Chapter 5. Materials

5.1 Real structure and defects in solids

5.2 Specific aspects of the structural chemistry of alloys

5.3 Magnetism in solid state compounds

5.4 Superconducting materials

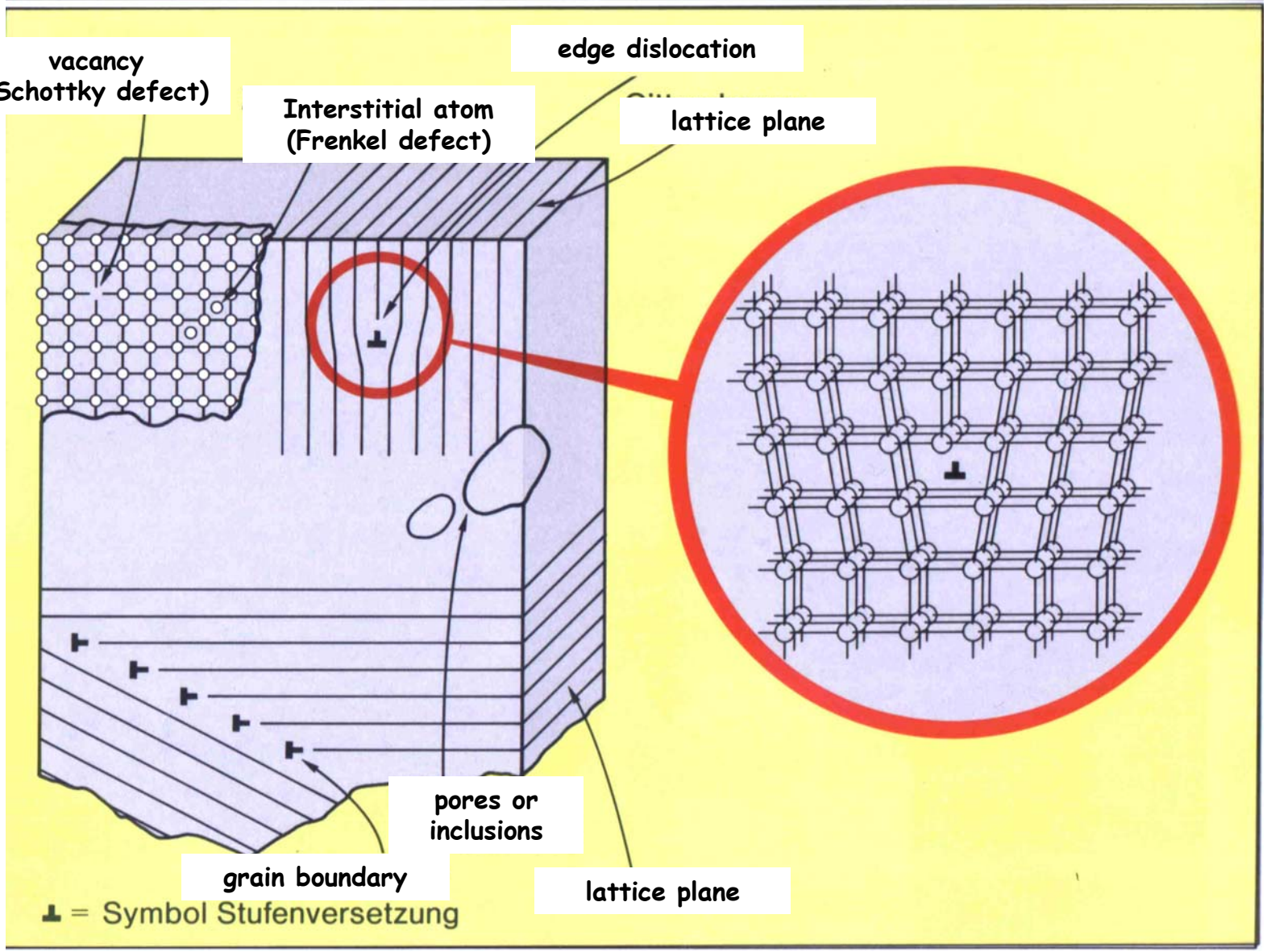
5.5 Ionic conductors

5.6 Luminescent materials

5.7 Nitride materials

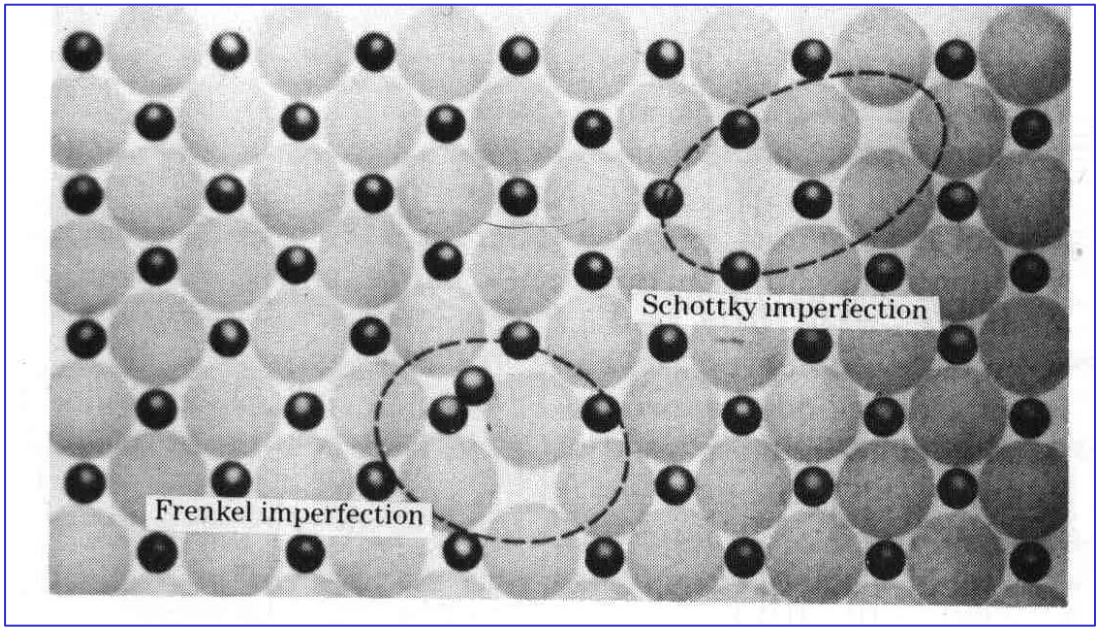
5.8 Biogenic materials

5.1 Real structure of a cubic crystal



5.1 Point defects in solids

Defects are of paramount importance for many application oriented properties of solids (e.g. mechanical and electrical properties)



Schottky-defect: vacancy, missing ions moved to the surface

Frenkel-defect: vacancy, missing ions on interstitial positions

5.1 Defects in solids

Importance of point defects for the properties of solids

- Defects are centers of reactivity

- Defects are responsible for mass transport (diffusion) either self diffusion or diffusion under the influence of an external electric field (ionic conductivity)

- Schottky defects (vacancy): diffusion of cations and anions

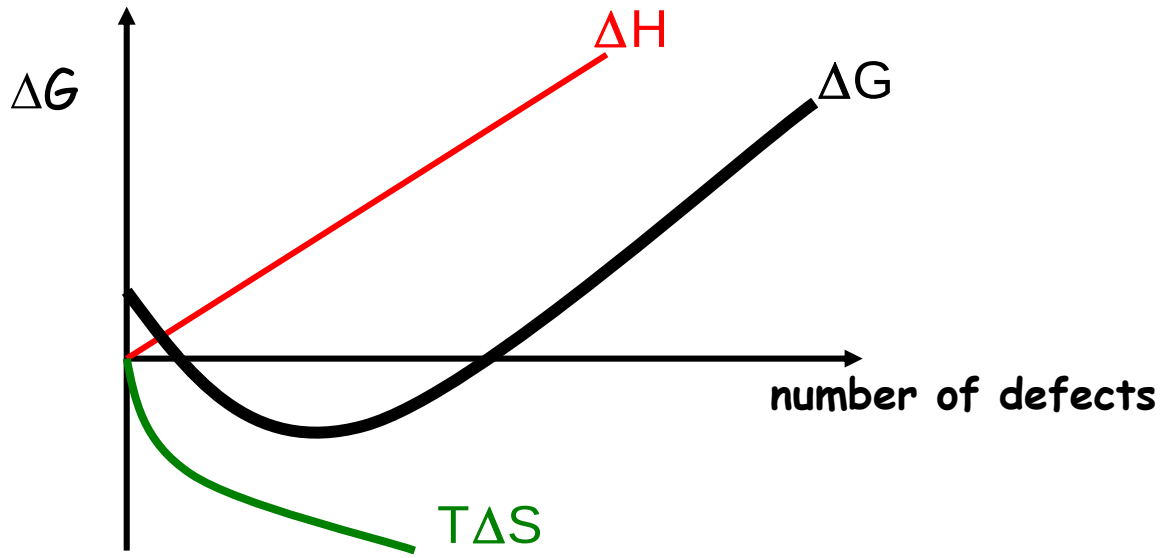
- Frenkel defects (interstitials): diffusion of one ionic species only

5.1 Defects in solids

→ Up to a certain (low!) concentration the presence of defects leads to a <u>reduction of the free enthalpy</u> (ΔG) !!!

$$\Delta G = \Delta H - T\,\Delta S$$

ΔG: free enthalpy of a crystal ; **ΔH:** enthalpy to create a defect,
ΔS: increase of entropy upon formation of a defect, **T:** absolute temperatur



5.1 Number of defects in solids

$$n_s/N = e^{\frac{-W}{2kT}}$$

n_s: number of defects; N: number of lattice positions
W: energy to create a defect („activation energy")
k: Boltzman constant´; T: absolute temperature

