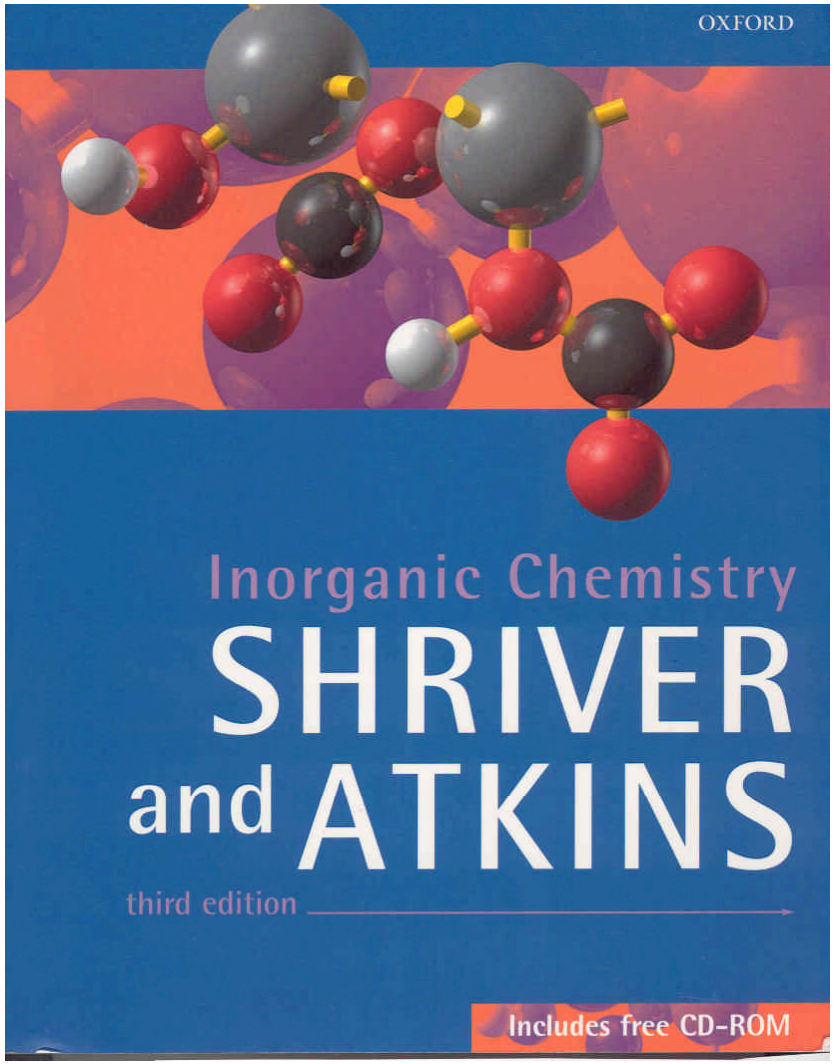
Advanced Inorganic Chemistry (Part 1)
Basic Solid State Chemistry
WS 05/06

(H.J. Deiseroth)

Topics of the complete lecture

- **Introduction – special aspects of the solid state**
- **Structure of solids**
- **Basic crystallography**
- **Characterization of solids: diffraction techniques, electron microscopy, spectroscopy, thermal analysis**
- **Bonding in solids**
- **Real structure of crystals, defects**
- **Electrical, magnetic and optical properties**
- **Synthesis of solids**
- **Structure-property relations**

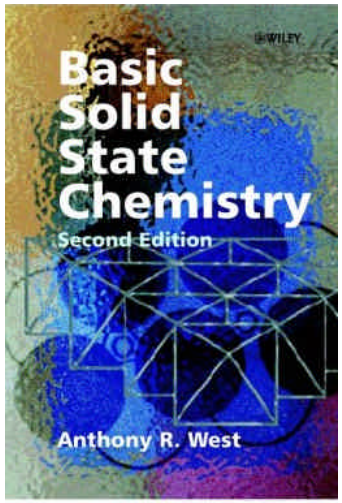
Resources


OXFORD
Inorganic Chemistry
SHRIVER
and ATKINS
third edition
Includes free CD-ROM

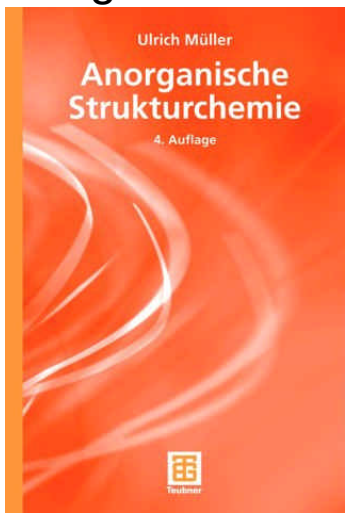
Resources

Textbooks: **Shriver, Atkins, *Inorganic Chemistry* (3rd ed, 1999)**
W.H. Freeman and Company (Chapter 2, 18 ...)

