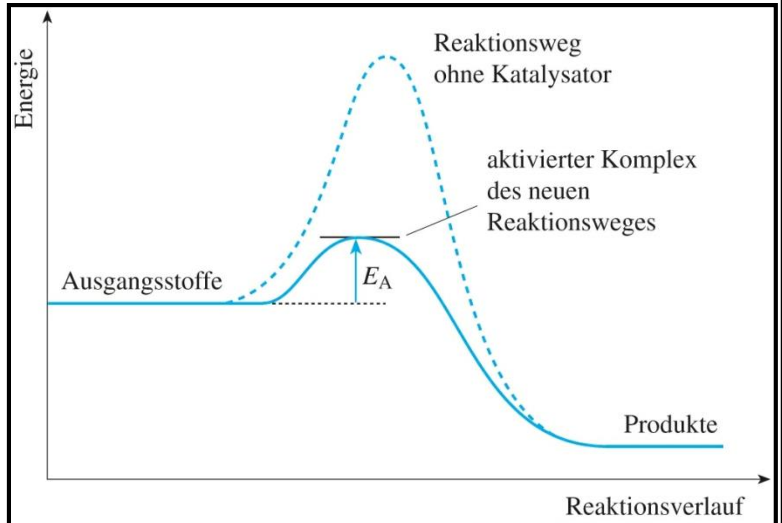
Application areas for heterogeneous catalytic materials
Selective synthesis of organic and inorganic compounds

- **Exhaust gas treatment**
- **Water treatment (waster, process, drinking water)**
- **Solar cells (Grätzel-cell)**



2.6 Catalytic Properties

Materials for Heterogeneous Catalysis



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung13-16.jpg

Effect

1. Decrease of activation energy
2. Localisation of reagents (educts) by absorption on surface

Prerequisites

- High selectivity, e.g. zeolites
- High reactivity, e.g. transition metals → Pt-group metals
- High specific surface area
  - Single-phase catalysts
    - Nano particles
    - Zeolites and clay minerals
  - Multi-phase catalysts
    - Pt on γ-Al_2O_3 or MgO: electron donators
    - Pt on silica gel SiO_2 or ZrO_2: electron acceptors
- Sufficient stability and lifetime (catalytic cycles)
  ⇒ protection from catalyst poison, e.g. sulphur

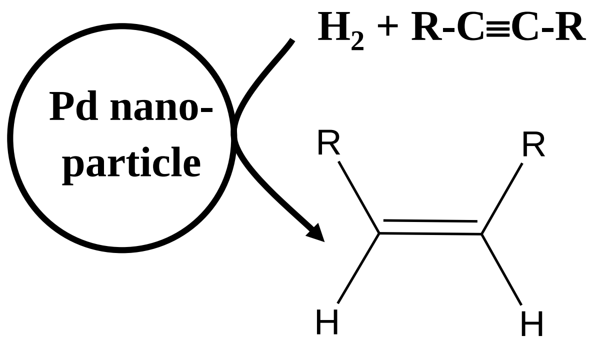
2.6 Catalytic Properties

Synthesis of Organic and Inorganic Compounds

1. **(Stereo selective) hydrations**

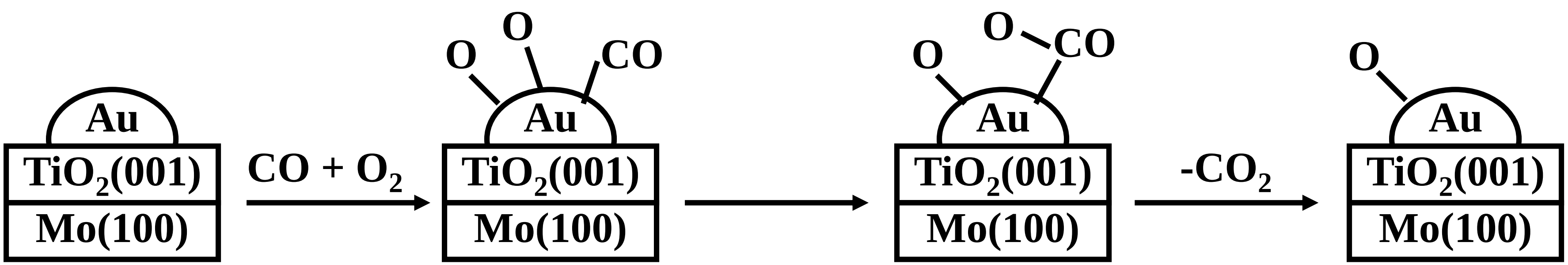
   CH_3-C≡C-CH_2-CH_2-CH_2-CH_3 + H_2 → cis-2-Hexen + trans-2-Hexen

   (2-Hexin)



2. **Oxidation reactions**

   2 CO + O_2 → 2 CO_2



2.6 Catalytic Properties

Synthesis of Organic and Inorganic Compounds

3. **Methanol-synthesis**
   $CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O$
   $\Rightarrow$ reduction of C $\Rightarrow$ electropositive catalysts $\Rightarrow$ NiO, CuO, ZnO

4. **Liquefaction of coal: Fischer-Tropsch-Synthesis (1923)**
   $C + 3\,H_2O \rightarrow CO + H_2$ (synthetic gas)
   $n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O$
   $\Rightarrow$ reduction of C $\Rightarrow$ highly electropositive catalysts $\Rightarrow$ Fe, Co
   $\Rightarrow$ sulphur- and nitrogen-free carbohydrates

5. **NH_3-Synthesis: Haber-Bosch-process (1913)**
   $N_2 + 3\,H_2 \rightleftarrows 2\,NH_3$
   $\Rightarrow$ reduction of N_2 $\Rightarrow$ highly electropositive
   Catalysts $\Rightarrow$ Fe with K_2O (electronegative promoter)
   Formation of iron nitride Fe≡N at surface

Facility for NH_3 production

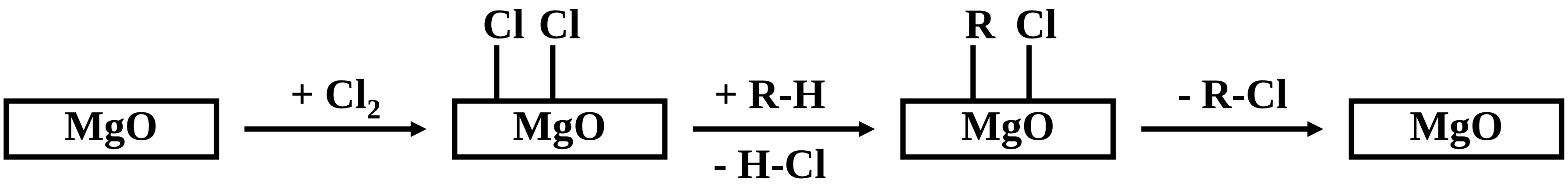
2.6 Catalytic Properties

Synthesis of Organic and Inorganic Compounds

6. Chlorination of alkenes

$C_2H_6 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$

activation of Cl_2 molecule by polarisation ⇒ electron-rich catalysts ⇒ MgO-catalysts



$MgO + HCl \rightarrow Mg(OH)Cl$

7. De-chlorination of organic compounds

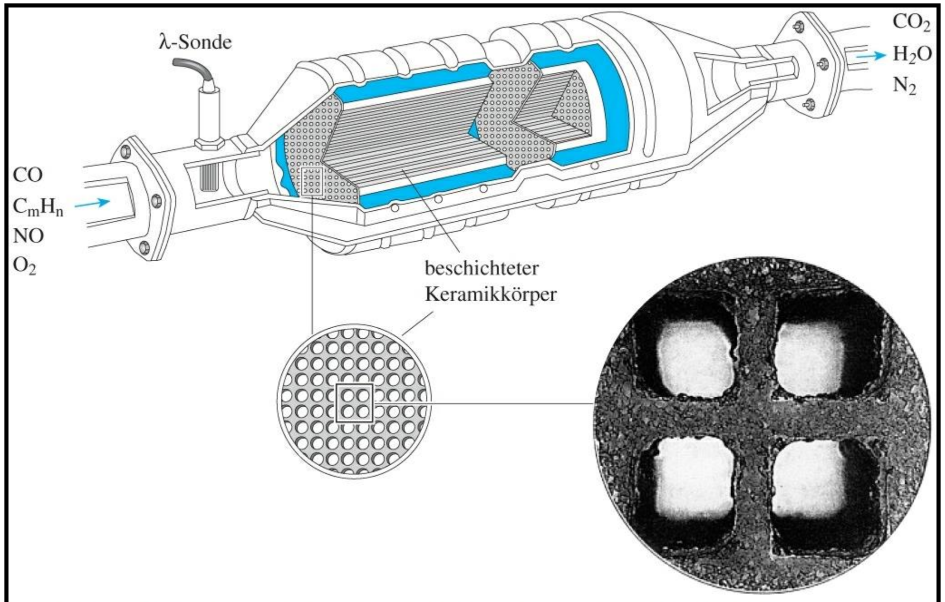
Activation of R-Cl bond ⇒ MgO-catalyst

$R\text{-}CH_2\text{-}CH_2Cl \rightarrow R\text{-}CH{=}CH_2 + HCl$

$MgO + 2\,HCl \rightarrow MgCl_2 + H_2O$

2.6 Catalytic Properties

Exhaust Treatment



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Autocatalyst Pd/Pt-pigment
On ceramic substrate

$2\,CO + O_2 \rightarrow 2\,CO_2$

$C_xH_y + (x + y/4)\,O_2 \rightarrow x\,CO_2 + y/2\,H_2O$

$2\,NO + 2\,CO \rightarrow N_2 + 2\,CO_2$

$C_xH_y + (2x + y/2)\,NO \rightarrow$
$x\,CO_2 + (x + y/4)\,N_2 + y/2\,H_2O$

Oxygen regulation through $Ce^{IV}O_2$

$2\,Ce^{IV}O_2 \rightleftarrows Ce^{III}{}_2O_3 + ½\,O_2$

Selective Catalytic Reduction (SCR)-catalysts ($FeVO_4$ on ceramic substrate)

$6\,NO + 4\,NH_3 \rightarrow 5\,N_2 + 6\,H_2O$ and $6\,NO_2 + 8\,NH_3 \rightarrow 7\,N_2 + 12\,H_2O$

Reduction of soot in diesel exhaust (regenerative additives)

1. Particle filter
2. Optimal engine management $\Rightarrow$ application of regenerative additives, such as CeO_2 (or Fe_2O_3): $C + 2\,CeO_2 \rightarrow CO + Ce_2O_3$

2.6 Catalytic Properties

Water Treatment

Germ-free water ⇒ Cl_2, Cl_2O, O_3, UV-A + cat., UV-C (240 - 280 nm)
- **Waste water**
- **Process water**
- **Drinking water**

Ultra-pure water ⇒ VUV (180 - 190 nm) ~ "band edge" of H_2O
- **Semi-conductor industry**

World market for water

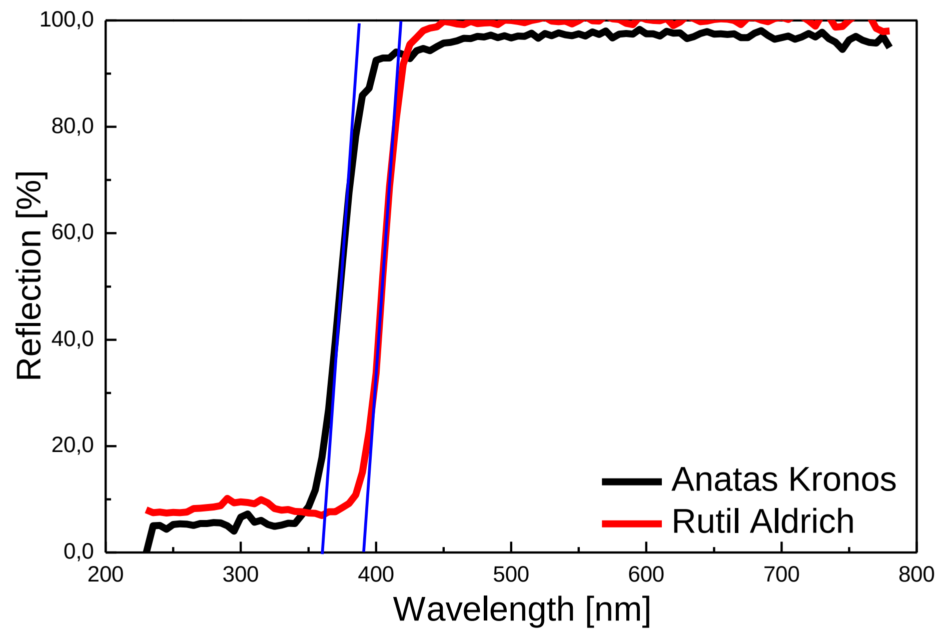
	1998/1999 [Bill. €]	2005 [Bill. €]	Increase [%]
Drinking water	37	63.5	72
Waste water	90.5	122.5	35
Process water	5.5	9.5	72
Other applications	15	23.5	57
Total market	148	219	48

2.6 Catalytic Properties

Water Treatment with UV-A Radiation and Catalyst

⇒ Pigments with low band gap: TiO_2, ZnO, ZnS, In_2O_3, $Ba_2In_2O_5$, WO_3, MoO_3, Fe_2O_3, $CaTiO_3$, Nb_2O_5, SiC, SnO_2, Nb_2O_5, Ta_2O_5

Modification	E_g [eV]	E_g [nm]	n
Anatase	3.5	360	2.55
Rutile	3.2	390	2.79



1. UV-absorption (protective pigment)

⇒ Application of rutile or ZnO

sunscreen, polymers, fronts

2. Photochemistry

⇒ Application of anatase

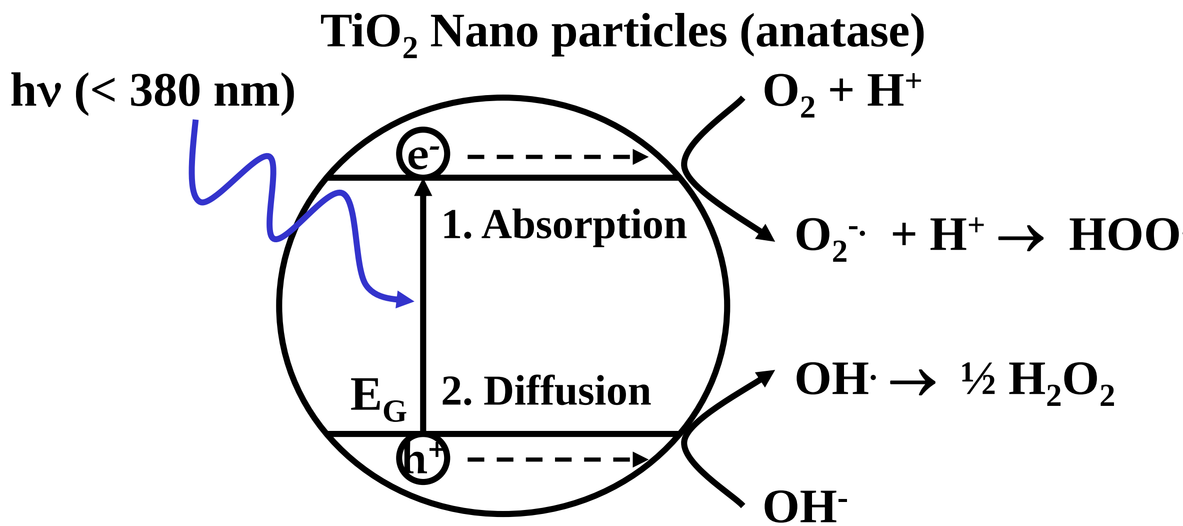
$TiO_2 + h\nu \rightarrow TiO_2^*(h_{VB}^+ + e_{CB}^-)$

