Structures and Properties of Solids

Dates

- Friday 20.10.06: 12.00-14.00, F002
- Friday 27.10.06: 12.00-14.00, F002
- Friday 03.11.06: 12.00-14.00, F002
- Friday 10.11.06: 12.00-14.00, F002

Outline

1. Introduction

2. Structure of solids

2.1 Basics of structures (geometrical concepts)

2.2 Simple close packed structures: metals

2.3 Basic structure types

3. Characterization of solids

3.1 Diffraction

3.2 Imaging

4. Synthesis

4.1 HT-synthesis

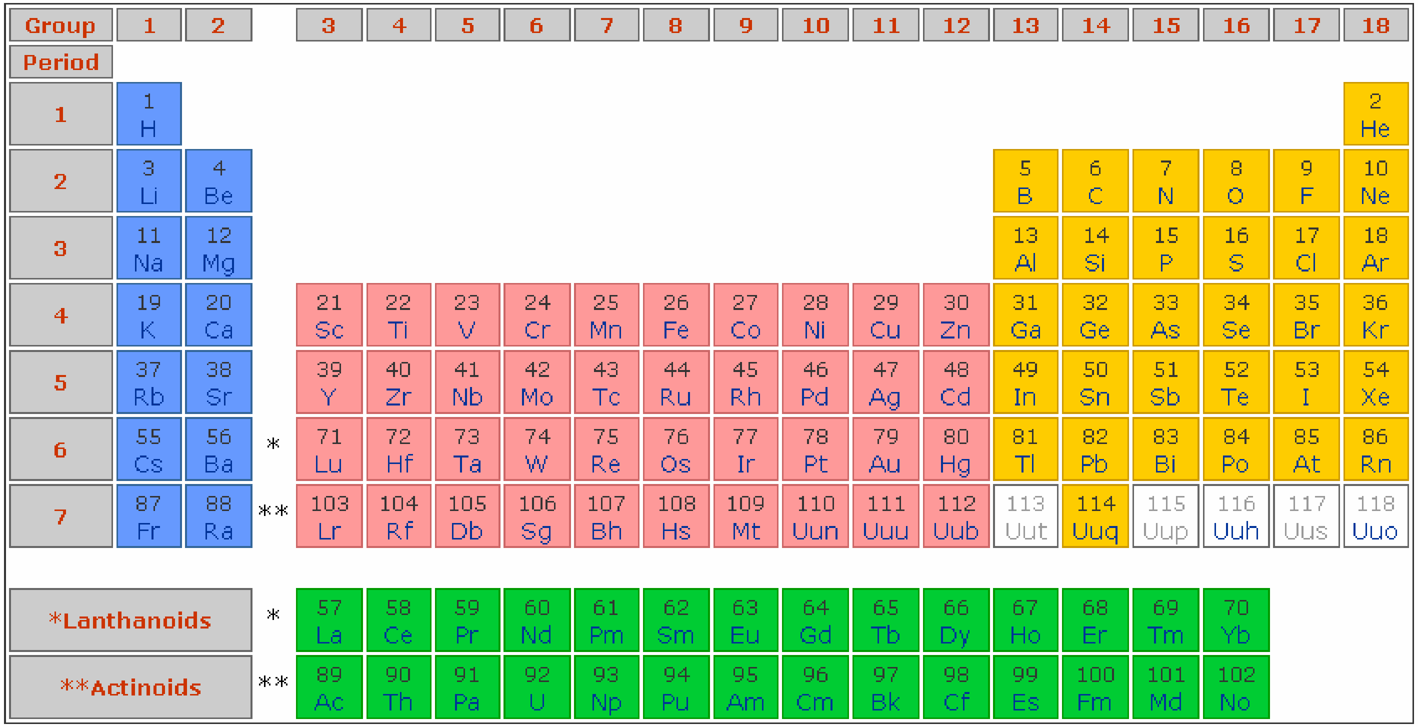
4.2 CVT

1.

Introduction

1.Introduction
Why is the solid state interesting?

Most elements are solid at room temperature



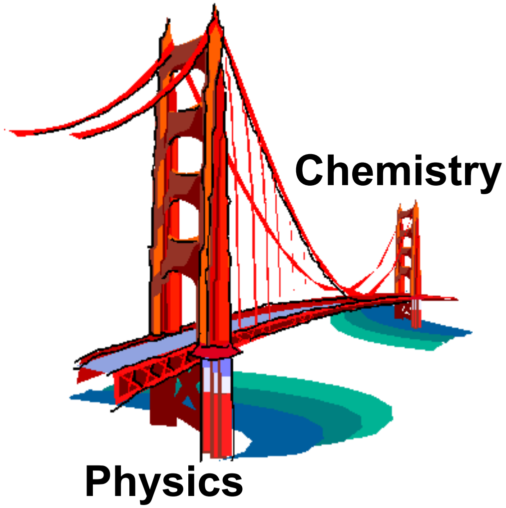
Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Solid Biomaterials (enamel, bones, shells…)

Nanomaterials (quantum dots, nanotubes…)

1. Introduction
Special aspects of solid state chemistry

Close relationship to solid state physics and materials science



Importance of structural chemistry

- Knowledge of several structure types
- Understanding of structures

Physical methods for the characterization of solids

- X-ray structure analysis, electron microscopy…
- Thermal analysis, spectroscopy, conductivity measurements ...

Investigation and tuning of physical properties

- Magnetism, conductivity, sorption, luminescence
- Defects in solids: point defects, dislocations, grain boundaries

Synthesis

- HT-synthesis, hydrothermal synthesis, soft chemistry (chemistry)
- Strategies for crystal growth (physics)

1. Introduction
Classifications for solids (examples)

Degree of order

- Long range order: crystals (3D periodicity)
- Long range order with extended defects (dislocations…)
- Crystals with disorder of a partial structure (ionic conductors)
- Amorphous solids, glasses (short range order)

Chemical bonding – typical properties

- Covalent solids (e.g. diamond, boron nitride): extreme hardness ...
- Ionic solids (e.g. NaCl): ionic conductivity ...
- Metals (e.g. Cu): high conductivity at low temperatures

Structure and Symmetry

- Packing of atoms: close packed structure (high space filling)
- Characteristic symmetry: cubic, hexagonal, centrosymmetric/non-centrosymmetric…

2.

Basic Structures

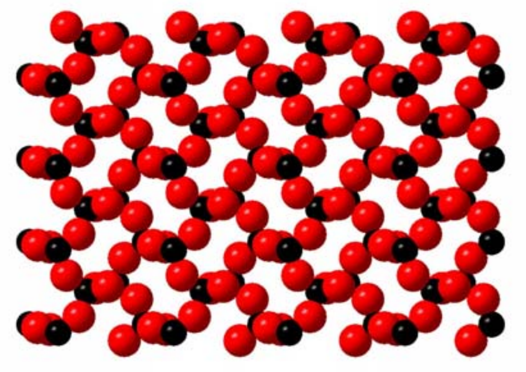
2.1 Basics of Structures
Visualization of structures

How can we display structures in the form of images?

Example: Cristobalite (SiO_2)

Approach 1

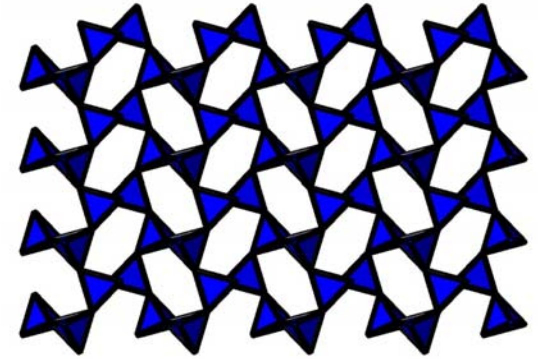
Packing of spheres
Bragg jun. (1920)



Atoms = spheres

Approach 2

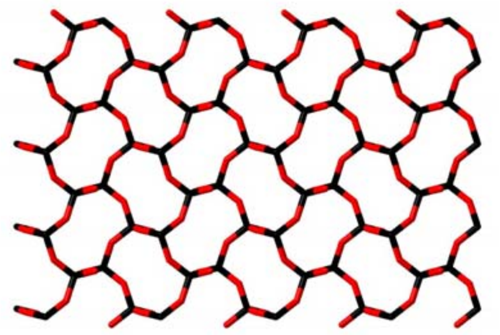
Coordination polyhedra
Pauling (1928)



SiO_4-tetrahedra

Approach 3

Description of topology
Wells (1954)



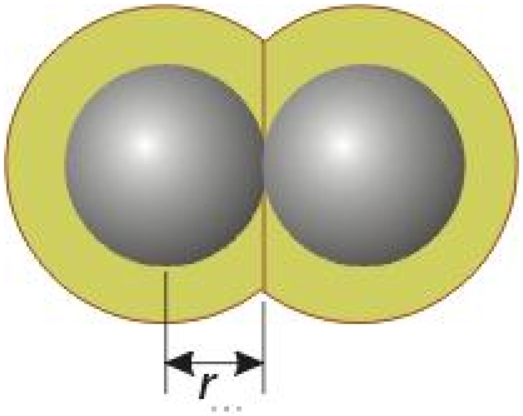
no atoms, 3D nets

One structure but very different types of structure images

2.1 Basics of Structures
Approximation: atoms can be treated like spheres

Approach 1: Concepts for the radius of the spheres depending on the nature of the chemical bond

element or compounds



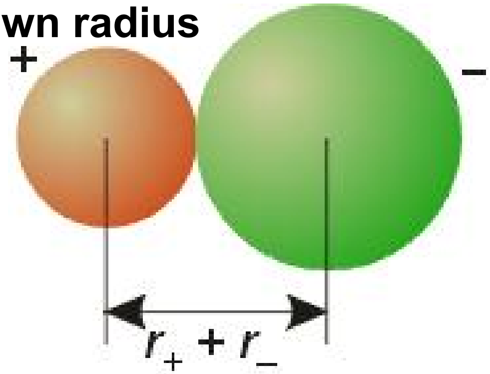
2 Covalent radius

=

d/2 of single bond in molecule

compounds

cation unknown radius

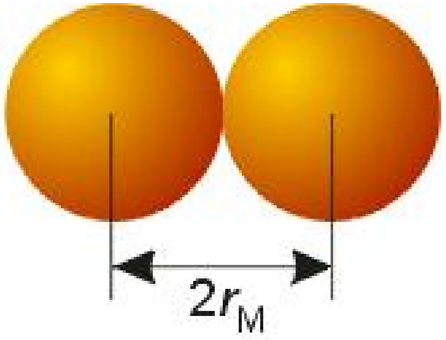


3 Ionic radius

=

d – r(F, O…)
problem: reference!

elements or compounds („alloys“)