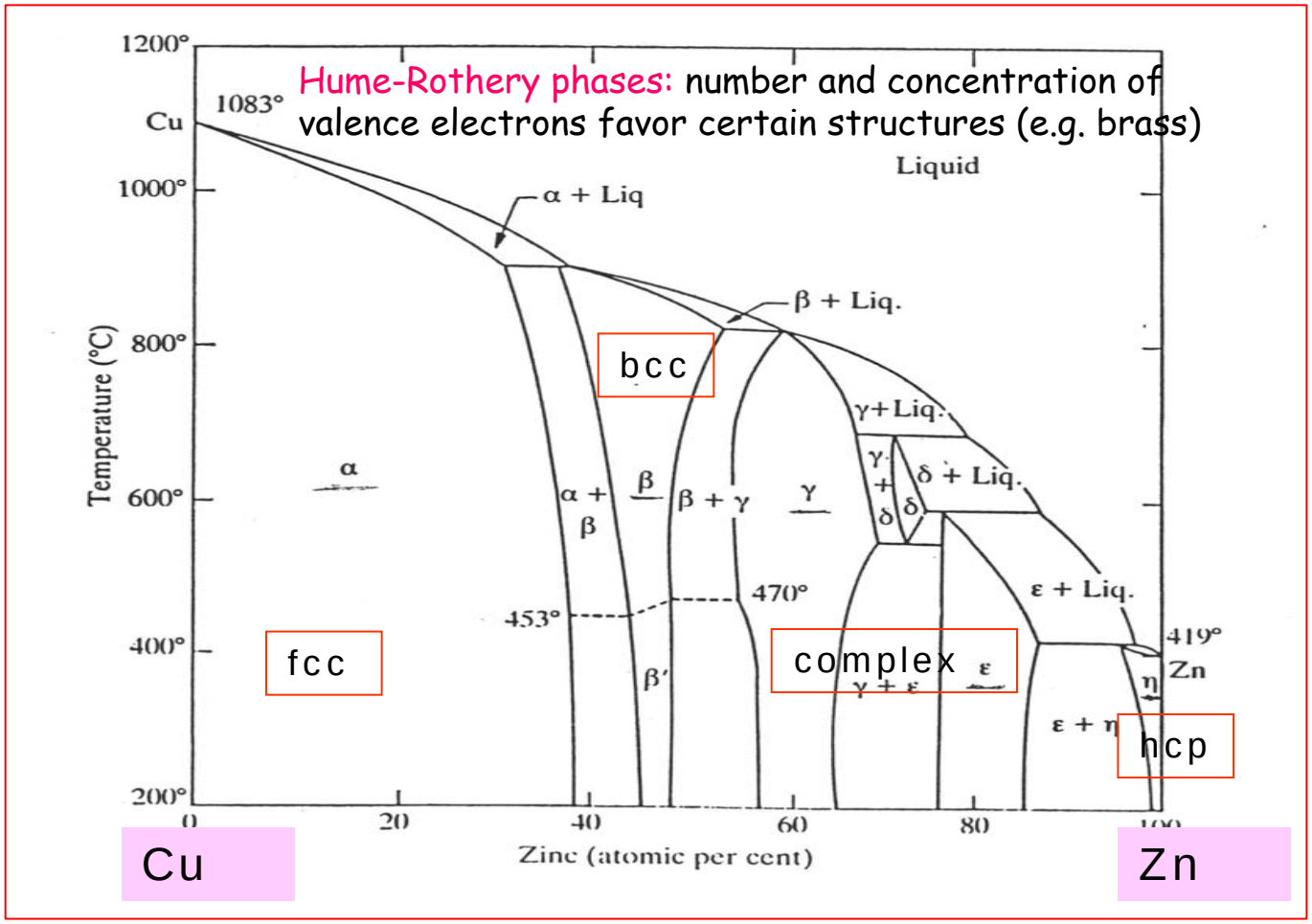
some typical numbers for NaCl (W = 188 kJ/mol ~ 2 eV):

T (K)	n_s/N	n_s/cm^3
0	-	-
298	$3 \cdot 10^{-17}$	$5 \cdot 10^{5}$
1073	$3 \cdot 10^{-5}$	$4 \cdot 10^{17}$

Alkali halides	Schottky (cations and anions)
Alkaline earth oxides	Schottky (cations and anions)
Silverhalides	Frenkel (cations)
Alkaline earth fluorides	Frenkel (anions)

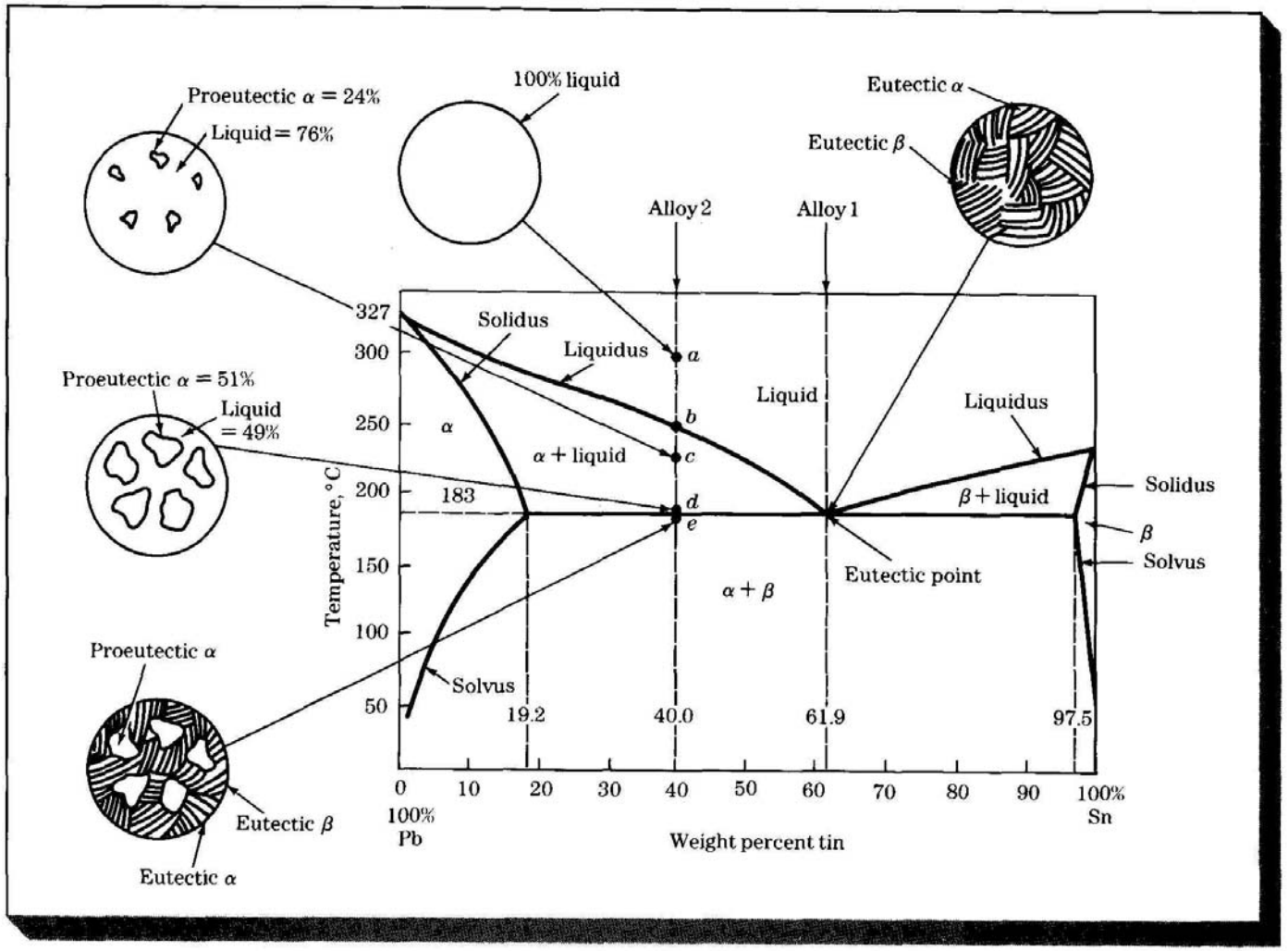
5.2 Specific aspects of the structural chemistry of alloys (intermetallic compounds)

- **Classical alloys do not obey simple valence rules (8-N etc.): Zr_4Al_3, Cu_5Zn_8 ... and are characterized by variable chemical compositions („homogeneity ranges") with statistical atom distribution (→ phase diagrams, → order-disorder-transitions)**

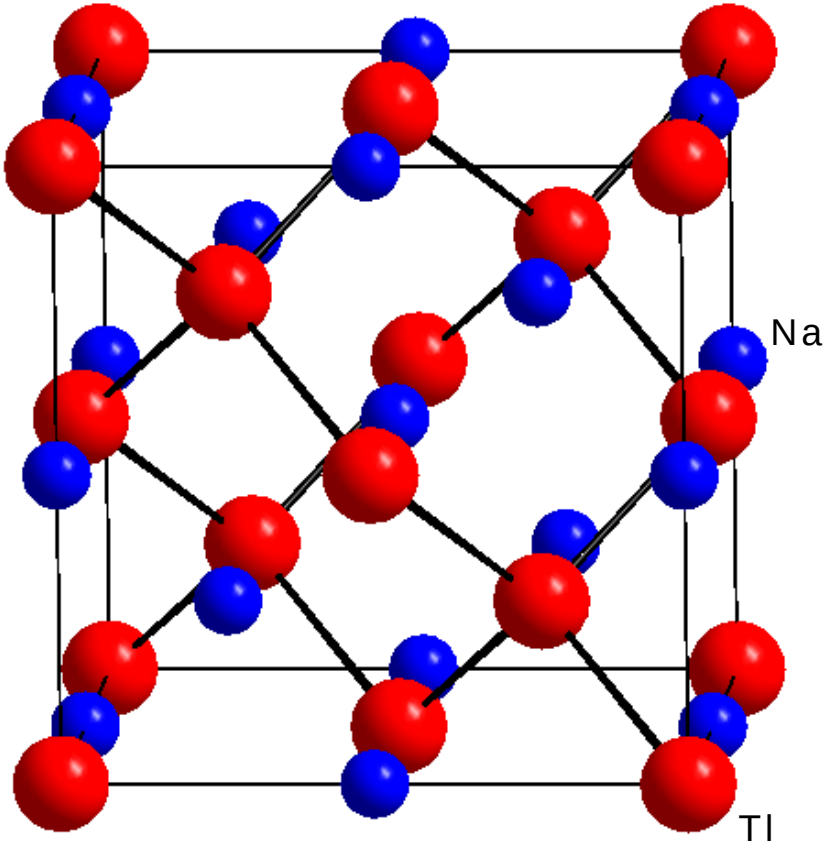


5.2 Characteristic morphology in different regions of the alloy system Pb - Sn

FIGURE 8.11 The lead-tin equilibrium phase diagram. This diagram is characterized by the limited solid solubility of each terminal phase (α and β). The eutectic invariant reaction at 61.9% Sn and 183°C is the most important feature of this system. At the eutectic point, α (19.2% Sn), β (97.5% Sn), and liquid (61.9% Sn) can coexist.



5.2 Zintl phases: alloys with moderate differences between participating metals (e.g. NaTl)



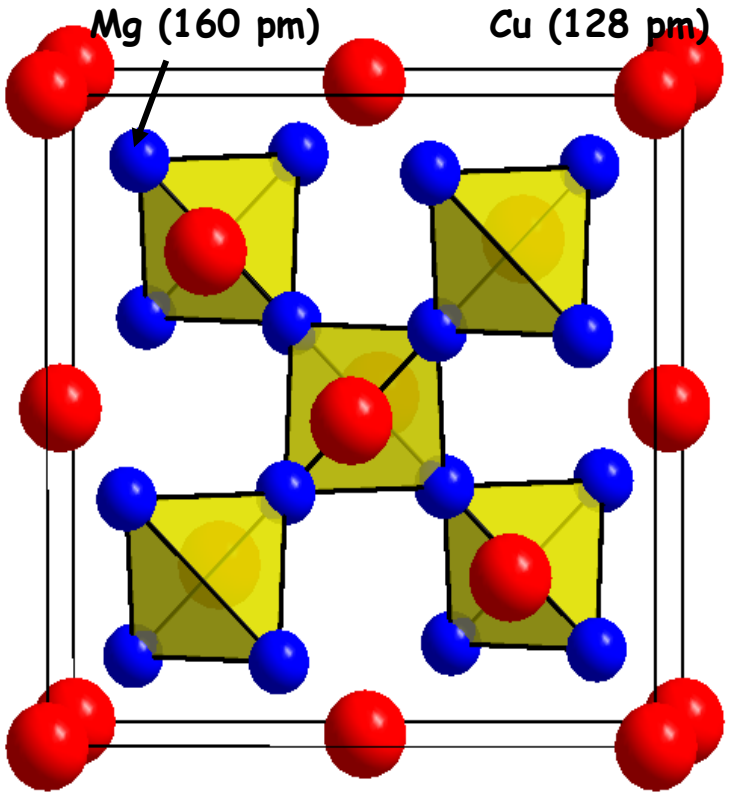
NaTl = Na^+Tl^-: Tl^- forms a diamond structure
(Tl^- acts as a „pseudo element" of group 14 (Pb))

- If one assumes a complete electron transfer from Na to Tl the latter one becomes a „pseudo element" of group 14 (Pb) and forms a diamond structure.