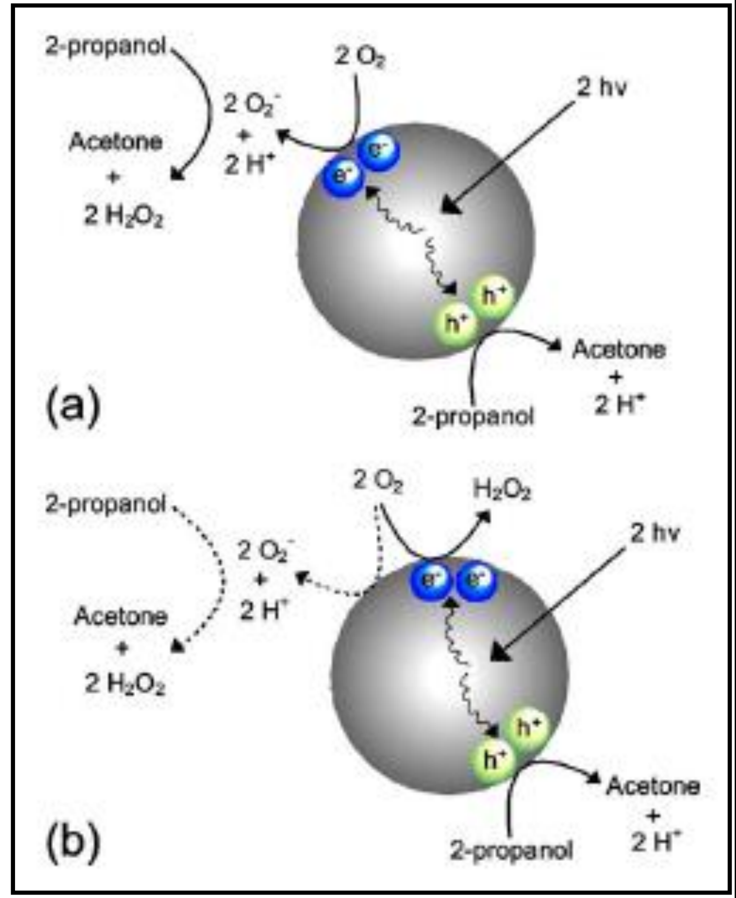
$h_{VB}^+ + H_2O \rightarrow H^+ + OH\cdot$

$e_{CB}^- + O_2 \rightarrow O_2^{\cdot -}$ (superoxide anion) ⇒ oxidative decomposition of organic substances in water or air as well as on surfaces

2.6 Catalytic Properties

Water Treatment with UV-A Radiation and Catalyst





$TiO_2^* + O_2 \rightarrow TiO_2^+ + O_2^{-\cdot}$

$TiO_2^* + OH^- \rightarrow TiO_2^- + OH^\cdot$

$O_2^{-\cdot} + H^+ \rightarrow HOO^\cdot$

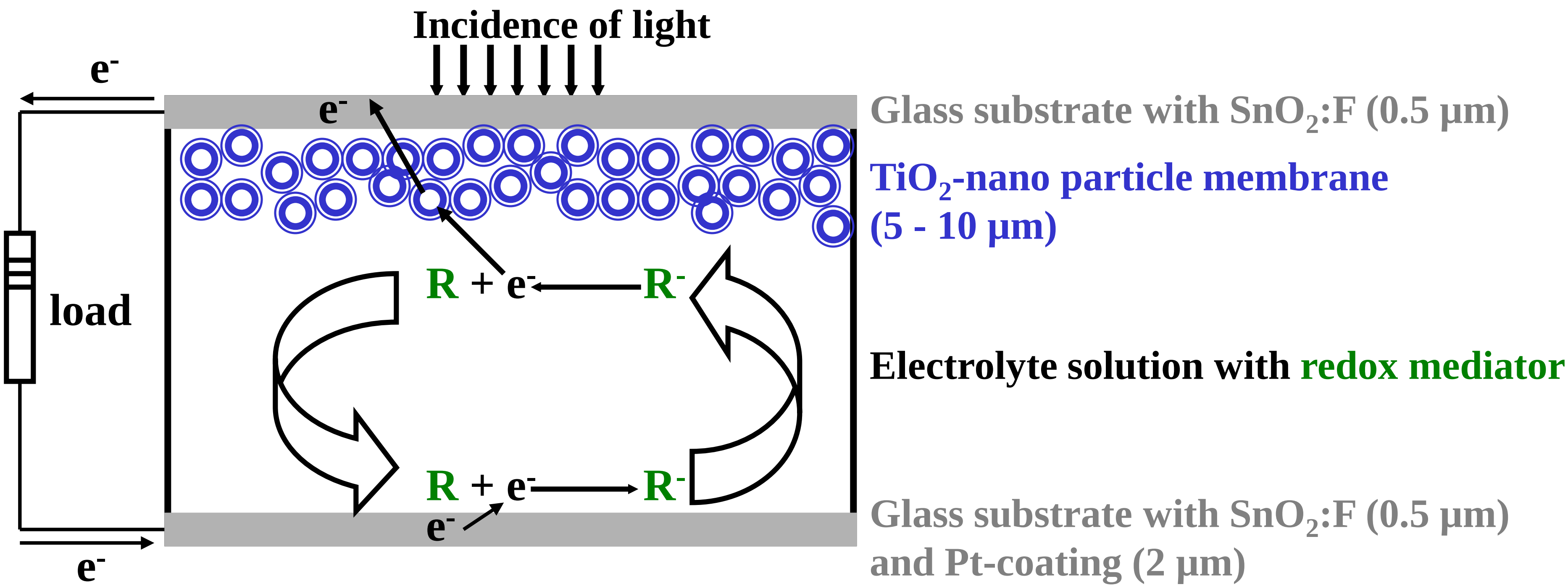
$2\ OH^\cdot \rightarrow H_2O_2$

$3n\ H_2O_2 + C_nH_{2n+2} \rightarrow n\ CO_2 + (4n+1)\ H_2O$ photoreactors, working with sunlight

⇒ recent research: doping for sensitisation of optical spectrum

2.6 Catalytic Properties

Solar Cells (Grätzel-Cell)



TiO_2 is the catalyst for the charge separation!

2.6 Catalytic Properties

Solar Cells (Grätzel-Cell)

1. Photosensibilisation by dyes

High efficiency requires strong absorption of light of a wavelength < 1100 nm (> 1.1 eV) $\Rightarrow$ excitation of allowed electronic transitions:

- **Organic compounds** — **$\pi \rightarrow \pi^*$ -transitions**
  anthocyanins, carotenoids, chlorophylls (extended π -electron system)

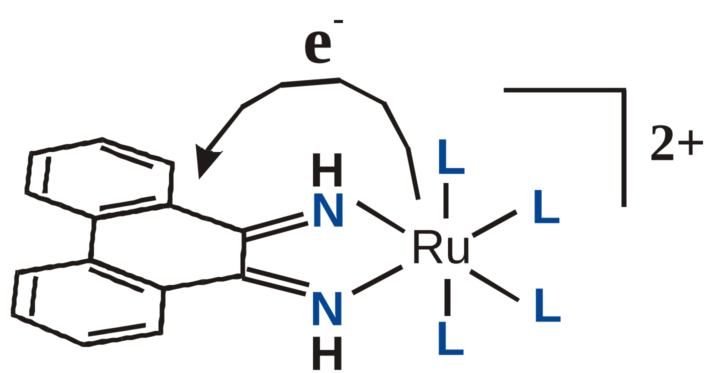
- **Coordination compounds** — **charge-transfer (CT)-transitions**

  Ligand-metal (LMCT)

  WO_4^{2-} 5d^0 $O^{2-} \rightarrow W^{6+}$

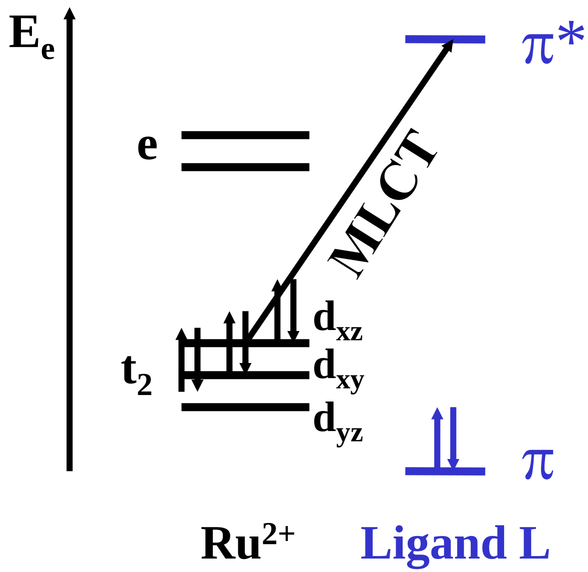
  Metal-ligand (MLCT)

  L_6Ru^{2+} 4d^6 $Ru^{2+} \rightarrow L$



Solar Cells (Grätzel-Cell)

1. Photosensibilisation by dyes

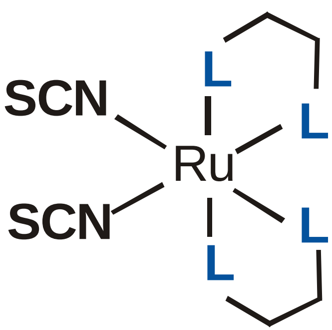


Complex	MLCT [nm]	$E^0_{Ru^{2+}/Ru^{3+}}$ [V vs NHE]
$[RuL_2Cl_2]$	534	+0,80
$[RuL_2(NCS)_2]$	534*	+1,09
$[RuL_2(CN)_2]$	493	+1,40

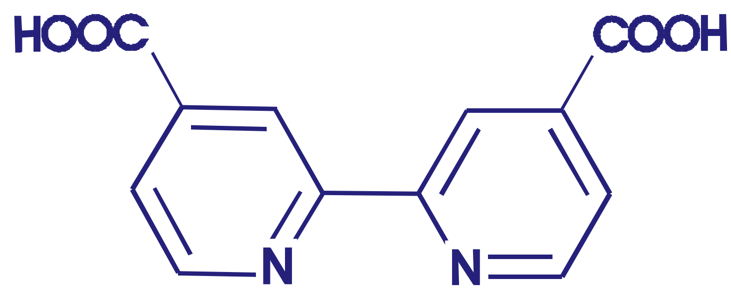
*the absorption edge is located at 800 nm (1,6 eV)

vs NHE = against normal hydrogen electrode:

$2\ H^+ + 2e^- \rightleftharpoons H_2(g)$



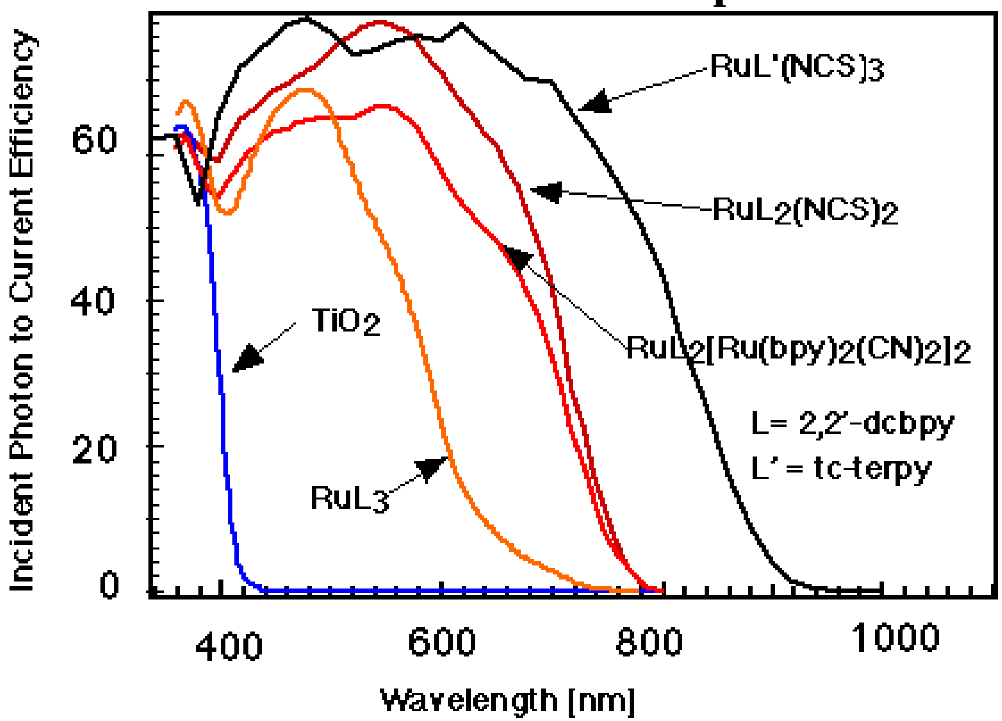
L = 2,2'-bipyridine-4,4'-dicarbonic acid



Solar Cells (Grätzel-Cell)

1. Photosensibilisation by dyes

Absorption spectra of TiO_2 and octahedral Ru^{2+}-complexes



Advantages of Ru^{2+}-chelating complexes

- **Reversible Ru^{2+}/Ru^{3+} redox pair**
- **Electronic low-spin configuration (anti-bonding orbitals are unoccupied)**
- **Chelating effect (entropic effect)**

⇒ kinetically very stable (slow ligand exchange reaction)

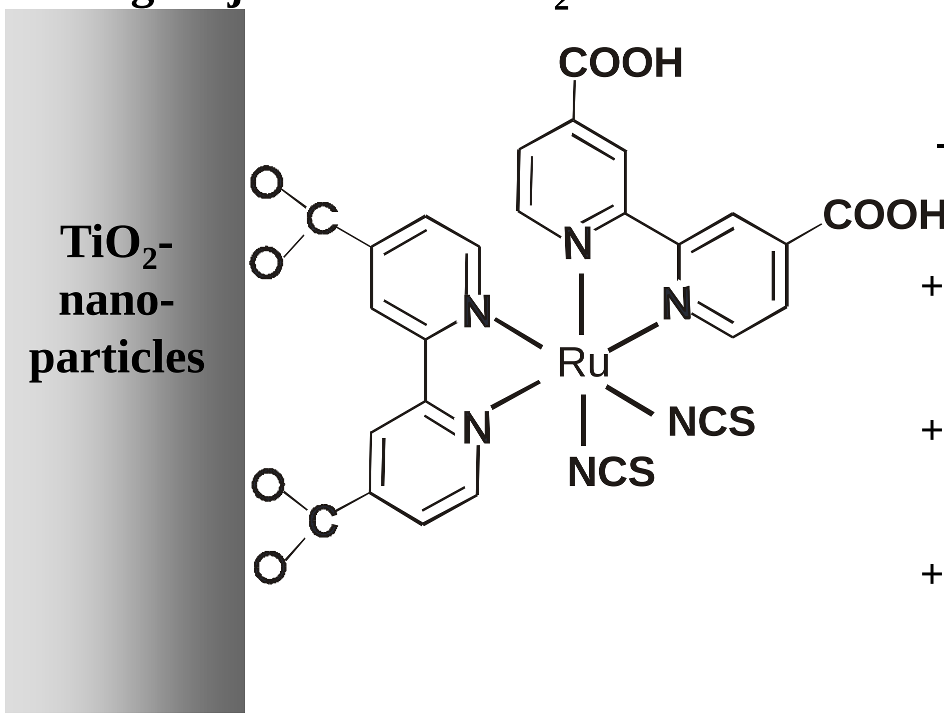
- **Allowed MLCT transitions at relative low energies**

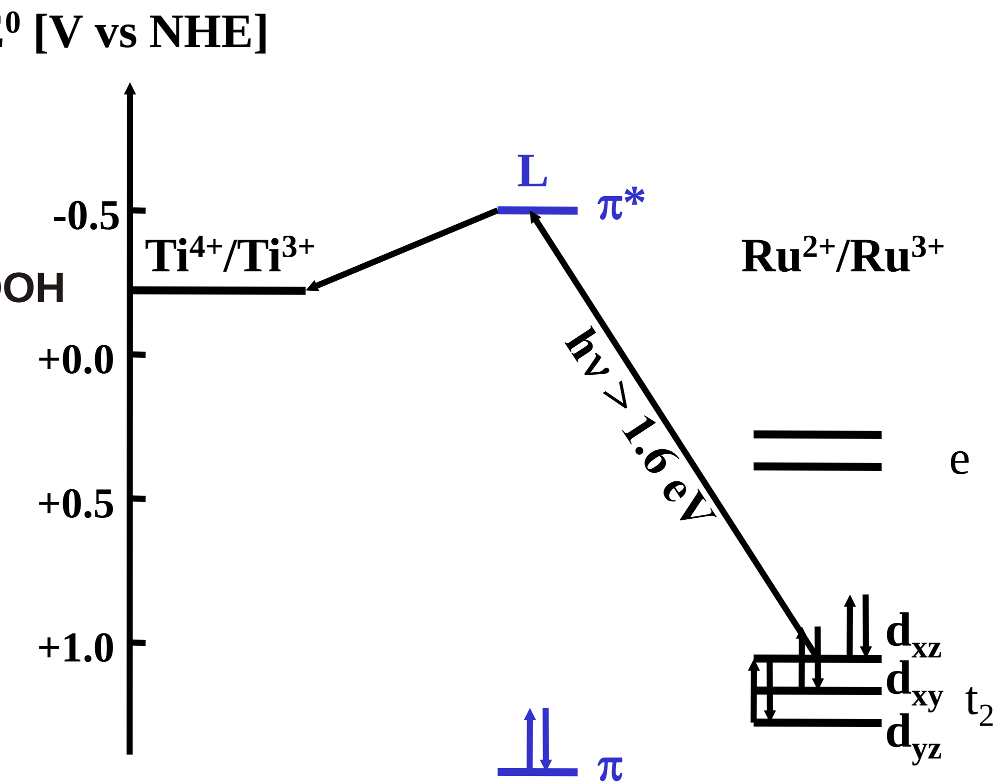
⇒ intense absorption bands in the visible range of the spectrum

