LECTURE SERIES
HETEROGENEOUS CATALYSIS

Defect Chemistry of Solids

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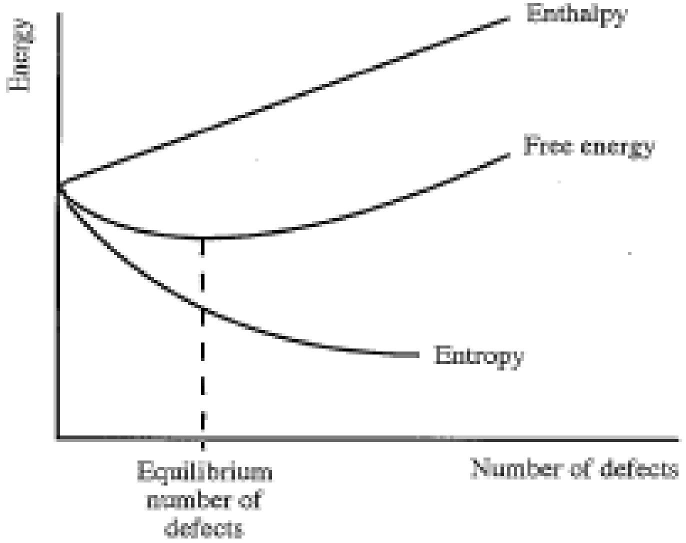
Outline

- Fundamentals
  - Ideal and real structure, intrinsic and extrinsic defects, thermodynamics of defects
- Ionic solids
  - Schottky and Frenkel defects, ionic conductivity, fast ion conductors
- Transition metal oxides
  - Non-stochiometry and redox processes, cation and anion vacancies, electronic properties of defective oxides
- Metals
  - Dislocations, grain boundaries, stacking faults, properties of engineering materials
- Defects in catalysis
  - Characterization and role of defects in catalysts, examples

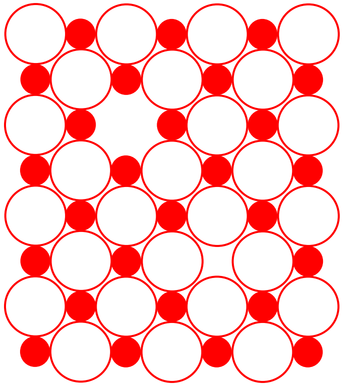
Ideal structure vs. real structure

- Ideal structure of a solid: Every lattice point has exactly the same environment
- Deviations from ideal structure: Defects
- Intrinsic defects: $\Delta G = \Delta H - T\Delta S$



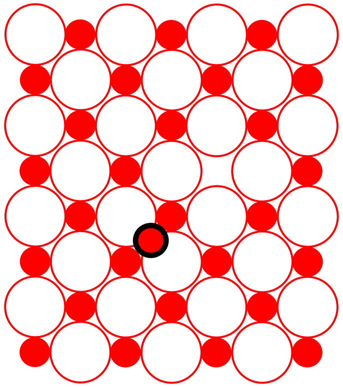
- Extrinsic defects: Non-stochiometry, doping

Intrinsic point defects



- Schottky defect (pairs of ions)

  NaCl: $V_{Na}^{-} + V_{Cl}^{+}$



- Frenkel defect (ion on interstitial site)

  AgBr: $Ag_{Ag} \rightarrow Ag_{i}^{+} + V_{Ag}^{-}$

Thermodynamics of intrinsic defects

- n defects are distributed over N lattice sites:

$$W = \binom{N}{n} = \frac{N!}{n!(N-n)!}$$

W possible arrangements

- Boltzmann: $S = k \ln W$ with $\Delta G = \Delta H - T\Delta S$

$$\Delta G = n\Delta H_f - kT \ln\left(\frac{N!}{(N-n)!n!}\right)$$

ΔH_f: Enthalpy of formation for one defect

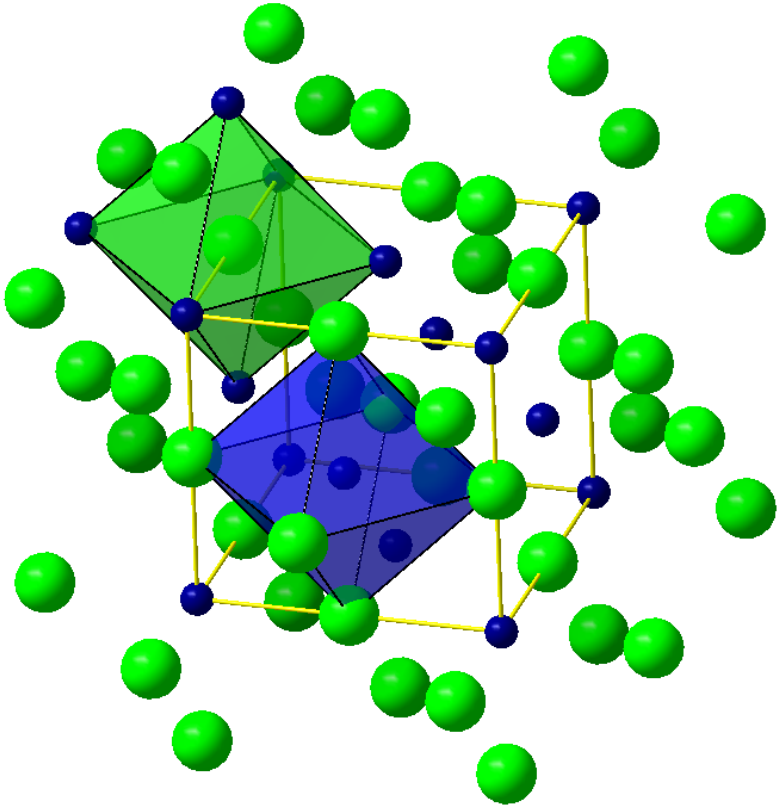
- Equilibrium, T=const. $d(\Delta G) = \left(\frac{\partial \Delta G}{\partial n}\right)_T = 0$ with $\ln x! \approx x \ln x - x$

$$\ln\left(\frac{n}{N-n}\right) = -\frac{\Delta H_f}{kT}$$

- n << N: $\boxed{\frac{n}{N} = e^{-\frac{\Delta H_f}{kT}}}$ Schottky defects: $\frac{n}{N} = e^{-\frac{\Delta H_f}{2kT}}$

Ionic solids: Alkali halides

- Rocksalt structure
  - fcc packing of oxygen atoms
  - cations in every octaheral void
- NaCl, KCl: Schottky defects dominating
- AgCl: Frenkel defects dominating
  - 4d electrons tend to occupy free 3d orbitals of Cl^- (partial covalent bonding), favored at interstitial sites



Defect structure of NaCl

- $\frac{n}{N} = e^{-\frac{\Delta H_f}{2RT}}$ ΔH_f(NaCl) ~ 200 kJ/mol
  - 300 K:

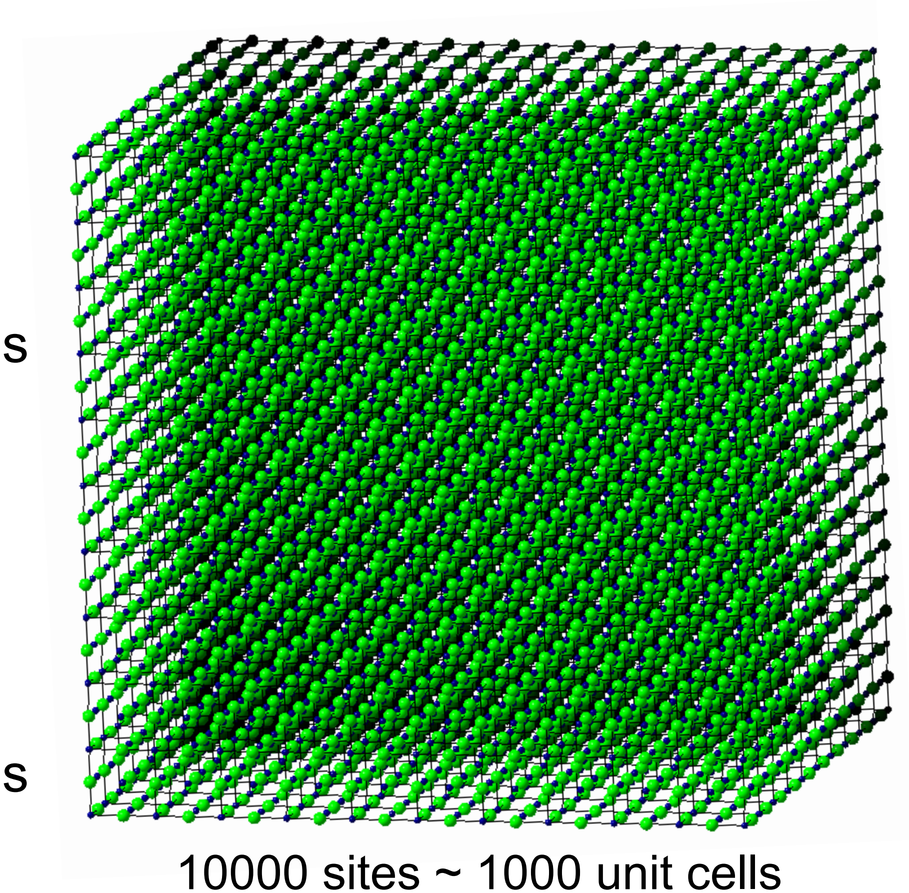
    < 10^{-13}

    Schottky defects / 10.000 sites

  - 1000 K:

    < 0.1

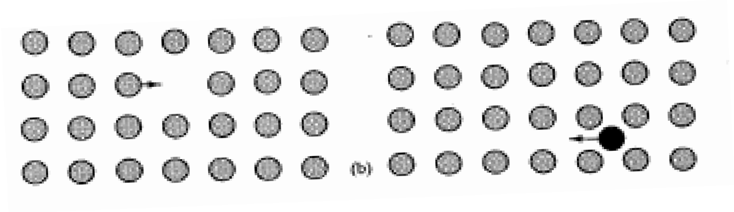
    Schottky defects / 10.000 sites



10000 sites ~ 1000 unit cells

Ionic conductivity

- Point defects enhance the mobility of ions

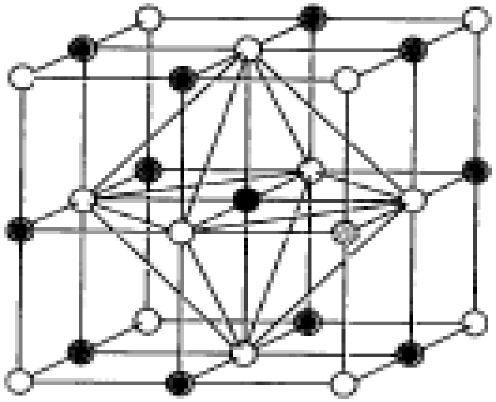


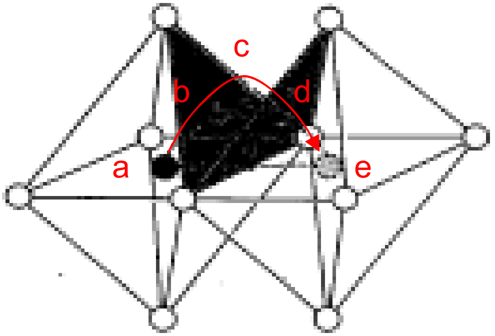
- Specific ionic conductivity $\sigma = nze\mu$

n: number of ions
ze: charge
μ: mobility

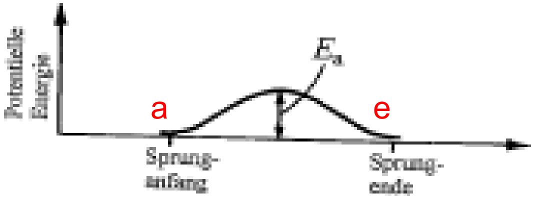
	Material	*σ / Sm^{-1}*
Ionic conductors	Ionic crystals	$<10^{-16} - 10^{-2}$
	Solid electrolytes	$10^{-1} - 10^{3}$
	Solutions of electrolytes	$10^{-1} - 10^{3}$
Electronic conductors	Metals	$10^{3} - 10^{7}$
	Semiconductors	$10^{-3} - 10^{4}$
	Insulators	$<10^{-10}$

Ionic conductivity of NaCl



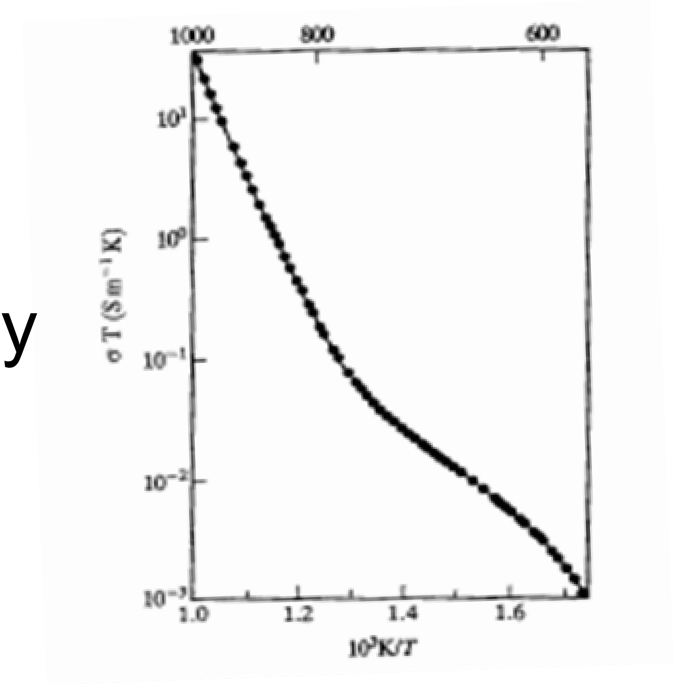


CN: 6 → 3 → 4 → 3 → 6



- T-dependence of atomic jumps

$$\mu = \mu_0 e^{-\frac{E_a}{kT}}$$ Arrhenius



- T-dependence ionic conductivity

$$\sigma = nze\mu$$

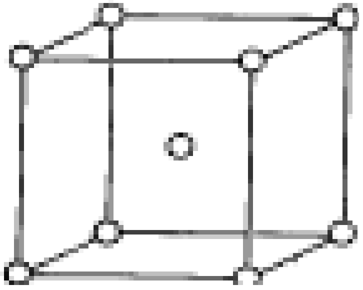
$$\ln\sigma = \ln\sigma_0 - \frac{E_a}{T}$$

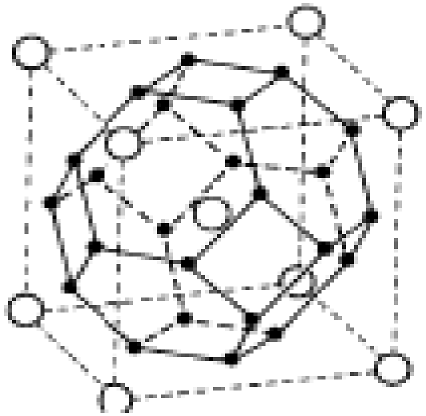
$$\sigma = \sigma_0 e^{-\frac{E_a}{T}}$$

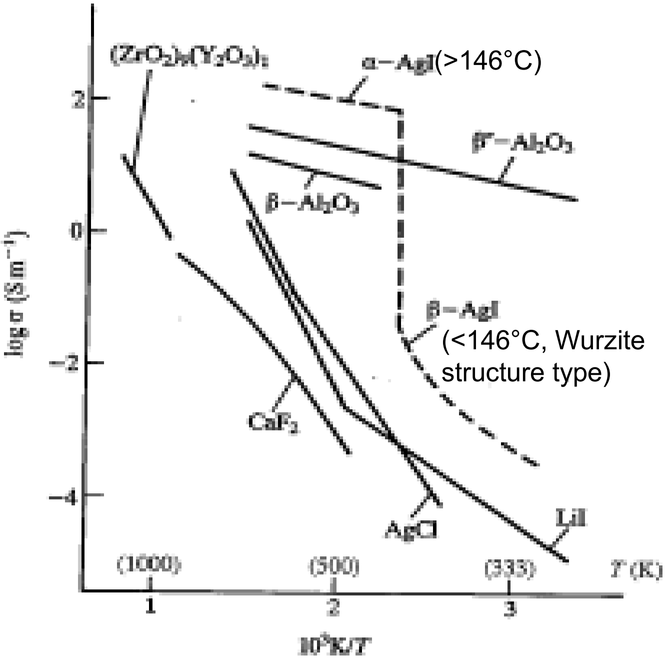
$$\sigma = \sigma' e^{-\frac{E_a}{kT}} e^{-\frac{\Delta H_f}{2kT}}$$

Fast ion conductors: α-AgI

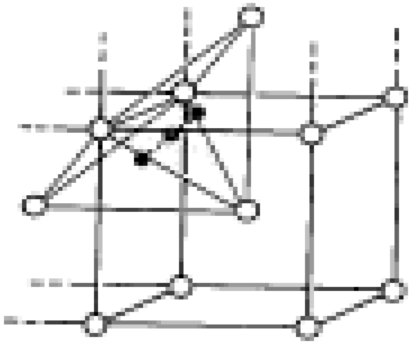
- bcc arrangement of anions
- large and polarizable anion
- low charge of cations, low CN
- many vacant lattice sites
- conductivity comparable to solutions of strong electrolytes







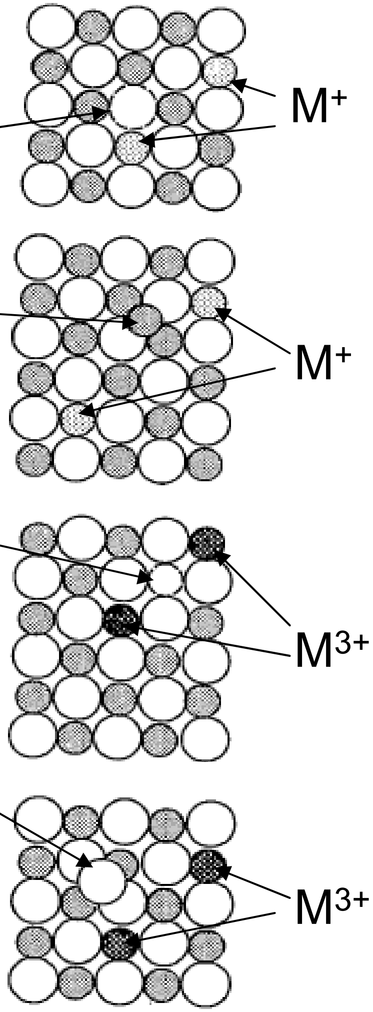
○ I
● Tetraederlücke
• Trigonale Lücke



Defects in transition metal oxides

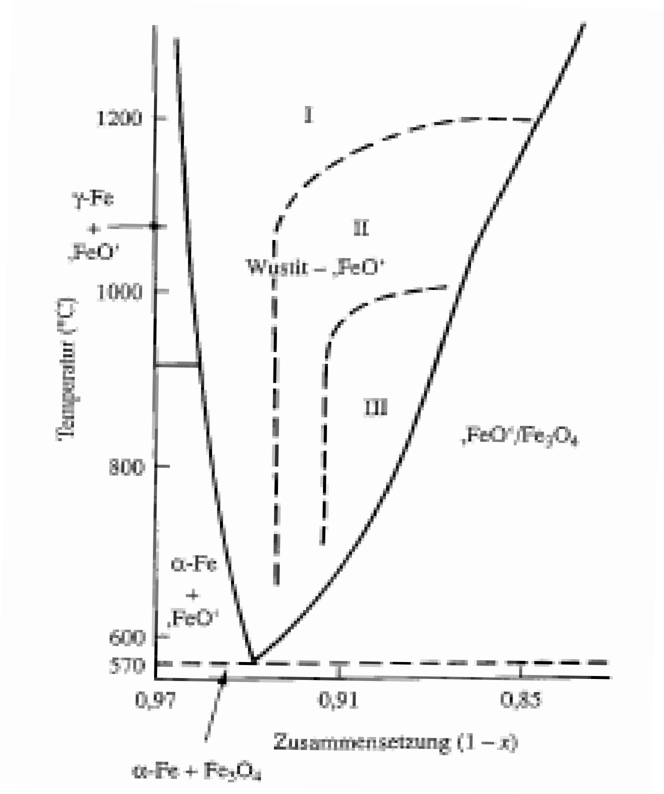
- 4 types of defective MO
  - Excess metal:
    - Anion vacancies MO_{1-x}
    - Interstitial cations $M_{1+x}O$
  - Excess oxygen:
    - Cation vacancies $M_{1-x}O$
    - Interstitial anions MO_{1+x}