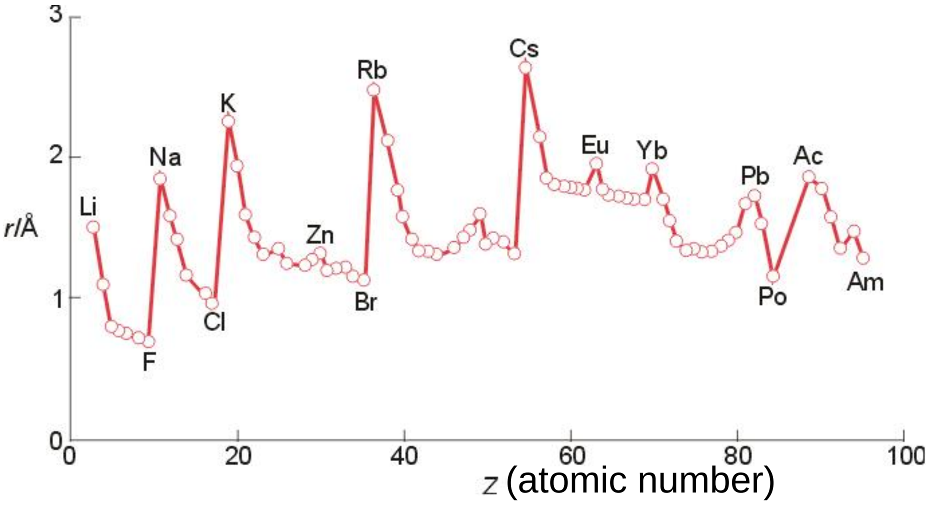
1 Metallic radius

=

d/2 in metal

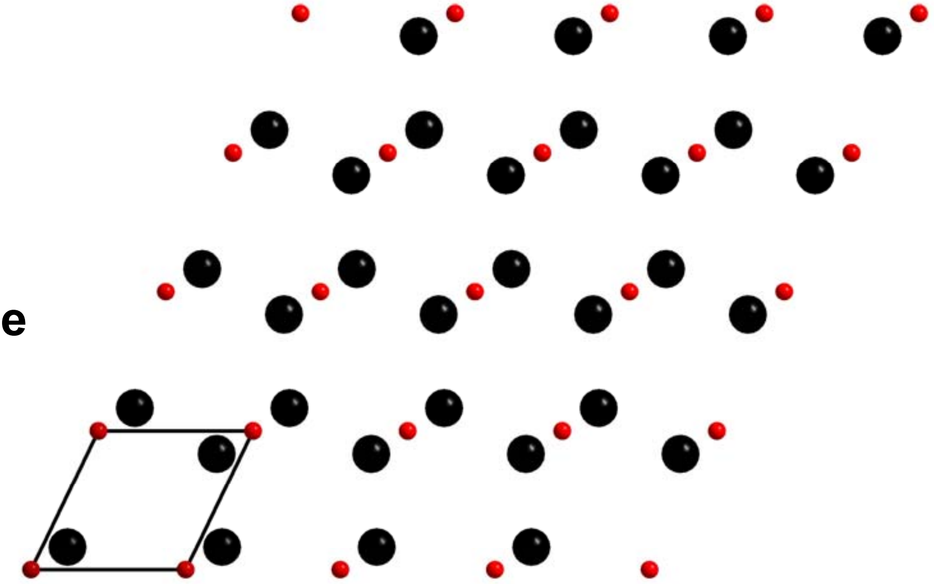
2.1 Basics of Structures
Trends of the atomic / ionic radii

- **Increase on going down a group (additional electrons in different shells)**
- **Decrease across a period (additional electrons in the same shell)**
- **Ionic radii increase with increasing CN**
  (the higher its CN, the bigger the ions seems to be, due to increasing d!!!)
- **Ionic radius of a given atom decreases with increasing charge**
  ($r(Fe^{2+}) > r(Fe^{3+})$)
- **Cations are usually the smaller ions in a cation/anion combination**
  (exception: $r(Cs^{+}) > r(F^{-})$)
- **Particularities: Ga < Al (d-block)**



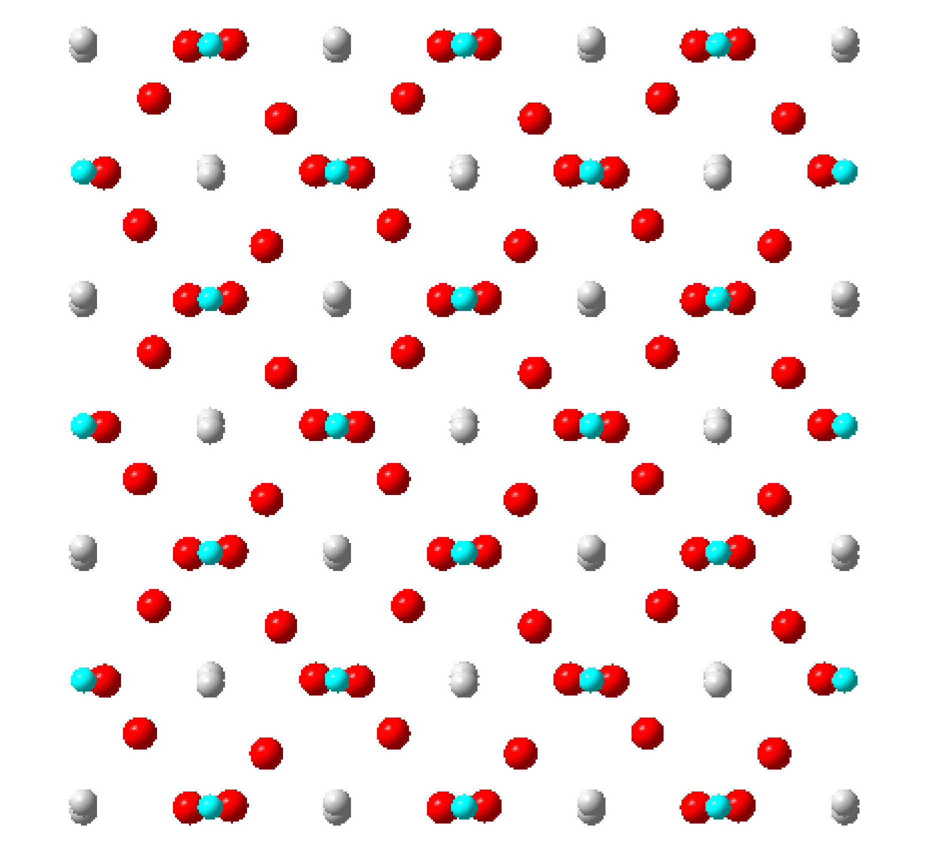
2.1 Basics of Structures
Structure, lattice and motif

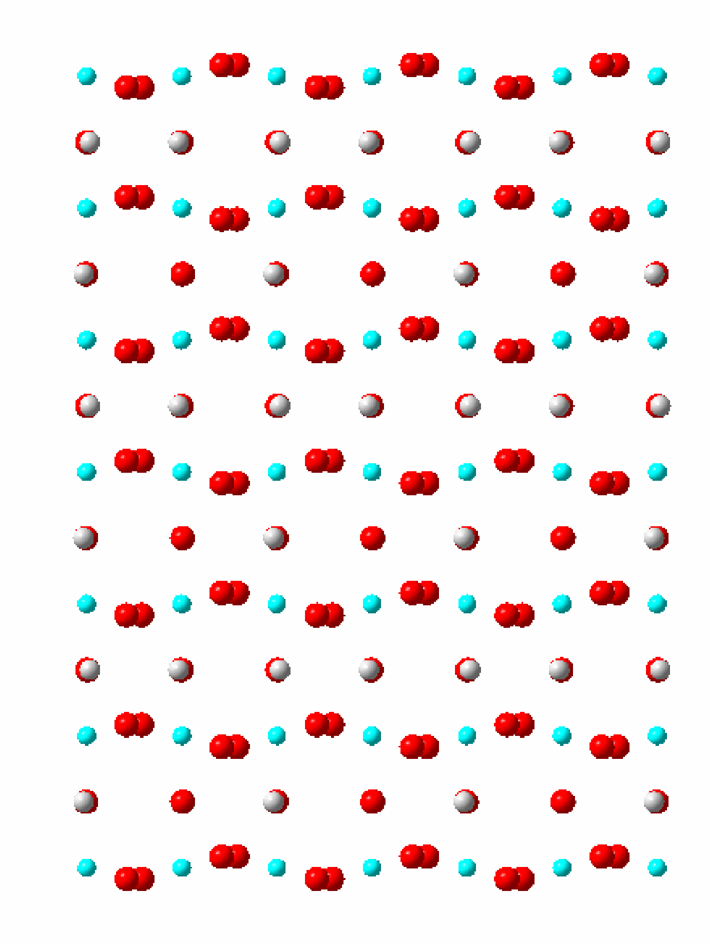
Example: Graphite



- **Lattice: Determined by lattice vectors and angles**
- **Motif: Characteristic structural feature, e. g. molecule**
- **Structure = Lattice + Motif**
- **Unit cell: Parallel sided region from which the entire crystal can be constructed by purely translational displacements (Conventions!!!)**

2.1 Basics of Structures
Determine the unit cells



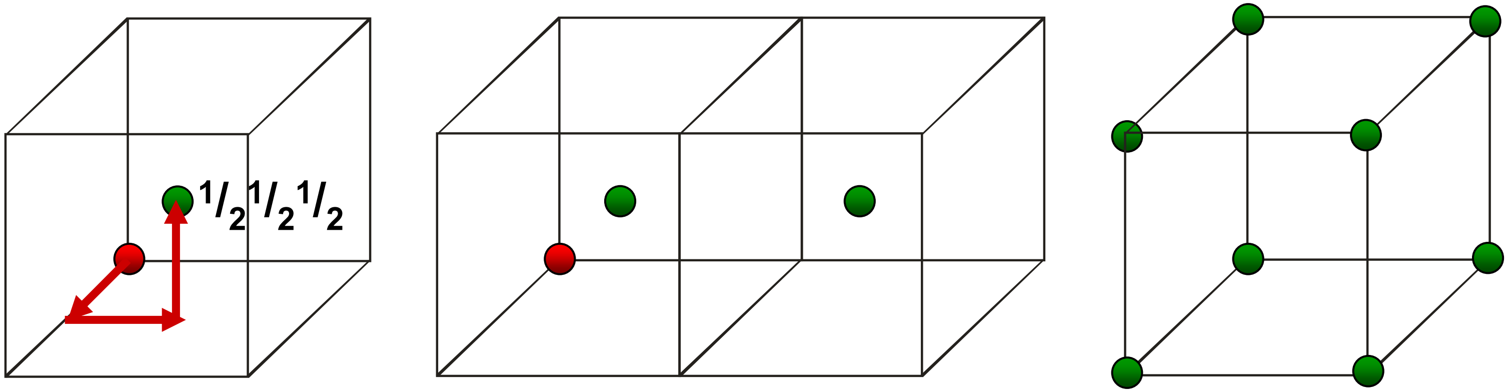


2.1 Basics of Structures
Unit cells and crystal system

- Millions of structures but 7 types of primitive cells (crystal systems)
- Crystal system = particular restriction concerning the unit cell
- Crystal system = unit cell with characteristic symmetry elements (SSC)

Crystal system	Restrictions axes	Restrictions angles
Triclinic	-	-
Monoclinic	-	$\alpha = \gamma = 90°$
Orthorhombic	-	$\alpha = \beta = \gamma = 90°$
Tetragonal	a = b	$\alpha = \beta = \gamma = 90°$
Trigonal	a = b	$\alpha = \beta = 90°,\ \gamma = 120°$
Hexagonal	a = b	$\alpha = \beta = 90°,\ \gamma = 120°$
Cubic	a = b = c	$\alpha = \beta = \gamma = 90°$

2.1 Basics of Structures
Fractional coordinates (position of the atoms)



  - possible values for x, y, z: [0; 1], atoms are multiplied by translations
  - atoms are generated by symmetry elements (see SSC)

- **Example:** Sphalerite (ZnS)

- **Equivalent points are represented by one triplet only**
  - equivalent by translation
  - equivalent by other symmetry elements (see SSC)

2.1 Basics of Structures
Number of atoms/cell (Z: number of formula units)

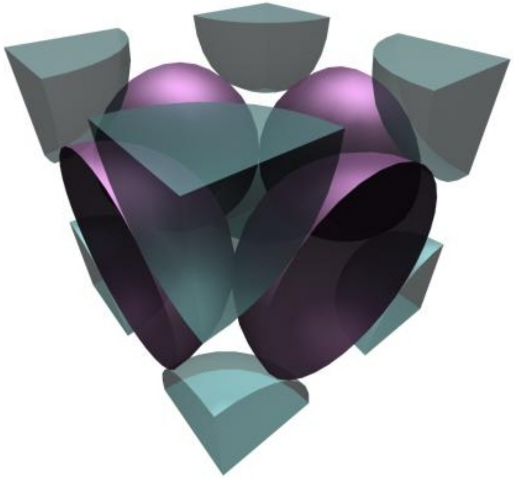
Molecular compounds: molecules determine the stoichiometry
Ionic or metallic compounds: content of unit cell ↔ stoichiometry

How to count atoms?