- Typical for Zintl phases: the „pseudo element" forms a structure (1D, 2D or 3D) which is found in real elements of the respective group of the periodic table.
(LiIn, NaSi, Ba_3Si_4, NaP ...)

- The Zintl model is an idealized assumption which accounts for the structural but in many cases not for the physical properties of the respective alloys

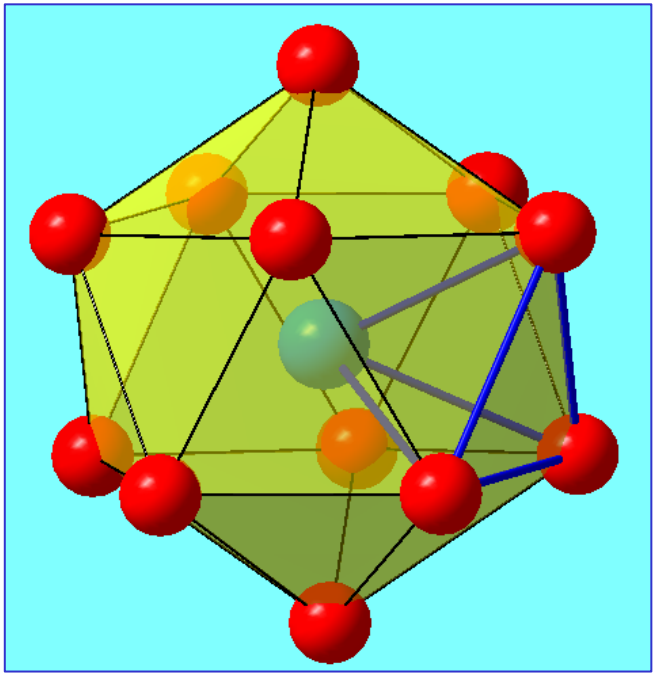
5.2 Laves phases: A specific radius ratio in AB_2 compounds favors certain structure types with closed-packed A and tetraedric B ions (classical examples: $MgCu_2$, a cubic Laves phase)

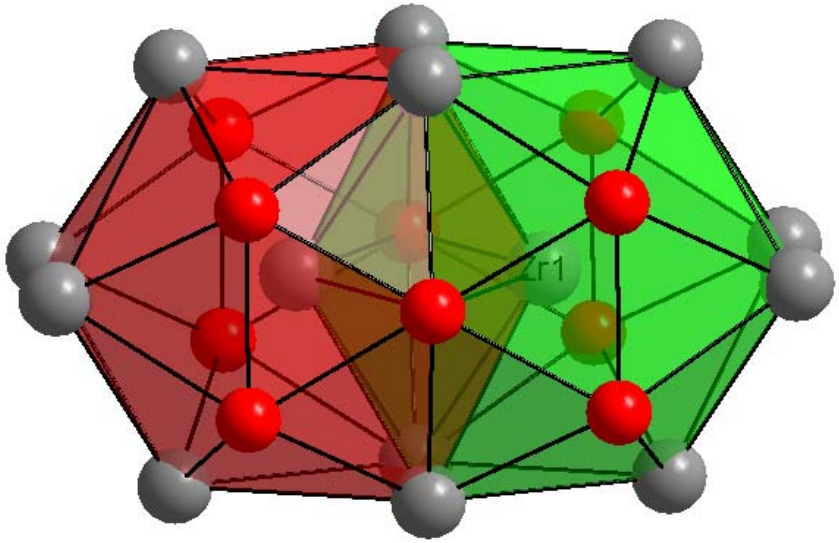


r(Mg)/r(Cu) = 1.25, range: 1.1 to 1.7, ideal value: $\sqrt{3}/\sqrt{2} = 1.22$

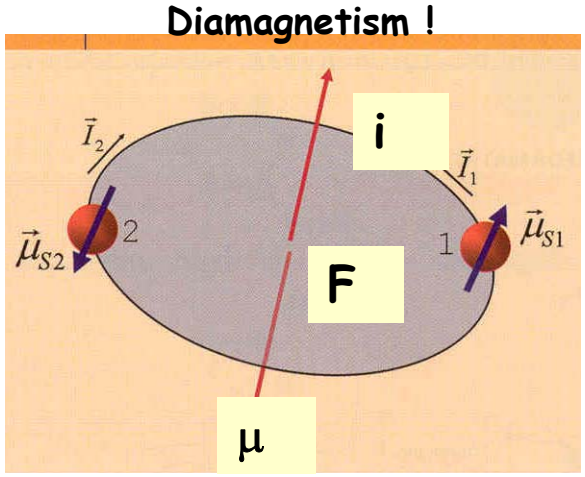
5.2 Frank-Kasper-Phases (topological close packings):

- Complex structures with 3D interpenetration of „Frank-Kasper-polyhedra"
- Each Frank-Kasper-polyhedron consists of a finite close packing of tetrahedra (e.g. icosahedron consists of 20 tetrahedra with a common apex and common faces and edges)





5.3 Magnetism in solid state compounds: Bohr magneton (smallest quantity of a magnetic moment)



General definition of the magnetic Moment μ (vector)

$\mu = i\,F$ [Am^2], i: circular current, F: aerea

μ_B magnet. moment of an electron on an atomic orbit (Bohr magneton BM)

$\mu_B = eh/4\pi m_e = 0{,}9274\ 10^{-27}\ Am^2$ (relation to basic constants)

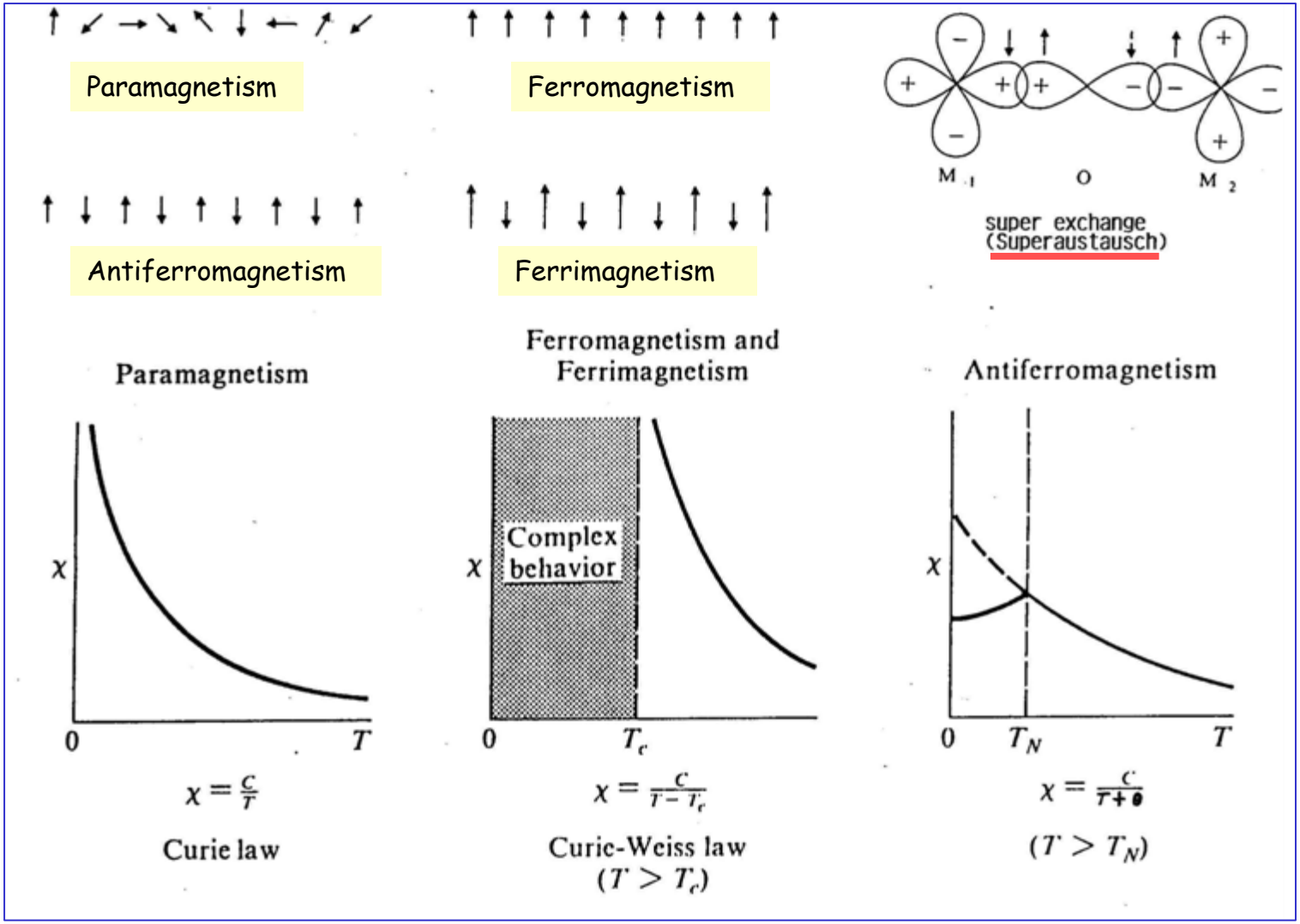
(μ_B: smallest possible quantity of a magnetic moment)

$\mu_s = 2\,(S(S+1))^{\frac{1}{2}} \cdot \mu_B$ **with** $S = \sum s = \frac{1}{2} \cdot n$ and n = number of unpaired electrons

(spin only magnetism, orbital momentum omitted, $\mu = g \cdot S$ with $g \sim 2 \rightarrow 5$ BM for Fe^{3+} (S = 5/2)

n	1	2	3	4	5
μ_m	1,73	2,83	3,87	4,90	5,91

5.3 Magnetism in solid state compounds



5.3 Magnetisation (M) and susceptibility (χ) for dia- and paramagnetic solids

M: in general ‚M is the sum of all magnetic moments in a volume V divided by V
i.e. magnetisation corresponds to an „intrinsic" (internal) magnetic field and has to be added to an external field H

$M = (\sum \mu)/V$ dim: [$Am^2/m^3 = A/m$] = magnetic field strength !