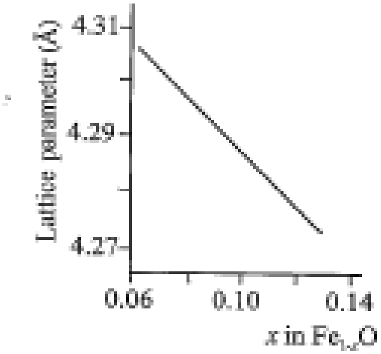
- Non-stochiometry in transition metal oxides is often compensated by change of oxidation state (partial oxidation or reduction of the metal)



Rocksalt-type oxides: Wuestite

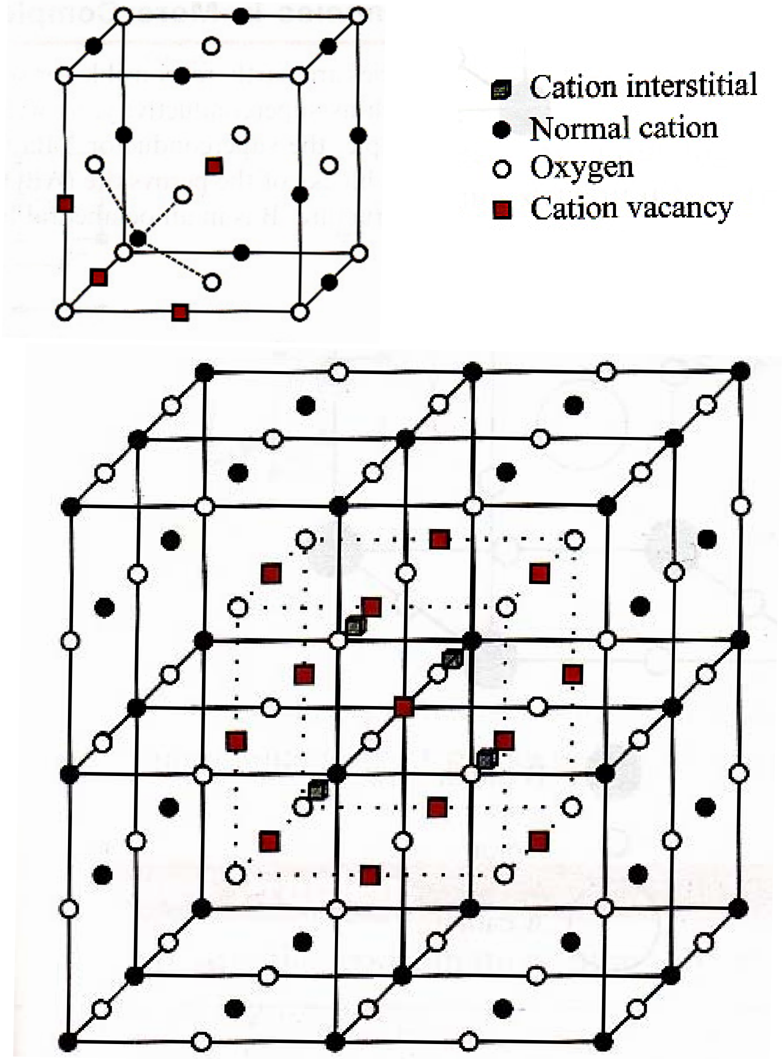
- “FeO” is always Fe-deficient
- Presence of extra O^{2-} on interstitial sites can be excluded from density measurements → Fe vacancies $Fe_{1-x}O$
- Gradual change of lattice parameter with x in $Fe_{1-x}O$
- For each Fe vacancy, two Fe(II) have to be oxidized to Fe(III)





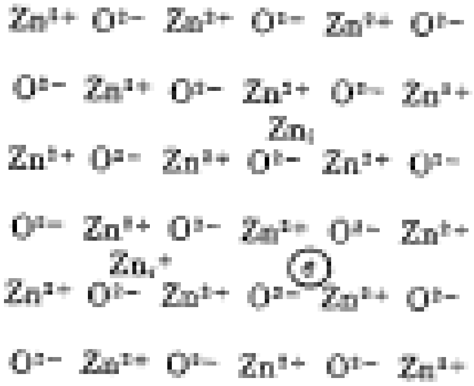
Clustering of defects in $Fe_{1-x}O$

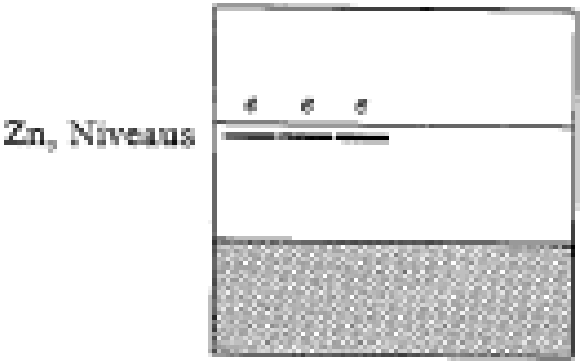
- Diffraction studies have shown that some Fe atoms are located on tetrahedral sites
- Mößbauer data reveals that Fe^{tet} is Fe(III)
- As the distance between octahedral and tetrahedral sites is short, vacancies cluster around occupied tetrahedral sites
- Koch-Cohen cluster: 4 interstitial Fe^{tet} and 13 vacancies
- “Fe_3O_4 ($FeO \cdot Fe_2O_3$) –like domains in $Fe_{1-x}O$”



Non-stochiometry of ZnO

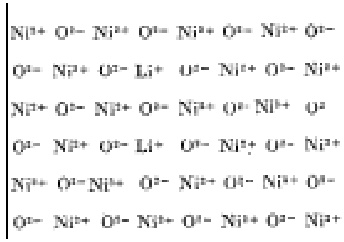
- Wurzite (ZnS) structure type
  - hexagonally packed oxygen anions
  - half of the tetrahedral voids filled with Zn^{2+}
- Upon heating some zinc is partially reduced and migrates to interstitial sites
  - $Zn_{1.00007}O$ at 800 °C: “ZnO” is yellow
- Interstitial Zn atoms act as electron donators
  - $Zn_i^{(2-x)+} \rightarrow Zn_i^{2+} + x\,e^-$

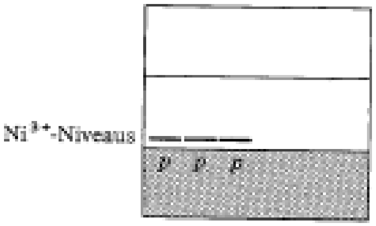


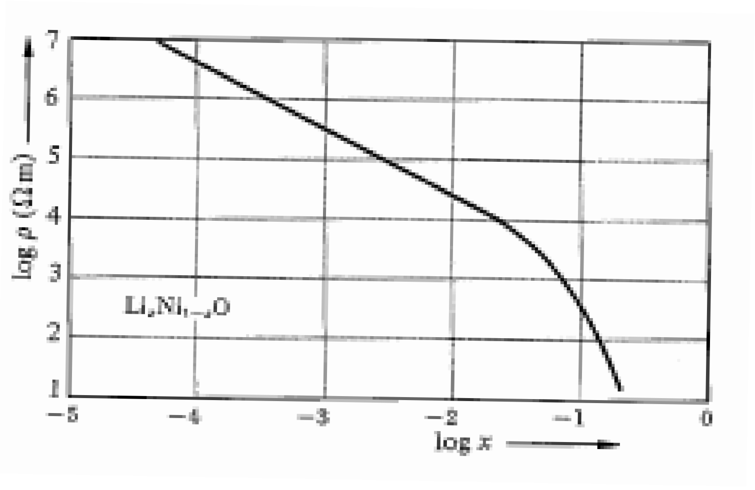


Non-stochiometry of NiO

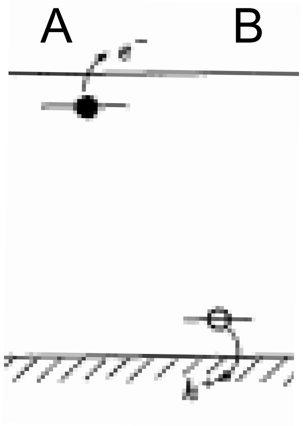
- Stochiometric NiO is an insulator and green (bandgap 3.8 eV)
- Non-stochiometric $Ni_{0.98}O$ (NaCl structure type) is a semiconductor and black
- Formation of Ni vacancies by oxidation :
  $2\ Ni^{2+} + ½\ O_2 \rightarrow O^{2-} + \square + 2\ Ni^{3+}$
- Ni^{3+} in the lattice is an acceptor for electrons
- Li doping ($0 \leq x \leq 0.1$):
  $Li_xNi_{1-x}O$
- As conductive as typical metals







Measuring the electronic properties of non-stochiometric transition metal oxides



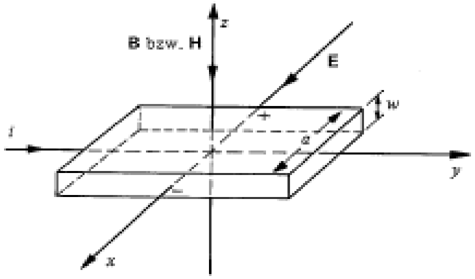
- A: extra electrons in the conduction band as charge carriers

Defects donor levels

- B: extra holes in the valence band as charge carriers

Defects acceptor levels

- Hall effect



$$E_y = -\frac{j_x B_z}{ne}$$

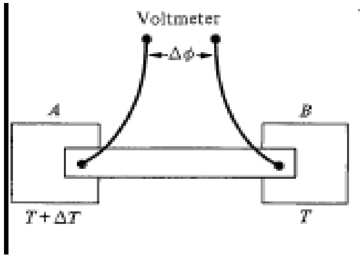
n; -*e*: electron concentration and charge