Rectangular cells:

- **Atom completely inside unit cell: count = 1.0**
- **Atom on a face of the unit cell: count = 0.5**
- **Atom on an edge of the unit cell: count = 0.25**
- **Atom on a corner of the unit cell: count = 0.125**

Fraction of the atoms in unit cell



Example 1: Sphalerite

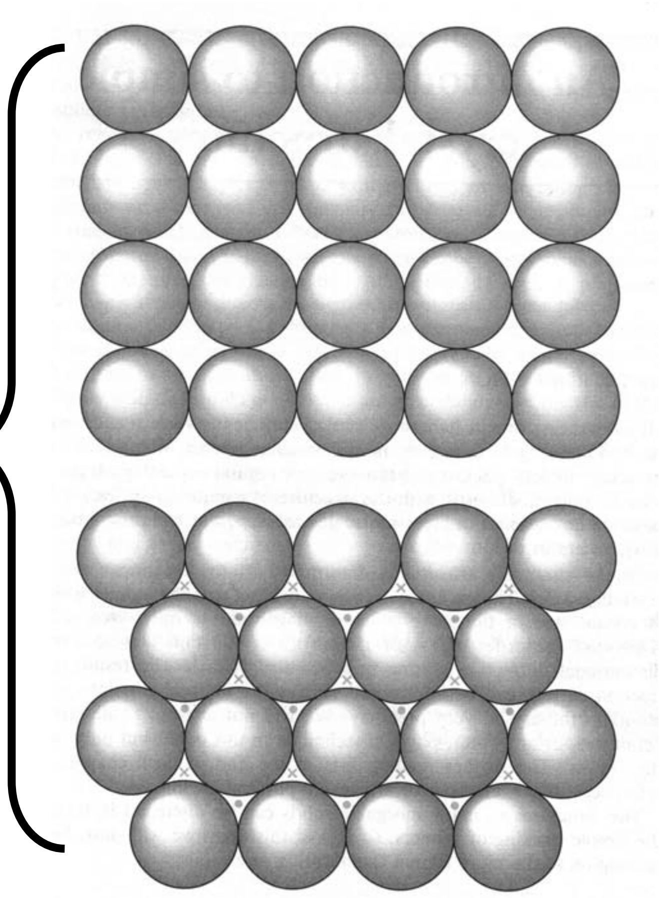
Example 2: Wurzite

Occupancy factor: number of atoms on one particular site

2.2 Simple close packed structures (metals)
Close packing in 2D

Metal atoms → Spheres

Arrangements in 2D



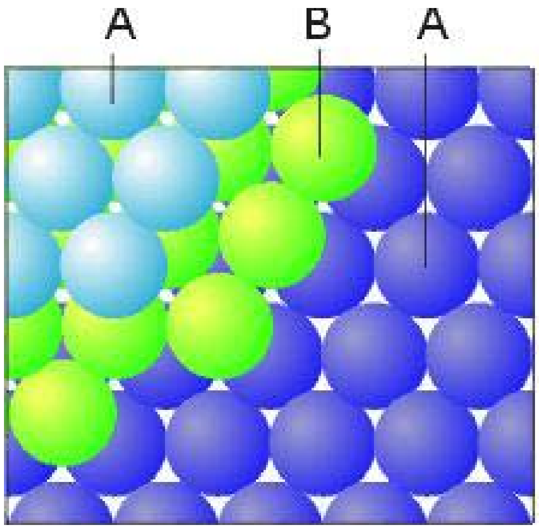
primitive (square) packing
(large holes, low space filling)

close (hexagonal) packing
(small holes, high space filling)

2.2 Simple close packed structures (metals)
Close packing in 3D

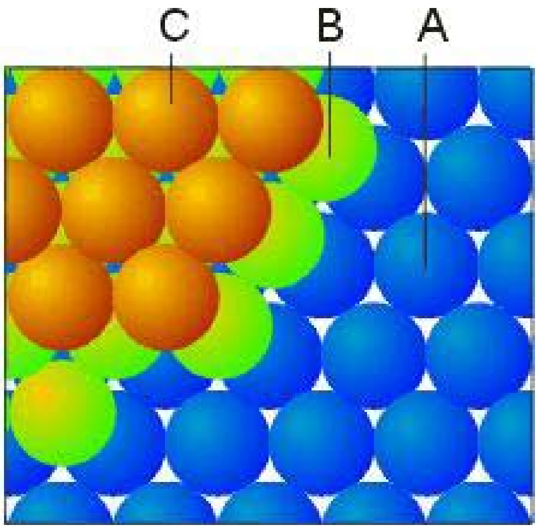
3D close packing:
different stacking sequences of close packed layers

Example 1: HCP



stacking sequence: AB

Example 2: CCP



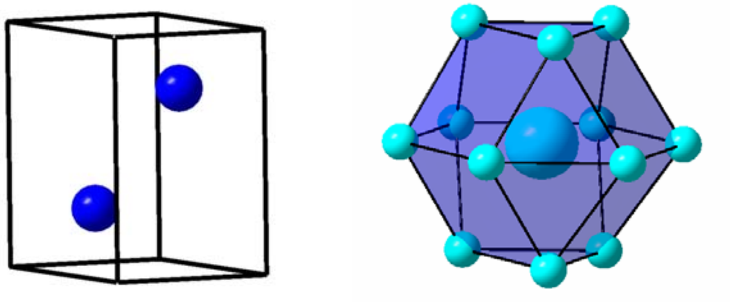
stacking sequence: ABC

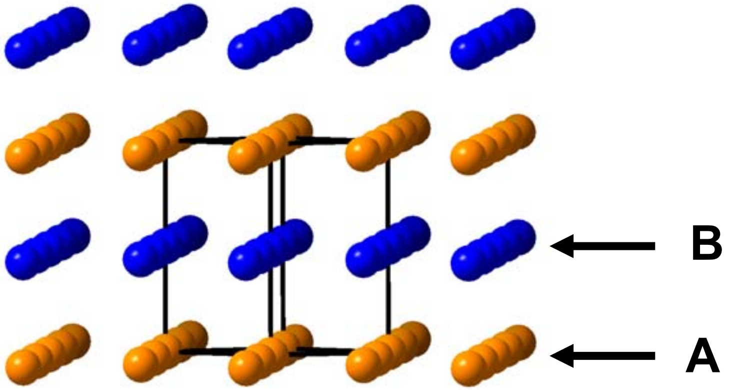
Polytypes: mixing of HCP and CCP, e. g. La, ABAC

2.2 Simple close packed structures (metals)
Unit cells of HCP and CCP

HCP

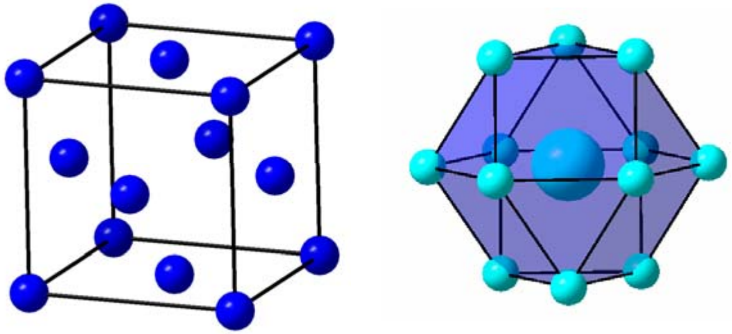
(Be, Mg, Zn, Cd, Ti, Zr, Ru ...)

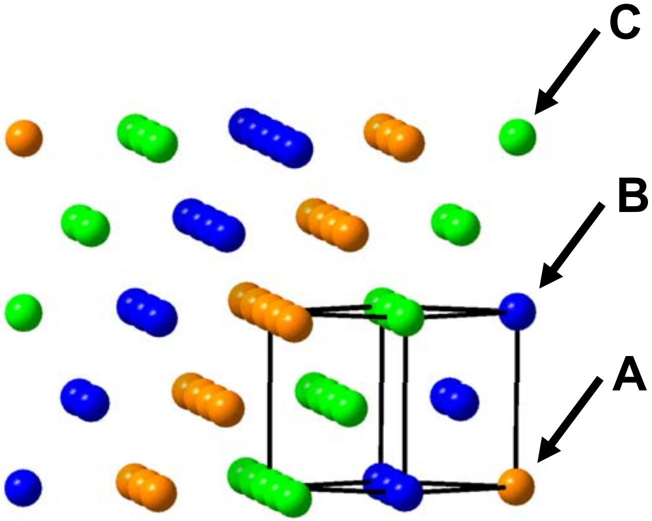




CCP

(Cu, Ag, Au, Al, Ni, Pd, Pt ...)

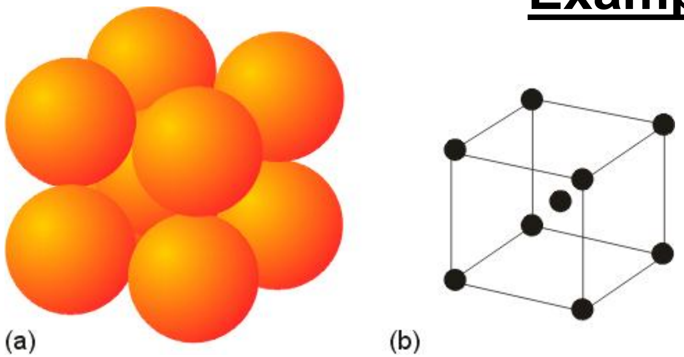




Common properties: CN = 12, space filling = 74%

2.2 Simple close packed structures (metals)
Other types of metal structures

Example 1: BCC



(Fe, Cr, Mo, W, Ta, Ba ...)

space filling = 68%

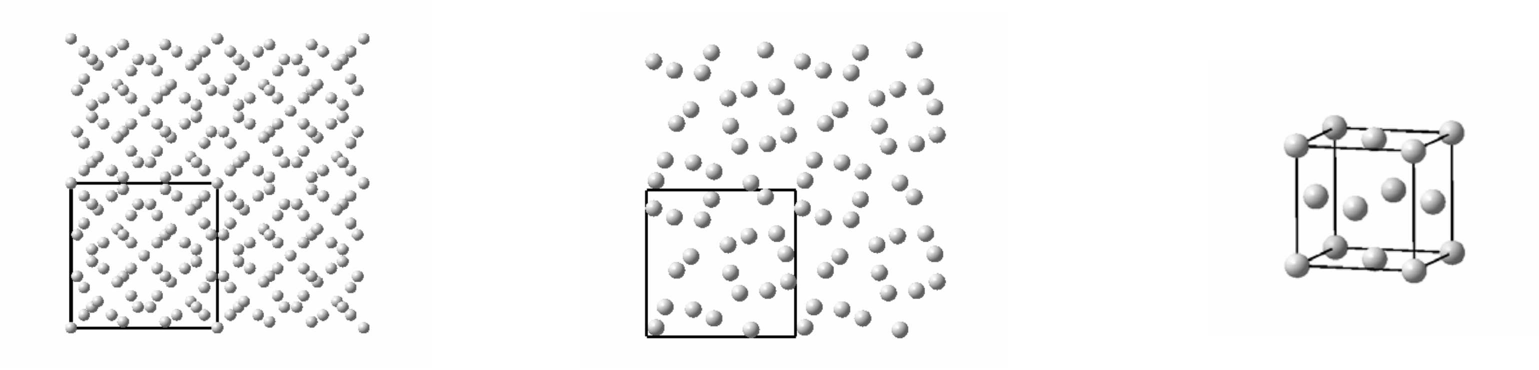
CN = 8, cube

Example 2: primitive packing (α-Po)

space filling = 52%

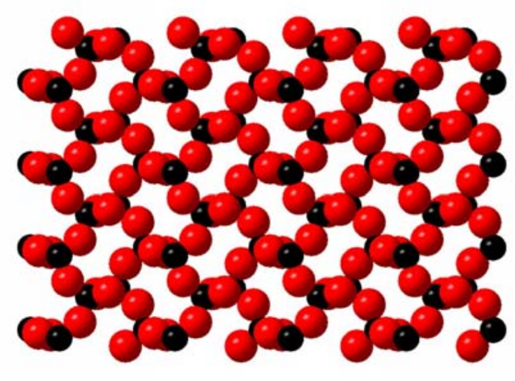
CN = 6, octahedron

Example 3: structures of manganese

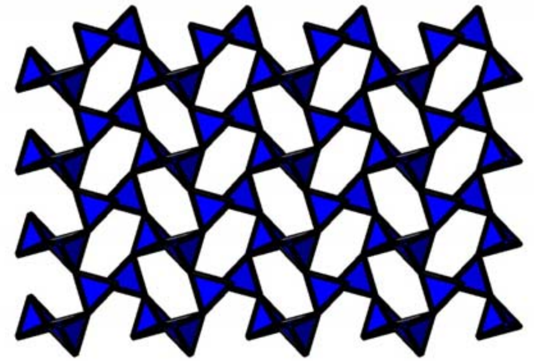


2.2 Basics of Structures
Visualization of structures - polyhedra

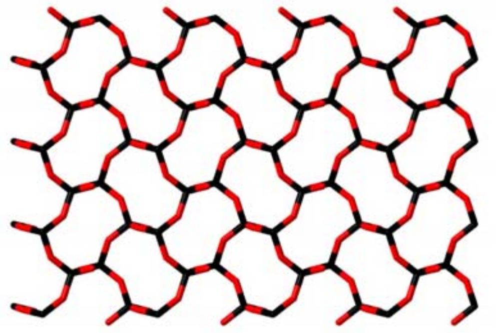
Example: Cristobalite (SiO_2)