The effective magnetisation M' of a sample in an experiment has an internal component M and an external component H; it turned out to be useful to define a dimensionless quantity χ (susceptibility), that represents this internal component:

$$M' = H\,\chi_V$$

χ_V:	dimensionless	(volume susceptibility)
χ_g:	[cm^3/g]	(gram susceptibilty)
χ_{mol}:	[cm^3/mol]	(molar susceptibility)→ used in Chemistry

Relations between susceptibility and magnetic moment:

$$\chi_{mol} = \frac{N\,\beta^2\,\mu^2}{3kT} \qquad \mu = 2.83\sqrt{\chi_{mol} \times T}$$

N: Avogadro-Zahl
$\beta=\mu_B$: Bohr magneton
k: Boltzmann constant

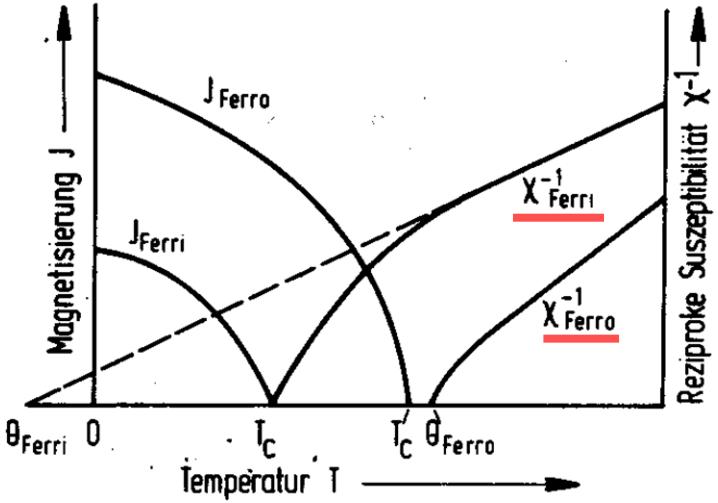
5.3 Magnetism in solid state compounds: Curie-Weiss law

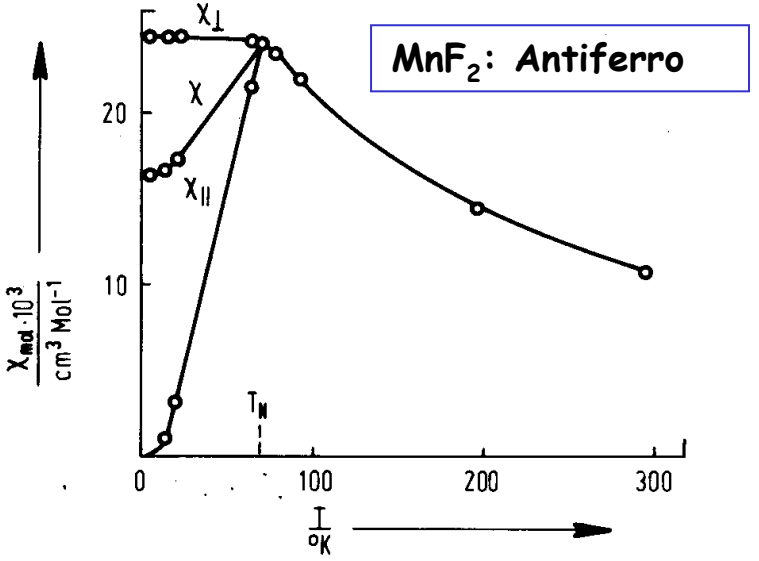
Pierre Curie
N.P. 1903 (Phys)
(Discovery of new elements Po, Ra)

Marie Sklodowska-Curie
N.P. 1903 (Phys), 1911 (Chem)
(Discovery of new elements Po, Ra)

Curie: $\chi \sim 1/T \rightarrow 1/\chi = C\ T$; Curie-Weiss: $1/\chi = C\ (T-\Theta)$

Susceptibility of real solids

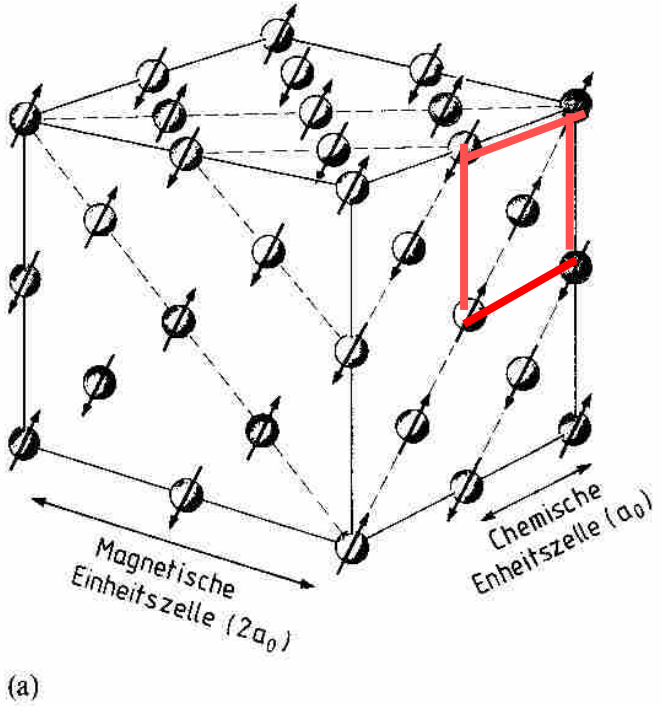


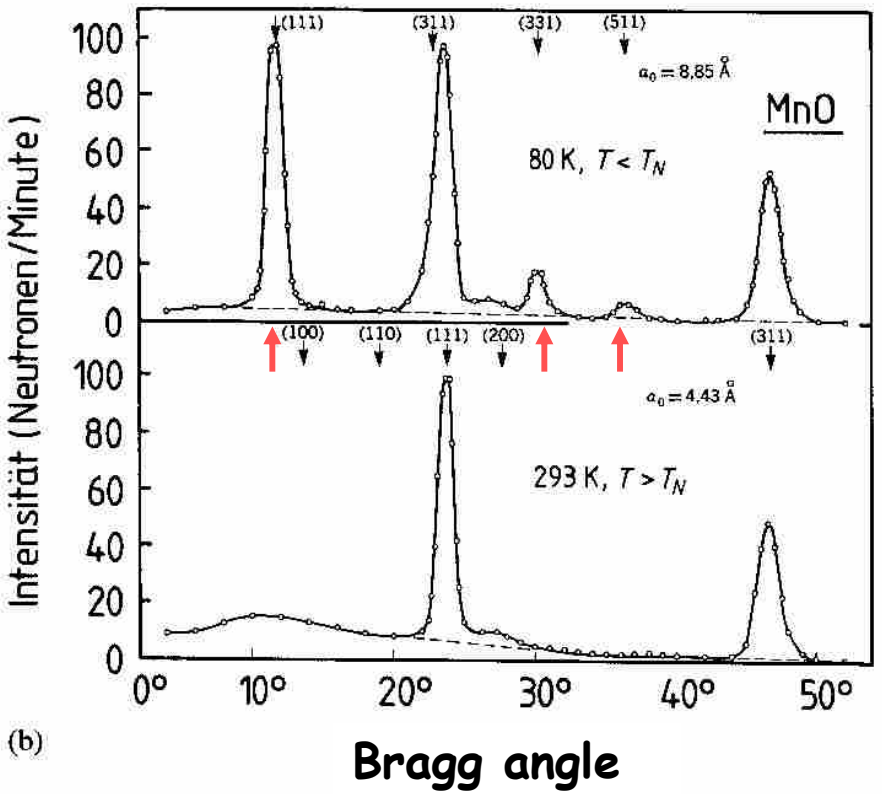


MnF_2: Antiferro

5.3 Solid State Magnetism: Magnetic structures by neutron diffraction

Neutrons interact with a) atomic nucleus („normal reflections") b) magnetic moment of electrons („magnetic reflections")



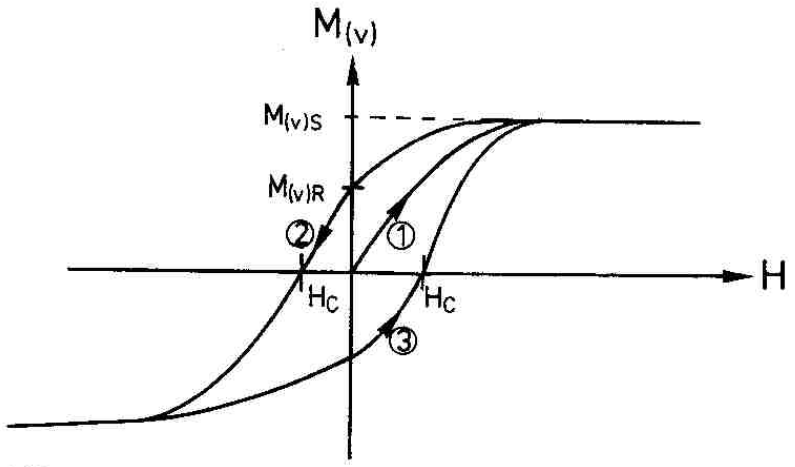


Magnetic Bragg-reflections indicating the magnetic order are visible only at low temperatures. At high temperatures the magnetic moments are randomly oriented and do not cause Bragg reflections.

5.3 Magnetisation curve of an initially „non-magnetic" Ferro-/ Ferrimagnet („hysteresis curve")

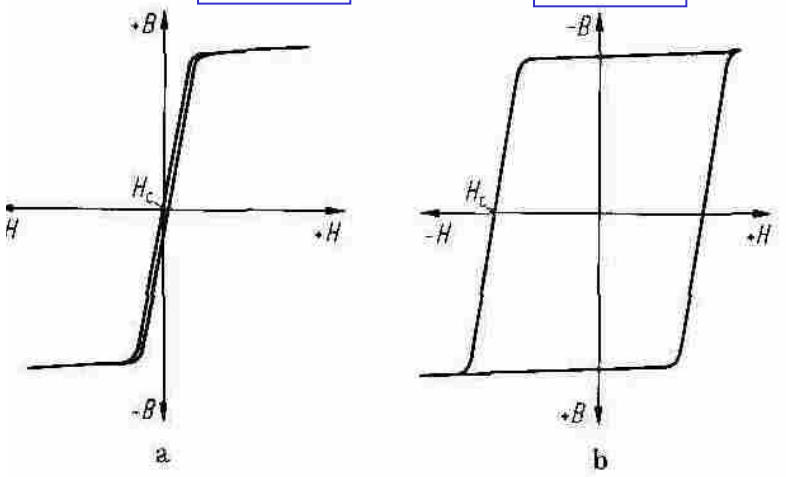
$M_{(v)S}$: saturation magnetization
$M_{(v)R}$: remanence
H_C: coercitive field

Aerea of the magnetization curve corresponds to magnetization energy



soft

hard



Applications:

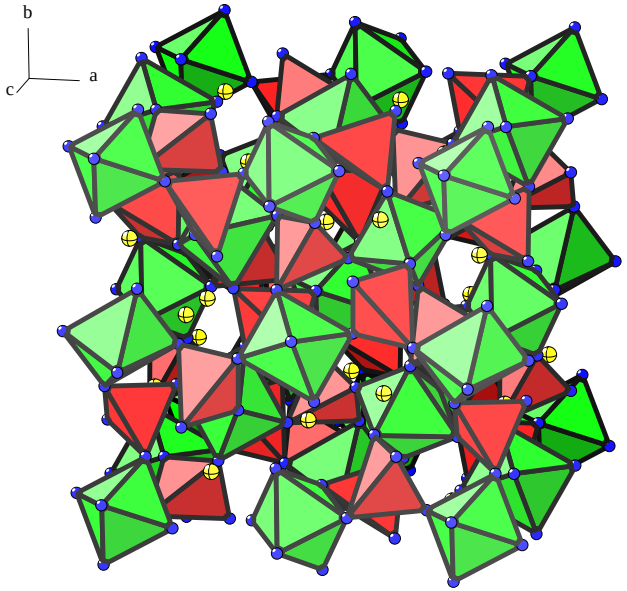
Soft magnets: transformers, electromagnets, coils ...

Hard magnets: sound- und video-tapes, permanent magnets ...