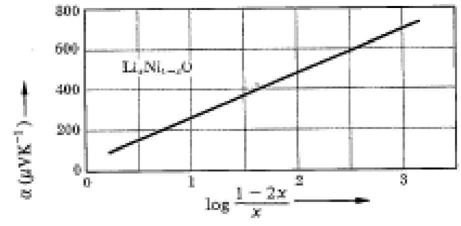
$$R_H = \frac{E_y}{j_x B_z} = -\frac{1}{ne}$$ for electrons

$$R_H = +\frac{1}{pe}$$ for holes

- Seebeck effect

$$\Delta\Phi = \Phi_A - \Phi_B = -\alpha\Delta T$$

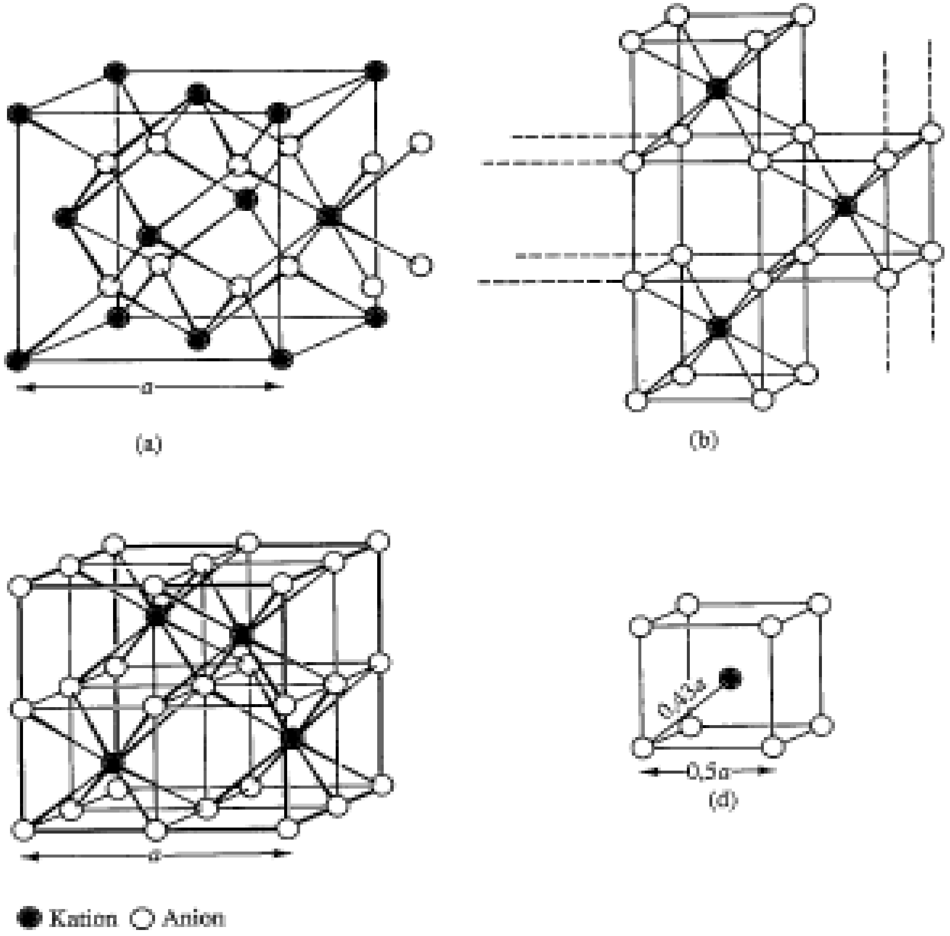




α (Seebeck coefficient) positive if holes are the major charge carrier, negative for electrons

Flourite-type oxides

- CaF_2 structure type: large and highly charged cations, small anions (PbF_2, UO_2, ZrO_2)
  - fcc packing of cations, anions in tetrahedral voids
  - large octahedral voids are vacant, anion mobility via interstitial sites



Crystal chemistry of ZrO_2

- Martensitic phase transformations of ZrO_2
  - $m\text{-}ZrO_2 \xrightarrow{1100°C} t\text{-}ZrO_2 \xrightarrow{2300°C} c\text{-}ZrO_2$
- Cubic ZrO_2 (CaF_2 structure type) is stable above 2300 °C or can be stabilized by cation substitution
  - $Ca_mZr_{1-m}O_{2-m}$

X.-J. Jin / Current Opinion in Solid State and Materials Science 9 (2005) 313–318

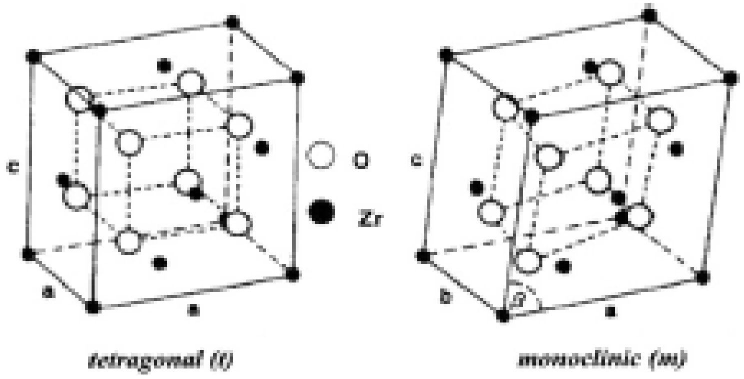
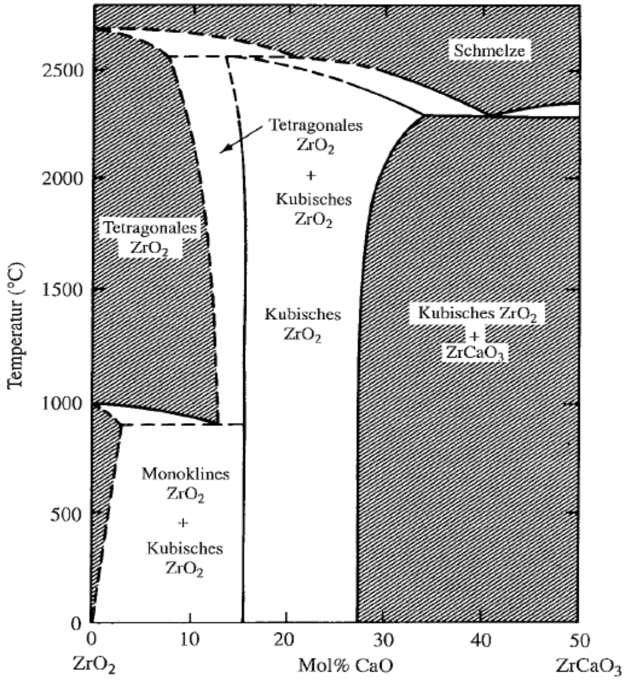
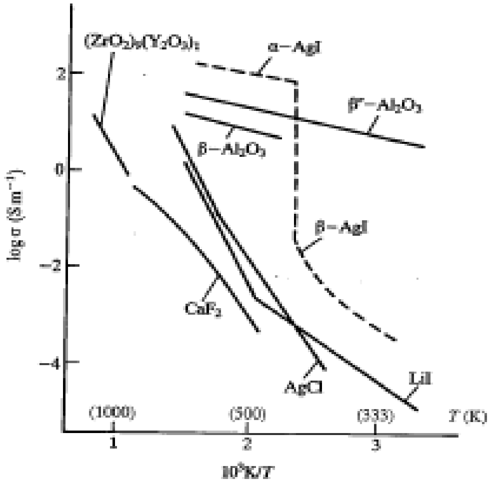


Fig. 1. Crystal structures of tetragonal (t) and monoclinic (m) phases [*7].



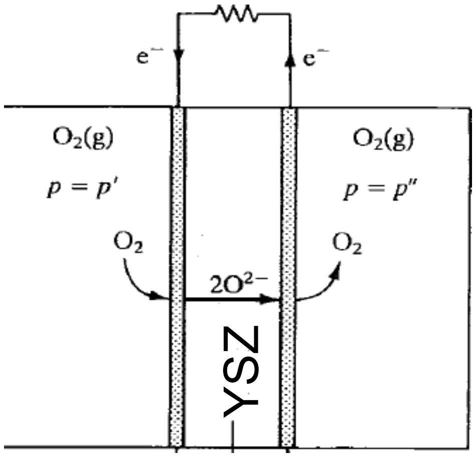
Applications of stabilized zirconia



- Solid electrolyte, e.g in fuel cells
- Oxygen sensor

$$E = \frac{2.3RT}{4F}\log\left(\frac{p'}{p_{ref}}\right)$$ Nernst

- Application: 3-way catalyst
  - Simultaneous oxidation of C_nH_m and CO and reduction of NO_x requires optimal air/exhaust gas ratio (λ = 1)
  - λ-sensor: Yttrium stabilized zirconia (YSZ), ca. 3 mol-% Y_2O_3



$$\begin{array}{ll} O_2(p') + 4\,e^- & \rightarrow 2\,O^{2-} \\ \underline{2\,O^{2-}} & \underline{\rightarrow O_2(p'') + 4e^-} \\ O_2(p') & \rightarrow O_2(p'') \end{array}$$