2.6 Catalytic Properties

Solar Cells (Grätzel-Cell)

2. Charge injection into TiO_2





<u>Photoreduction of TiO_2</u>

$[Ru^{2+}L_2(NCS)_2] \xrightarrow{h\upsilon} [Ru^{2+}L_2(NCS)_2]^*$

$[Ru^{2+}L_2(NCS)_2]^* + Ti^{4+}O_2 \longrightarrow [Ru^{3+}L_2(NCS)_2]^+ + Ti^{3+}O_2^-$

Solar Cells (Grätzel-Cell)

2. Charge injection into TiO_2

Efficiency of charge injection

$\phi_{inj} = k_{inj}/(\tau^{-1} + k_{inj})$

with

k_{inj} = rate of charge injection

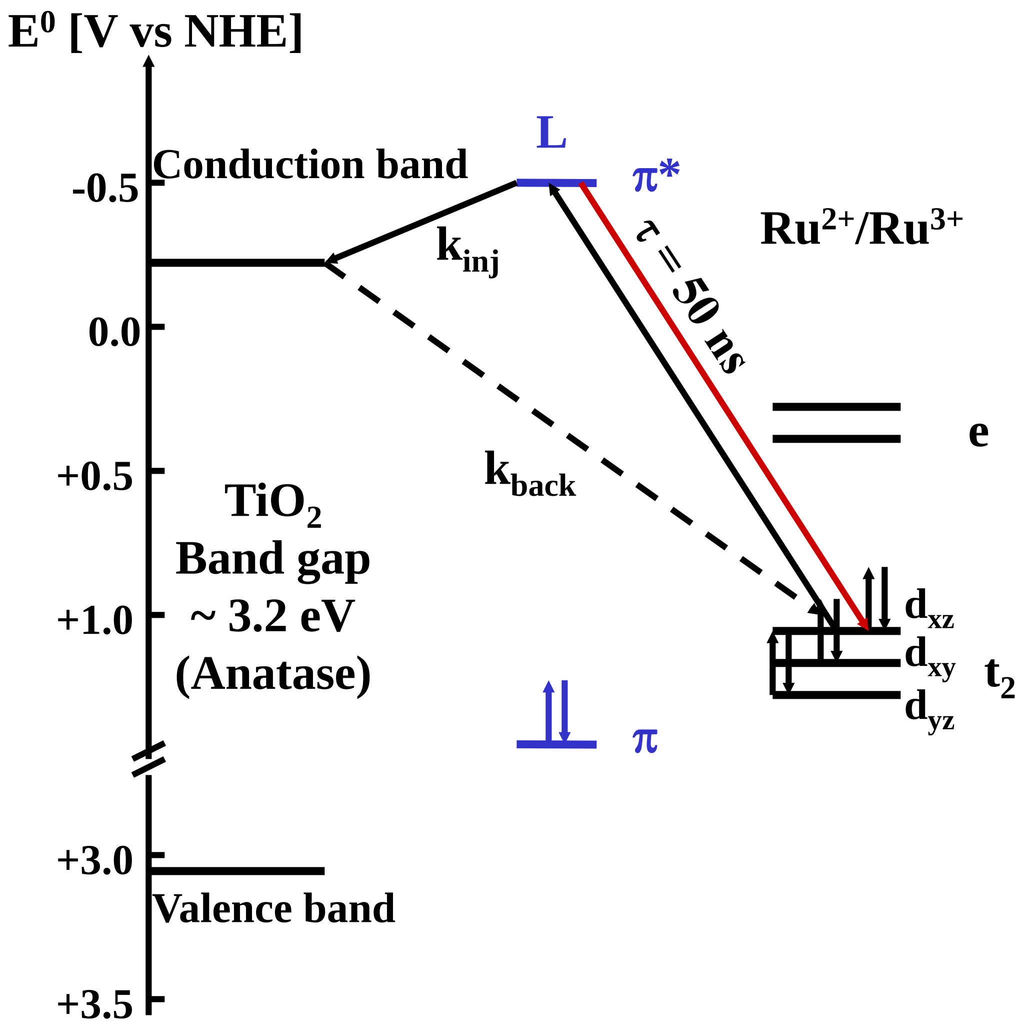
$> 1.4 \times 10^{11}\ s^{-1}$

τ = lifetime of MLCT-state

= 50 ns (fluorescence)

$\Rightarrow \phi_{inj} > 99.9\%$

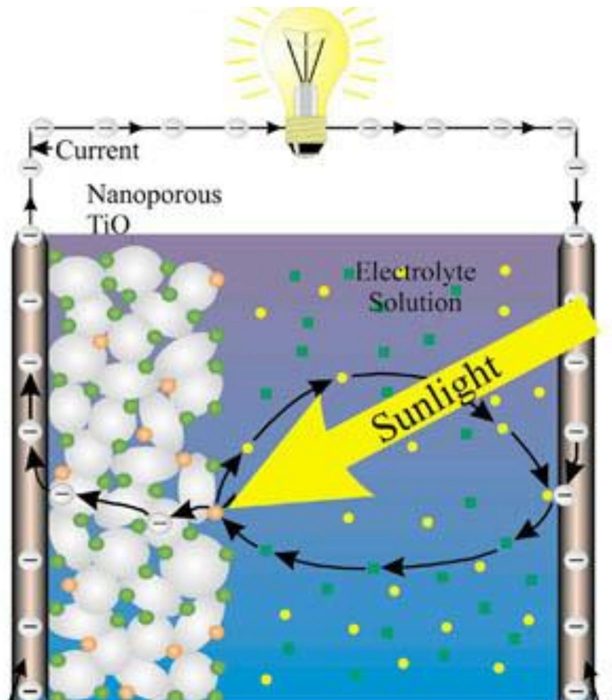
$k_{inj}/k_{back} > 10^3$



2.6 Catalytic Properties

Solar Cells (Grätzel-Cell)

3. Charge separation



Negative electrode

Positive electrode

A mobile redox system dissolved in a elctrolyte is responsible for the charge separation

Counter electrode

$I_3^- + 2e^- \rightleftharpoons 3I^-$ (0.3 M LiI and 0.03 M I_2 in CH_3CN)

$E^0 = +0.536$ V vs NHE

Reaction at negative electrode

$[Ru^{3+}L_2(NCS)_2]^+ + I^- \rightarrow 2\ [Ru^{2+}L_2(NCS)_2] + I$

$2\ I \rightarrow I_2$

$I_2 + I^- \rightarrow I_3^-$

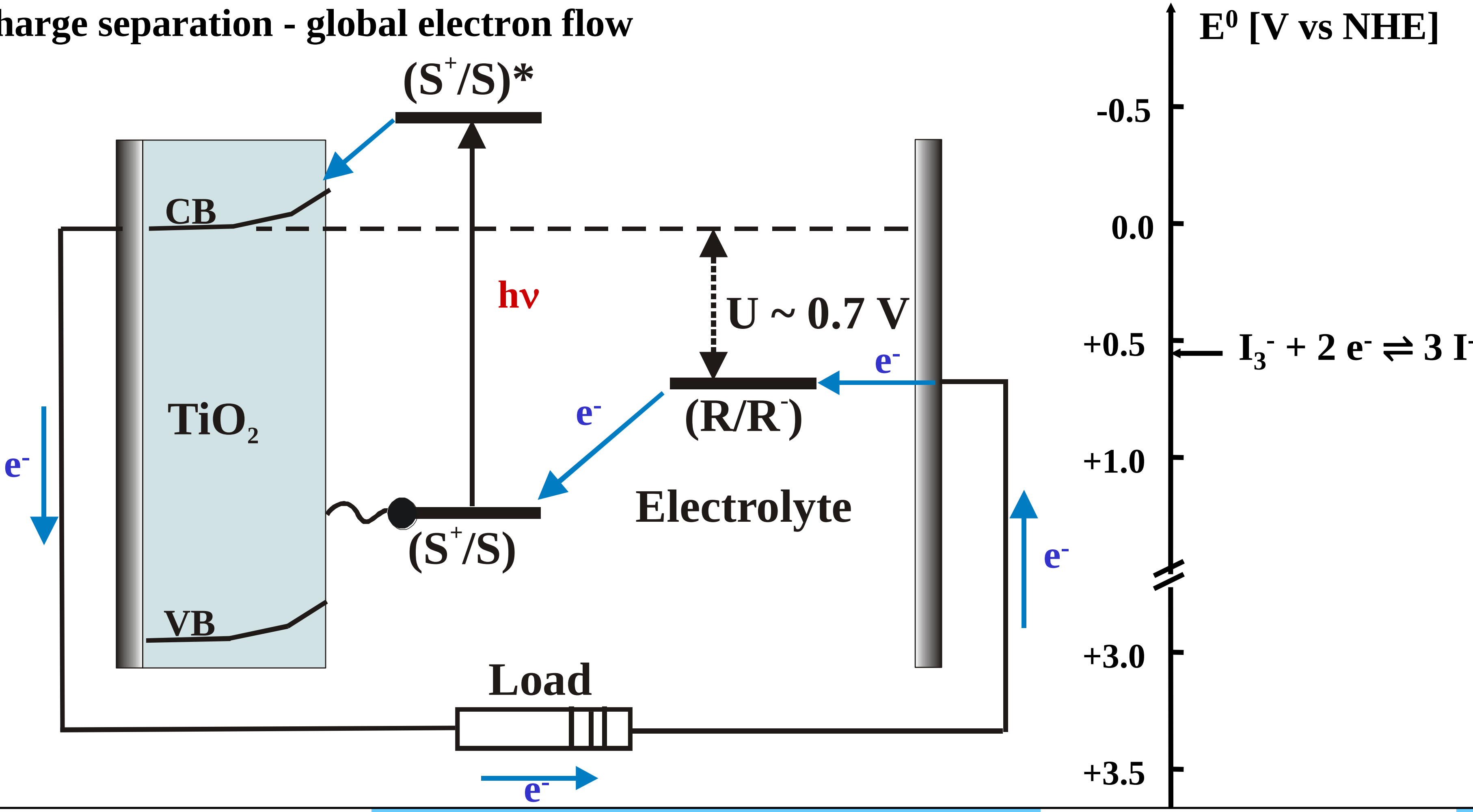
Reaction at positive elecctrode

$I_3^- + 2\ e^- \rightarrow 3I^-$

2.6 Catalytic Properties

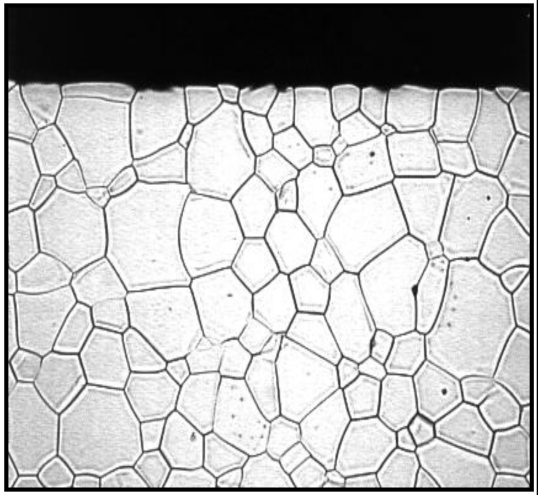
Solar Cells (Grätzel-Cell)

3. Charge separation - global electron flow



3.1 Ceramic Materials

Definition and Classification



Ceramics are solids, neither metallic nor inter-metallic nor organic, made of a single structure of one or more phases (crystalline, glassy)

Glass ceramics

Fine-grained microstructure made of a ceramic and a glass phase

Clay ceramics (silicate ceramics)

Most important component: layered silicates ⇒ Kaolinite $Al_4[Si_4O_{10}](OH)_8$, Montmorillonite

1. **Pottery (porous)**
   a. **Earthenware: pottery**
   b. **Stoneware: crockery, sanitary ware**
2. **Pottery (dense)**
   a. **Stoneware: tiles, sanitary ware**
   b. **Porcelain: crockery ⇒ hard porcelain:**

3.1 Ceramic Materials

Definition and Classification

High-performance ceramics (high-temperature and functional ceramics)

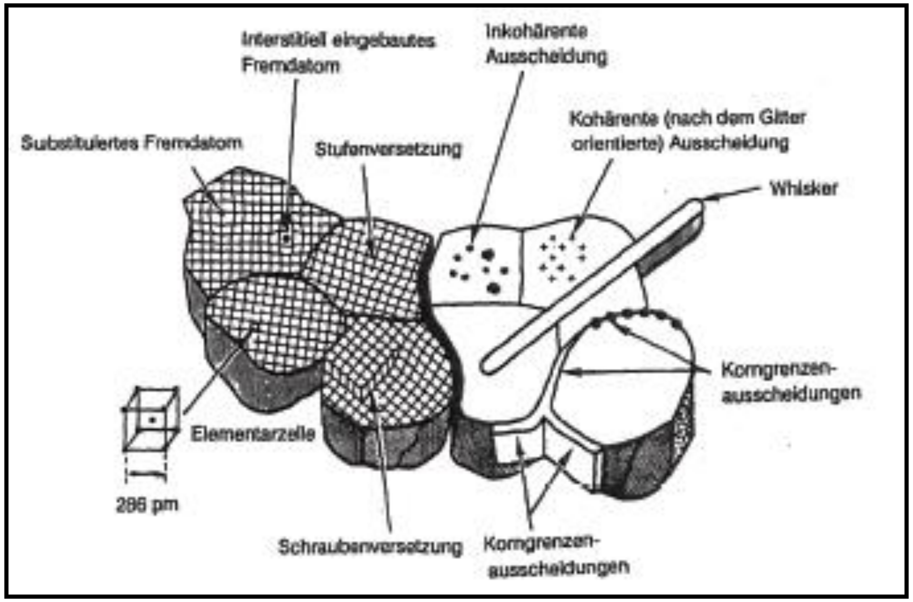
Chemically produced, highly pure oxides, borides, carbides, nitrides, and silicides of a certain composition and particle size (5 nm – 50 µm), which are processed by pressing and sintering to give compact bodies

Oxides	Borides	Carbides	Nitrides	Silicides
Al_2O_3	TiB_2	SiC	Si_3N_4	$MoSi_2$
ZrO_2	ZrB_2	B_4C	BN	WSi_2
TiO_2	LaB_6	WC	AlN	
$MO{\cdot}Fe_2O_3$ (ferrite)		TiC	TiN	
$MTiO_3$ (titanate)		HfC	ZrN	
$YBa_2Cu_3O_{7-x}$ (cuprate)		TaC		
$M_2O{\cdot}nX_2O_3$ (ß-aluminate)		NbC		

3.1 Ceramic Materials

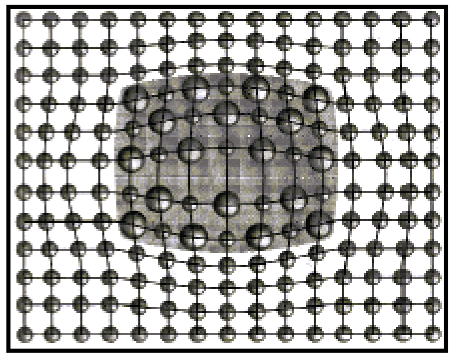
Structure

In general, ceramics consist of , more or less, randomly oriented crystalline grains (crystallites), amorphous areas and defects

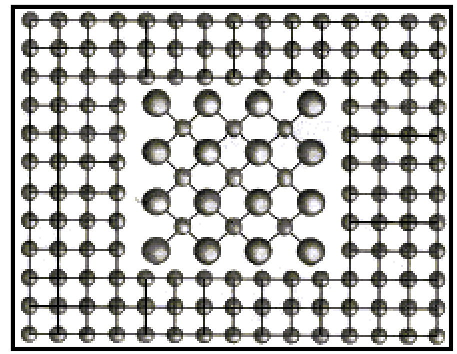


Göpel/Ziegler, Einführung in die Materialwissenschaften, Physikalisch-chemische Grundlagen und Anwendungen, B.G. Teubner Verlagsgesellschaft, Stuttgart Leipzig 1996

coherent + incoherent defects



Coherent defects possess the same structure as the host but leads to elastic distortion thereof