Bragg jun. (1920)
Sphere packing



Pauling (1928)
Polyhedra

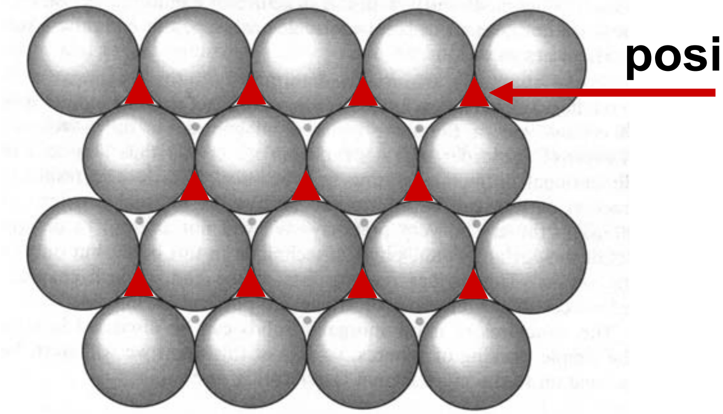


Wells (1954)
3D nets

2.2 Simple close packed structures (metals)

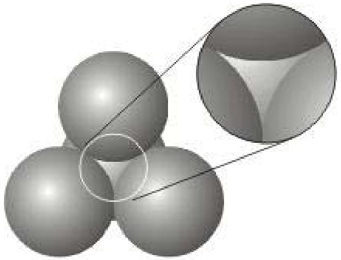
Holes in close packed structures

Different point of view → description of the environment of holes

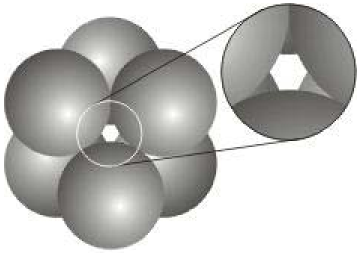


2D close packing

position of B-layer-atom



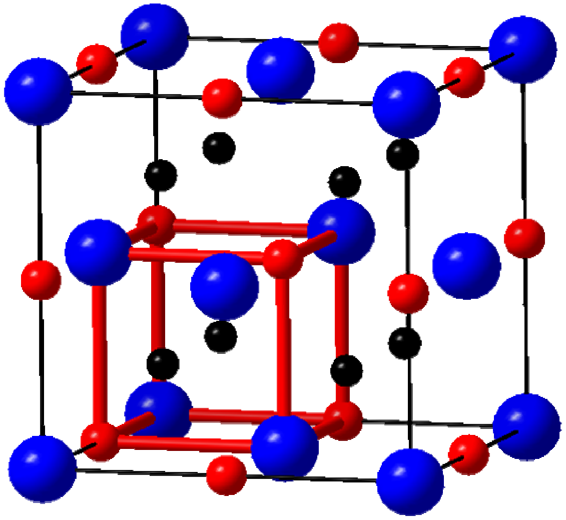
Tetrahedral hole
TH



Octahedral hole
OH

Filled holes: Concept of polyhedra

2.2 Simple close packed structures (metals)
Properties of OH and TH in CCP



Number
OH/TH
(with respect to n-atoms/unit cell)

n: 12/4 +1
2n: 8

Location

OH: center, all edges
TH: center of each octant

Distances
OH/TH

OH-OH: no short distances
TH-TH: no short distances

!OH-TH!

2.3 Basic structure types
Overview

„Basic“: anions form CCP or HCP, cations in OH and/or TH

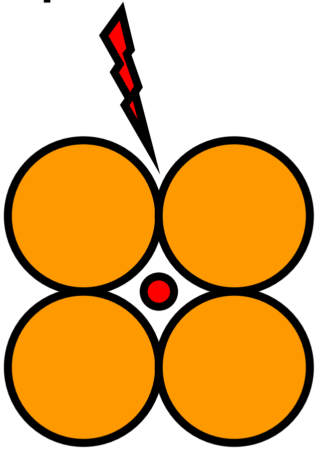
Structure type	Examples	Packing	Holes filled OH and TH
NaCl	AgCl, BaS, CaO, CeSe, GdN, NaF, **Na_3BiO_4, V_7C_8**	CCP	n and 0n
NiAs	TiS, CoS, CoSb, AuSn	HCP	n and 0n
CaF_2	CdF_2, CeO_2, **Li_2O**, Rb_2O, $SrCl_2$, ThO_2, ZrO_2, $AuIn_2$	CCP	0 and 2n
$CdCl_2$	$MgCl_2$, $MnCl_2$, $FeCl_2$, Cs_2O, $CoCl_2$	CCP	0.5n and 0
CdI_2	$MgBr_2$, PbI_2, SnS_2, $Mg(OH)_2$, $Cd(OH)_2$, Ag_2F	HCP	0.5n and 0
Sphalerite (ZnS)	AgI, BeTe, CdS, CuI, GaAs, GaP, HgS, InAs, ZnTe	CCP	0 and 0.5n
Wurzite (ZnS)	AlN, BeO, ZnO, CdS (HT)	HCP	0 and 0.5n
Li_3Bi	Li_3Au	CCP	n and 2n
ReB_2	!wrong! (SSC)	HCP	0 and 2n

2.3 Basic structure types
Pauling rule no. 1

A polyhedron of anions is formed about each cation, the cation-anion distance is determined by the sum of ionic radii and the coordination number by the radius ratio: r(cation)/r(anion)

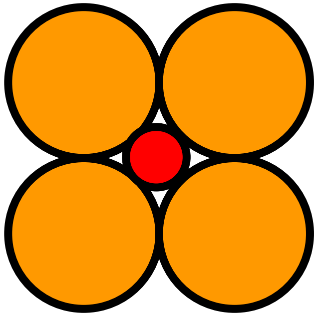
Scenario for radius ratios:

r(cation)/r(anion)
< optimum value



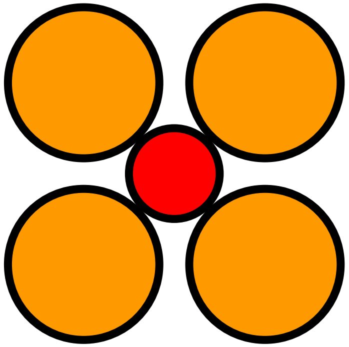
worst case
(not stable)

r(cation)/r(anion)
= optimum value



optimum

r(cation)/r(anion)
> optimum value



low space filling
(switching to higher CN)

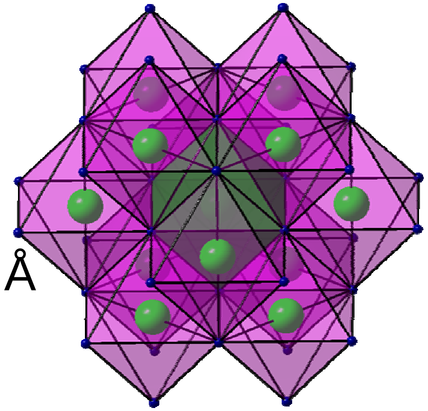
2.3 Basic structure types
Pauling rule no. 1

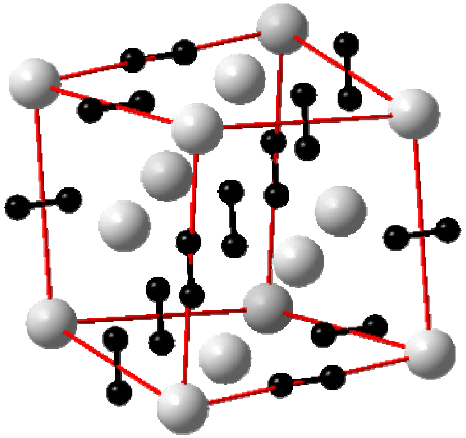
coordination	anion polyhedron	radius ratios	cation
3	triangle	0.15-0.22	B in borates
4	tetrahedron	0.22-0.41	Si, Al in oxides
6	octahedron	0.41-0.73	Al, Fe, Mg, Ca in oxides
8	cube	0.73-1.00	Cs in CsCl
12	close packing (anti)cuboctahedron	1.00	metals

2.3 Basic structure types
NaCl-type

Crystal data

Formula sum	NaCl
Crystal system	cubic
Unit cell dimensions	*a* = 5.6250(5) Å
Z	4





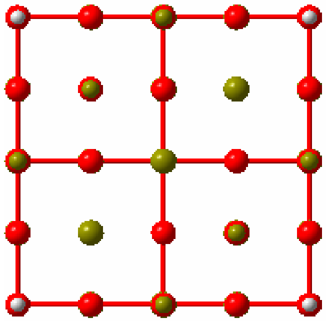
Variations of basic structure types:

Exchange/Decoration

Cl → C_2^{2-}

Superstructure

Na → Li, Fe



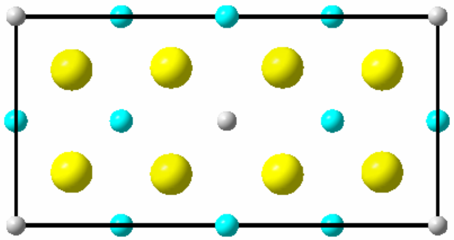
Features:

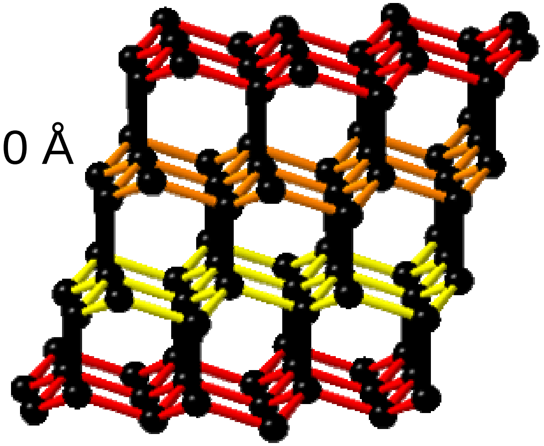
- **All octahedral holes of CCP filled, type = antitype**
- **Na is coordinated by 6 Cl, Cl is coordinated by 6 Na**
- **One $NaCl_6$-octaherdon is coordinated by 12 $NaCl_6$-octahedra**
- **Connection of octahedra by common edges**

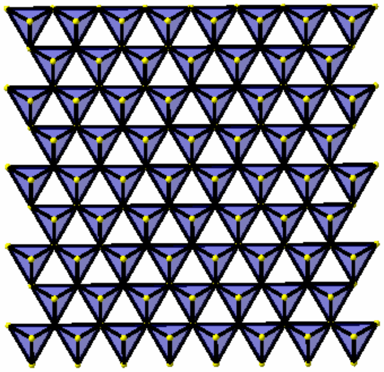
2.3 Basic structure types
Sphalerite-type