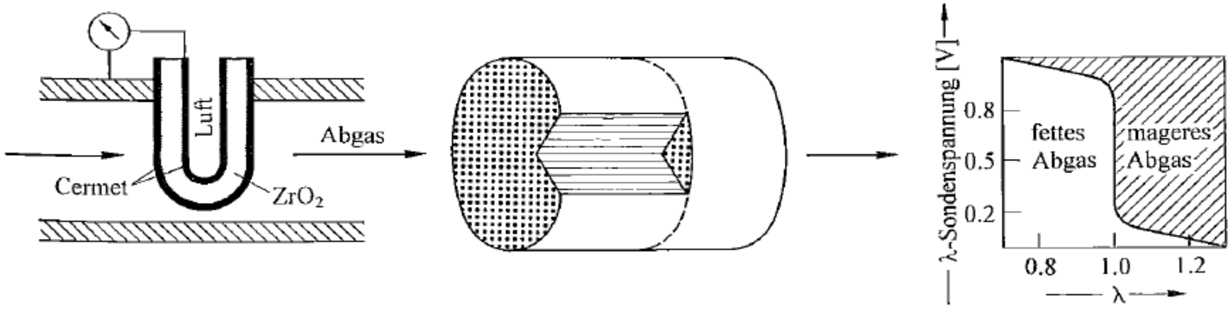
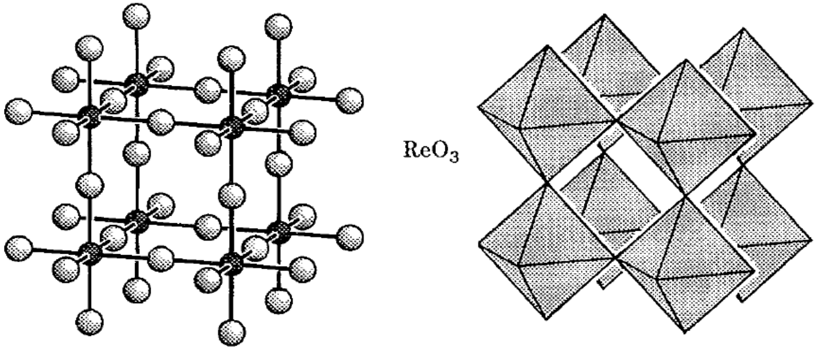
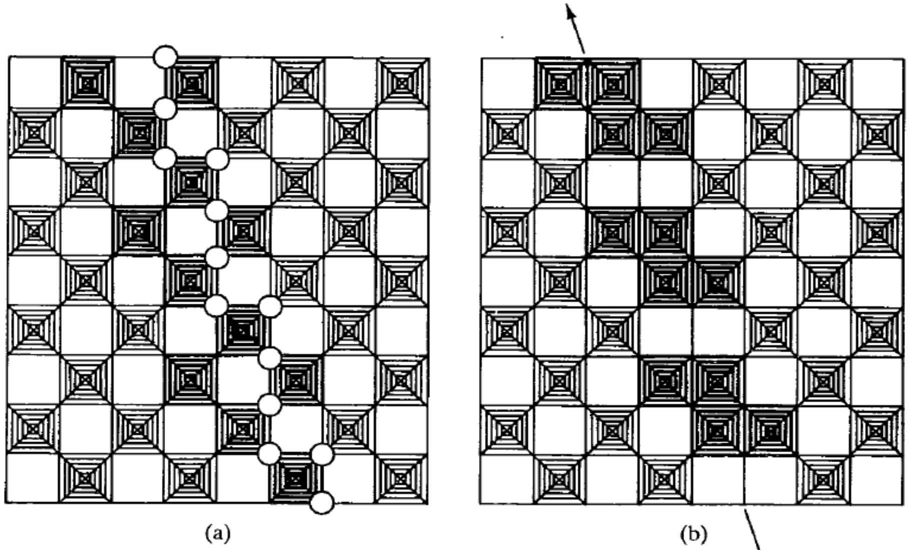


Fig. 156 λ-Sonde, Dreiweg-Katalysator und λ-Sondenspannung in Abhängigkeit von λ.

Extended defects

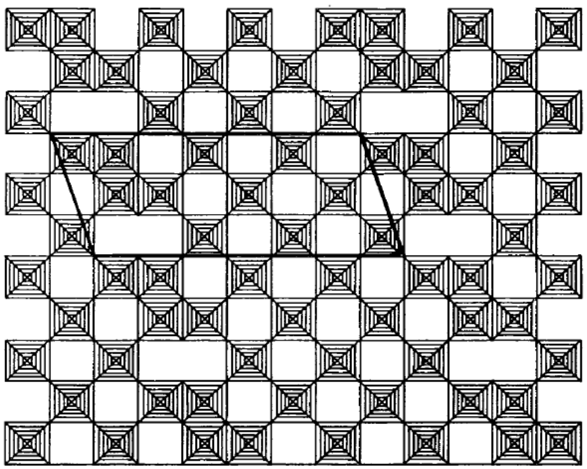
- Crystallographic shear
  - Elimination of vacancies by crystallographic shear: $MO_{3-x} = M_nO_{3n-1}$, M = Mo, W, n ≥ 4



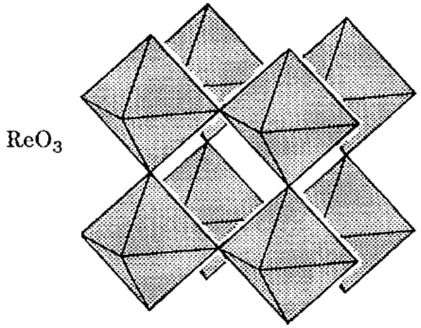

(a) (b)

○ : Leerstelle

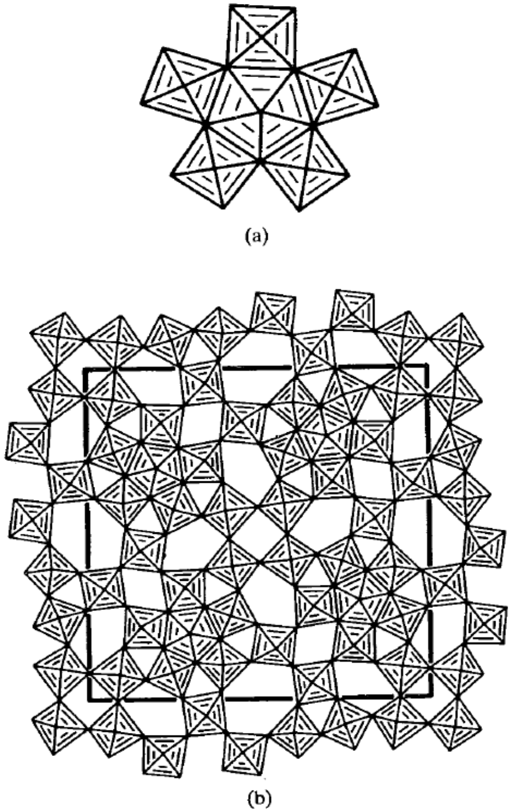
WO_3 WO_{3-x}


$W_{11}O_{32}$

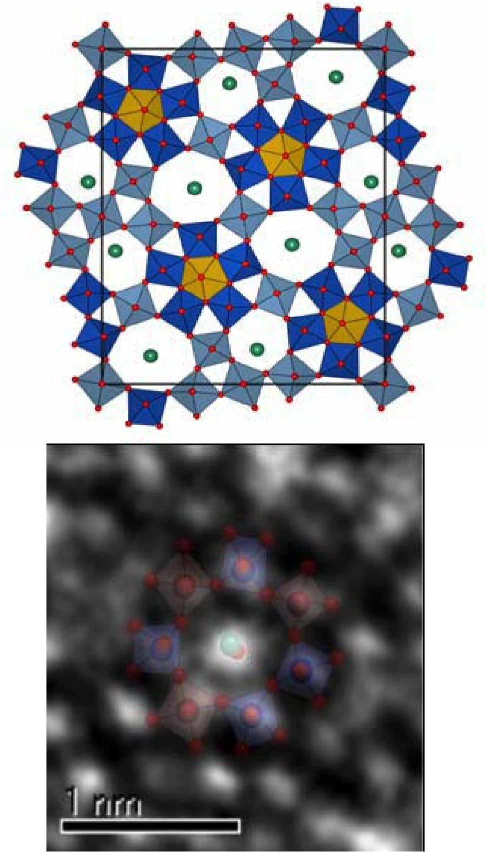
ReO_3 type oxides



Vacancy elimination in oxygen deficient ReO_3 type solids



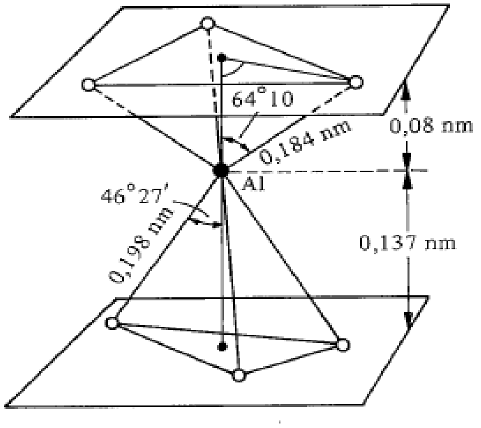
Mo_5O_{14}

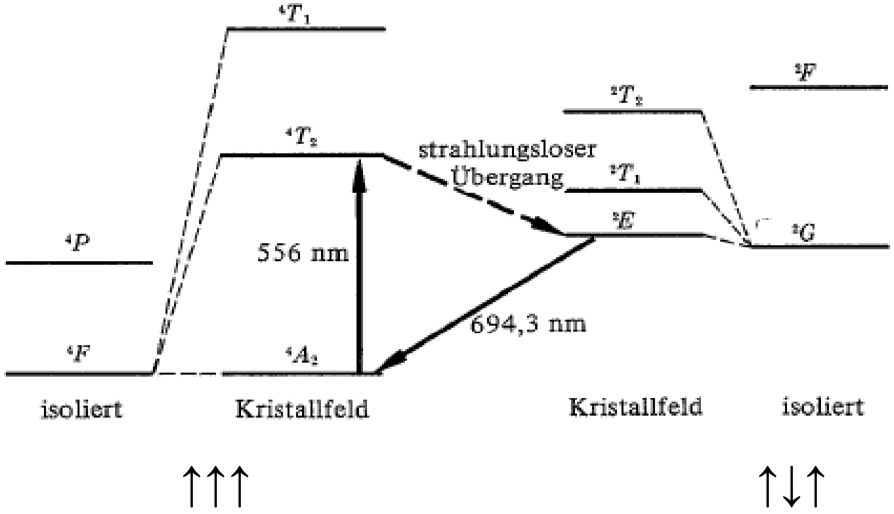


MoVTeNb catalyst (M1)