Incoherent defects posses a different structure than the host but does not lead to distortions

D.R. Askeland, Materialwissenschaften, Spektrum Akademischer Verlag GmbH Heidelberg, Berlin Oxford, 1996

3.1 Ceramic Materials

Properties

Because of their ionic or covalent bonds, ceramic compounds often exhibit the following properties:

- **Small thermal and electrical conductivity**
- **Great hardness and brittleness**
- **High melting point (> 1500 °C)**
- **High chemical and thermal stability**
- **Low density**

Material	Density [g/cm^3]	Tensile strength [N/mm^2]
Al_2O_3	4.0	210
SiC	3.1	175
Si_3N_4	3.2	560
SiAlON	3.2	420
ZrO_2	5.8	455

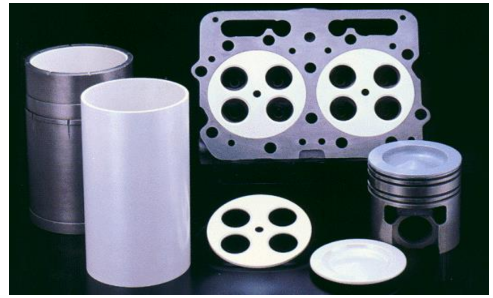
SiAlON = $Si_{3-x}Al_xN_{4-x}O_x$

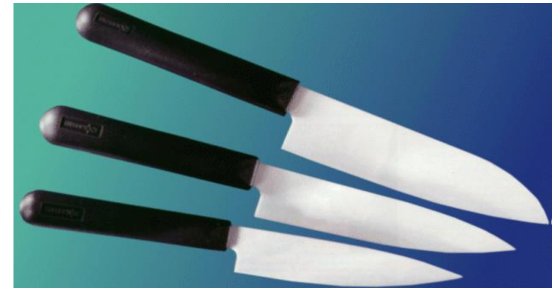
Ceramics where the focus is laid on function and not on mechanical properties may show different behaviour, such as:

FeO, ZnO	Semiconductor
$YBa_2Cu_3O_{7-x}$	Superconductor
ß-$NaAl_{11}O_{17}$	Ionic conductor
CrO_2, $Y_3Fe_5O_{12}$	Magnetics
$(Pb,La)(Zr,Ti)O_3$	Pressure sensors
$MoSi_2$	Heating elements

3.1 Ceramic Materials

Applications





Hardness: Al_2O_3, Si_3N_4, SiAlON

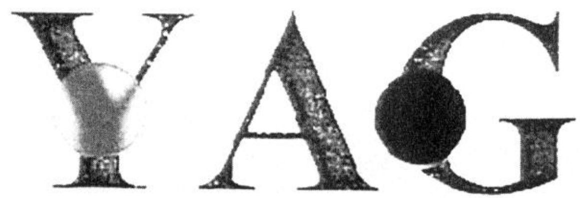
⇒ Tools for milling and cutting

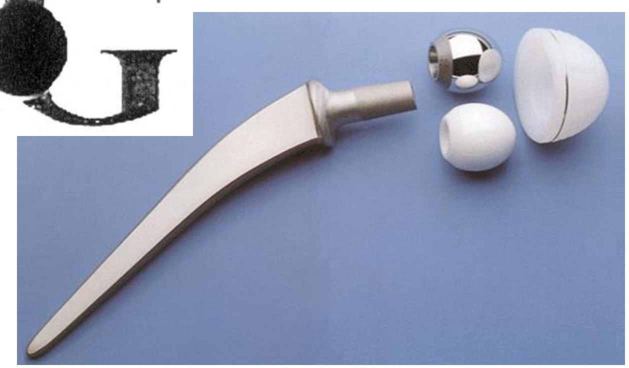
High melting point: Al_2O_3, Si_3N_4, SiC

⇒ Crucible, furnaces, engines, turbines

Chemical stability: Al_2O_3, $Y_3Al_5O_{12}$

⇒ Ceramic lamps (CDM), Laser





Biological compatibility: TiO_2, ZrO_2

⇒ Dental and bone implants

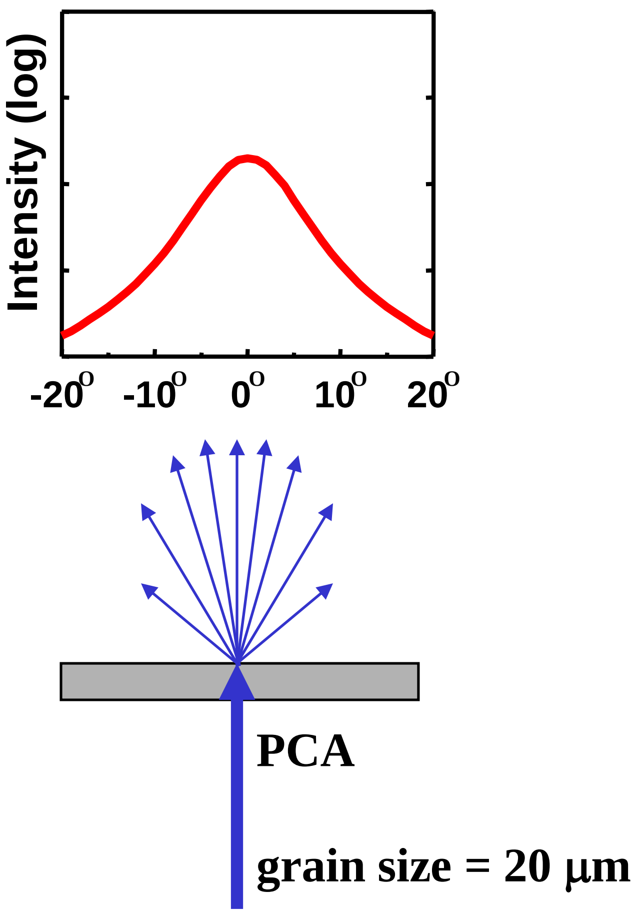
Optical transparency: $Y_3Al_5O_{12}$, Gd_2SiO_5, Lu_2SiO_5

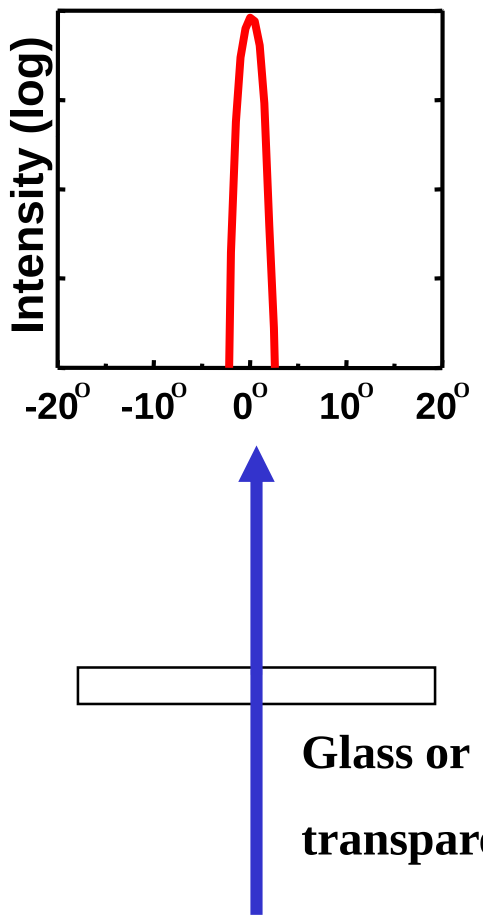
⇒ LEDs, scintillators

3.1 Ceramic Materials

Oxidic Ceramics: Al_2O_3 Corundum-Structure-Type (Oxygen hcp)

Fire resistant materials, transparent ceramics ⇒ polycrystalline aluminium oxide (PCA)





Translucency:
no pores

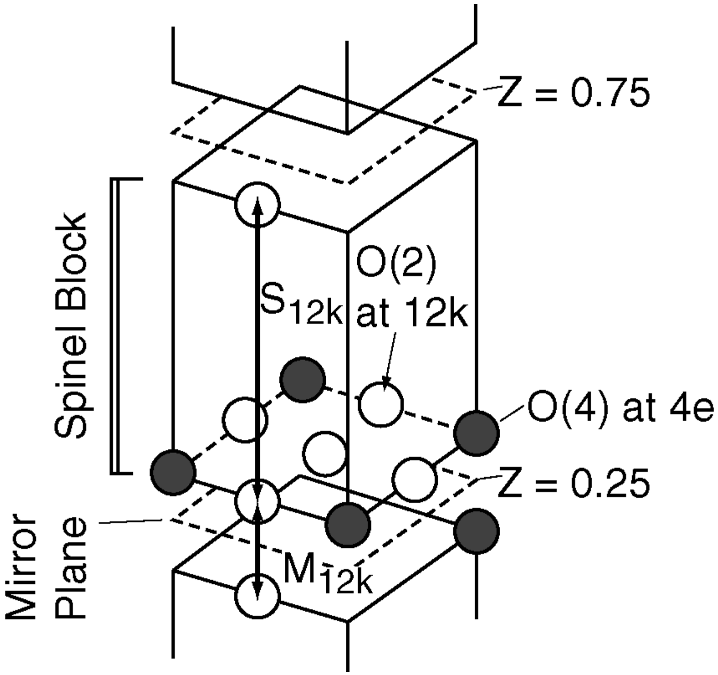
Transparency:
nano-crystallites

3.1 Ceramic Materials

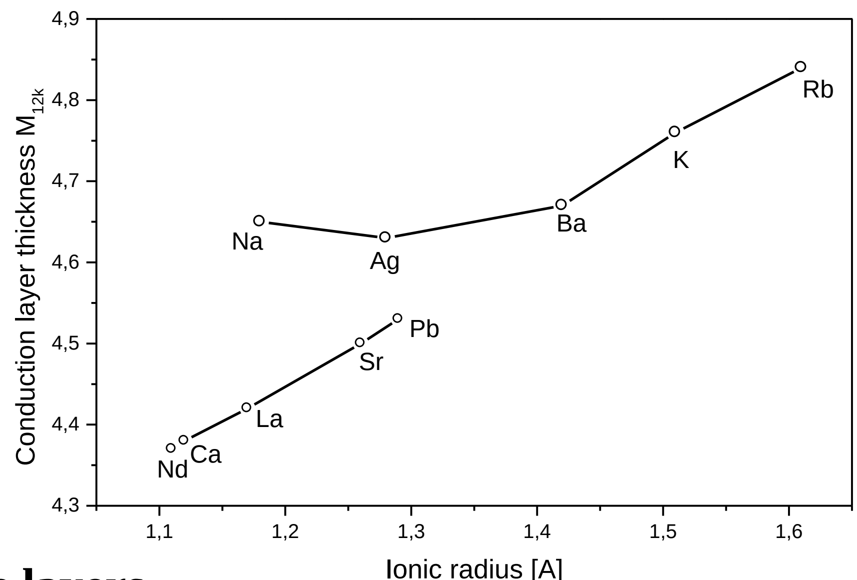
Oxidic Ceramic: $MO \cdot nX_2O_3$ ß-Alumina-Structure-Type

M = alkali$^+$, Cu^+, Ag^+, Ga^+, In^+, Tl^+, NH_4^+, H_3O^+; X = Al^{3+}, Ga^{3+}, Fe^{3+}; $5 < n < 11$

⇒ **Layered structure comprising spinel blocks (n X_2O_3) and intermediate layers (MO)**



ß-alumina phase is formed only with big cations



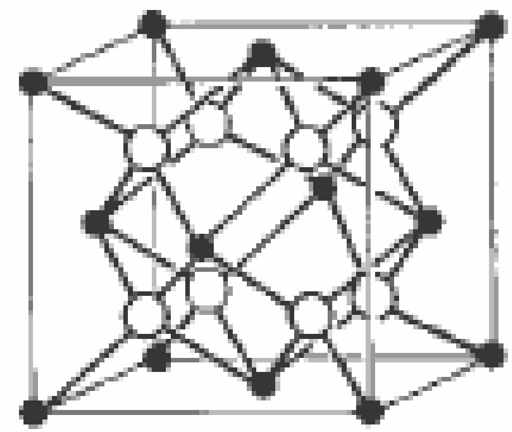
High ionic conductivity of the intermediate layers

⇒ **Solid electrolytes in fuel cells**

3.1 Ceramic Materials

Oxidic Ceramics: ZrO_2 Cubic Fluorite-Structure-Type (Oxygen ccp)

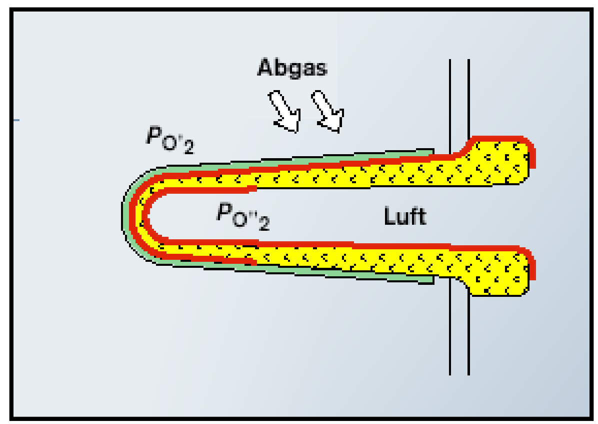
$$ZrO_2\text{ (monoclinic)} \overset{1100\,°C}{\rightleftharpoons} ZrO_2\text{ (tetragonal)} \overset{2350\,°C}{\rightleftharpoons} ZrO_2\text{ (cubic)} \overset{2680\,°C}{\rightleftharpoons} \text{melt}$$



To prevent phase transitions during cooling at 1100°C, cubic ZrO_2 is stabilised by the addition of CaO, MgO or Y_2O_3, e.g.

$$CaO + Zr_{Zr} + O_O \rightleftharpoons Ca''_{Zr} + V^{\cdot\cdot}_O + ZrO_2$$

Due to the created anion vacancies, doped ZrO_2 is a solid electrolyte (anion conductor)



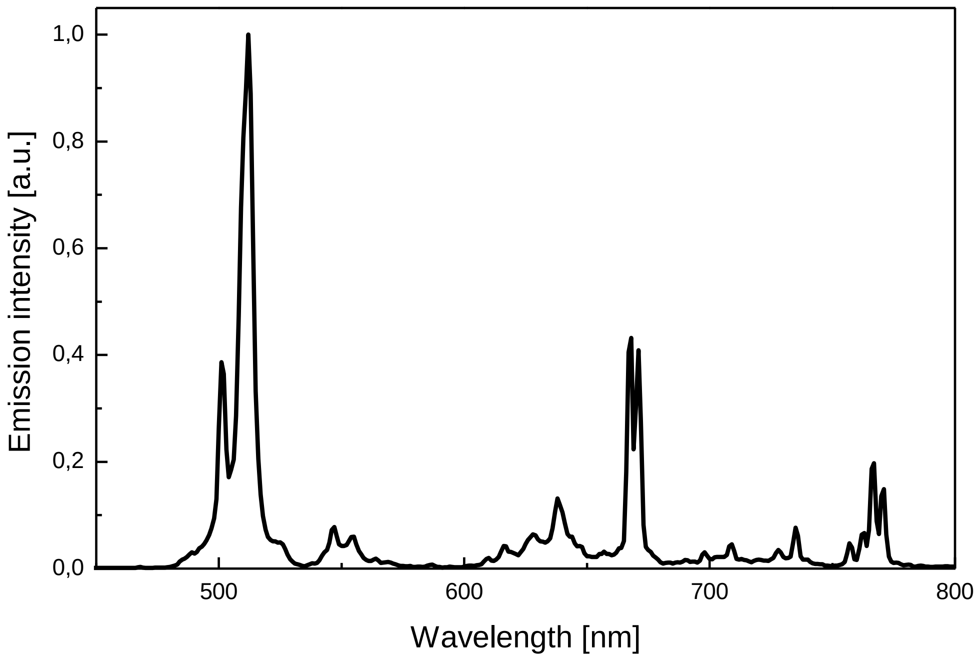
⇒ **Solid electrolyte in fuel cells**

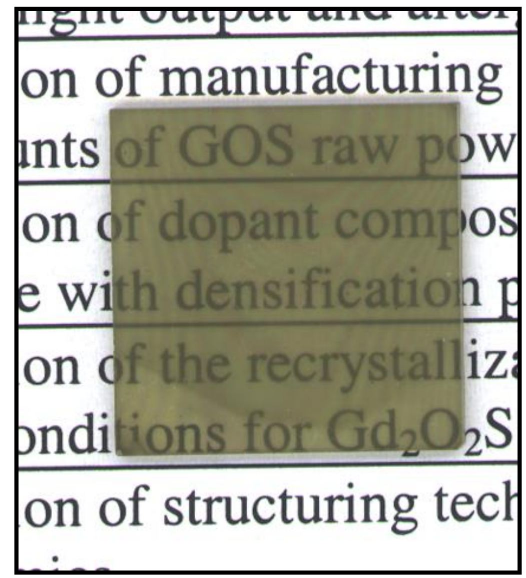
⇒ **Galvanic chain in O_2-sensors (Lambda-probe)**