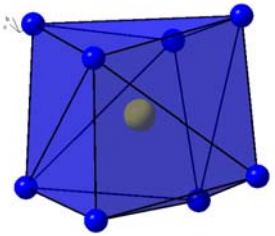
5.3 Solid State Magnetism: Magnetic materials

- No general chemical systematics for the composition of magnetic materials:
→ alloys with d-metals (Fe, Co, Ni, rare earth metals etc), ferrites, garnets …

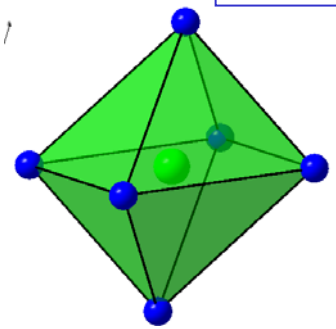
The garnet structure: $(Y^{3+})_3(Fe^{3+})_5O_{12}$

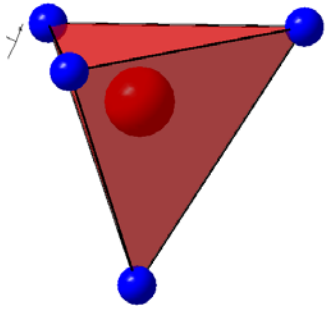


Y coordination, CN 8



Fe coordination



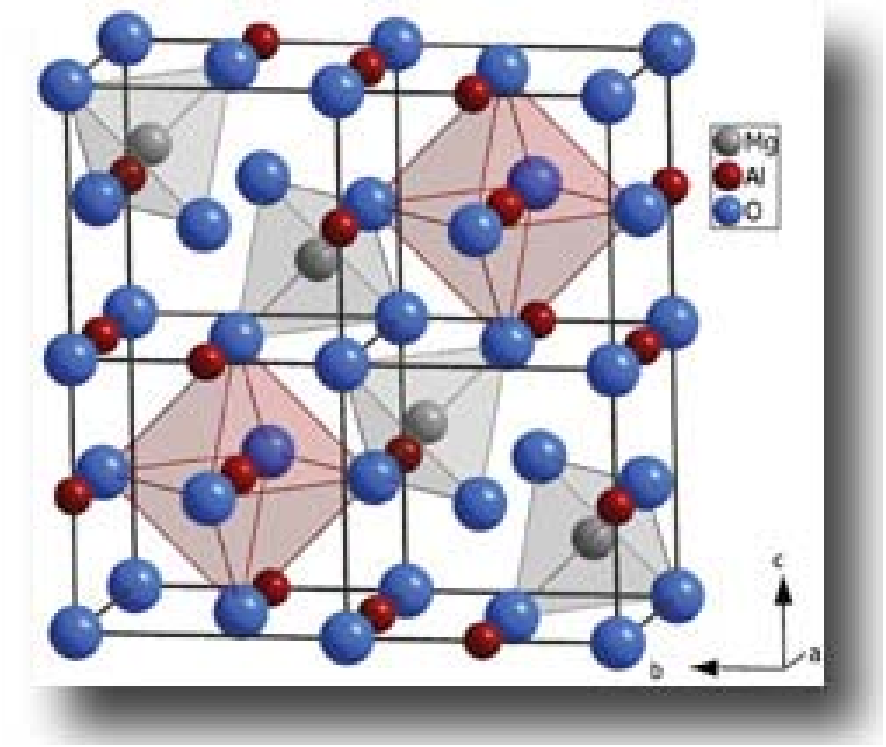


<u>Garnets</u>: $A_3^{2+}B_2^{3+}Si_3O_{12}$: A=Ca, Mg, Fe, Mn …, B=Al, Fe, Cr

- Silicates with isolated SiO_4-tetrahedra
- A^{2+}: big cations with CN=8 - B^{3+}: small cations with CN=6

RG: Ia3d: O (96h: xyz), Si (24d: 3/8 0 ¼) B (16a: 000) A (24c: 1/8 0 ¼)

5.3 Solid State magnetism: Structure of spinell: $MgAl_2O_4$

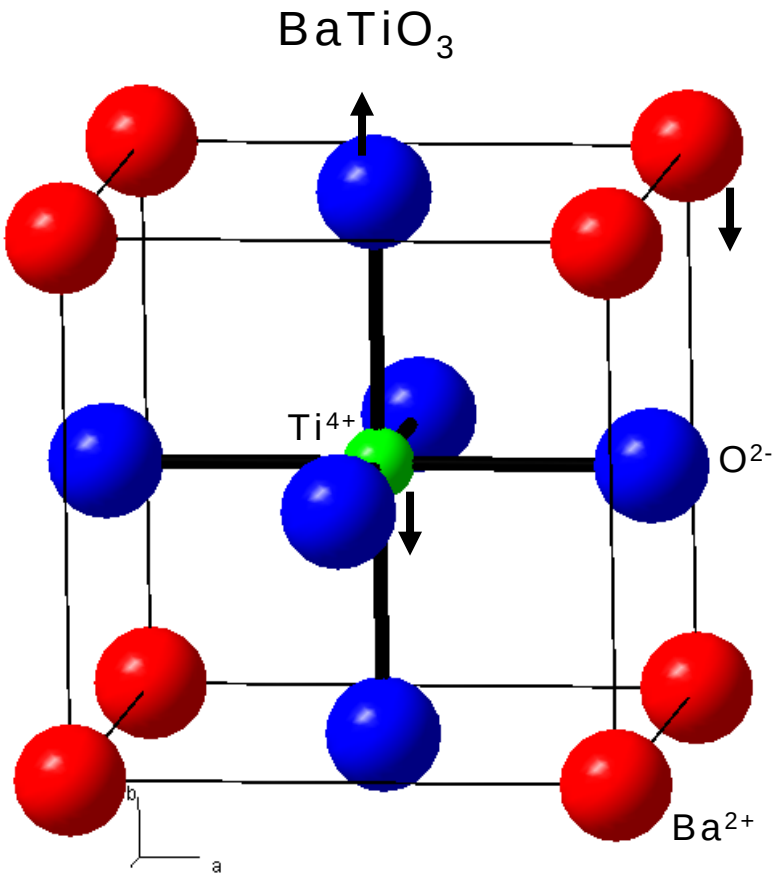


structural basis: ccp-arrangement of O^{2-}

Normal spinell: AB_2O_4, $\frac{1}{8}$ T-holes (A), $\frac{1}{2}$ O-holes (B)

Invers spinell: $B(BA)O_4$, e.g. $Fe_3O_4 = Fe^{3+}(Fe^{3+}Fe^{2+})O_4$

5.3 Ferroelectricity: The perovskite structure ($CaTiO_3$)



$BaTiO_3$ is a dielectric material that shows „Ferroelectricity"

- Displacive phase transition below the ferroelectric Curie temperature (T_c = 393 K for $BaTiO_3$) → spontaneous polarisation

- Piezoelectricity (pressure induced), Pyroelectricity (temperature induced) are also characterized by a spontaneous polarisation in the respective material

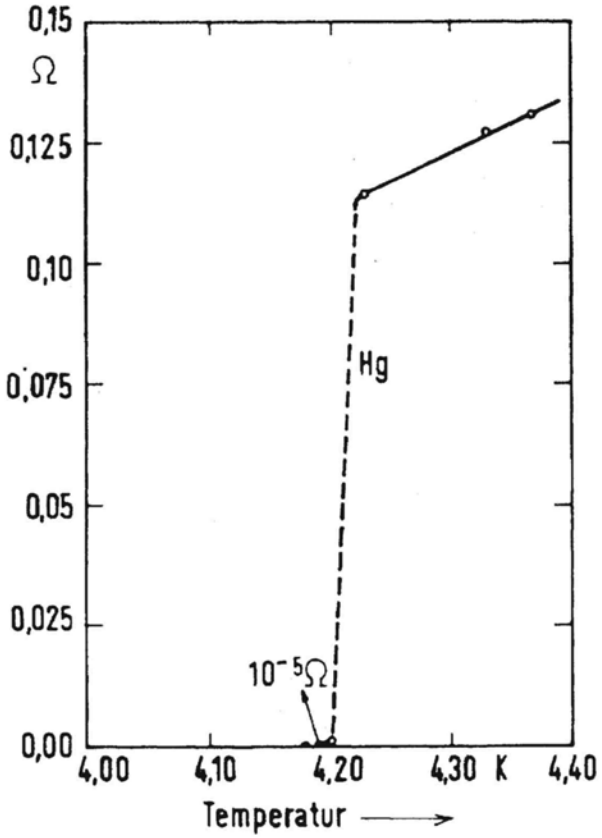
- In an external electric field and below 393 K all cations (Ba^{2+}, Ti^{4+}) move in one and the anions (O^{2-}) move in the opposite direction (see arrows); the structure becomes tetragonal (inversion center gets lost !) and shows a permanent electrical polarisation

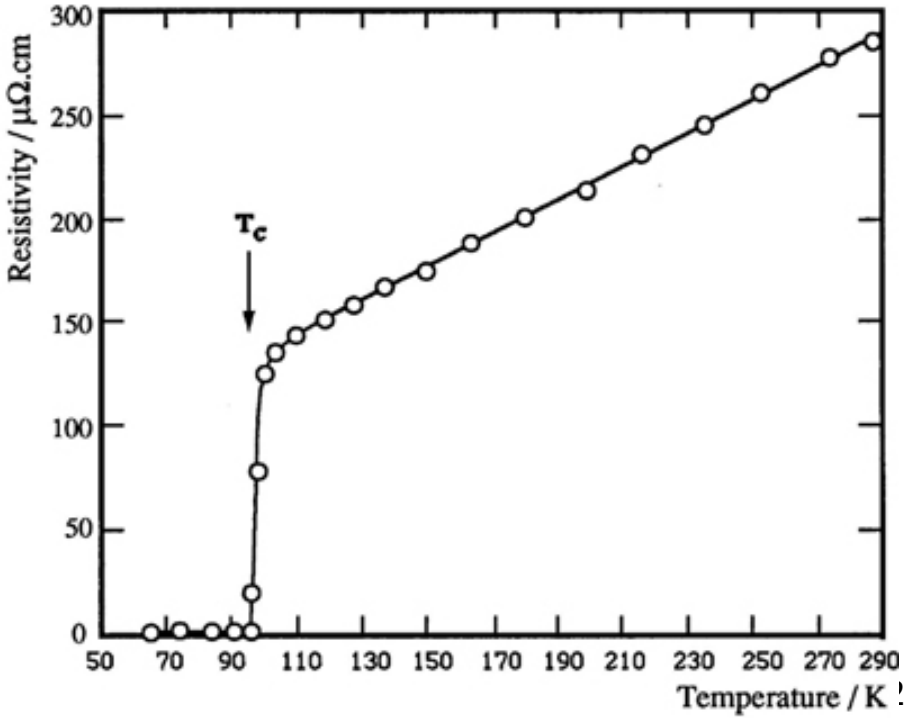
5.4 Superconducting materials

H. Kammerlingh-Onnes
N.P. 1913

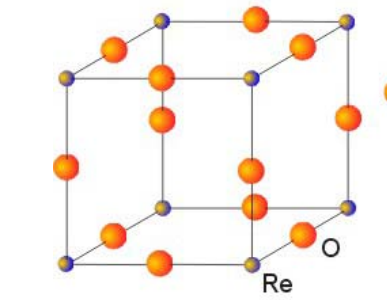
J.G. Bednorz,
K.A. Mueller
N.P. 1987

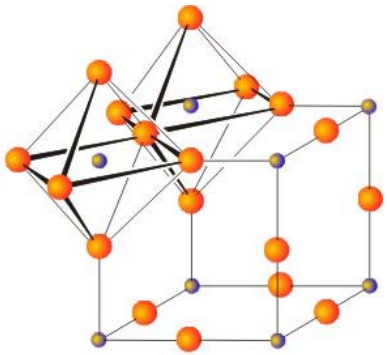
$Ba_xLa_{2-x}CuO_{4-y} \rightarrow YBa_2Cu_3O_{7-\delta}$





5.4 Structural relation between the structure of the high temperature superconductor $YBa_2Cu_3O_{7-\delta}$ (δ+0.5) and the **perovskite structure**