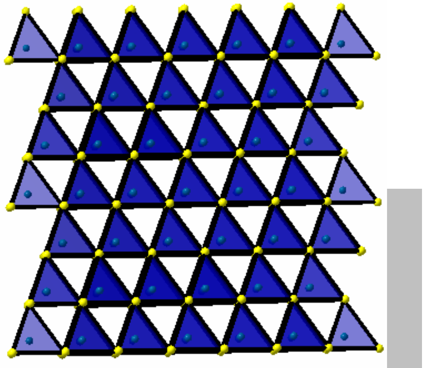
Crystal data

Formula sum	ZnS
Crystal system	cubic
Unit cell dimensions	*a* = 5.3450 Å
Z	4









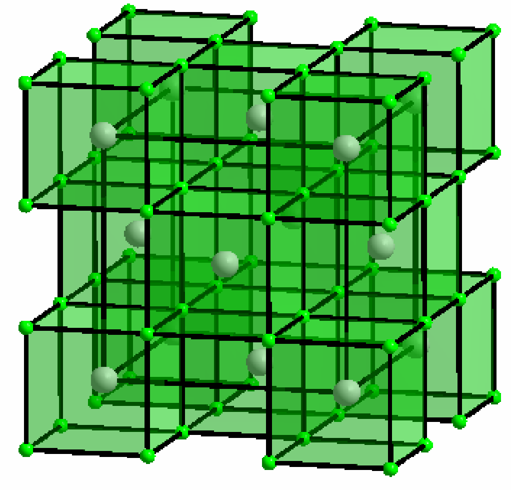
Features:

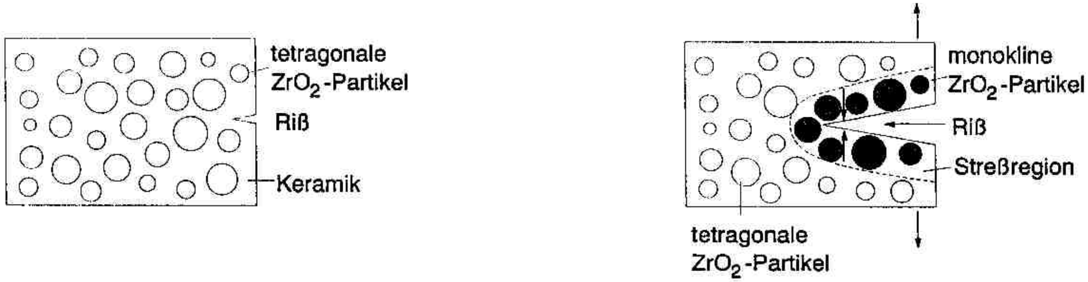
- **Diamond-type structure, or: 50% of TH in CCP filled**
- **Connected layers, sequence (S-layers): ABC, polytypes**
- **Zn, S coordinated by 4 S, Zn (tetrahedra, common corners), type = antitype**
- **Hexagonal variant (wurzite) and polytypes**
- **VEC = 4 for ZnS-type (AgI, CdS, BeS, GaAs, SiC)**
- **Many superstructures: Cu_3SbS_4 (famatinite, VEC = 32/8)**
- **Vacancy phases: Ga_2Te_3 (1SV), $CuIn_3Se_5$ (1 SV), AgGa5Te8 (2 SV)**
- **Applications: semiconductors, solar cells, transistors, LED, laser…**

2.3 Basic structure types
CaF_2-type

Crystal data

Formula sum	CaF_2
Crystal system	cubic
Unit cell dimensions	a = 5.4375(1) Å
Z	4

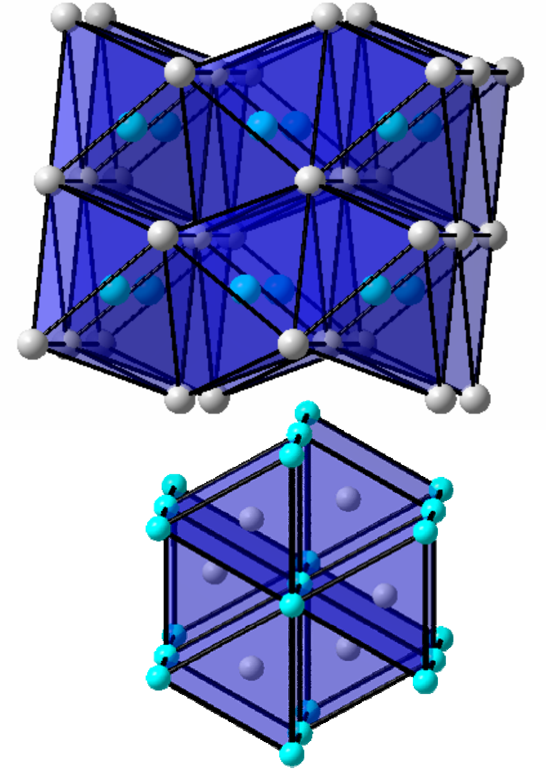




Fracture is closed by monoclinic ZrO_2 (increase of volume)

Features:
- **All TH of CCP filled**
- **F is coordinated by 4 Ca (tetrahedron)**
- **Ca is coordinated by 8 F (cube)**
- **Oxides MO_2 as high-temperature anionic conductors**
- **High performance ceramics**

2.3 Basic structure types
NiAs-type



Crystal data

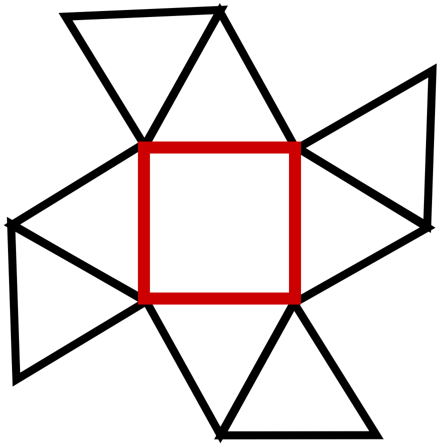
Formula sum	NiAs
Crystal system	hexagonal
Unit cell dimensions	*a* = 3.619(1) Å, *c* = 5.025(1) Å
Z	2

Features:

- All OH of HCP filled, metal-metal-bonding (common faces of octahedra!)
- Ni is coordinated by 6 As (octahedron)
- As is coordinated by 6 Ni (trigonal prism)
- Type ≠ antitype

2.3 Basic structure types
Oxides: Rutile (TiO_2)

Crystal data	
Formula sum	TiO_2
Crystal system	tetragonal
Unit cell dimensions	*a* = 4.5937 Å, *c* = 2.9587 Å
Z	2

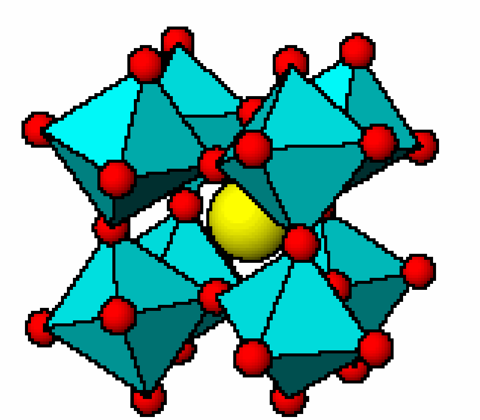


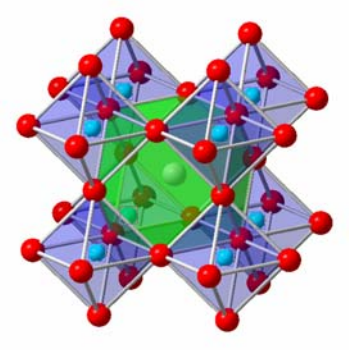
Features:
- No HCP arrangement of O (CN(O,O) = 11, tetragonal close packing)
- Mixed corner and edge sharing of TiO_6-octahedra
- Columns of trans edge sharing TiO_6-octahedra, connected by common corners
- Many structural variants ($CaCl_2$, Markasite)
- Application: pigment…

2.3 Basic structure types
Oxides: undistorted perovskite ($SrTiO_3$)

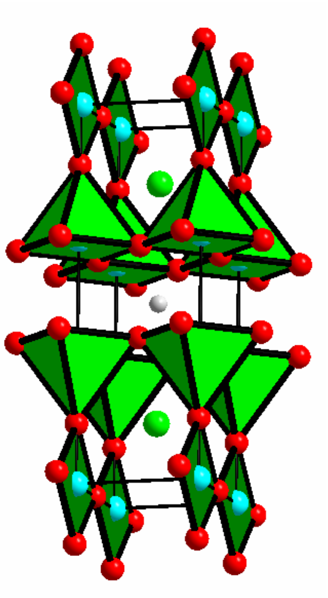
Crystal data

Formula sum	$SrTiO_3$
Crystal system	cubic
Unit cell dimensions	*a* = 3.9034(5) Å
Z	1





$YBa_2Cu_3O_{7-\delta}$

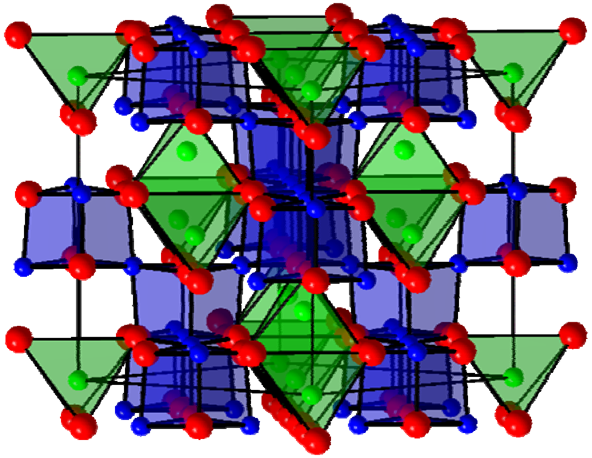


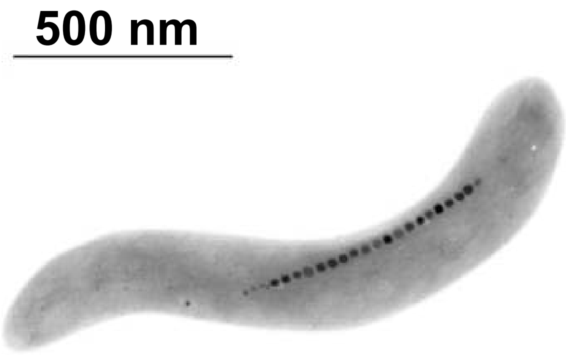
Features:

- **Filled ReO_3 phase, CN (Ca) = 12 (cuboctaehdron), CN (Ti) = 6 (octahedron)**
- **Ca and O forming CCP, Ti forms primitive arrangement**
- **Many distorted variants ($BaTiO_3$, even the mineral $CaTiO_3$ is distorted!)**
- **Many defect variants (HT-superconductors, $YBa_2Cu_3O_{7-x}$)**
- **Hexagonal variants and polytypes**

2.3 Basic structure types
Oxides: Spinel ($MgAl_2O_4$)

Crystal data	
Formula sum	$MgAl_2O_4$
Crystal system	cubic
Unit cell dimensions	*a* = 8.0625(7) Å
Z	8





Magnetospirillum
(Fe_3O_4)

Features:

- **Distorted CCP of O**
- **Mg in tetrahedral holes (12.5%), no connection of tetrahedra**
- **Al in octahedral holes (50%), common edges/corners**
- **Inverse spinel structures $Mg_{TH}Al_{2OH}O_4 \rightarrow In_{TH}(Mg, In)_{OH}O_4$**
- **Application: ferrites (magnetic materials), biomagnetism**

2.3 Basic structure types
Oxides: Silicates- overview 1

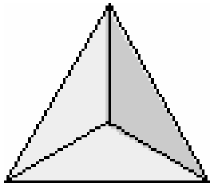
From simple building units to complex structures

Structural features:

- fundamental building unit (b.u.): SiO_4 tetrahedron
- isolated tetrahedra and/or tetrahedra connected via common corners
- MO_6 octahedra , MO_4 tetrahedra (M = Fe, Al, Co, Ni…)

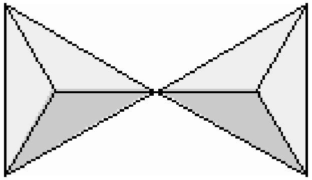
Composition of characteristic b.u.:
Determine the composition and relative number of different b.u.