3.1 Ceramic Materials

Oxidic Ceramic: Gd_2O_2S:Pr,Ce,F (GOS)

Scintillator in computed tomographs (CTs) ⇒ transparent ceramics

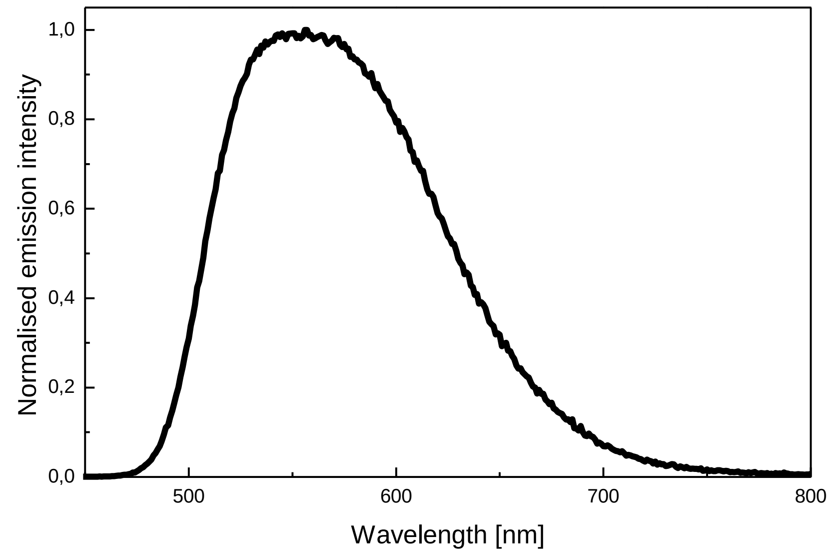




Production of ceramics is almost always more cost efficient than growing single crystals

Oxidic Ceramics: $Y_3Al_5O_{12}$:Ce and $Y_3Al_5O_{12}$:Pr (Garnets)

e.g. as scintillators in positron emission tomographs (PETs) ⇒ transparent ceramics

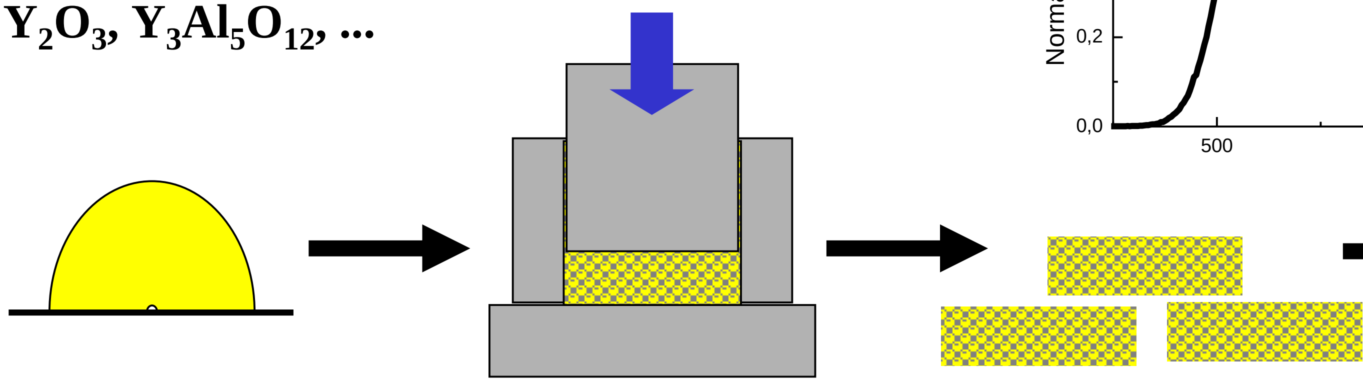


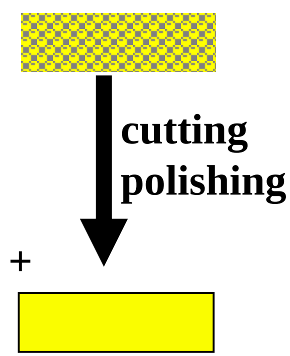
Scintillator ***Detector***

511 keV photon → visible photons → signal

Materials with cubic crystal structure

⇒ Y_2O_3, $Y_3Al_5O_{12}$, ...





Preparation of ceramic precursors (nano particles)

Addition of binder/flux + formation of green bodies

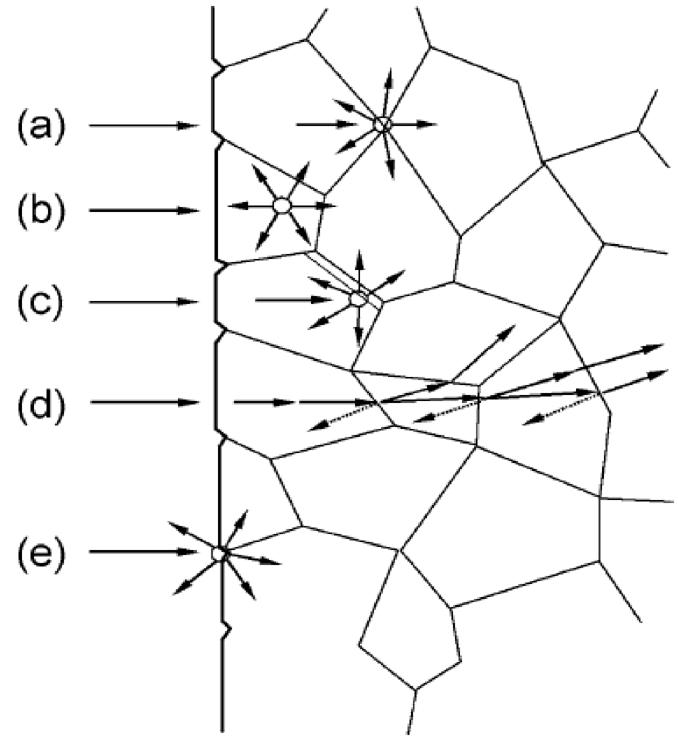
Thermal treatment: combustion of binder + sintering (vacuum)

3.1 Ceramic Materials

Oxidic Ceramics: Garnets and Sesquioxides

e.g. as optical components solid state Lasers (SSL) $\Rightarrow$ transparent ceramics

$Y_3Al_5O_{12}$	Optic to form beam
$(Y,Lu)_3Al_5O_{12}$:Nd	Laser with high pulse repetition rate
$(Y,Lu,Gd)_3Al_5O_{12}$:Yb	Disk Laser + other SSL
Sc_2O_3:Yb	Disk Laser + other SSL
$(Y,Lu)_2O_3$:Yb	Disk Laser + other SSL
Gd_2O_3:Yb	Disk Laser + other SSL



Processes that reduce transmission (aim: T > 99%)

a) Refraction at grain boundaries

b) Refraction at pores or impurities

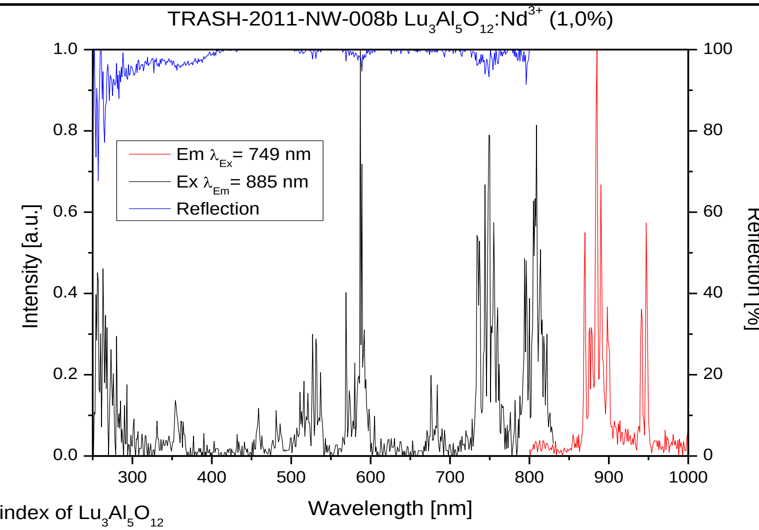
c) Refraction at secondary phases (glassy phase)

d) Reflection or birefringence at boundary layers

e) Refraction at surface roughness

Translucent Ceramic $Lu_3Al_5O_{12}$ (LuAG)

LuAG:Pr **Scintillator**
LuAG:Nd **NIR Laser**



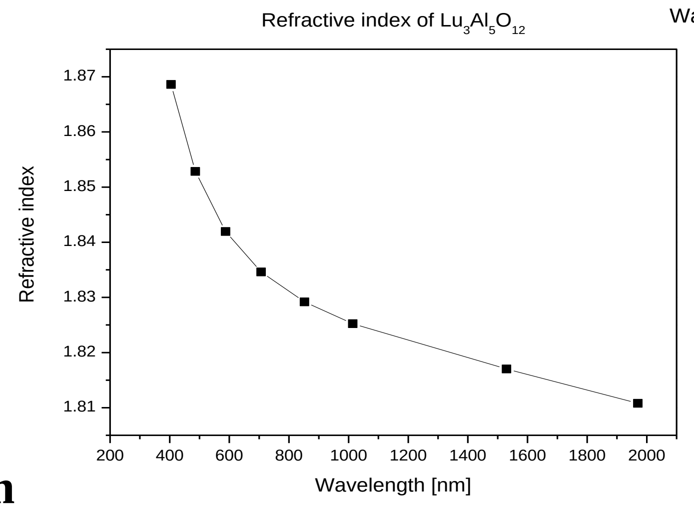
Crystal system: cubic (garnet)

Melting point T_m: 1987 °C

Density: 6.72 g/cm^3

Optical band gap E_g = 7.3 eV

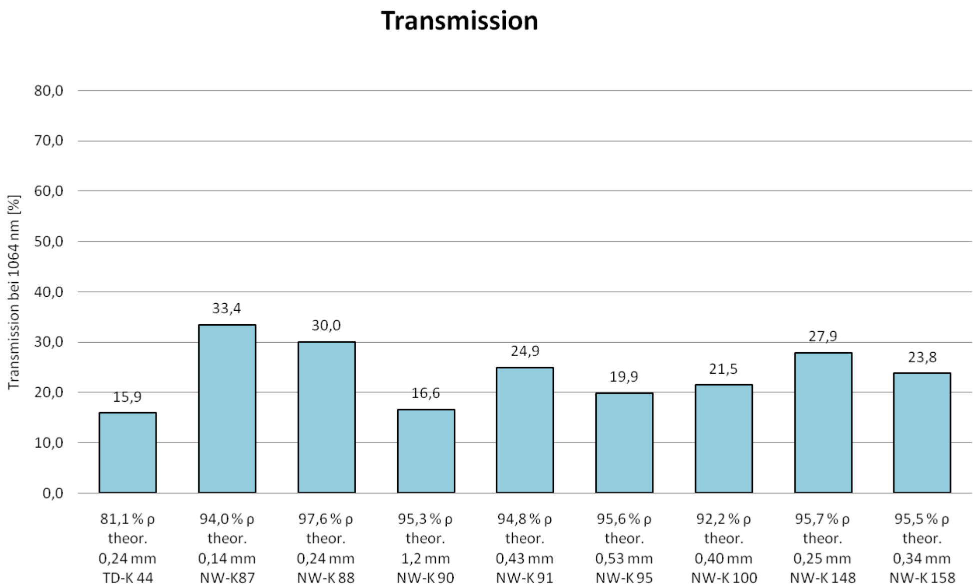
Max. phonon frequency: ~ 600 cm^{-1}

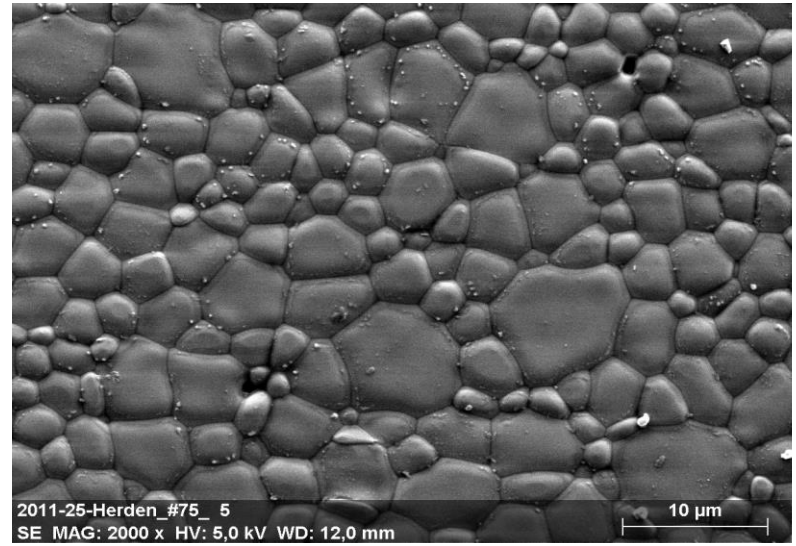


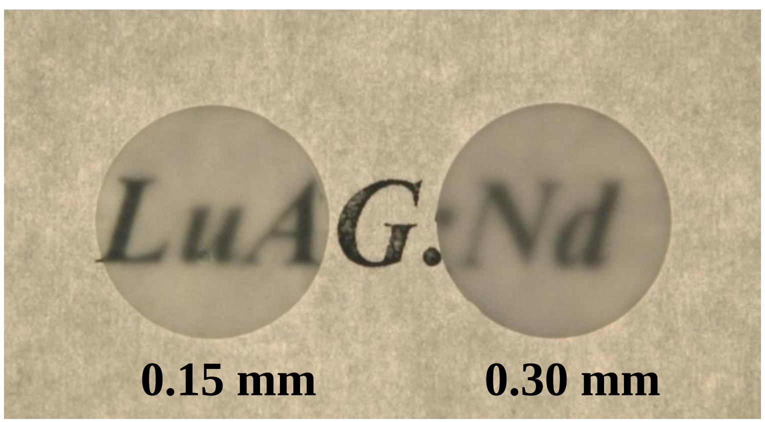
Refractive index: n = 1.825 @ 1014 nm
T = 1-R_{total} (R_{total} = 2·R_{reg}), if A = 0
→ max. pure transmission = 82.9% @ 1014 nm

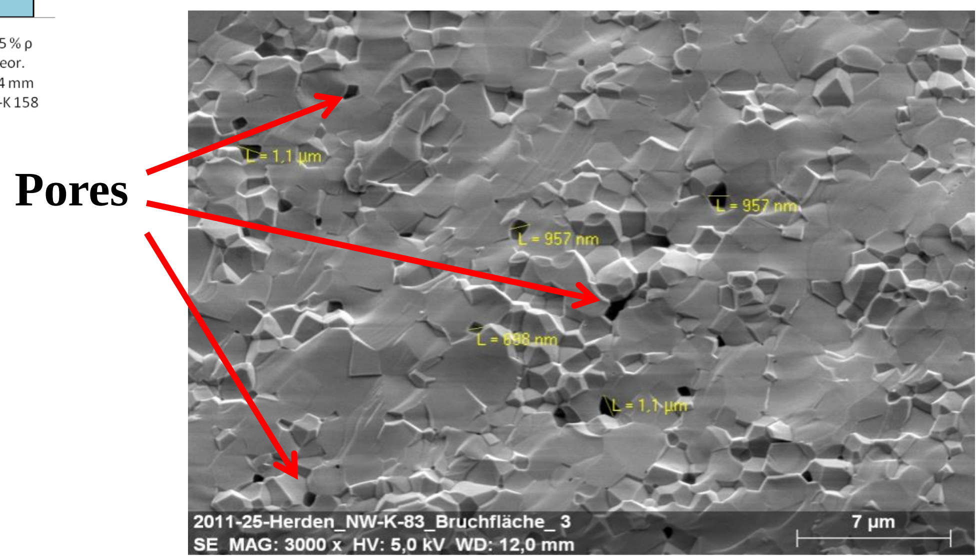
$$R_{reg} = \frac{(n_1 - n_0)^2}{(n_1 + n_0)^2}$$