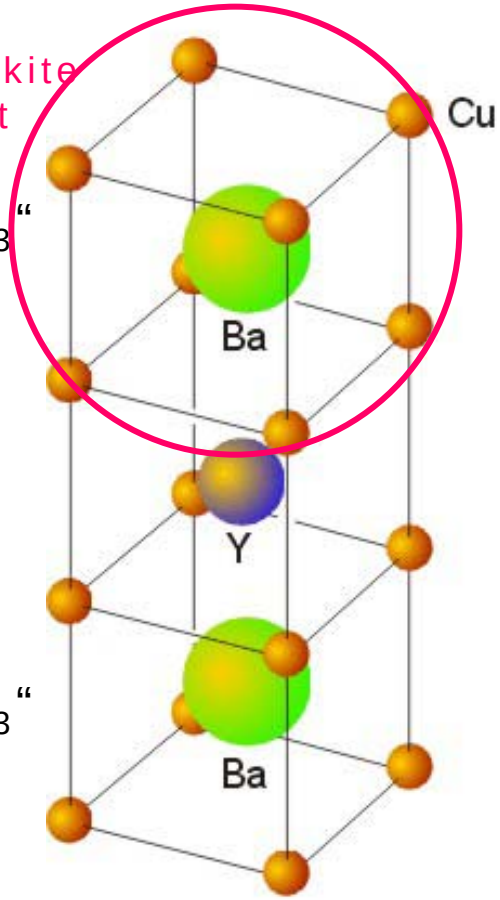
„$BaCuO_3$“

„$YCuO_3$“

„$BaCuO_3$“

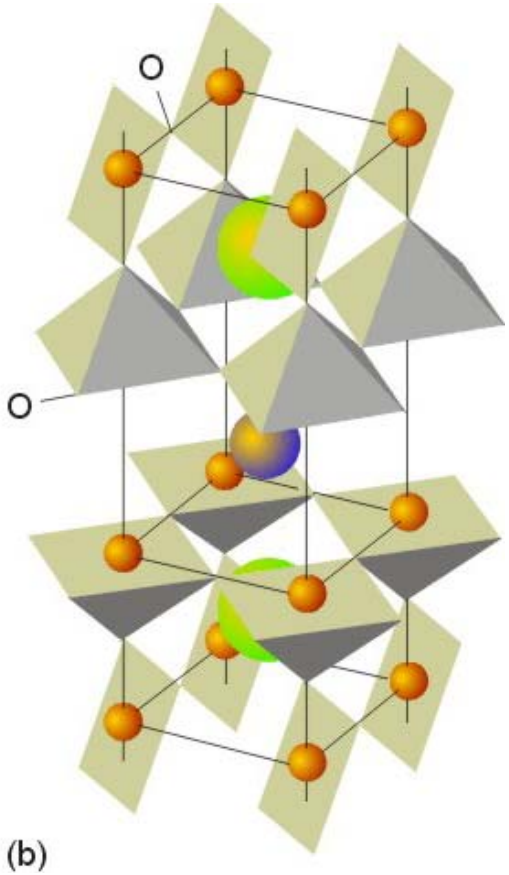
oxygen atoms are omitted

perovskite unit



(a)

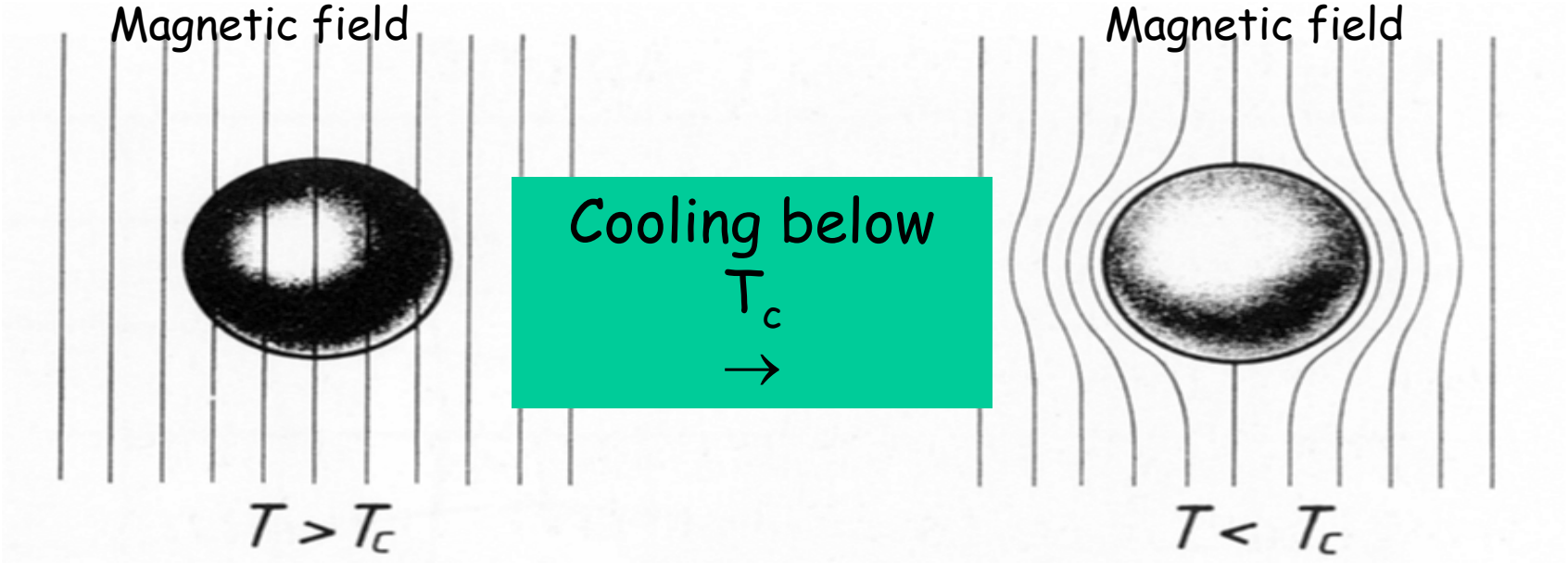
oxygen deficient !!

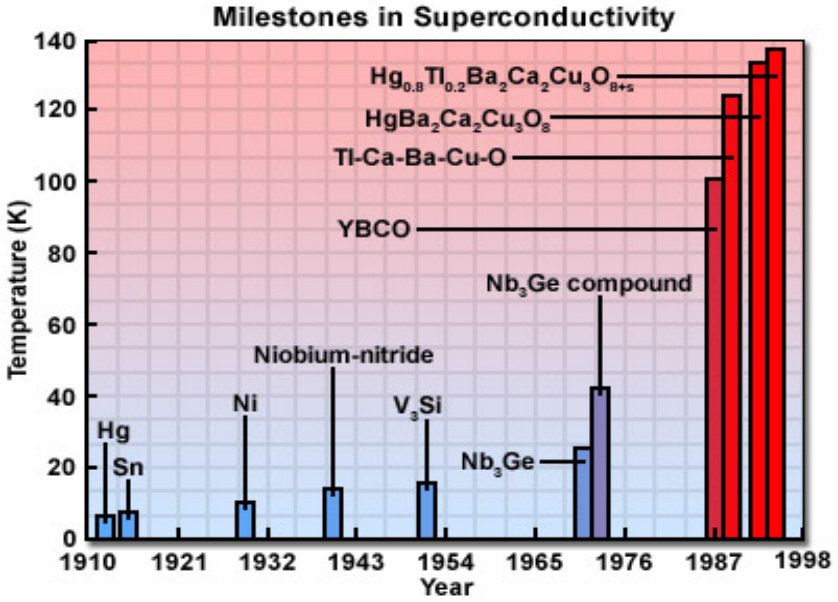


(b)

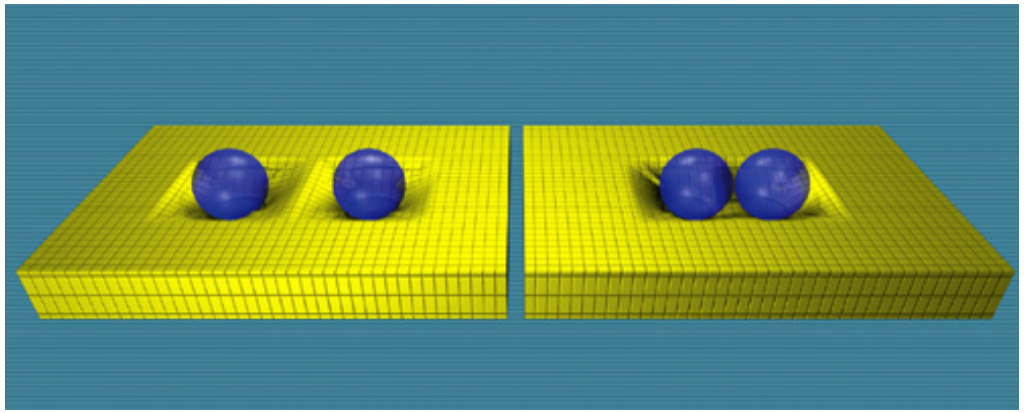
fragments of CuO_6-octahedra

5.4 Meissner-Ochsenfeld-effect

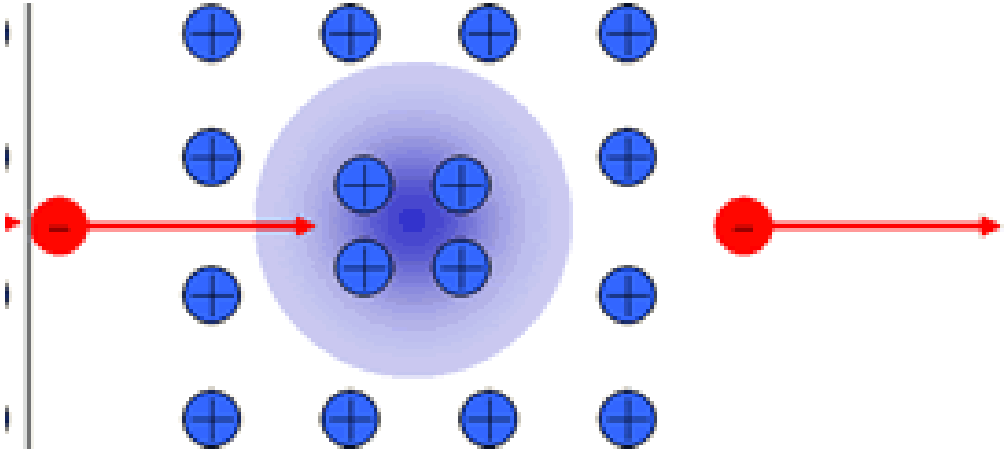




5.4 Mechanism of superconductivity: Cooper pairs

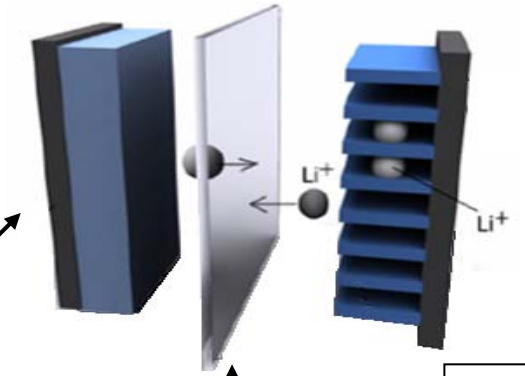


Pairs of two electrons feel a weak attractive interaction mediated by a weak polarisation of the positively charged atomic cores



5.5 Ionic conductors: Mobile ions Li^+, Na^+, O^{2-} ...

Li-battery (-accumulator)

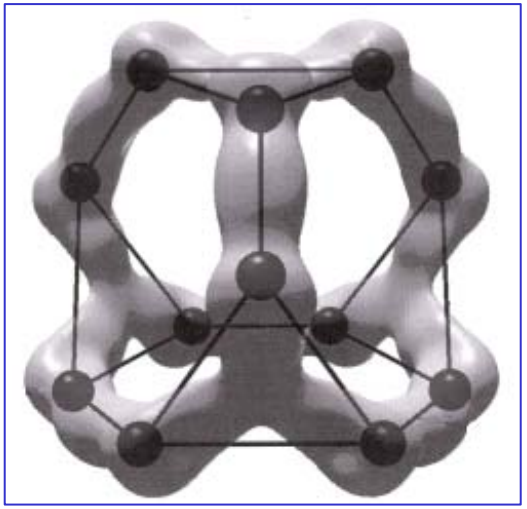


Anode

Cathode

Electrolyte

Diffusion path of Ag^+ ions in a silver ionic conductor



Mobile ions in ionic conductors (e.g.):

α-AgI: mobile Ag^+

„β-Alumina": $M_2O \bullet 11Al_2O_3$, mobile M^+

„ZrO_2": cubic, stabilized by Y_2O_3 doping, mobile O^{2-}

LiC_6: Li-intercalated graphite, mobile Li^+

5.5 Zirconia: ZrO_2 : application as solid electrolyte

- Three modifications:

monoclinic (baddeleyite)	: <1170 °C (mineral)
tetragonal	: <2370 °C
cubic	: <2590 °C (m.p.)