SiO_4

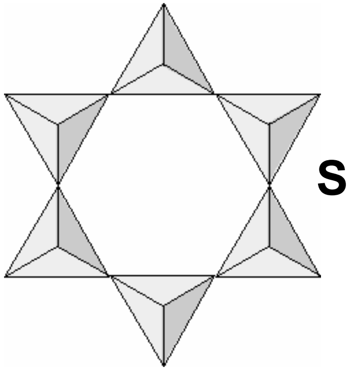


common corners (c.c): 0

$SiO_3O_{0.5}$



c.c: 1



$SiO_2O_{2\times 0.5}$

c.c: 2

Nesosilicates

SiO_4^{4-}
Olivine: $(Mg,Fe)_2SiO_4$

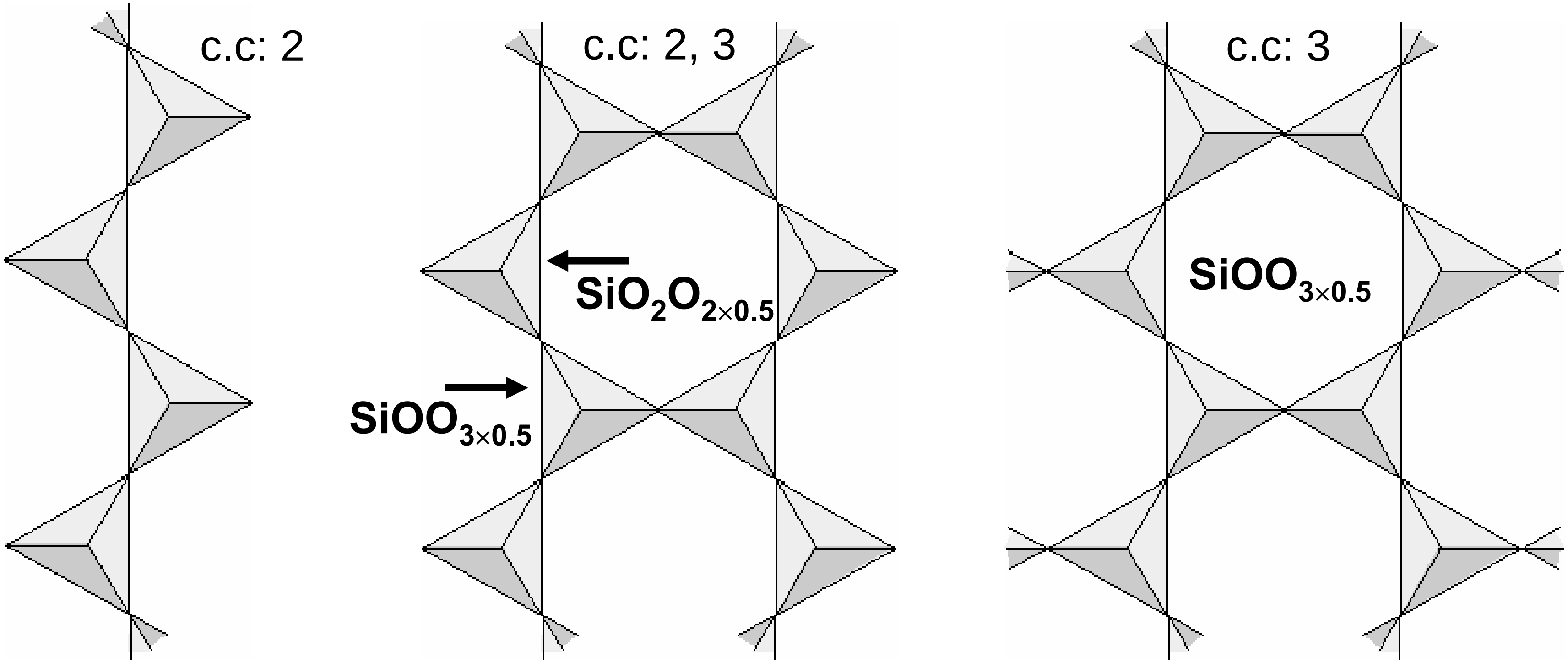
Sorosilicates

$Si_2O_7^{6-}$
Thortveitite: $(Sc,Y)_2Si_2O_7$

Cyclosilicates

SiO_3^{2-}
Beryl: $Be_3Si_6O_{18}$

2.3 Basic structure types
Oxides: Silicates- overview 2



$SiO_2O_{2\times0.5}$

Inosilicates

Phyllosilicates

single chain: SiO_3^{2-}
Pyroxene: $(Mg,Fe)SiO_3$

double chain: $Si_4O_{11}^{6-}$
Tremolite:
$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$

$Si_2O_5^{2-}$
Biotite: $K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$

2.3 Basic structure types
Oxides: Silicates- overview 3

Tectosilicates c.c: 4, SiO_2, Faujasite: $Ca_{28.5}Al_{57}Si_{135}O_{384}$

Pores Pores

$$A_{x/n}\underbrace{[Si_{1-x}Al_xO_2}]\bullet mH_2O$$

T (= Si, Al)O_4-Tetrahedra sharing all corners,
isomorphous exchange of Si^{4+}, charge compensation

x: Al content, charge of microporous framework, n: charge of A

Zeolites

- Alumosilicates with open channels or cages (d < 2 nm, “boiling stones”)
- Numerous applications: adsorbent, catalysis…

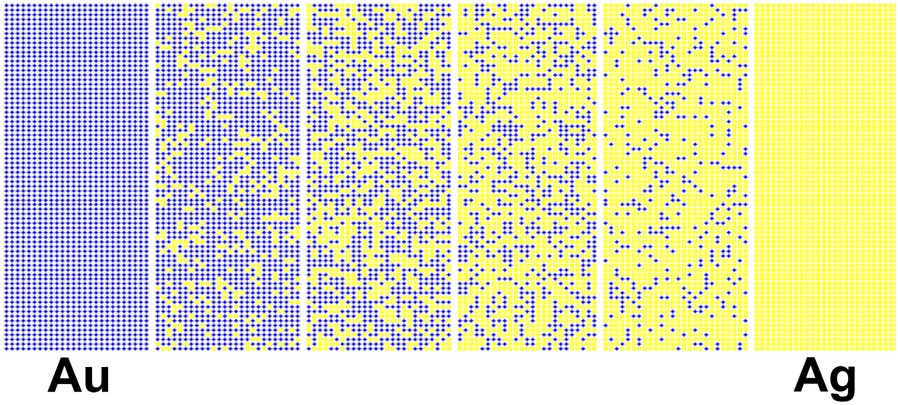
2.3 Basic structure types
Intermetallics- overview

Solid solutions: random arrangement of species on the same position

Examples: Rb_xCs_{1-x} BCC, Ag_xAu_{1-x} CCP

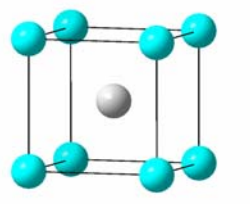
The species must be related

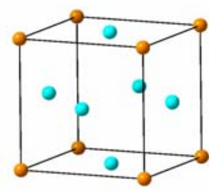
- **Chemically related species**
- **Small difference in electronegativity**
- **Similar number of valence electrons**
- **Similar atomic radius**
- **(High temperature)**

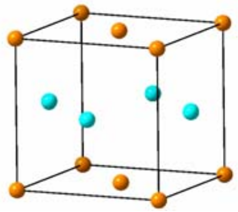


Ordered structures: from complex building units to complex structures

Exception: simple structures







3.

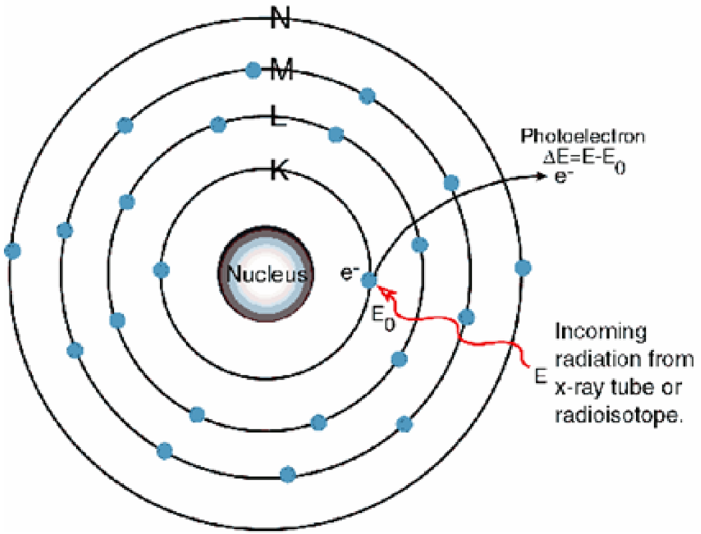
Characterization of Solids

4. Introduction
Noble prizes associated with X-ray diffraction

- 1901 W. C. Roentgen (Physics) for the discovery of X-rays.
- 1914 M. von Laue (Physics) for X-ray diffraction from crystals.
- 1915 W. H. and W. L. Bragg (Physics) for structure derived from X-ray diffraction.
- 1917 C. G. Barkla (Physics) for characteristic radiation of elements.
- 1924 K. M. G. Siegbahn (Physics) for X-ray spectroscopy.
- 1927 A. H. Compton (Physics) for scattering of X-rays by electrons.
- 1936 P. Debye (Chemistry) for diffraction of X-rays and electrons in gases.
- 1962 M. Perutz and J. Kendrew (Chemistry) for the structure of hemoglobin.
- 1962 J. Watson, M. Wilkins, and F. Crick (Medicine) for the structure of DNA.
- 1979 A. Cormack and G. Newbold Hounsfield (Medicine) for computed axial tomography.
- 1981 K. M. Siegbahn (Physics) for high resolution electron spectroscopy.
- 1985 H. Hauptman and J. Karle (Chemistry) for direct methods to determine structures.
- 1988 J. Deisenhofer, R. Huber, and H. Michel (Chemistry) for the structures of proteins that are crucial to photosynthesis.