Solid solutions: Oxides

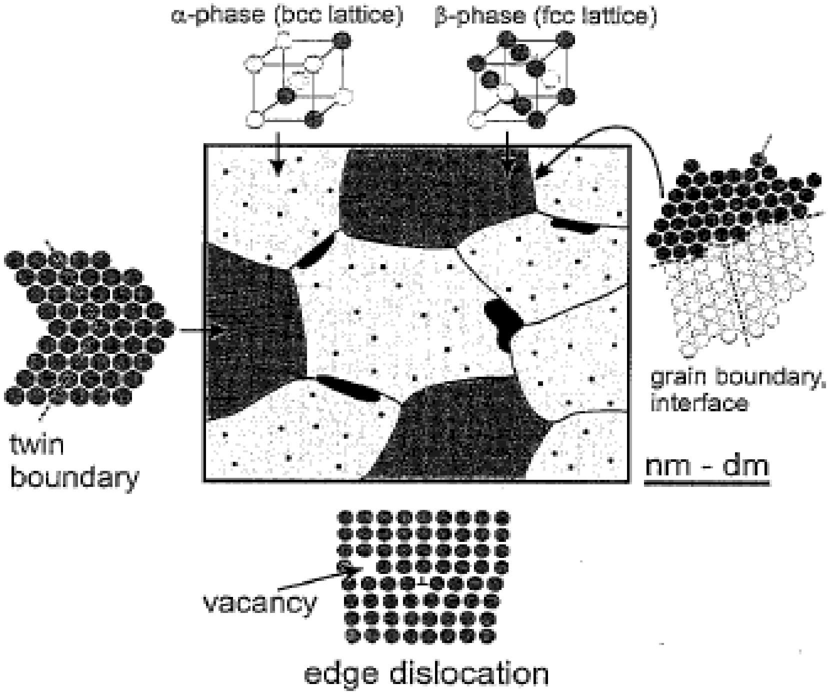
- Ruby: 0.04–0.5 % Cr^{3+} in α-Al_2O_3
- Structure of corundum
  - hexagonal packing of oxygen, ⅔ of octahedral voids occupied by Al^{3+}
- Isomorphous substitution Al^{3+} by Cr^{3+}
- Application: Ruby laser

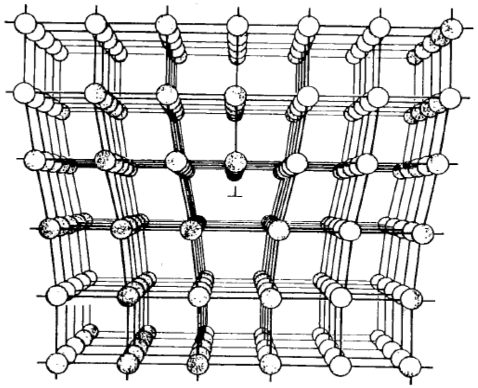




Defects in metals

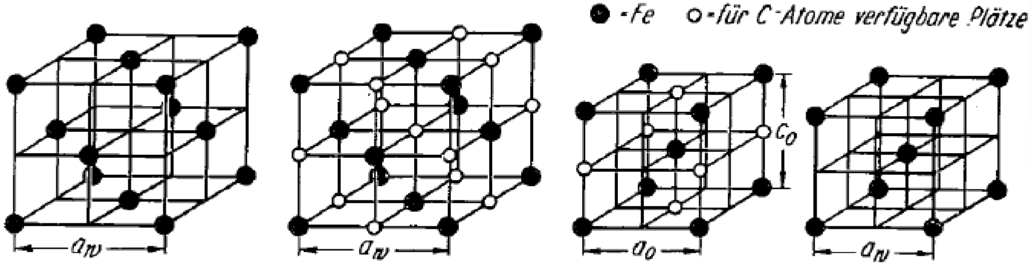
- Microstructure of engineering materials
  - point defects
  - grain boundaries
  - interfaces
  - twin boundaries
  - dislocations





Interstitial solid solutions: Steel

- Up to 2% C can be dissolved in fcc γ-Fe (Austenite), 0.8% at 723 °C, as interstitial solid solution
- At 723 °C only 0.02% C can be dissolved in bcc α-Fe (Ferrite)
- Upon slow cooling Austenite splits into Ferrite and Zementite (diffusion controlled)
- Upon fast cooling, a novel metastable phase will form without diffusion: Tetragonally distorted bcc Fe with C in octahedral intersitials, Martensite (hardening of steel)



γ-Eisen
a_w = 0,359 nm

Austenit
a_w = 0,363 nm

Martensit
a_0 = 0,280 nm
c_0 = 0,304 nm

α-Eisen (Ferrit)
a_w = 0,286 nm

Fe_3C: Zementite

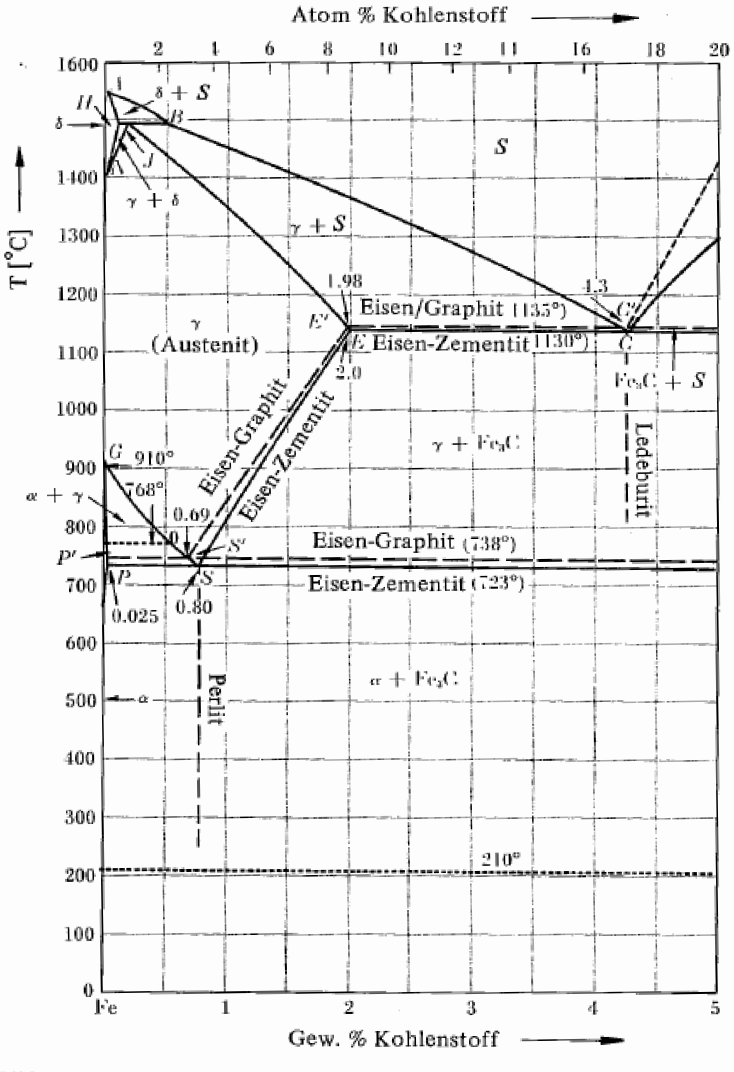
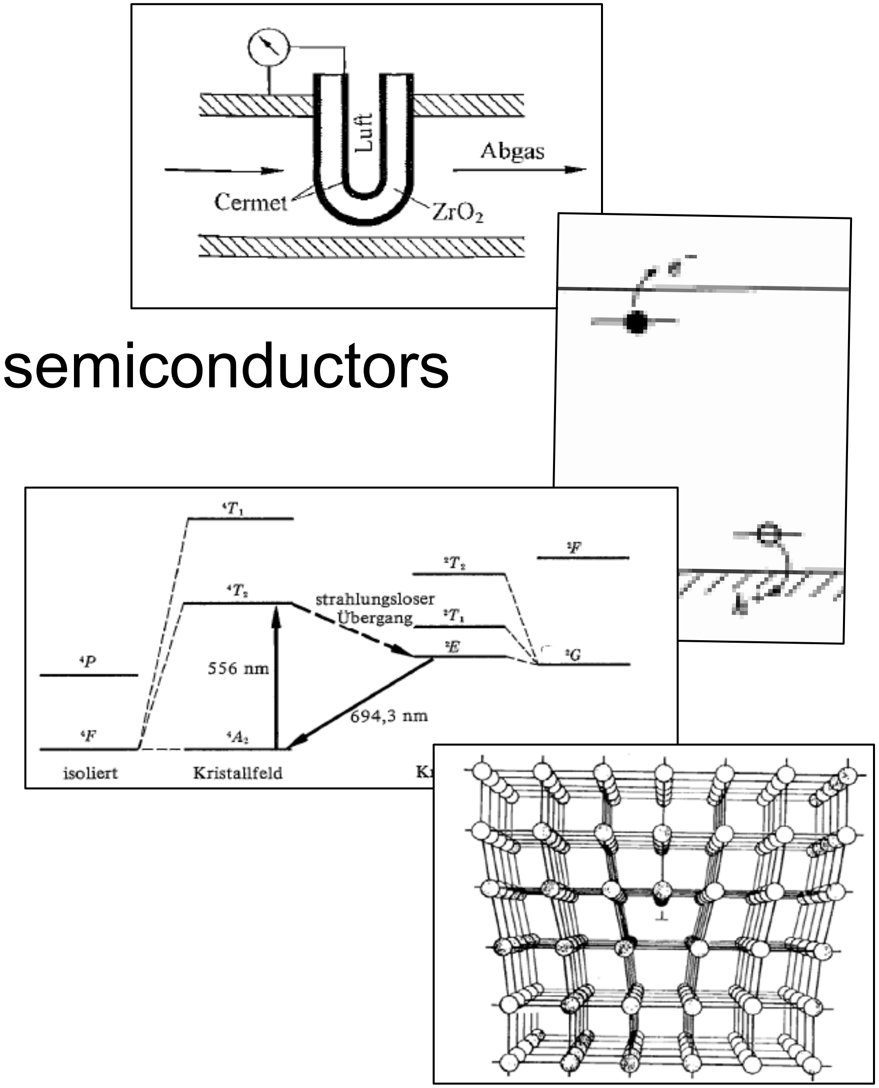


Bild 4.3. Der wichtigste Teil des Fe/C-Zustandsdiagramms (*Austin* [3])

