Chapter 5: Materials

- 5.1 Real structure and defects in solids
- 5.2 Specific aspects of the structural chemistry of alloys
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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)



<u>Schottky-defect:</u> vacancy, missing ions moved to the surface <u>Frenkel-defect:</u> vacancy, missing ions on interstitial positions

5.1 Defects in solids

- Importance of point defects for the properties of solids
- Defects are <u>centers of reactivity</u>
- Defects are responsible for <u>mass transport (diffusion)</u> either <u>self diffusion</u> or <u>diffusion under the influence of an</u> <u>external electric field (ionic conductivity)</u>
- Schottky defects (vacancy): diffusion of cations <u>and</u> anions
- Frenkel defects (interstitials): diffusion of <u>one</u> ionic species only

5.1 Defects in solids

 \rightarrow 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):

Т (К)	n _s /N	n _s /cm ³	
0	-	-	
298	3 ·10 ⁻¹⁷	5·10 ⁵	
1073	3·10 ⁻⁵	4·10 ¹⁷	
Alkali halides	Schottky (cations and		

Schottky (cations and anions)
Schottky (cations and anions)
Frenkel (cations)
Frenkel (anions)

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

Classical alloys do not obey simple <u>valence rules</u> (8-N etc.): Zr₄Al₃, Cu₅Zn₈ ... and are characterized by variable chemical compositions (<u>"homogeneity ranges</u>") 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.



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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, Ba₃Si₄, 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 AB₂ compounds favors certain structure types with closed-packed A and tetraedric B ions (classical examples: MgCu₂, 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)



 μ_B magnet. moment of an electron on an atomic orbit (Bohr magneton BM) μ_B = eh/4 π m_e = 0,9274 10⁻²⁷ Am² (relation to basic constants) (μ_B : smallest possible quantity of a magnetic moment)

 $\mu_s = 2 (S(S+1))^{\frac{1}{2}} \mu_B$ with $S = \sum s = \frac{1}{2} n$ and n = number of unpaired electrons (spin only magnetism, orbital momentum omitted, $\mu = g S$ with $g \sim 2 \rightarrow 5$ BM for Fe³⁺ (S = 5/2)

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

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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' = Η χ_ν

χ _V :	dimensionless	(volume susceptibility)
χ _a :	[cm ³ /g]	(gram susceptibilty)
χ _{mol}	[cm ³ /mol]	(molar susceptibility) \rightarrow 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 β=μ_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)



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



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")



5.3 Solid State Magnetism: Magnetic materials

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



<u>Garnets</u>: A₃²⁺B₂³⁺Si₃O₁₂ : A=Ca, Mg, Fe, Mn ..., B=Al, Fe, Cr

- Silicates with isolated SiO₄-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 $\frac{1}{4}$) B (16a: 000) A (24c: 1/8 0 $\frac{1}{4}$)

5.3 Solid State magnetism: Structure of spinell: MgAl₂O₄





structural basis: ccp-arrangement of O²⁻

Normal spinell: AB₂O₄, $\frac{1}{8}$ T-holes (A), $\frac{1}{2}$ O-holes (B)

Invers spinell: B(BA)O₄, e.g. $Fe_3O_4 = Fe^{3+}(Fe^{3+}Fe^{2+})O_4$ 19

5.3 Ferroelectricity: The perovskite structure ($CaTiO_3$)



<u>BaTiO₃ is a dielectric material that</u> <u>shows "Ferroelectricity"</u>

- Displacive phase transition below the ferroelectric Curie temperature $(T_c = 393 \text{ K for } BaTiO_3) \rightarrow \text{spontaneous}$ 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 (Ba²⁺, Ti⁴⁺) 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 20

5.4 Superconducting materials

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50

90

70

110

130 150



H. Kammerlingh-Onnes N.P. 1913



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





170 190 210

230

250 270 290

Temperature / K

 $Ba_{x}La_{2-x}CuO_{4-y} \rightarrow YBa_{2}Cu_{3}O_{7-\delta}$

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



5.4 Meissner-Ochsenfeld-effect



Milestones in Superconductivity

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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⁺, O²⁻ ...



Diffusion path of Ag⁺ ions in a silver ionic conductor



Mobile ions in ionic conductors (e.g.): α -AgI: mobile Ag⁺ " β -Alumina": $M_2O \cdot 11Al_2O_3$, mobile M⁺ "ZrO₂": cubic, stabilized by Y_2O_3 doping, mobile O²⁻ LiC₆: Li-intercalated graphite, mobile Li⁺

5.5 Zirconia: ZrO_2 : application as solid electrolyte

- <u>Three</u> modifications: monoclinic (baddeleyite) tetragonal cubic

: <1170 °C (mineral) : <2370 °C : <2590 °C (m.p.)

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

Ca²⁺ 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: ZrO₂: application as solid electrolyte

- <u>stabilized</u> cubic zirconia is an O²⁻ 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: ZrO₂ : 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	Fm3m	
Volume per formu	ula 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



Wavelength of emission depends on material composition: e.g. $(In_{1-x}Ga_xN \dots)$; 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 (Eu³⁺, Eu²⁺, Ce²⁺...)

Leuchtstoff	Aktivator	Anregung	Wellenlänge, Farbe der Emission, B = Breitband-Emission, L = Linien- bande
$\overline{Y_2O_3:Eu}$	Eu ³⁺	4f-4f	611 nm, orangerot, L
BaFC1: 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⁺	3d3d	694 nm, tiefrot, L (Rubin-Laser)
$Y_3Al_5O_{12}$: Nd	Nd ³⁺	4f-4f	1064 nm, IR, L (YAG:Nd-Laser)
BaSi ₂ O ₅ : Pb	Pb^{2+}	6s-6p	350 nm, UV-A, B
LaPO₄: 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: $(BaO)_x$ · Al_2O_3 : Eu^{2+} (x = 0,8)

5.7 Nitride materials: hexagonal and cubic BN



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

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

- primary product is h-BN; at 50 kbar / 1400 $^{\circ}C \rightarrow$ cubic-BN (similar to diamond)



 \rightarrow extreme hardness (like diamond), very low thermal expansion coefficient, due to a thin protecting layer of SiO_2 stable up to to 1400 $^{\rm o}C$ in air

Further important nitride materials: AIN, 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)