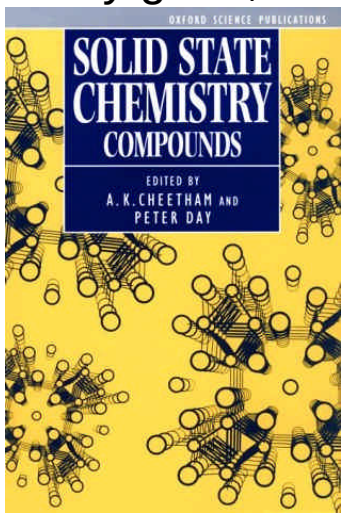
recommendation

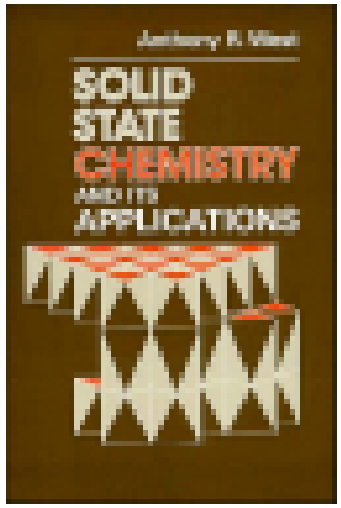


german



very good, but not basic level



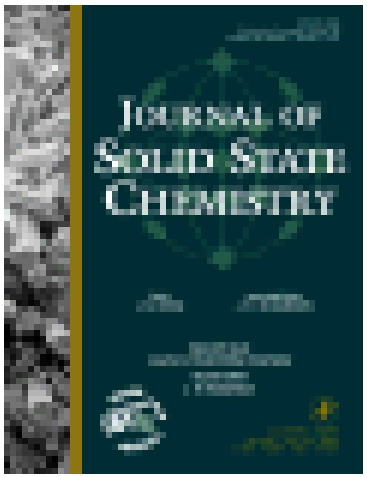


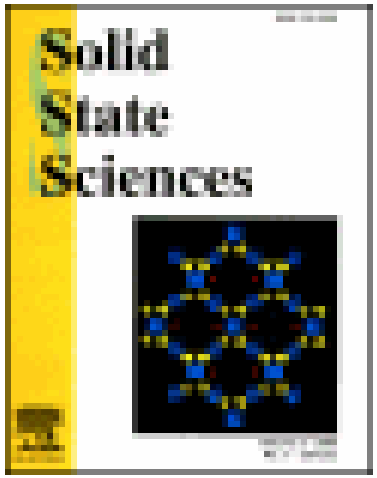
Internet resources

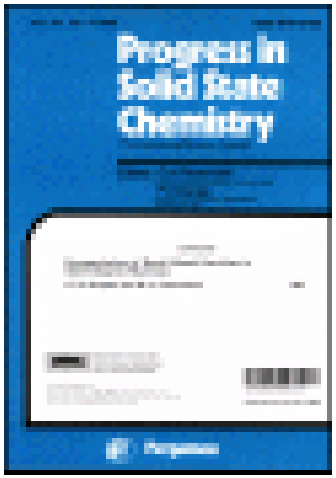
- **http://ruby.chemie.uni-freiburg.de/Vorlesung/ (german)**
- **http://www.chemistry.ohio-state.edu/~woodward/ch754... (pdf-downloads)**
- **IUCR-teaching resources (International Union for Crystallography, advanced level)**

Resources

Journals







Outline - 15.10.04

1. Introduction
2. Structure of solids
   - 2.1 Basics of structures
   - 2.2 Simple close packed structures: metals
   - 2.3 Basic structure types (structure of simple salts)
   - 2.4 More complex structures
   - 2.5 Complex structures

   } Oxides...