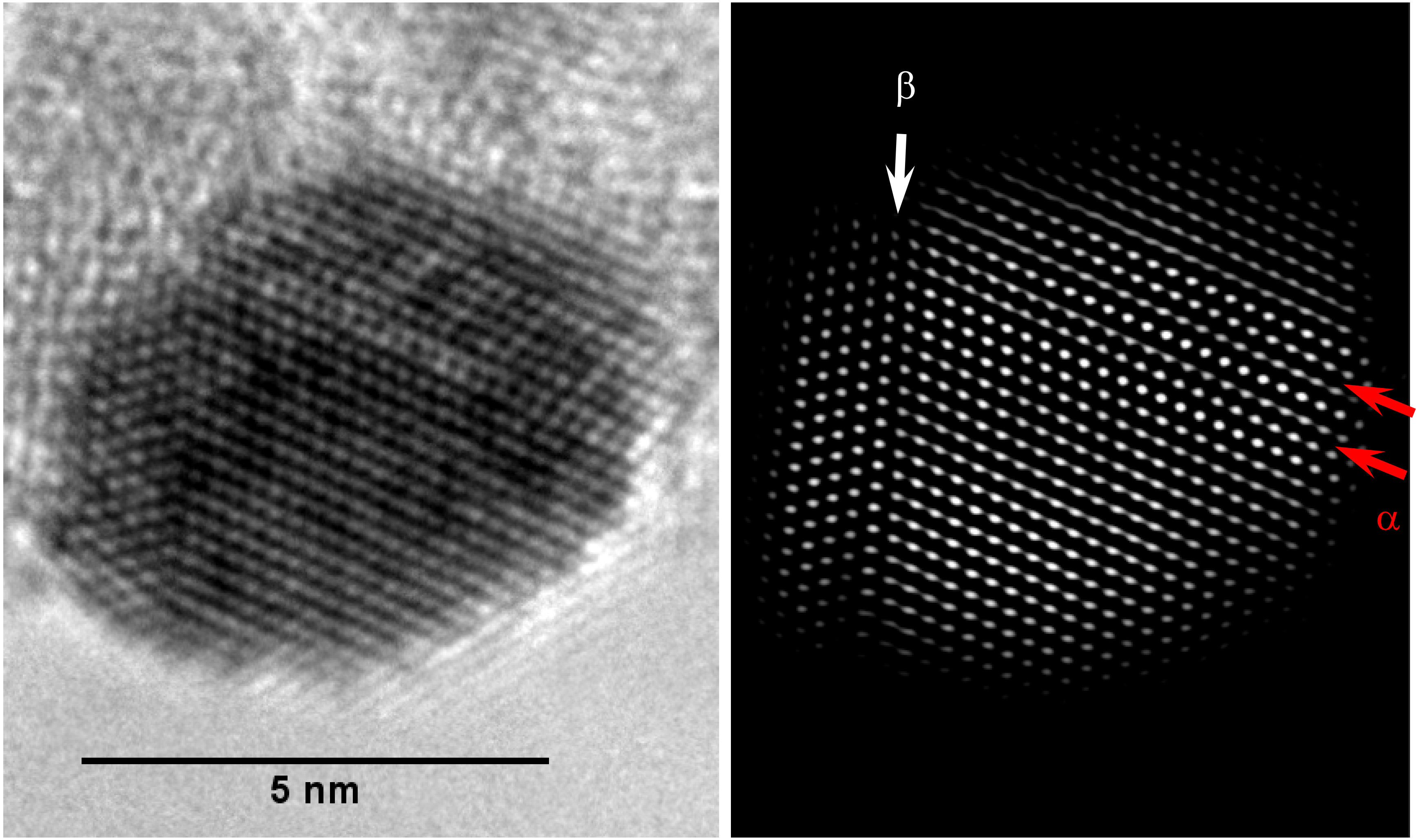
Properties governed by defects

- Ionic conductivity
  - fast ion conductors
  - solid electrolytes
  - gas sensors
- Electronic properties of semiconductors
  - electronics
- Optical properties
  - luminescence
  - laser
- Mechanical properties
  - hardness of metals
- …

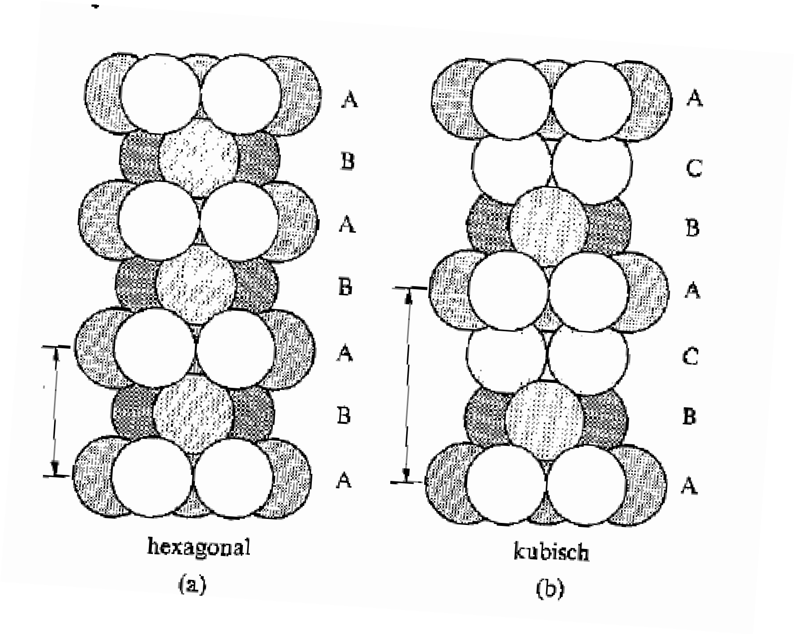
- … and catalysis?



Microscopy: Planar defects in Cu catalysts

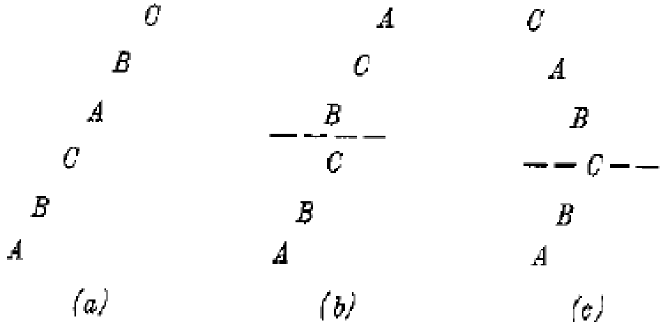


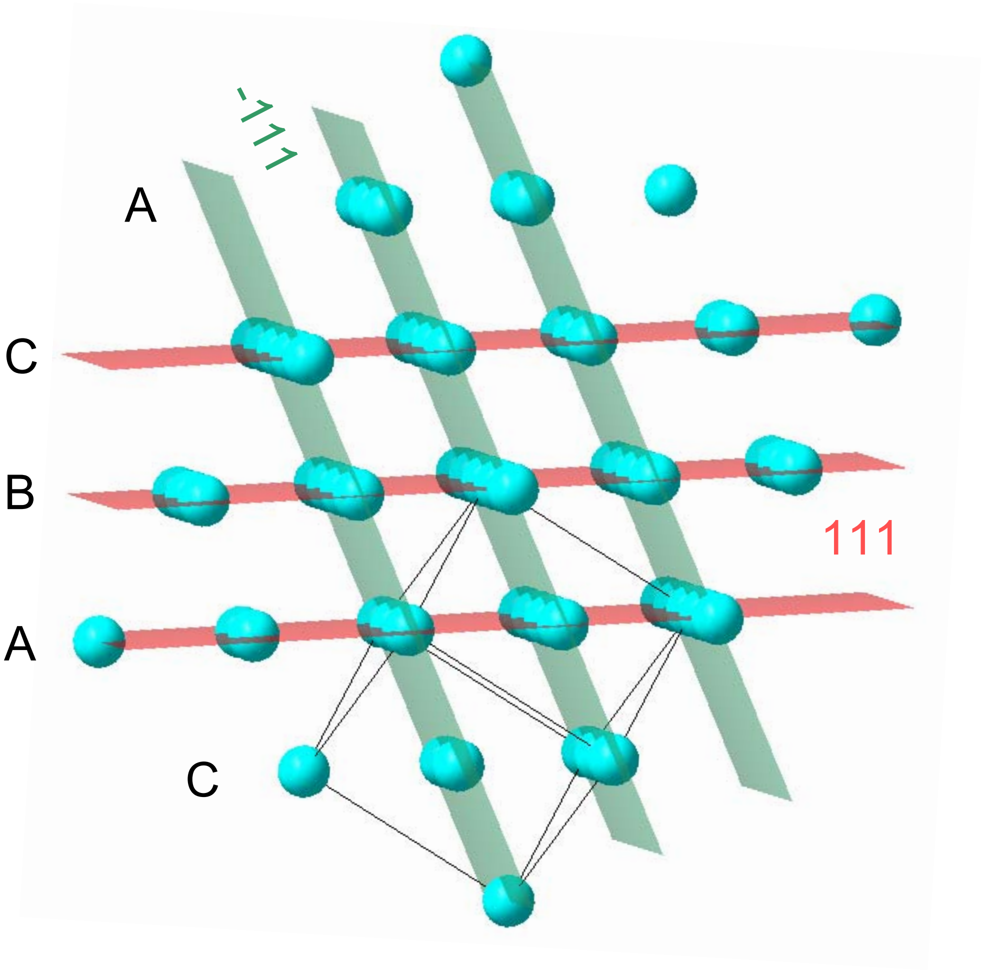
Diffraction: Planar defects in Cu



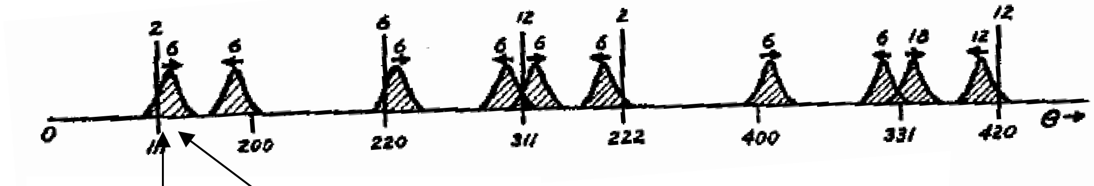
hexagonal (a)

kubisch (b)