Cubic zirconia: stabilized at ambient temperatures by additives: (Ca^{2+}, Y^{3+},...):

Ca^{2+} replaces Zr^{4+} and generates a void in the O^{2-} partial structure

$$Ca + Zr_{Zr} + 2\ O = Ca_{Zr} + V_O'' + ZrO_2$$

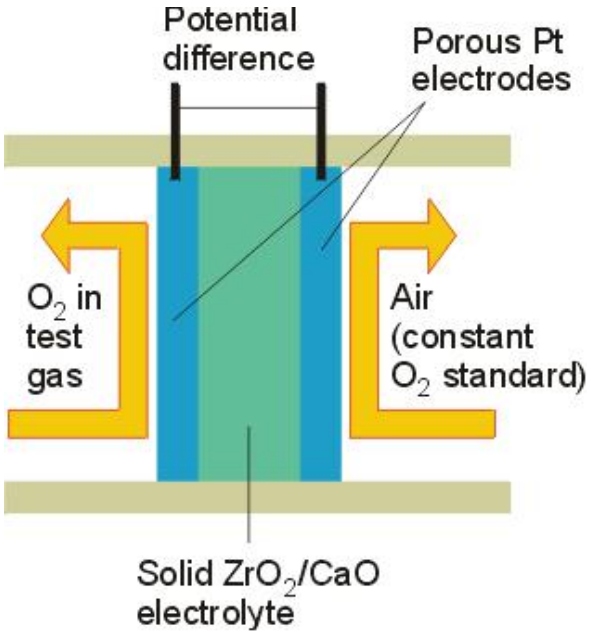
5.5 Zirconia: ZrO_2: application as solid electrolyte

- <u>stabilized</u> cubic zirconia is an O^{2-} ionic conductor at higher temperatures

- can be used as „solid electrolyte" like liquid electrolytes in conventional electrochemistry

- oxygen voids are migrating in a external field

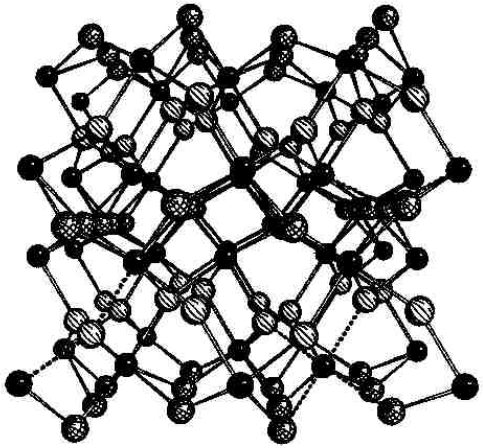
- most important part of oxygen sensors for car emission control

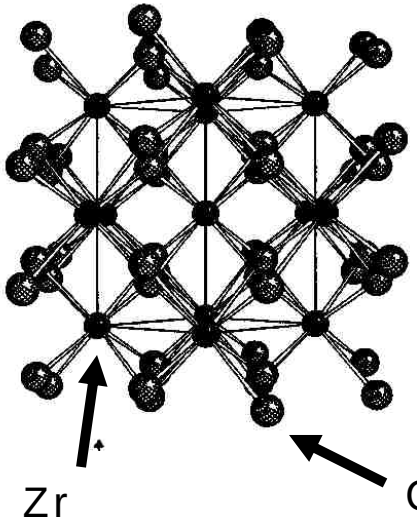


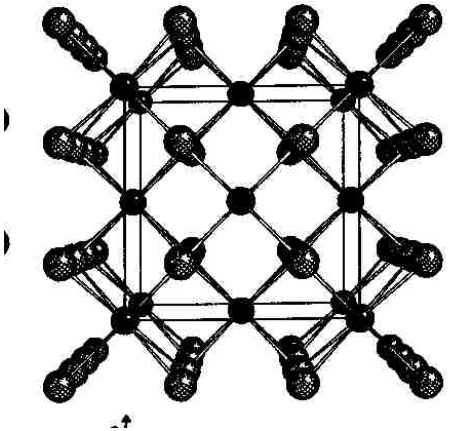
5.5 Zirconia: ZrO_2 : structural properties

	Baddeleyit monoklin	Tetragonales ZrO_2	Kubisches ZrO_2
Existenzbereich	- 1170 °C	1170 - 2370 °C	2370 - 2950 °C
Kristallstruktur	monoklin	tetragonal	kubisch
Raumgruppe	P $2_1/c$	P $4_2/n$ m c	F m 3 m

Volume per formula unit:	35,59	33,67	32,89

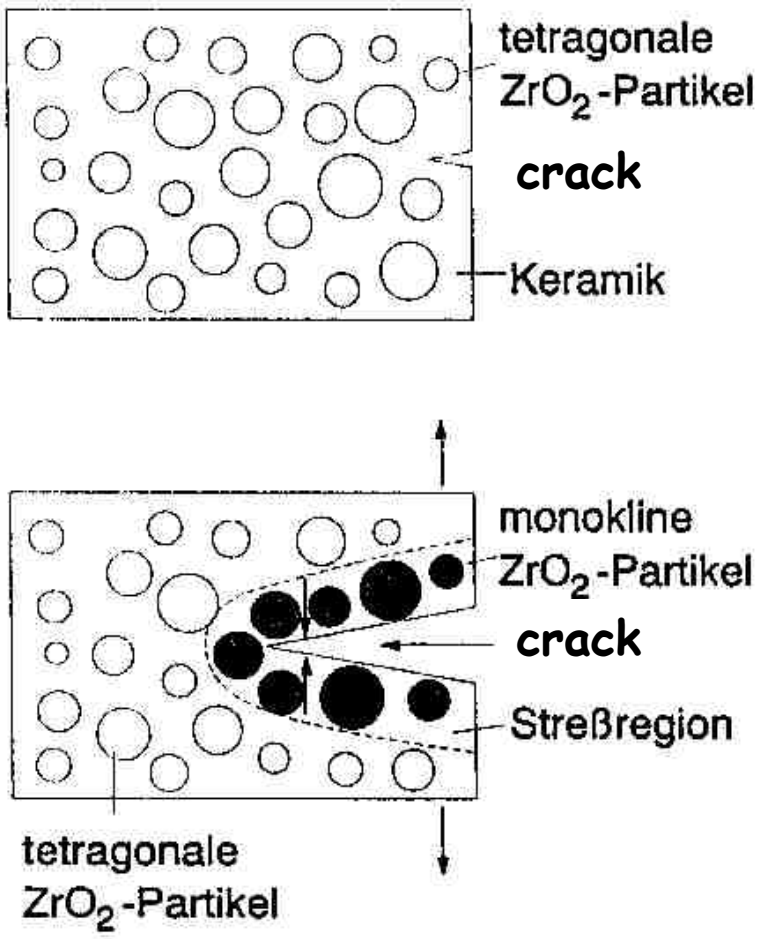






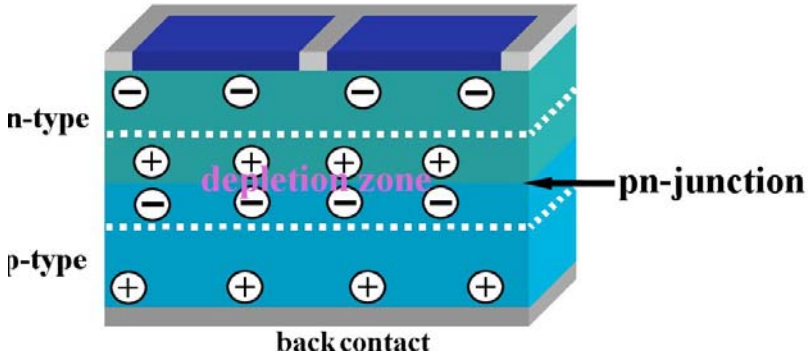
5.5 Zirconia: ZrO_2 : application as ceramic material

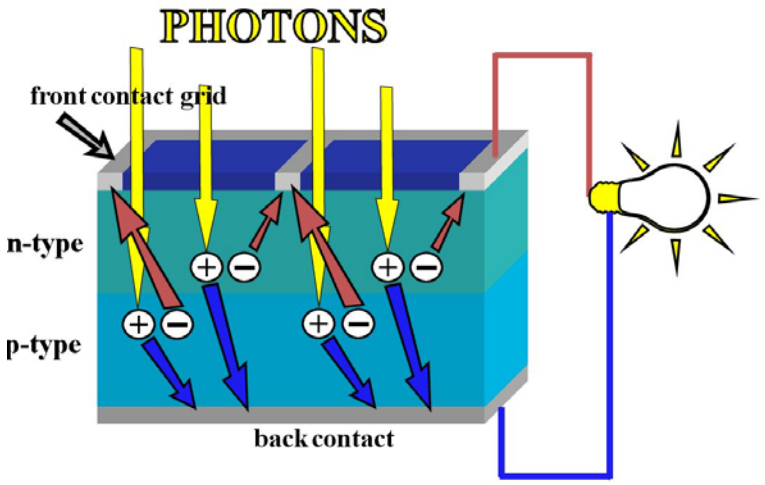
Phase hardening on transition:
based on the energy consuming formation and volume expansion of monoclinic ZrO_2 in a surrounding of stabilized cubic ZrO_2



5.6 Luminescent materials: LED's

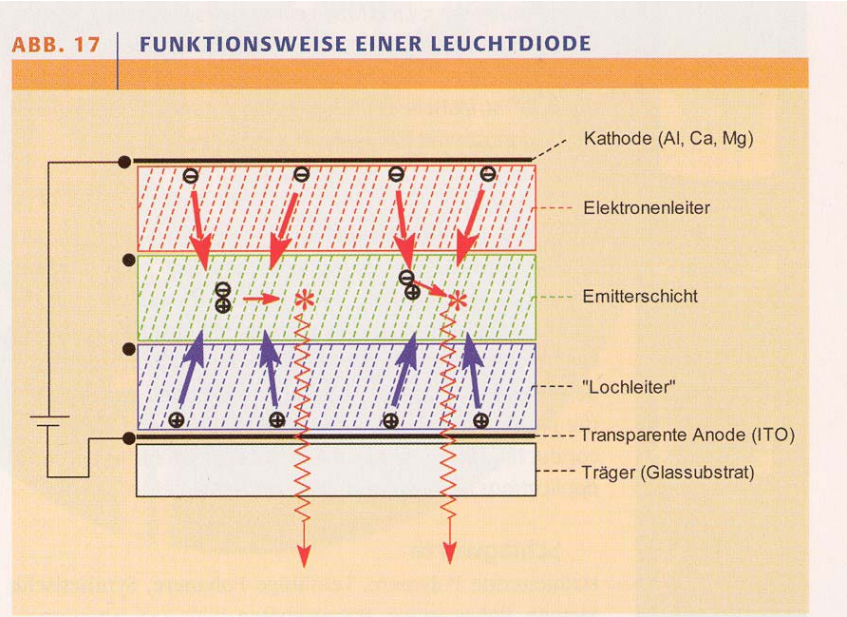
LED: Light Emitting Diode: based on a pn-junction