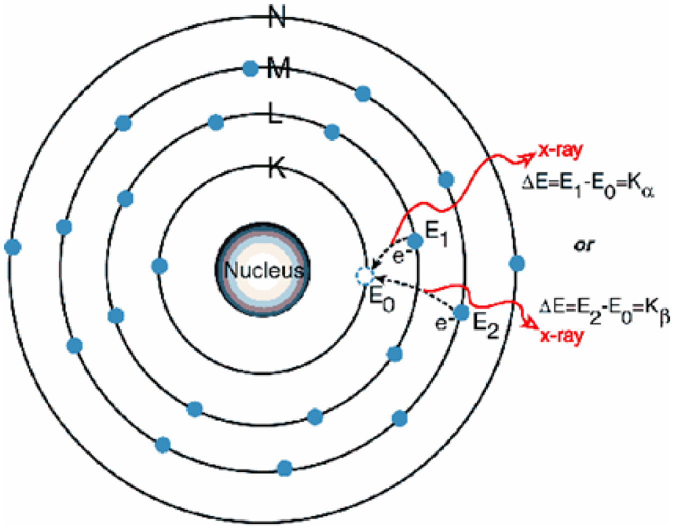
4.1 Diffraction

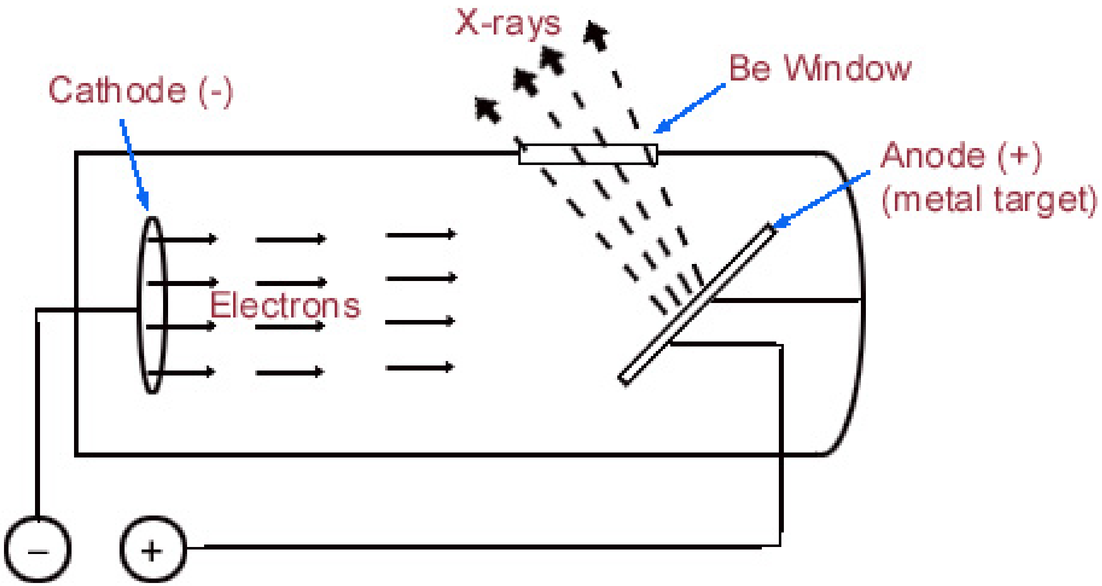
Generation of X-rays



Atomic scale scenario

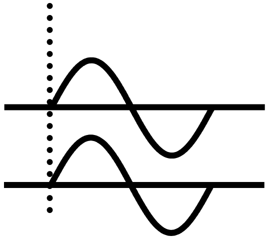
- Inner shell electrons are striked out
- Outer shell electrons fill hole
- Production of X-rays due to energy difference between inner and outer shell electron



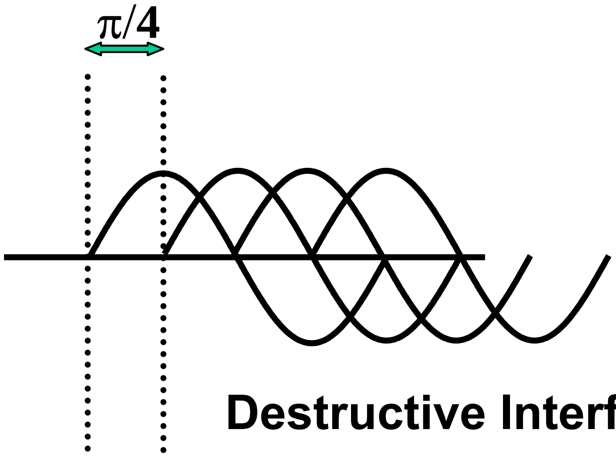


X-ray tube

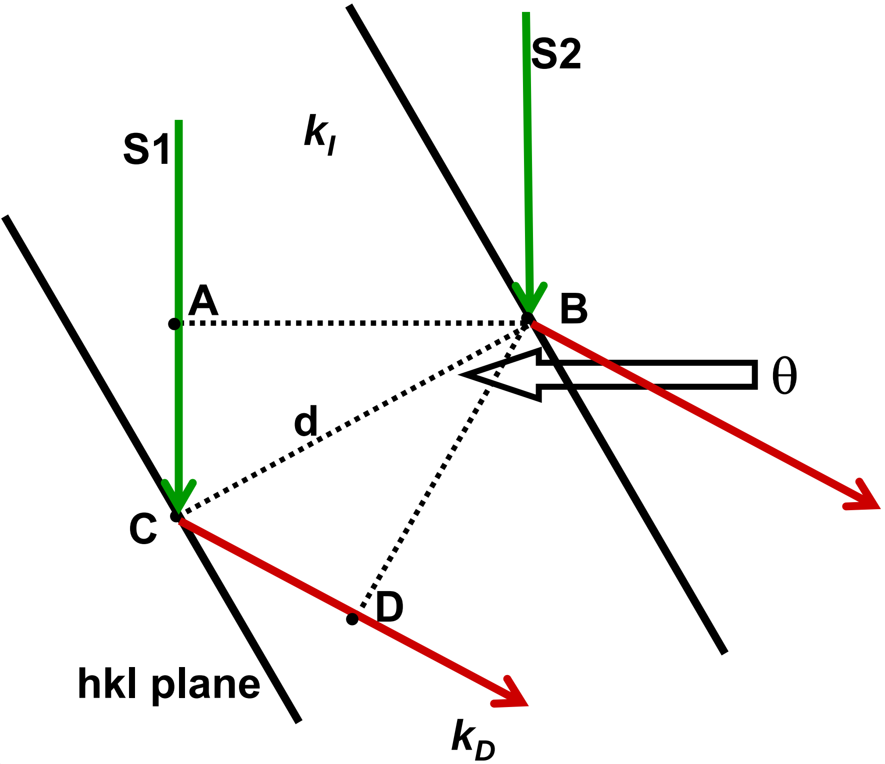
4.1 Diffraction
Geometrical approach, Bragg's law (BL)



Constructive Interference



Destructive Interference



$$AC + CD = n\lambda = 2d\sin\theta_B$$

$$2\sin\theta_B/\lambda = n/d = n|d^*|$$

4.1 Diffraction
Results of diffraction studies- Overview

Lattice parameters

Position of the reflections (Bragg's law), e. g. $(1/d)^2 = (1/a)^2 [h^2 + k^2 + l^2]$

Symmetry of the structure

Intensity of the reflections and geometry of DP = symmetry of DP

Identification of samples (fingerprint)

Structure, fractional coordinates…:

Intensity of the reflections, quantitative analysis (solution and refinement)

Crystal size and perfection

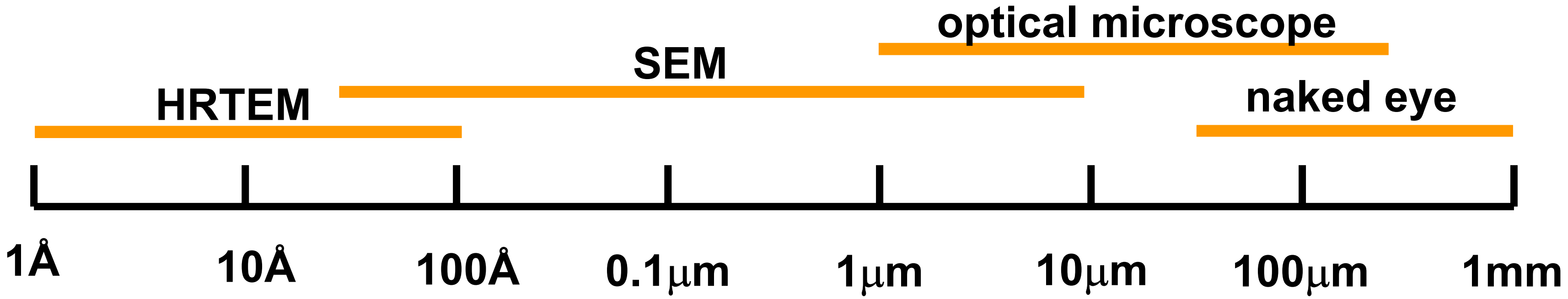
Profile of the reflections

Special techniques

- Electron diffraction: highly significant data, SAED (DP of different areas of one crystal)
- Neutron diffraction: localization of H, analyses of magnetic structures
- Synchrotron: small crystals, large structures (protein structures)

4.2 Imaging
Optical microscopy and SEM- Possibilities

- **Analysis of the homogeneity of the sample (color…)**
- **Selection of single crystals for structure determination**
- **Determination of the crystal class by analyzing the morphology**
- **Analysis of peculiar features of the morphology (steps, kinks…)**
- **SEM: Determination of the stoichiometry (EDX, cf. X-ray tube)**



optical microscope

SEM

HRTEM

naked eye

1Å 10Å 100Å 0.1μm 1μm 10μm 100μm 1mm

4.2 Imaging
TEM- Basics of physics

Light microscope

Disadvantage: low resolution

Abbe (Theory of light microscops resolution)

The smaller the wavelength, the higher the resolution

De Broglie (Electrons as waves)

Fast electrons possess small wavelength

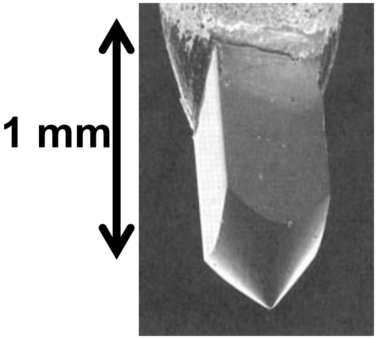
Consequence: Microscopy with high-energy radiation

Consequence: Microscopy with “fast electrons”