Translucent Ceramic $Lu_3Al_5O_{12}$ (LuAG)









3.2 Glasses and Glass Ceramics

Glasses Are Amorphous Solids, Solidifying from Melts during Cooling or Formed by Quenching without Visible Crystallisation

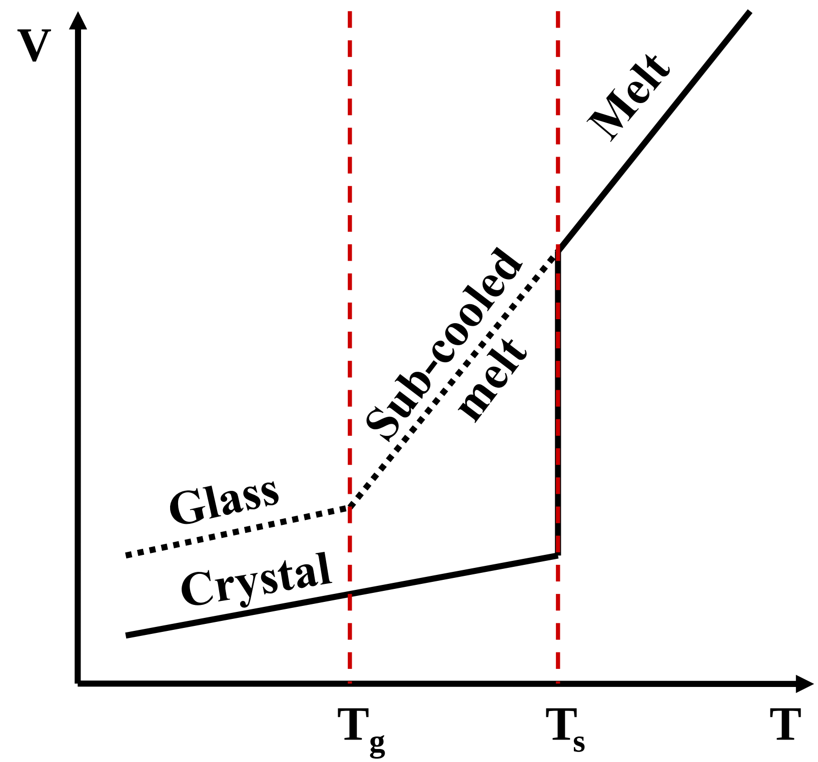
Properties

- Wide optical window
- Small electrical and thermal conductivity
- Good corrosion resistance
- Highly brittle

Classification according to linear thermal Expansion coefficient α

- Soft glasses $\alpha > 6 \cdot 10^{-6}\ K^{-1}$
- Hard glasses $\alpha < 6 \cdot 10^{-6}\ K^{-1}$

Temperature-dependence of volume



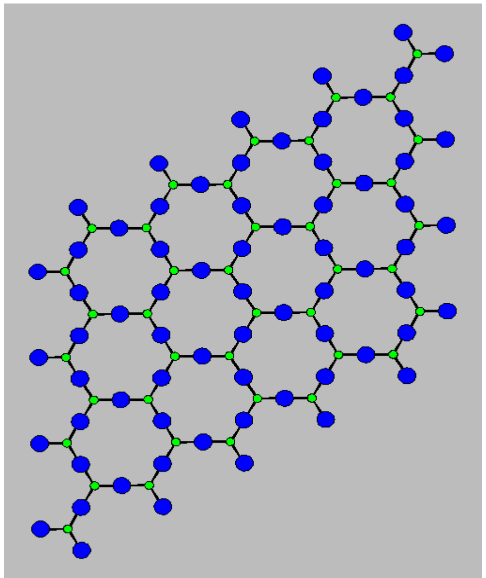
3.2 Glasses and Glass Ceramics

Analogous to Liquids, Glasses Possess Near-range Order (< 0.5 nm) but no Long-range Order, thereby Behaving like Thermoplastics

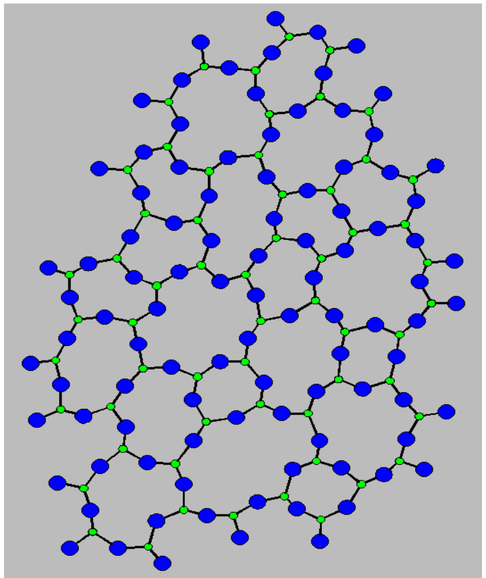
Building blocks of glasses (network creators) are similar to those of crystals but the arrangement in glasses is more irregular than in crystals

Si-O-distance in SiO_4-tetrahedron: 1.61 Å in α-quartz, 1.62 Å in amorphous SiO_2

Crystalline solids



Amorphous solids

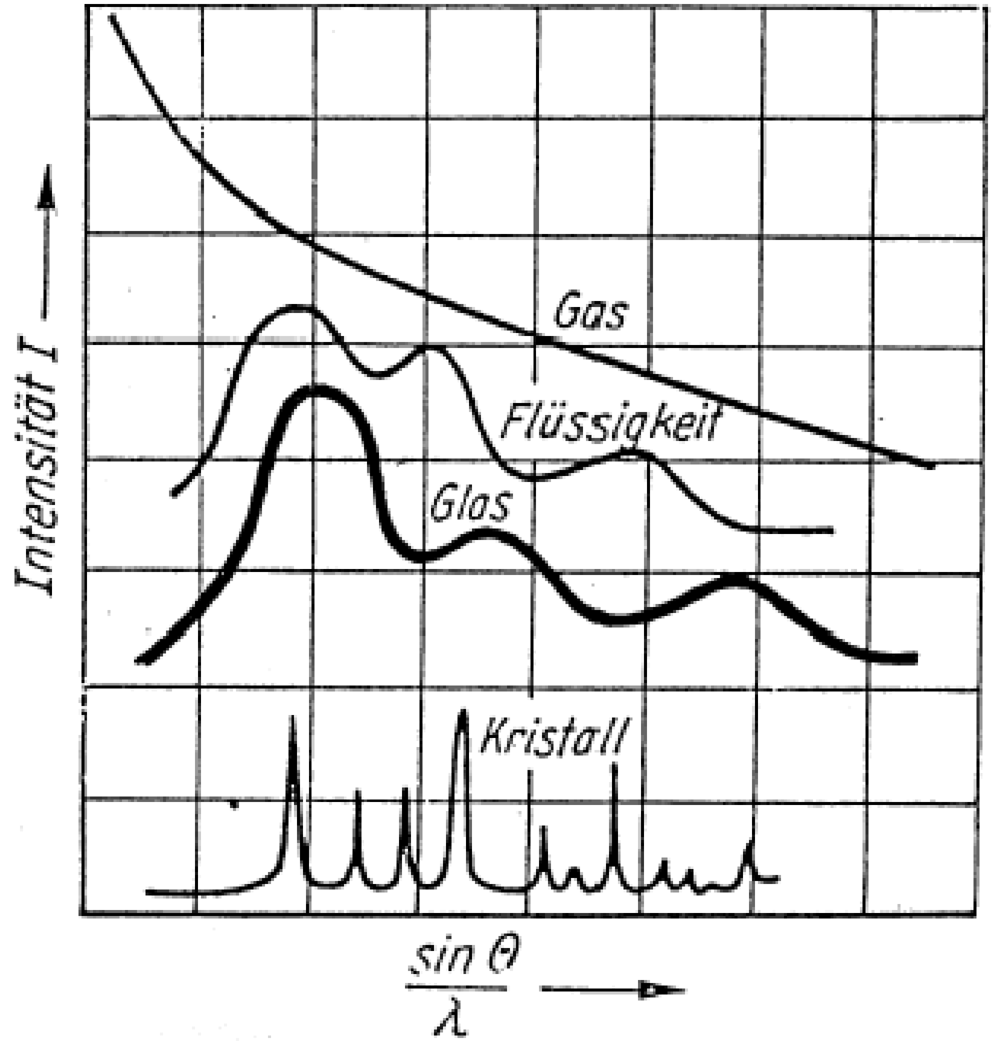


3.2 Glasses and Glass Ceramics

Glasses Can Easily Be Discriminated from Crystalline Solids by X-Ray Diffraction

In terms of order, glasses resemble liquids, with the lacking long-range order being the reason for optical transparency and low quantum efficiencies of dissolved activator ions.

Doped glasses are useful as colour filters, e.g. in LCDs but not as efficient phosphors.



3.2 Glasses and Glass Ceramics

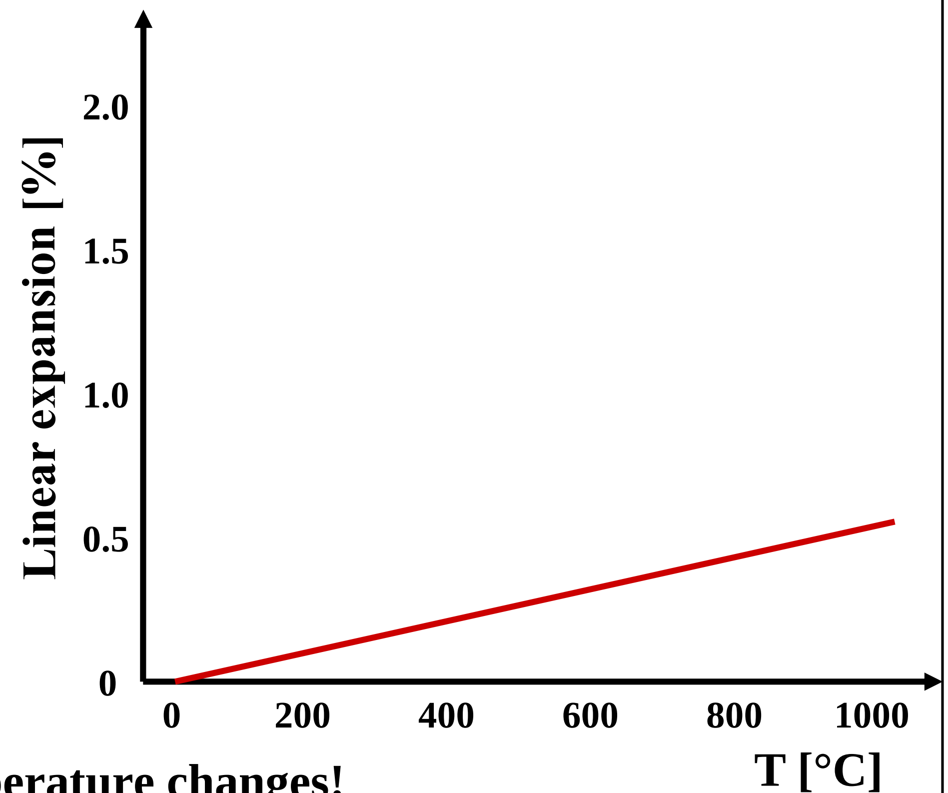
Building Blocks (Network or Glass Creators)

Elements	**C (glassy), S, Se, P $\Rightarrow$ allotropy**
Oxides (acidic)	B_2O_3, SiO_2, P_2O_5, V_2O_5, GeO_2, As_2O_3, Sb_2O_3
Sulphides	As_2S_3, Sb_2S_3, **various compounds with Tl, Sn, Pb, As, Sb, Bi, Si, P**
Selenides/Tellurides	**various compounds with Tl, Sn, Pb, As, Sb, Bi**
Halides	BeF_2, AlF_3, $ZnCl_2$, ZrF_4-BaF_2-AlF_3, ScF_3-BaF_2-YF_3
Polymers	**Polycarbonate (PC), Polyethylene PE), Polymethylmethacrylate (PMMA), Polystyrene (PS)**

3.2 Glasses and Glass Ceramics

Glasses Based on Silicates Are Most Common

Quartz or silica glass (pure SiO_2) possess high melting points (T_m = 1723 °C), high thermal stability (T_g = 1500 °C), and very small linear thermal expansion coefficients ($\alpha = 5.4 \cdot 10^{-7}\ K^{-1}$)



Quartz glass shows excellent stability upon temperature changes!

3.2 Glasses and Glass Ceramics

Normally, Glasses Are Synthesised by Mixing Network Creators like SiO_2 with Other (Alkaline) Oxides as Interstitial Ions and Network Modifiers

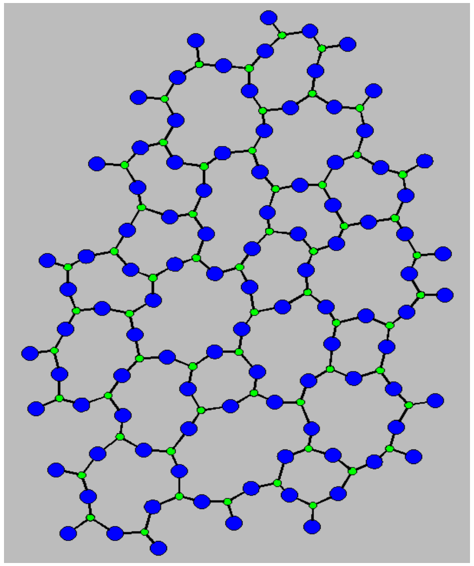
⇒ Decrease in glass transition temperature
⇒ Modification of mechanical properties
⇒ Modification of physical properties

Interstitial ions
⇒ MgO, PbO, Al_2O_3, Y_2O_3, TiO_2, ZrO_2, SnO_2, ZnO, BeO

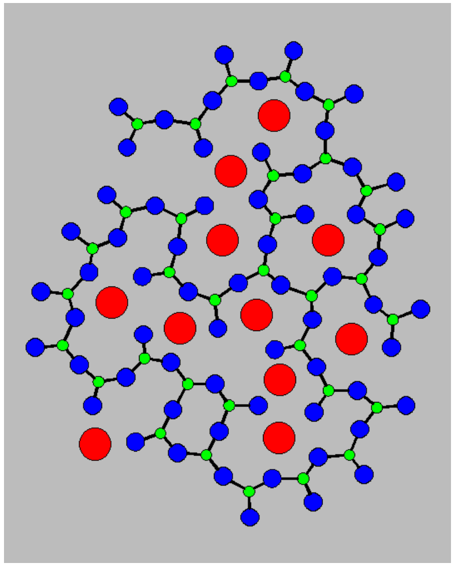
Network Modifiers
Inorganic glasses
⇒ Na_2O, K_2O, CaO, SrO, BaO

Polymeric glasses
⇒ softener, e.g. phthalate acid ester

without network modifiers



with network modifiers



3.2 Glasses and Glass Ceramics

Composition of Technical (Silicate) Glasses (All Numbers Given in wt-%)

Type of Glass	SiO_2	B_2O_3	Al_2O_3	PbO	CaO	MgO	BaO	Na_2O	K_2O
Container	72		2		10			14	
Flat	72		1.5		8.5	3.5		13.5	
Laboratory	80	10	3		1	1		5	
Cathode-ray tubes	60		4	11	1.7	1.2	1.3	8	8
Lead crystal	60.5		8	24				2.5	2
Crystal	76.5		0.3		6			6	11
Optical	28			70				1	1
Crone	72	8.2			1.6	0.5		7.2	10.5
Quartz	100								