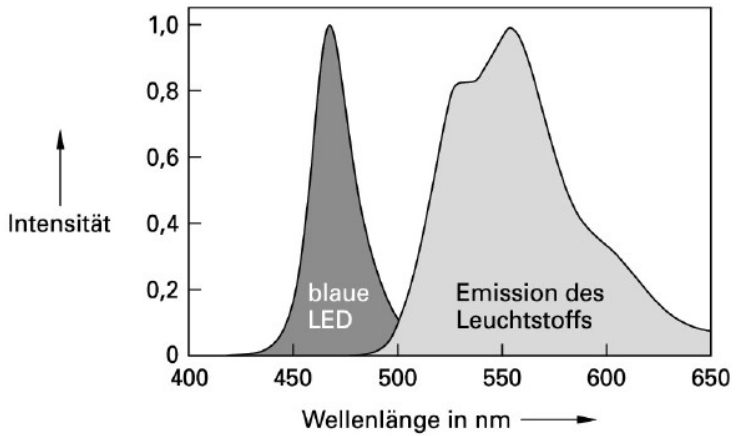


Solar cell: incoming: electromagnetic radiation (photons) outgoing: voltage
LED: incoming: voltage outgoing: electromagnetic radiation (photons)

5.6 Luminescent materials: LED's



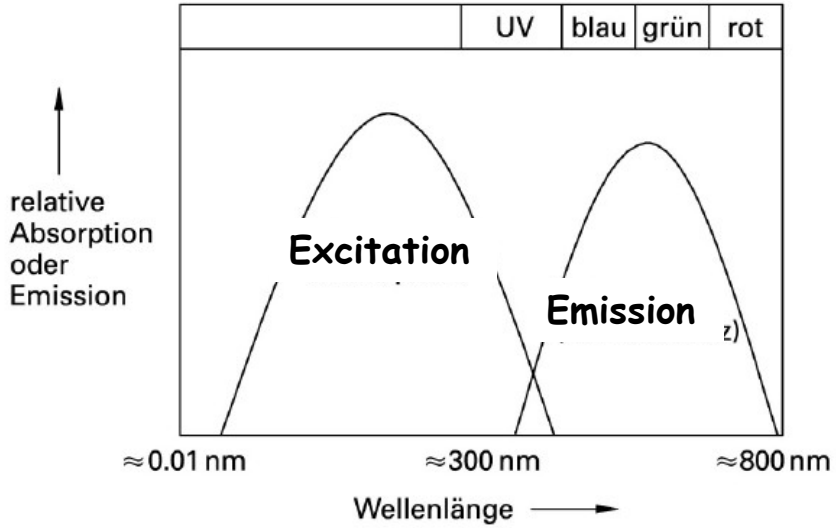
combination gives „cool white"

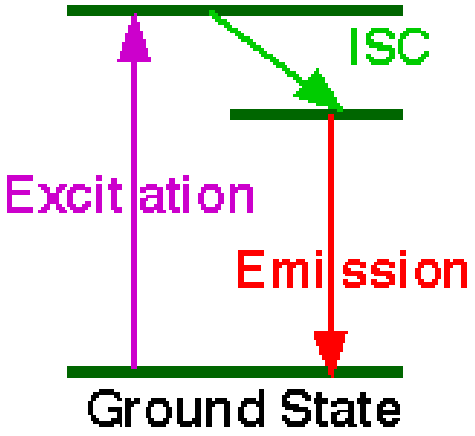


Wavelength of emission depends on material composition: e.g. ($In_{1-x}Ga_xN$ ...); white light is generated by combination of an LED (blue) with a yellow luminescent material (see next transparency).

5.6 Luminescent materials: Solids doped with luminescent centers (Eu^{3+}, Eu^{2+}, Ce^{2+} ...)

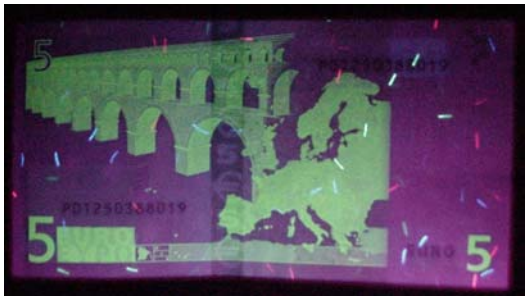
Leuchtstoff	Aktivator	Anregung	Wellenlänge, Farbe der Emission, B = Breitband-Emission, L = Linienbande
$Y_2O_3:Eu$	Eu^{3+}	4f−4f	611 nm, orangerot, L
$BaFCl:Eu$	Eu^{2+}	4f−5d	390 nm, violett, B
$Y_3Al_5O_{12}:Ce$	Ce^{3+}	4f−5d	540 nm, grüngelb, B
$Zn_2SiO_4:Mn$	Mn^{2+}	3d−3d	530 nm, grün, L
$Al_2O_3:Cr$	Cr^{3+}	3d−3d	694 nm, tiefrot, L (Rubin-Laser)
$Y_3Al_5O_{12}:Nd$	Nd^{3+}	4f−4f	1064 nm, IR, L (YAG:Nd-Laser)
$BaSi_2O_5:Pb$	Pb^{2+}	6s−6p	350 nm, UV-A, B
$LaPO_4:Ce$	Ce^{3+}	4f−5d	320 nm, UV-B, B
$YPO_4:Bi$	Bi^{3+}	6s−6p	240 nm, UV-C, B





5.6 Luminescent materials

Luminescence of Eu^{3+} and Eu^{2+} in European paper money when illuminating it with UV radiation



Red: Eu^{3+}-beta-Diketonate

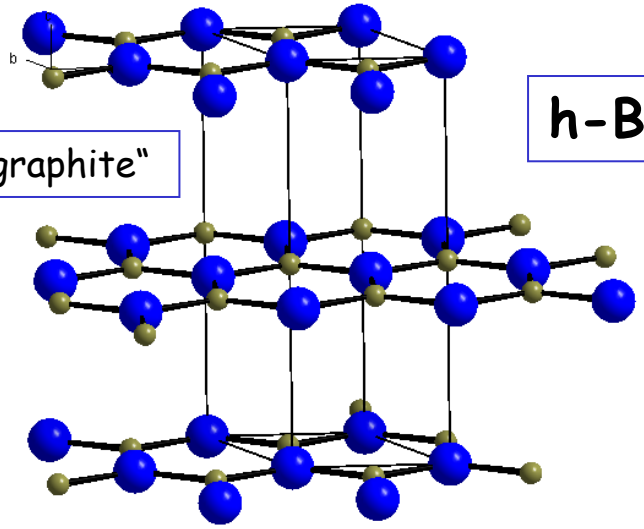
Green: $SrGa_2S_4:Eu^{2+}$

Blue: $(BaO)_x \cdot Al_2O_3:Eu^{2+}$ (x = 0,8)

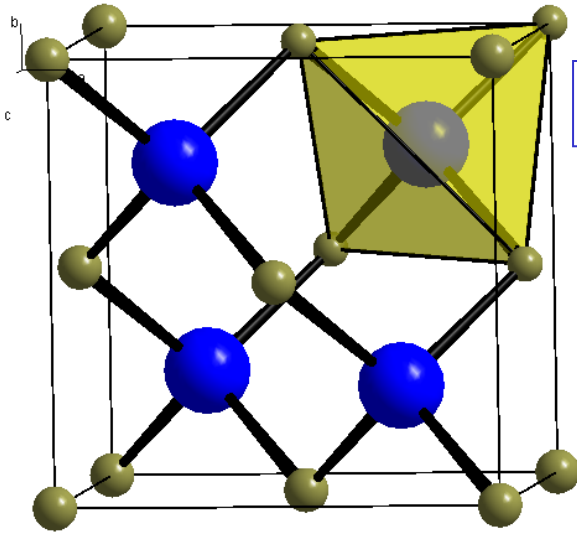
5.7 Nitride materials: hexagonal and cubic BN

ρ = 2,25 g cm^{-3} (graphite 2,26 g cm^{-3})	**cubic-BN:** ρ = 3.47 g cm^{-3}

„white graphite"



h-BN



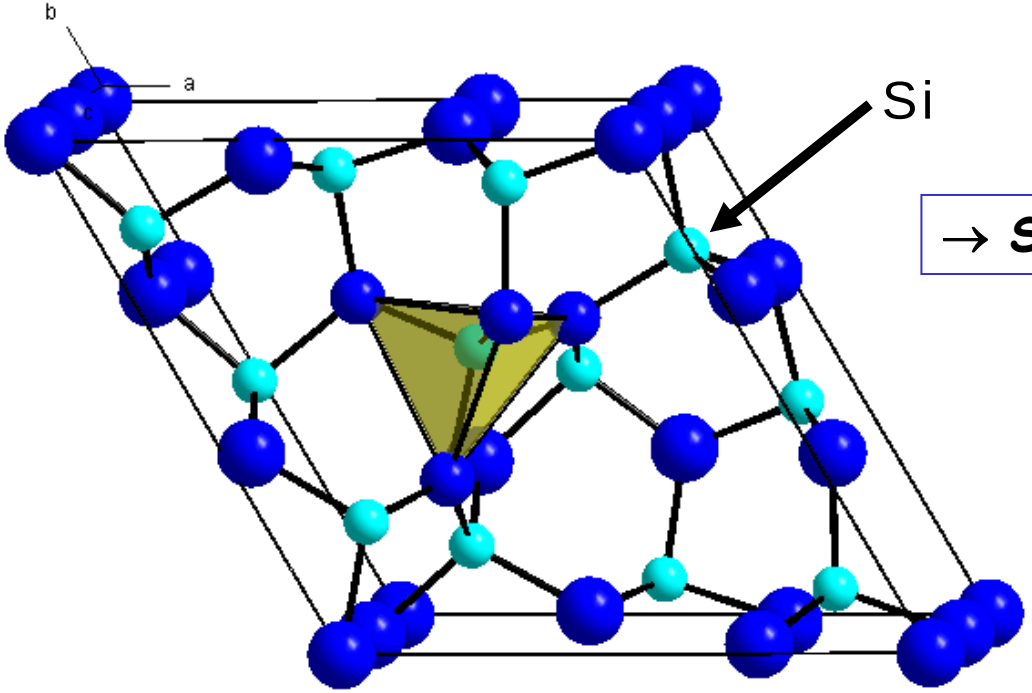
c-BN

Both BN-modifications are colorless and show a low electrical conductivity

- $B_2O_3 + 2\ NH_3 \rightarrow 2\ BN + 3\ H_2O$ (ca. 1000 °C)

- primary product is h-BN; at 50 kbar / 1400 °C → cubic-BN (similar to diamond)

5.7 Nitride materials: α-Si_3N_4: T<1650 °C



→ **$SiN_{4/3}$ and $NSi_{3/4}$!!**

direct reaction ´between Si and N: 3 Si + 2 N_2 → Si_3N_4 ΔH = -750 kJ/mol
(T>1100 °C)

→ **extreme hardness (like diamond), very low thermal expansion coefficient, due to a thin protecting layer of SiO_2 stable up to to 1400 °C in air**

Further important nitride materials: AlN, TiN, ZrN, HfN, NbN, TaN

5.8 Biogenic materials: apatite $Ca_5(PO_4)_3X$ (X: F, OH…)
(Inorganic basis of bones and teeth)

„Composite system" bones:
apatite + collagen (fiber protein)

structure of apatite