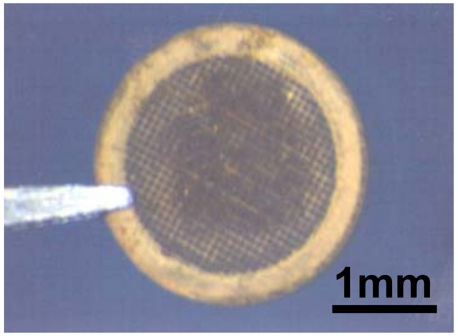
Advantage of electrons: negative charge

Acceleration and focusing in magnetic or electric fields

4.2 Imaging
TEM- Basics of Hardware

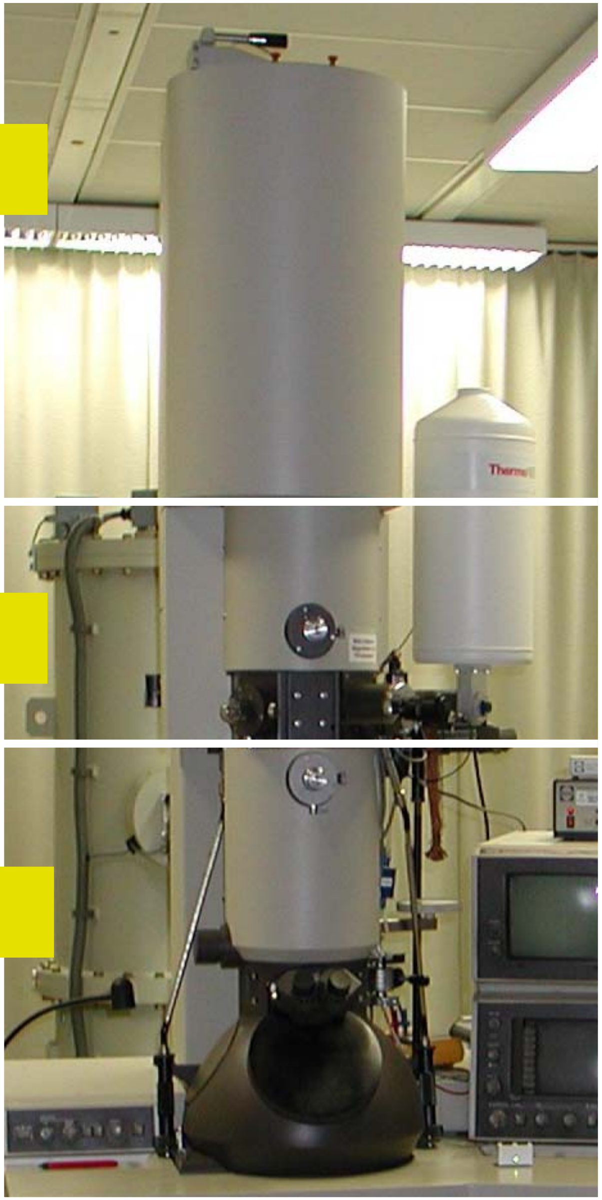


Beam formation



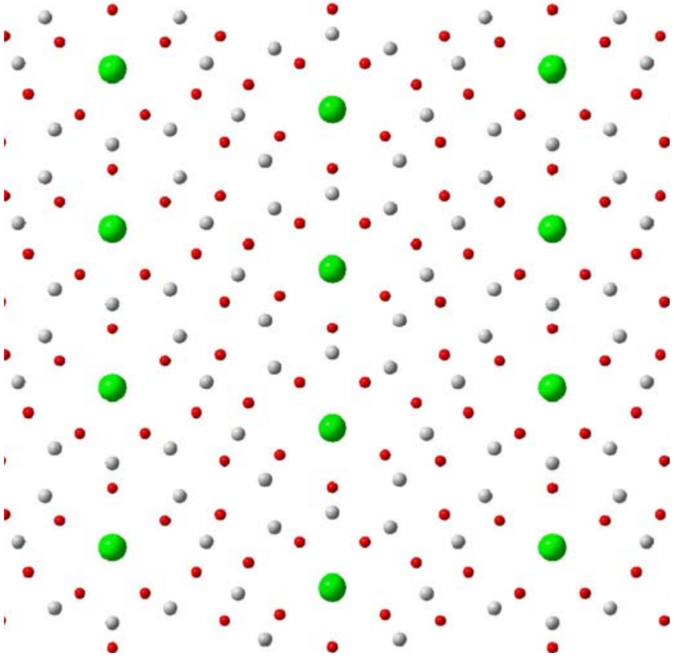
Interactions

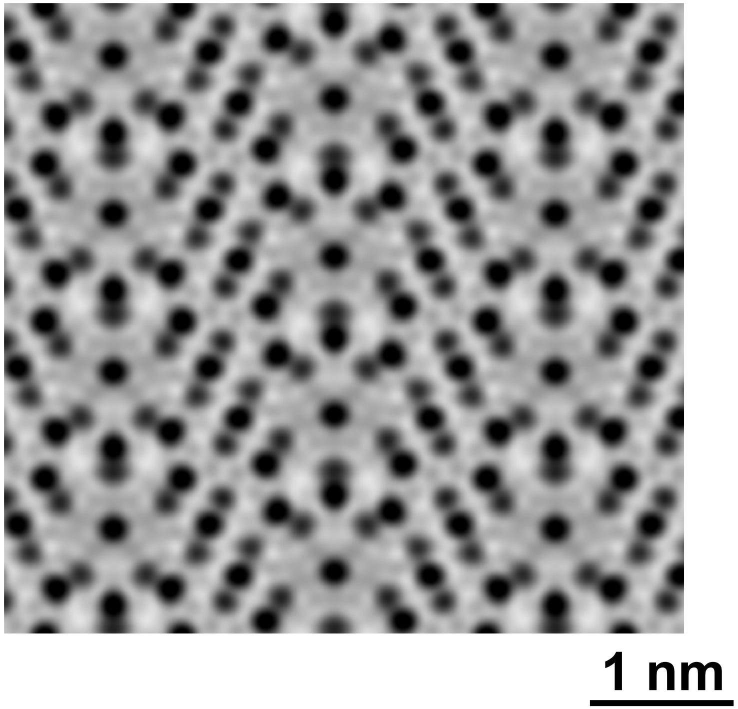
Focusing



HRTEM- Basics

Imaging of real structures on the atomic scale (HRTEM)





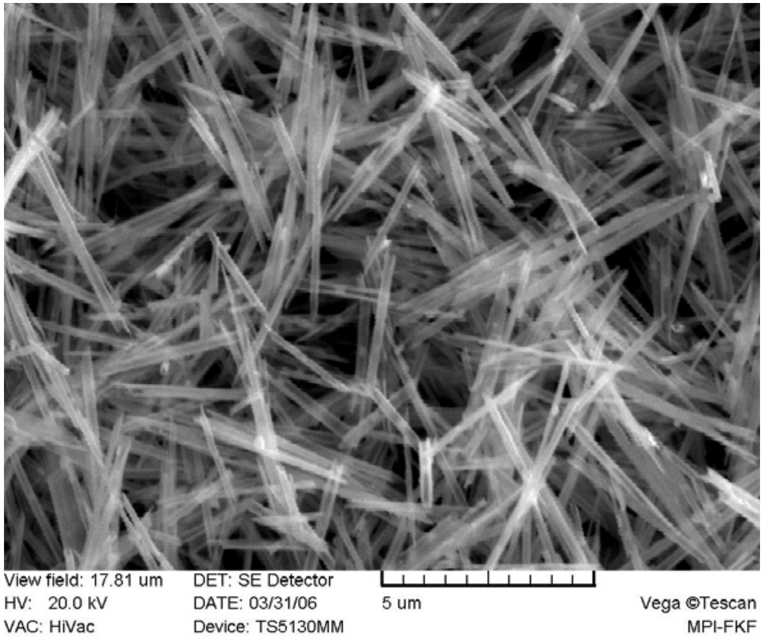
Black dots: positions of atoms
White dots: positions of cavities of the structure

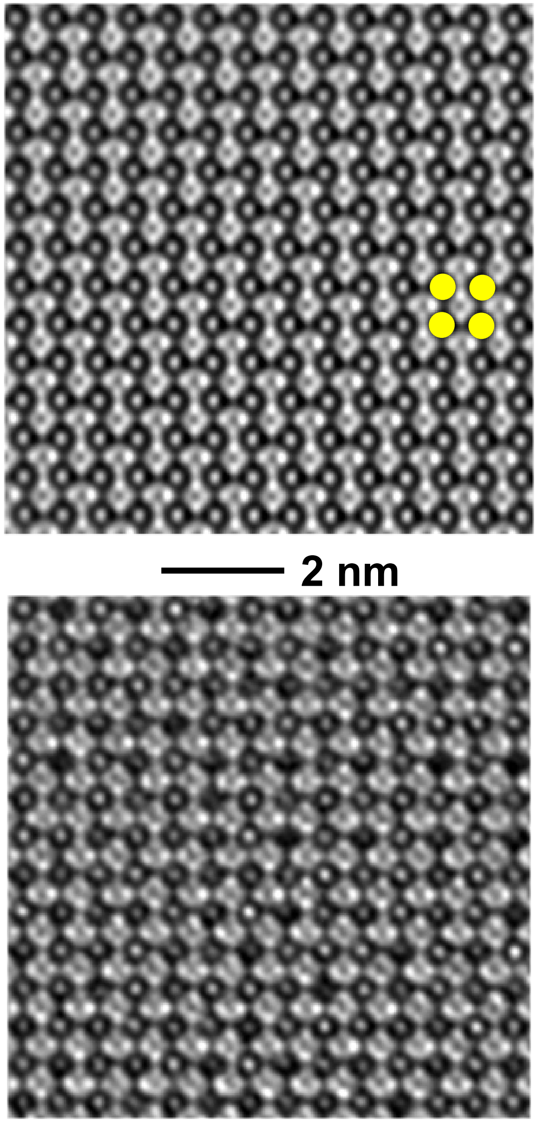
4.

Synthesis

4. Introduction
Goals of synthesis / preparation

- **Synthesis of new compounds**
- **Synthesis of highly pure, but known compounds**
- **Synthesis of highly pure single crystals (Iceberg-principle)**
- **Structural modification of known compounds bulk-structures and nanostructures**





4.1 HT-synthesis
Introduction

Standard procedure:

“Shake and bake”, “heat and beat”, “trial and error”

“The starting materials are finely grinded, pressed to a pellet and heated to a temperature „near“ the melting temperature.”

Parameters influencing the reaction:

- **Purity of educts (sublimation)**
- **Handling of educts (glove box, Schlenck technique)**
- **Temperature: T(reaction) > 2/3 T(melting point), rule of Tamann. Effects on real structure (more defects at elevated T) and diffusion (increase with T)**
- **Solid state reactions are exothermic, “thermodynamically controlled“: Consequence: No metastable products (see e.g. Zeolites)**
- **Porosity, grain size distribution and contact planes: High reactivity of nanoparticles / colloids (low CN)**

4.1 HT-synthesis
Practical work

Experimental consequences:

(1) large contact areas
(2) small path lengths
(3) small pore volume

Reactive sintering:
pellets of fine powders

Problems / Pitfalls:

- "Chemical problems" of containers materials: use of reactive materials remedy: double / coated containers
- "Physical problems" of containers: compatible expansion/compression coefficients, sufficiently stable to withstand pressure
- Separation of educts, remedy: special furnaces, reduced free volume, tricks
- No intrinsic purification processes

Ex.: $2\ Li_2CO_3 + SiO_2 \rightarrow Li_4SiO_4 + 2CO_2$ (800 °C, 24 h)

- Li-compounds are highly reactive against containers (use of Au)
- Production of a gas, consequence: cracking of containers

4.1 HT-synthesis
Tricks

- **Application of a "gaseous solvent" *chemical* or *vapour phase transport***

  Ex.: $Cr_2O_3(s) + 3/2\ O_2(g) \rightarrow 2\ CrO_3(g)$

  $MgO(s) + 2\ CrO_3(g) \rightarrow MgCr_2O_4(s) + 3/2\ O_2(g)$

- **Separation of educts in a temperature gradient (to avoid explosions)**

  Ex.: $2\ Ga(l) + 3\ S(g) \rightarrow Ga_2S_3(g)$

- **Use of precursors for reactive educts**

  Ex.: Thermal decomposition of MN_3 (M = Na, K, Rb, Cs)

  Thermal release of reactive gases: (O_2: MnO_2, CO_2: $BaCO_3$, H_2: LnH_2)

  Coprecipitation and thermal decomposition (e.g. oxalates to oxides)

- **Use of fluxes**

  Ex.: $Li_2CO_3 + 5\ Fe_2O_3 \rightarrow 2\ LiFe_5O_8 + CO_2(g)$ (incompl. :grind-fire-regrind, etc.)

  Or: Flux of Li_2SO_4/Na_2SO_4 (dissolves Li_2CO_3, remove flux with water)

- **Metathesis reaction**

  Ex.: $2GaCl_3 + 3Na_2Te \rightarrow Ga_2Te_3 + 6NaCl$, very exothermic!

4.2 CVT

Introduction

A <u>solid</u> is <u>dissolved</u> in the <u>gas phase</u> at one place (T=T1) by reaction with a <u>transporting agent</u> (e.g. I_2). At another place (T=T2) the solid is <u>condensed</u> again. Use of a temperature gradient.

$$ZnS(s) + I_2(g) = ZnI_2(s) + S(g)$$

- Used for purification and synthesis of single crystals (fundamental research)
- Reactions with large absolute value of ΔH° gives no measurable transport
- The sign of ΔH° determines the direction of transport:

  exothermic reactions: transport from cold to hot
  endothermic reactions: transport from hot to cold.

4.2 CVT Examples

- Mond-process: $Ni(s) + 4\ CO(g) = Ni(CO)_4(g)$
  $\Delta H° = -300$ kJ/mol, transport from 80° to 200°C

- Van Arkel / De Boer: $Zr(s) + 2\ I_2(g) = ZrI_4(g)$; (280 to 1450 °C)

- $Si(s) + SiX_4(g) = 2\ SiX_2(g)$; (1100° to 900°)

- Mixtures of Cu and Cu_2O:
  $3\ Cu(s) + 3\ HCl(g) = Cu_3Cl_3(g) + (3/2)\ H_2(g)$; (High T to Low T)
  3/2 Cu2O(s) + 3 HCl(g) = $Cu_3Cl_3(g) + 3/2\ H_2O(g)$; (Low T to High T)

- Transport of $Cu_2O(s)$:
  $3/2\ Cu_2O(s) + 3\ HCl(g) = Cu_3Cl_3(g) + 3/2\ H_2O(g)$; (Low T to High T)
  $Cu_2O(s) + 2\ HCl(g) = 2\ CuCl(g) + H_2O(g)$; (High T to Low T)