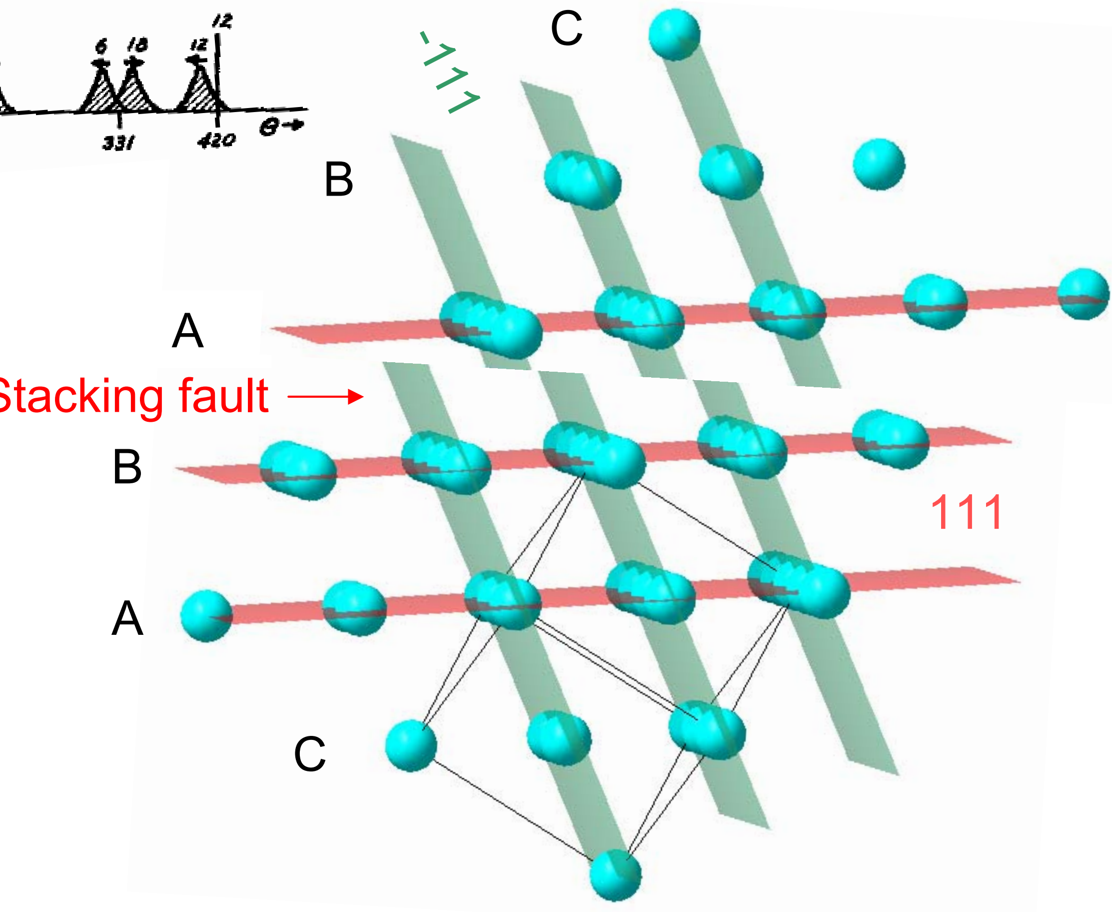


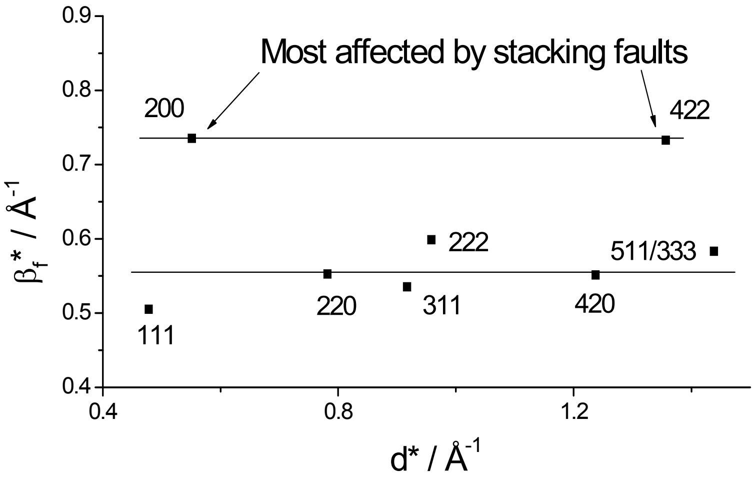
Stacking faults in fcc materials



111, -1-1-1
not affected
(h+k+l=3N)

-111, 1-11,
11-1, -1-11,
1-1-1, -11-1
broadened
and shifted
(h+k+l=3N±1)

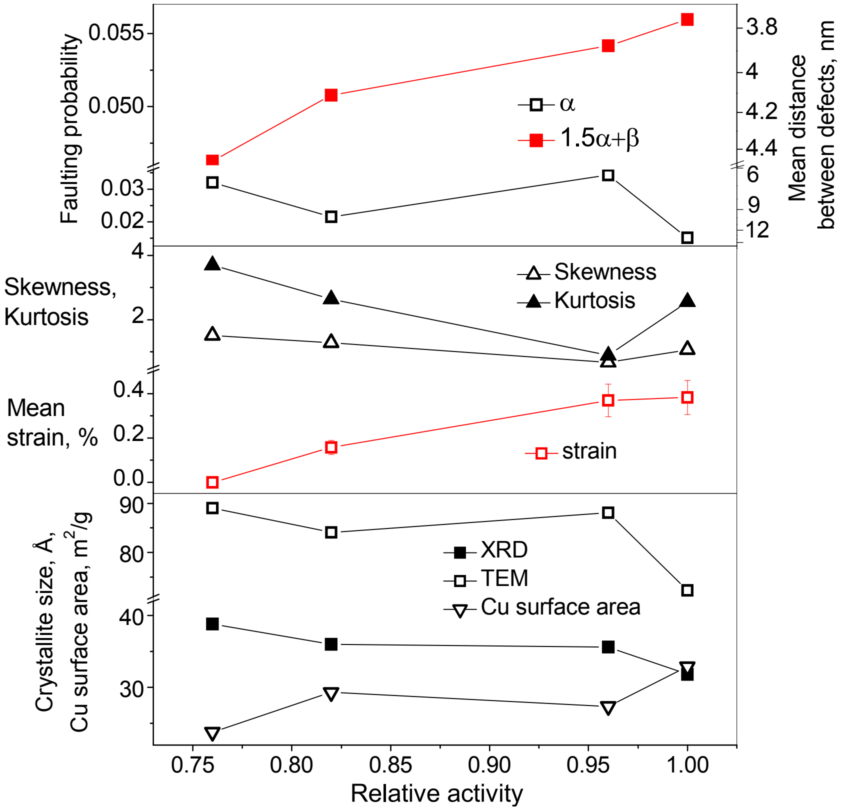


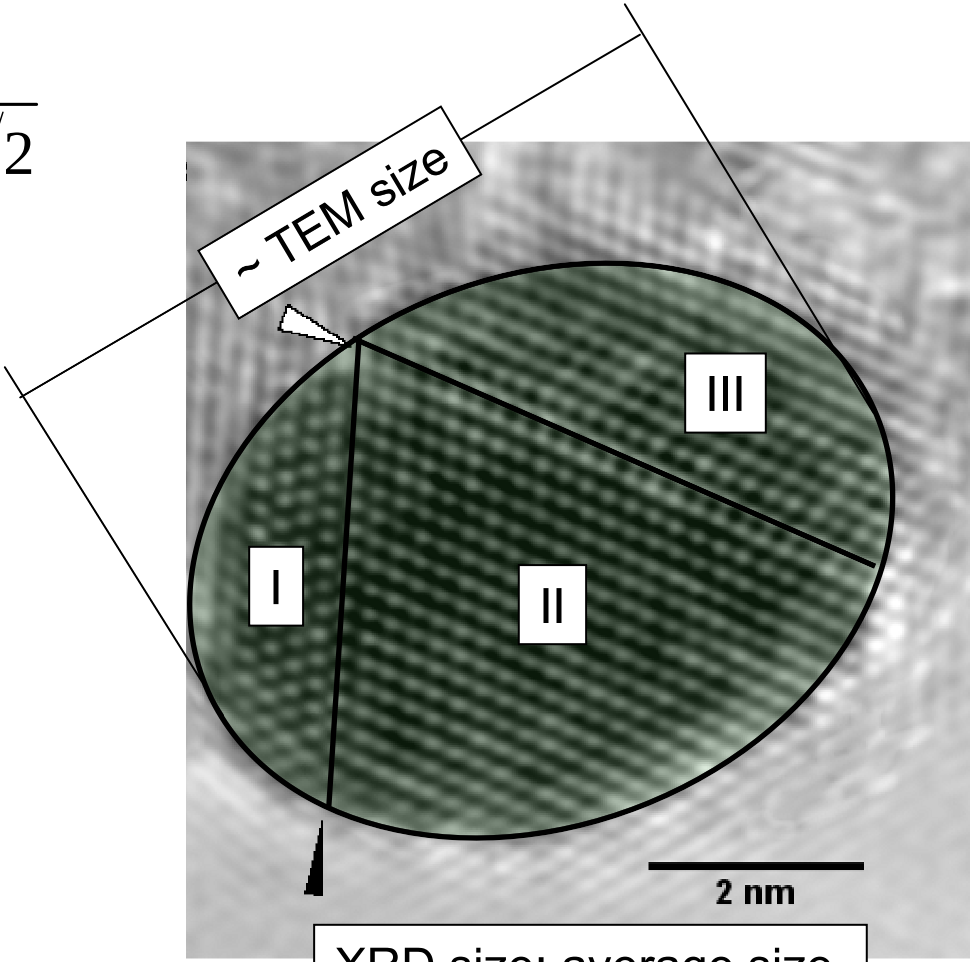


Williamson-Hall plot
from neutron data

Combined XRD and TEM apprach

$$D = \frac{a \cdot D_{111}}{a - (1.5\alpha + \beta) D_{111} \sqrt{3}/2}$$





XRD size: average size of volumes I, II & III

(Kasatkin, I., Kurr, P., Kniep, B., Trunschke, A., Schlögl, R., Angew. Chem. 119, 2007, 7465)

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