3.2 Glasses and Glass Ceramics

Composition and Applications of Special Glasses

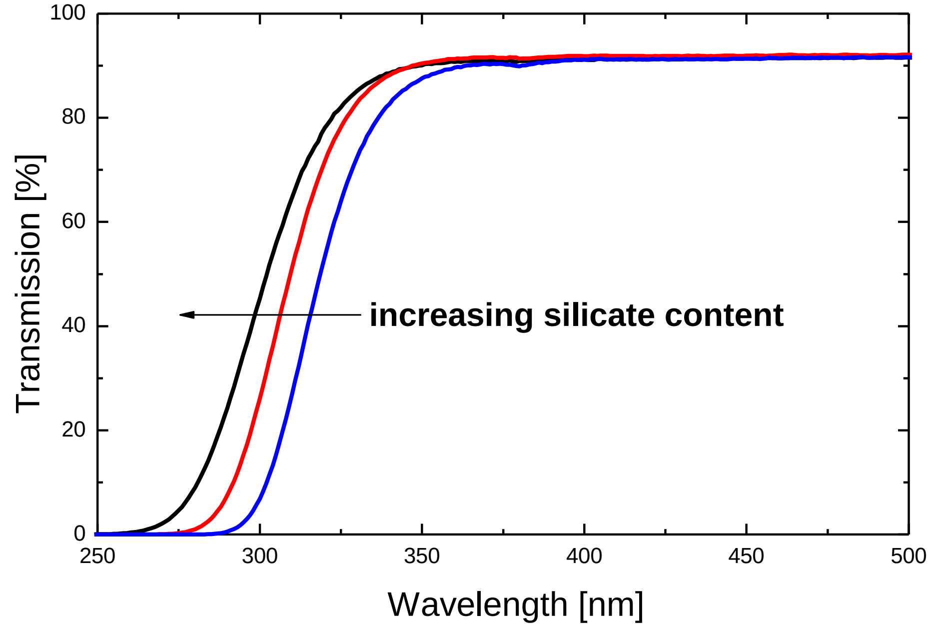
Type of Glass	Composition	Applications
Quartz glass (silica glass)	SiO_2	Optical fibres UV-transparent optics Crucibles Semi-conductor technology UV-lamps
Fluoride glasses	ZrF_4-BaF_2-AlF_3, ZrF_4-BaF_2-LaF_3	Optical fibre for infrared light
Chalkogenide glasses	$AsTe_3$, As_2S_3, $GeSe_2$, GeS_2	IR-transparent optics
Glass fibre	SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O	Admixture of metals, ceramics and glasses
Glass solder	Lead-borate-glass	Reinforcement of polymers
Glass finish	Glass coating	Thermal insulation UV-protection Mirror Filter

3.2 Glasses and Glass Ceramics

Modification of physical properties

- **Enhancement of thermal changing behaviour**
  ⇒ B_2O_3-addition
- **Increased UV-transparency →**
  ⇒ higher silicate content
- **Increased refractive index**
  ⇒ PbO/GeO_2-addition
- **Increased absorption of X-rays**
  ⇒ BaO/SrO/PbO-addition
- **Colourisation**
  ⇒ coloured ions or metal clusters (e.g. Au)
- **Dull finish**
  ⇒ $ZrSiO_4$/$Ca_3(PO_4)_2$-addition
- **Anti-reflection coating**
  ⇒ coating with SiO_2-nano particles

Transparency of sodium silicate glasses



3.2 Glasses and Glass Ceramics

Bleaching of Glasses

Flat glass and other technical glasses (glass for lamps etc.) often contain small amounts of Fe^{2+} which gives the glasses a bluish-greenish colour

Addition of oxidising agents, such as MnO_2

$$\Rightarrow \; 2\,Fe^{2+} + Mn^{4+} \rightarrow 2\,Fe^{3+} + Mn^{2+}$$

Problem: solarisation of these glasses by UV-light (sun light or plasma radiation)

$$\Rightarrow \; Mn^{2+} \xrightarrow{h\nu} Mn^{3+} \text{(violet)} + e^{-} \text{(colour centre)}$$

Alternative oxidising agent is As_2O_5 which decomposes upon heating

$$\Rightarrow \; As_2O_5 \xrightarrow{\Delta T} As_2O_3 + O_2$$

$$\Rightarrow \; 4\,FeO + O_2 \rightarrow 2\,Fe_2O_3$$

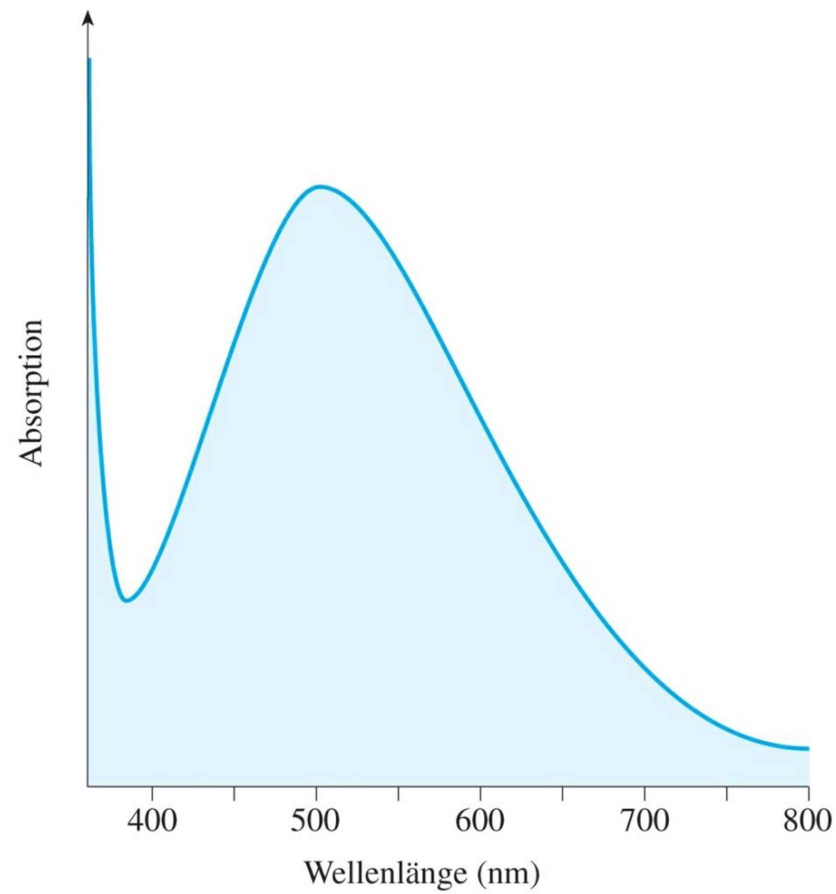
3.2 Glasses and Glass Ceramics

Colourisation of Glasses

1. Addition of transition metal ions

Ion	Coordination number	Colour
Ti^{3+}	6	violet
Ti^{4+}	6	transparent
V^{3+}	6	green
V^{5+}	4	transparent
Cr^{3+}	6	green
Cr^{6+}	4	yellow
Mn^{2+}	6	transparent
Mn^{3+}	6	violet
Fe^{2+}	4	bluish-green
Fe^{3+}	4, 6	light yellow
Co^{2+}	4, 6	blue, violet
Co^{3+}	4	green
Ni^{2+}	4, 6	blue, yellow
Cu^{2+}	6	blue

Absorption spectrum of $[Ti(H_2O)_6]^{3+}$



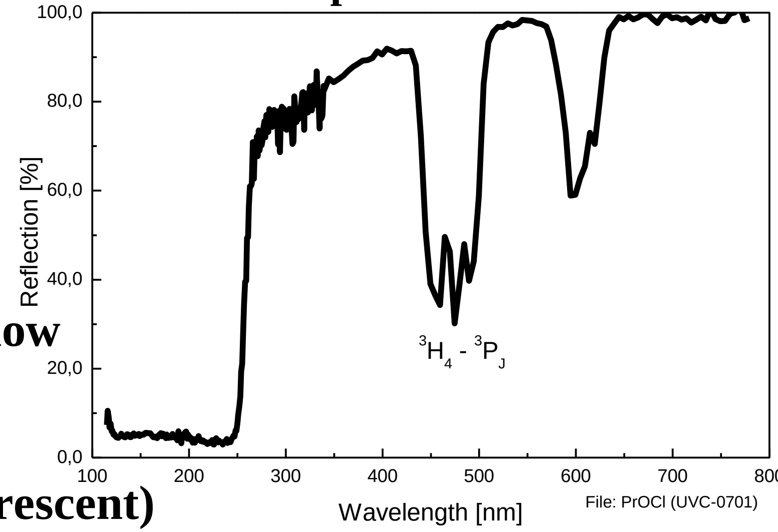
Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung23-19.jpg

Colourisation of Glasses

2. Addition of lanthanide or actinide ions

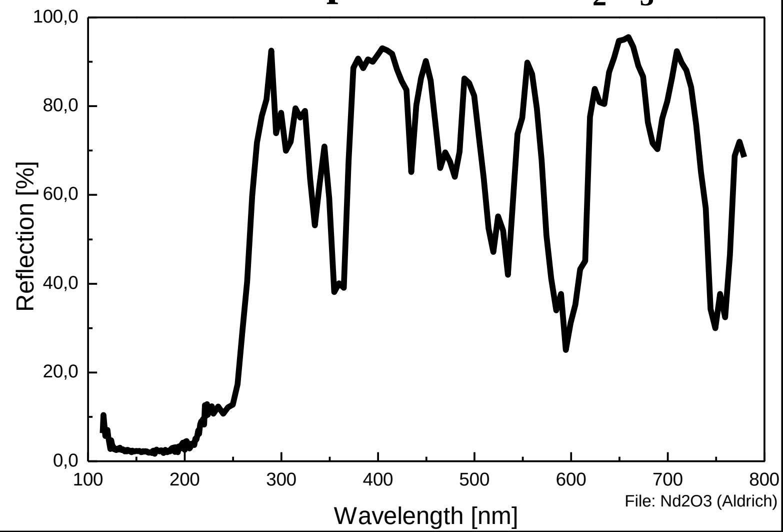
Ion	Coordination number	Colour
Ce^{3+}	6	transparent
Ce^{4+}	6	transparent to yellow
Pr^{3+}	6	green
Nd^{3+}	6	violet
UO_2^{2+}	6	yellow-green (fluorescent)

Reflection spectrum of PrOCl



- **Ce^{3+} is used as UV-A filter in halide- and Hg-high-pressure lamp glass**
- **Nd^{3+} is used in glasses for spectacles and displays to increase contrast**

Reflection spectrum of Nd_2O_3

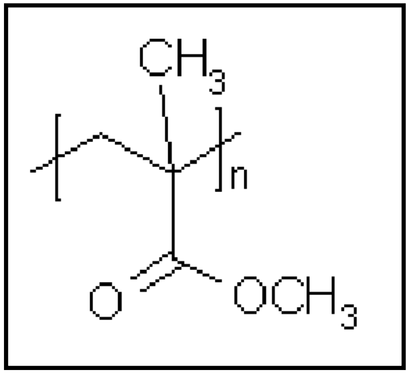


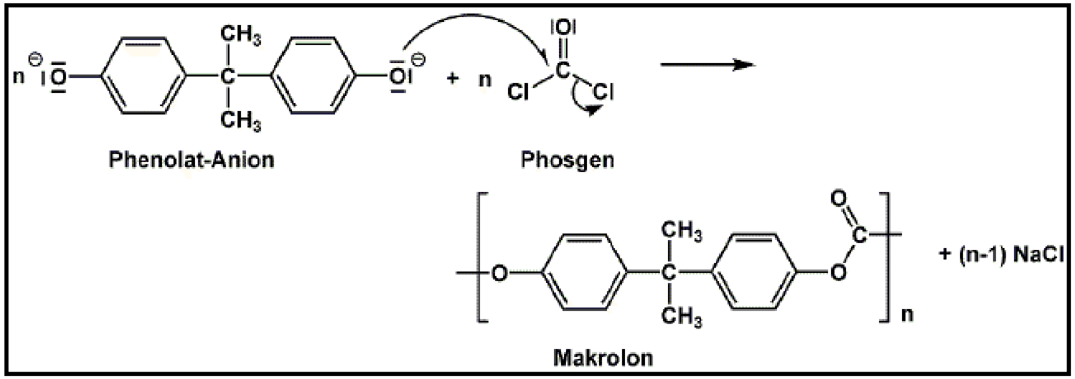
3. Formation of metal colloids (10 – 50 nm)
raw materials: $CuCl_2$, $AgNO_3$, $AuCl_3$
+ reducing agent: $SnCl_2$, As_2O_3

3.2 Glasses and Glass Ceramics

Organic Glasses – Properties, Applications and Structure

	Polymethacrylatemethylest. (PMMA)	Polycarbonate (PC)
Properties	high (UV-)transparency (E_G~4.4 eV)	high transparency
	high resistance to light	high tensile strength and viscosity
	Solubility in non-polar solvents	high impact and ultimate strength
Applications	plexiglas panels	storage medium (CDs and DVDs)
	spectacle glasses, (contact)lenses	visors

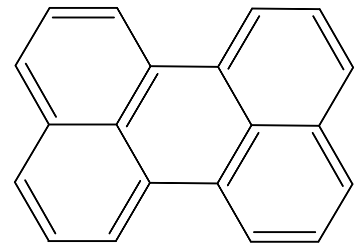




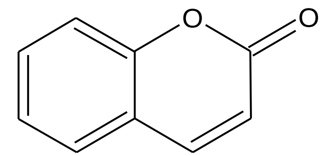
3.2 Glasses and Glass Ceramics

Organic Glasses - Dopants

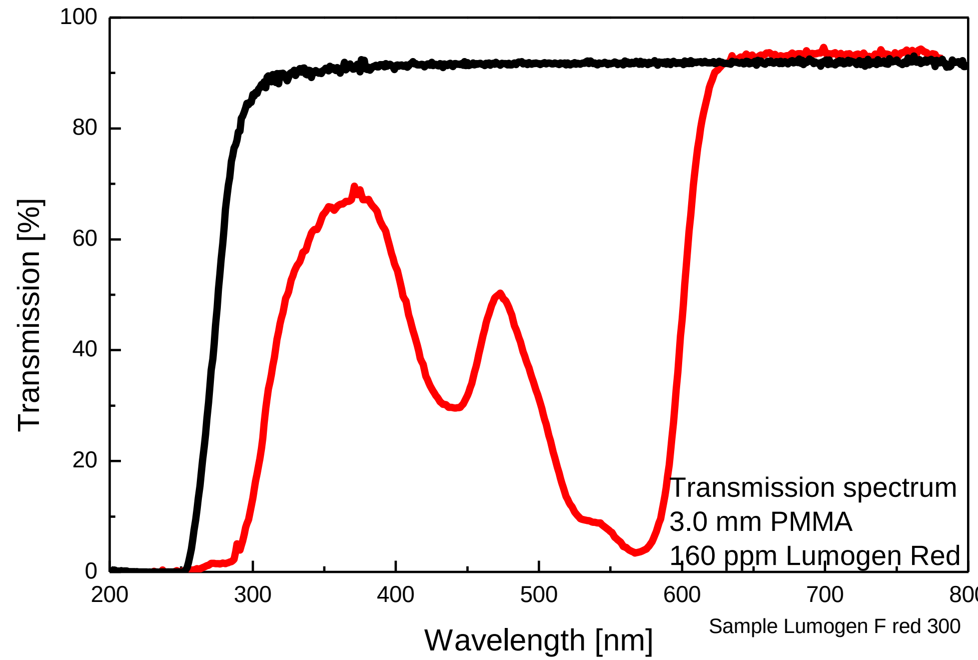
Perylene



Coumarin



With organic luminophores
- Perylene derivatives (Lumogen™)
- Coumarin derivatives (Laser-dyes)
- Rhodamines, e.g. rhodamine B or 6G
- Fluorescein



Application
- Design elements
- Traffic signs
- (Light sources)