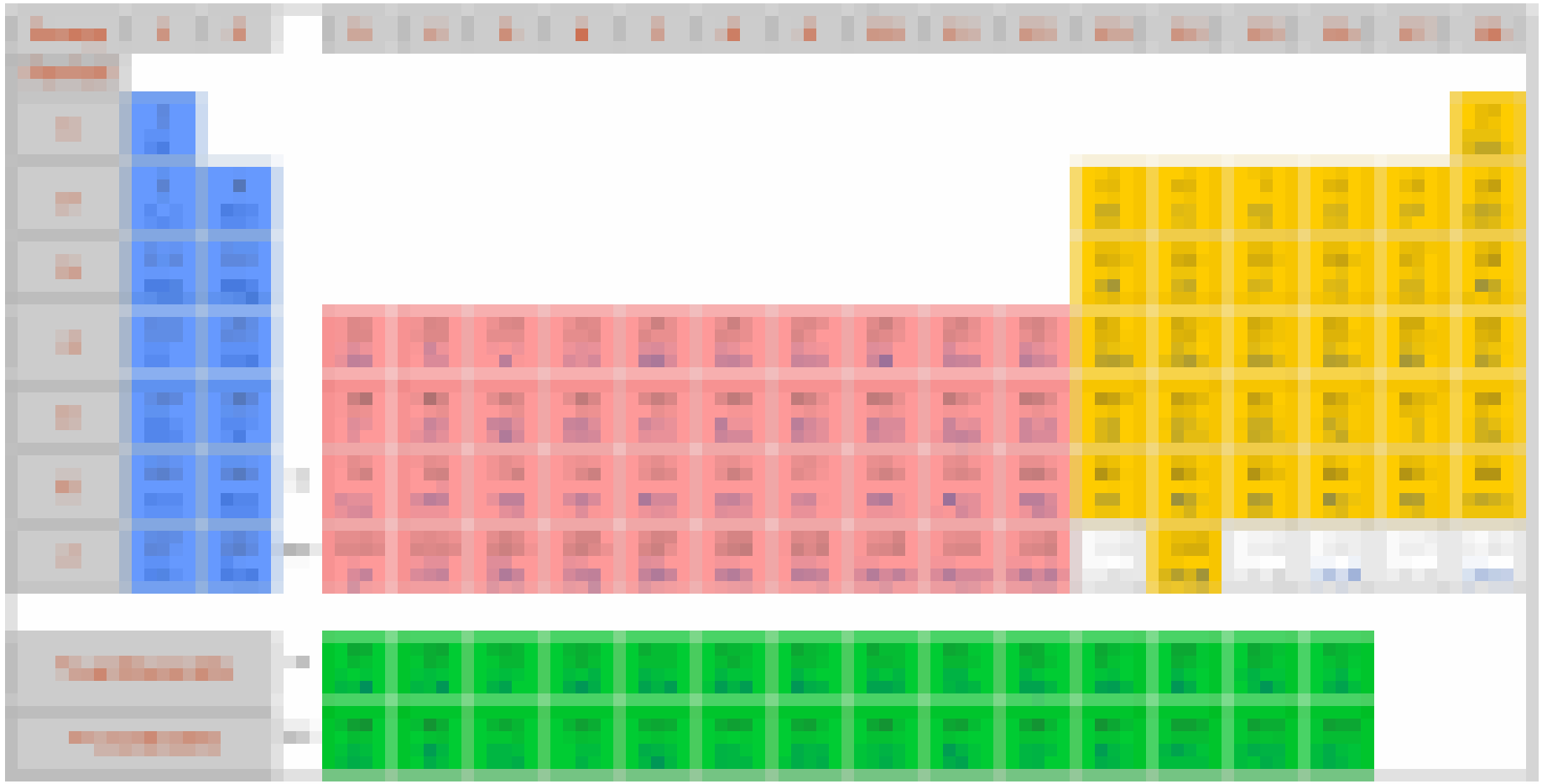
   - 2.6 Structure of nanomaterials

1.

Introduction

1.Introduction
Why is the solid state interesting?

Most elements are solid at room temperature



1. Introduction
Special aspects of solid state chemistry

- Close relationship to solid state physics
- 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
  - 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**
  - **conductivity: metals, semiconductors, insulators, superconductors…**
  - **magnetism: ferromagnetism, paramagnetism…**
- **Structure and Symmetry**
  - **packing of atoms: close packed structure (high space filling)**
  - **characteristic symmetry elements: cubic, hexagonal…**

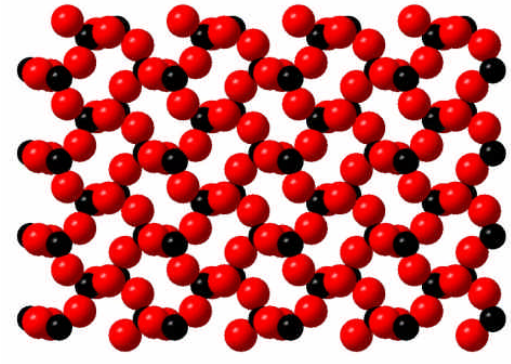
2.

Basic Structures

2.1 Basics of Structures
Visualization of structures

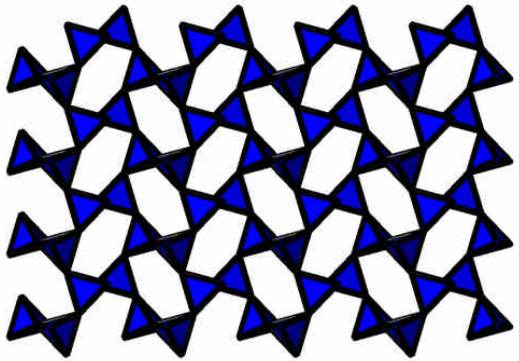
Example: Cristobalite (SiO_2)

Description of packing



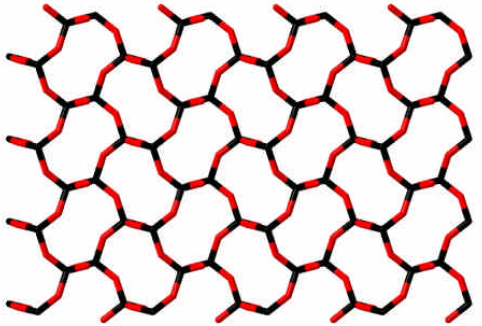
Bragg jun. (1920)
Sphere packing

Description of environment



Pauling (1928)
Polyhedra

Description of topology

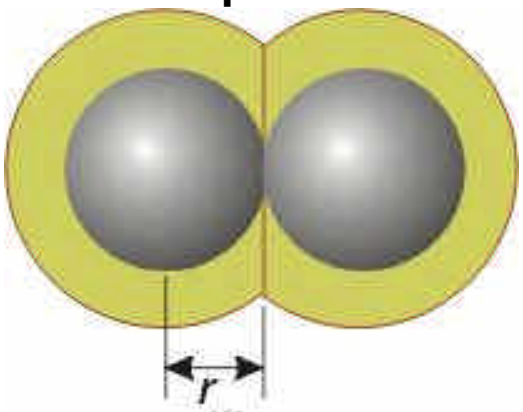


Wells (1954)
3D nets

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

Concepts for the radius of the spheres

element or compounds

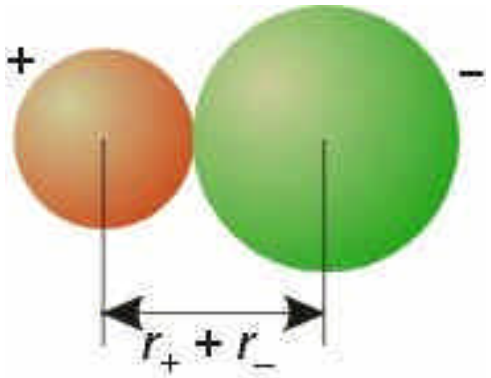


2 Covalent radius

=

d/2 of single bond in molecule

compounds only

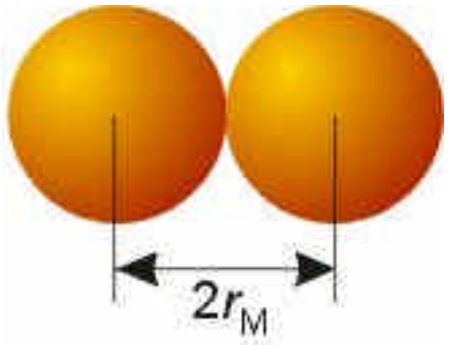


3 Ionic radius

=

d – r(F, O…)
problem: reference!

elements or compounds („alloys“)