Lumogen plates
Source: BASF AG

Glass Technology

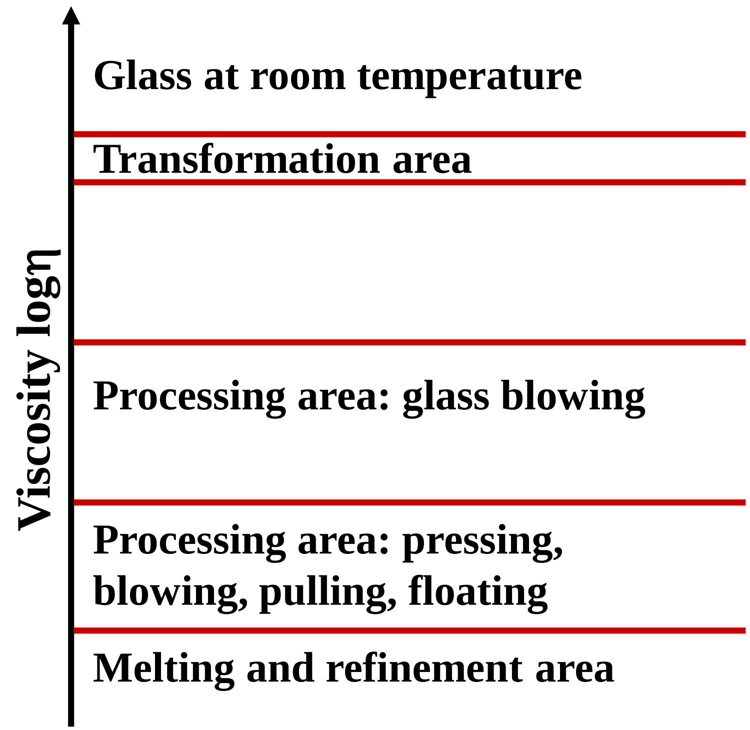
Glasses are processed at temperatures, where their viscosity allows deformation without breaking

The viscosity of a glass-forming melt can be described by the Vogel-Fulcher-Tammann-equation

Viscosity $[Nm^{-2}s]$

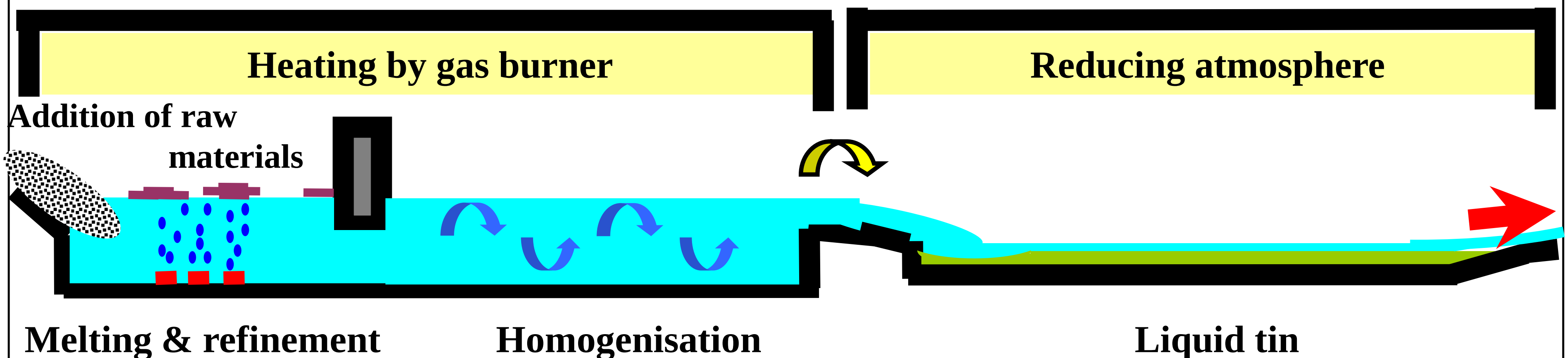
$$\eta = C \cdot \exp\left(\frac{E_\eta}{k_B(T - T_0)}\right)$$

With C = pre exponential factor $[Nm^{-2}s]$
k_B = Boltzmann constant [J/K]
E_η = Activation energy [J]
T = Temperature [K]



Glass Technology – Melting Area η = 5 - 50 $Nm^{-2}s$

- Disks and sheet glass is produced from a melt. Processes are waltzing between water-cooled rolls and floating on tin



- Glass fibres are pulled from a melt using Pt-nozzles

- For the production of optical lenses glass melts are poured into moulds that are cooled slowly to prevent cracks and tensions

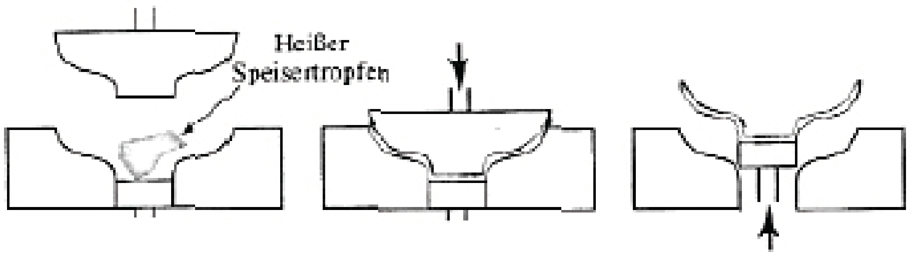
Glass Technology – Melting Area η = 10^3 - 10^6 $Nm^{-2}s$

Glass vessels or glass bulbs for incandescent and halogen lamps are produced by pressing, pulling or blowing.

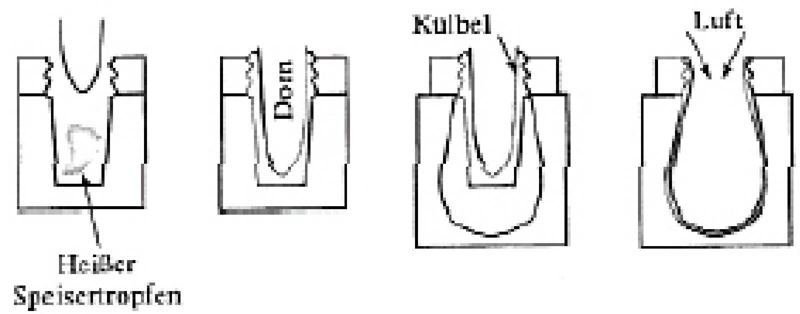
The glass is in a temperature range where it can be formed but does not "run away".

<u>Glass transformation processes</u>

a) Pressing-process



b) Pressing-blowing-process



D.R. Askeland, Materialwissenschaften, Spektrum Verlag GmbH Heidelberg, Berlin, Oxford, 1996

3.2 Glasses and Glass Ceramics

Glass Technology – Relaxation Areas $\eta = 10^6 - 10^{12}$ $Nm^{-2}s$

Some glasses must be relaxed (annealed) to get rid of tensions which occurred during deformation

Some glasses are thermally treated to precipitate crystalline areas within the glass
⇒ glass ceramics

Pre-stressed glass can be produced by quenching of sheet glass in air. Thereby, the surface layer is cooling off rapidly and contracts. The inner layers are cooling down more. The as produced glass exhibits higher thermal resistance against tensile stress and impacts

3.2 Glasses and Glass Ceramics

Glass Ceramic – Definition and Properties

Glass amorphous solid

Ceramic polycrystalline solid

Glass ceramic crystallites in glass matrix mostly Li_2O-SiO_2-Al_2O_3 based

⇒ Complex production process

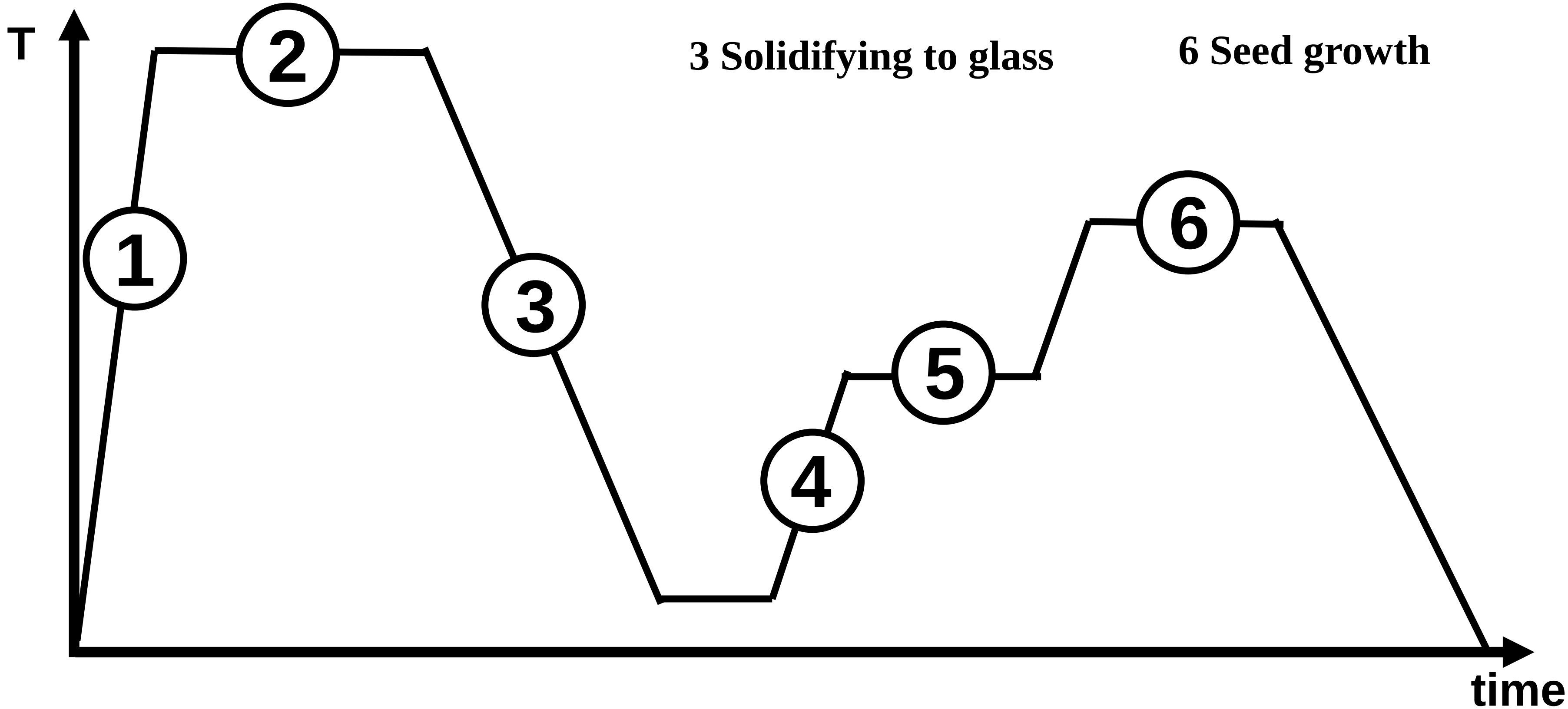
⇒ Ultrapure raw materials needed

⇒ Colourisation is complex

Properties

- Small or even negative thermal expansion
- High resistance against temperature changes
- Some types can be processed by machines

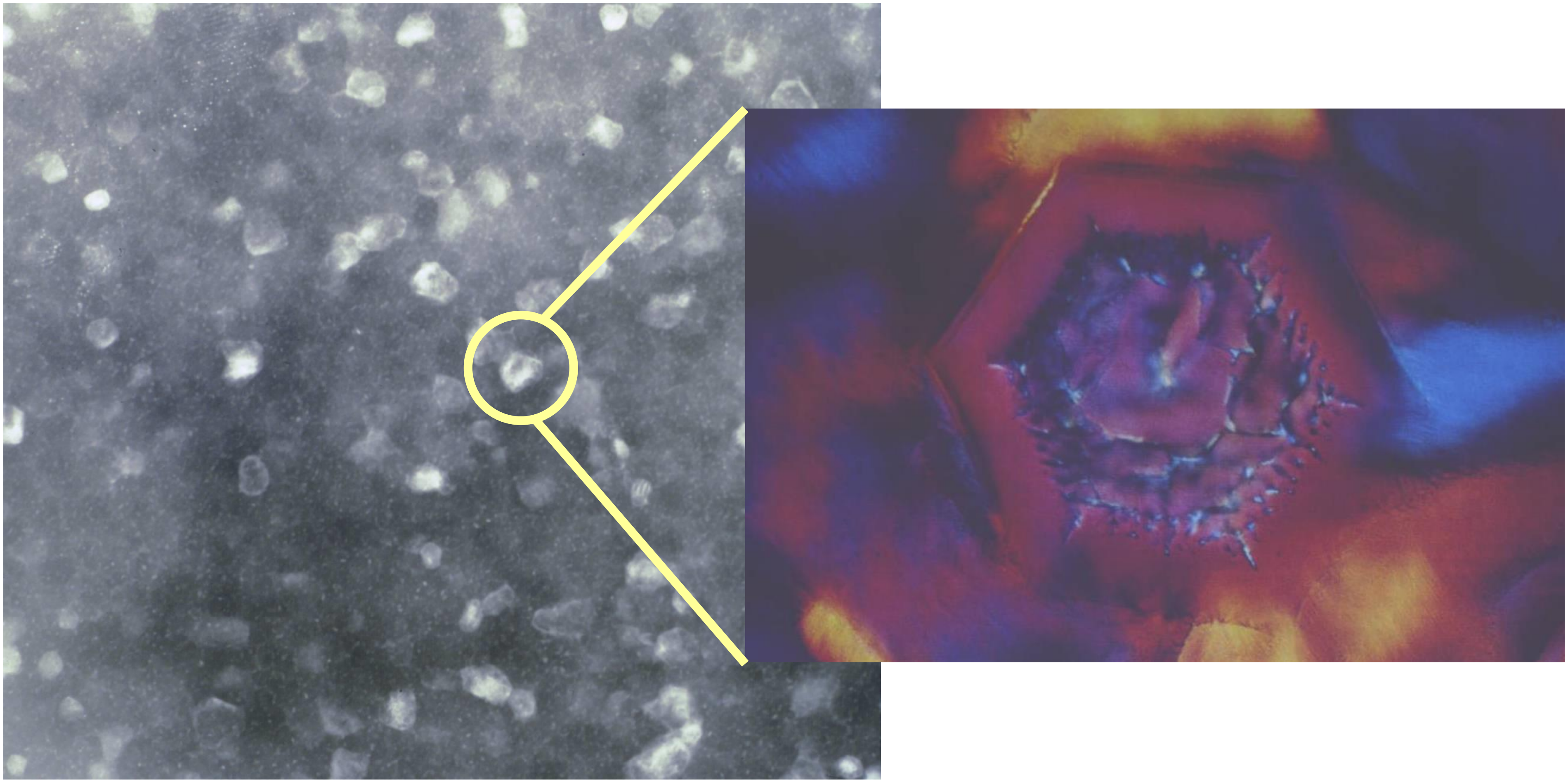
Glass Ceramic – Production



1 Melting
2 Purification
3 Solidifying to glass
4 Heating
5 Seed formation
6 Seed growth

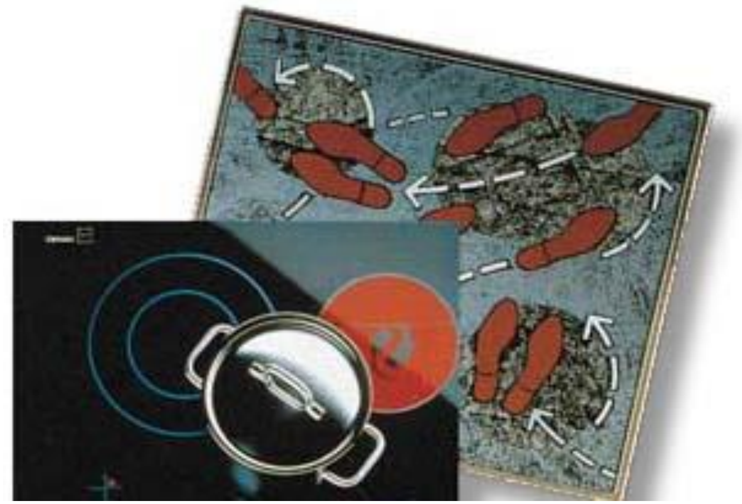
Seed formation can be achieved by the addition of seed formation centres, such as TiO_2, or thermal treatment

Glass Ceramic - Structure



3.2 Glasses and Glass Ceramics

Glass Ceramic - Applications



- Scaffolds for huge reflecting telescopes VLT, ELT)
- Stove tops (Ceran™)
- Heat shield for aerospace technology
- Temperature-resistant front panels for fireplaces
- LED Converter

Ce^{3+}-doped Garnets	$(Y,Gd,Tb)_3Al_5O_{12}$:Ce
Eu^{2+} doped Silicates	$(Ca,Sr,Ba)_2SiO_4$:Eu, $(Ca,Sr,Ba)_3SiO_5$:Eu
Eu^{2+} doped Nitrides	$Ba_2Si_5N_8$:Eu, $CaAlSiN_3$:Eu
Eu^{3+} doped Metallates	$Ln_x(Mo,W)_yO_z$

- Resonators for solid state lasers

Sesquioxides	Y_2O_3:Yb
Garnets	$Y_3Al_5O_{12}$:Nd, $Y_3Al_5O_{12}$:Yb