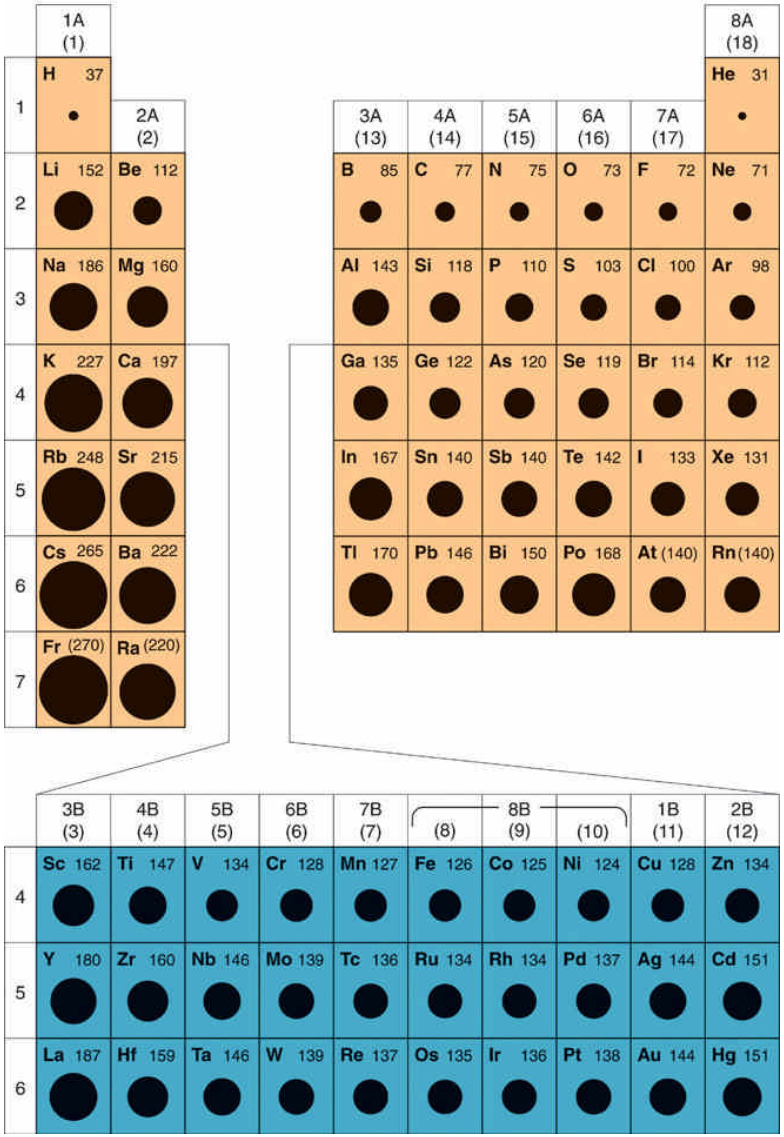


1 Metallic radius

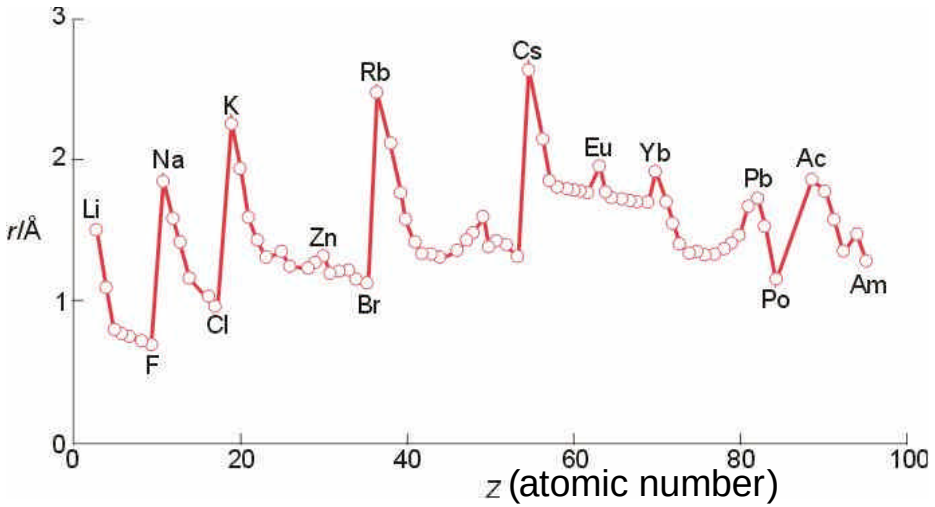
=

d/2 in metal

2.1 Basics of Structures
Trends of the atomic radius



- **atomic radii increase on going down a group.**
- **atomic radii decrease across a period**
- **particularities: Ga < Al (d-block)**

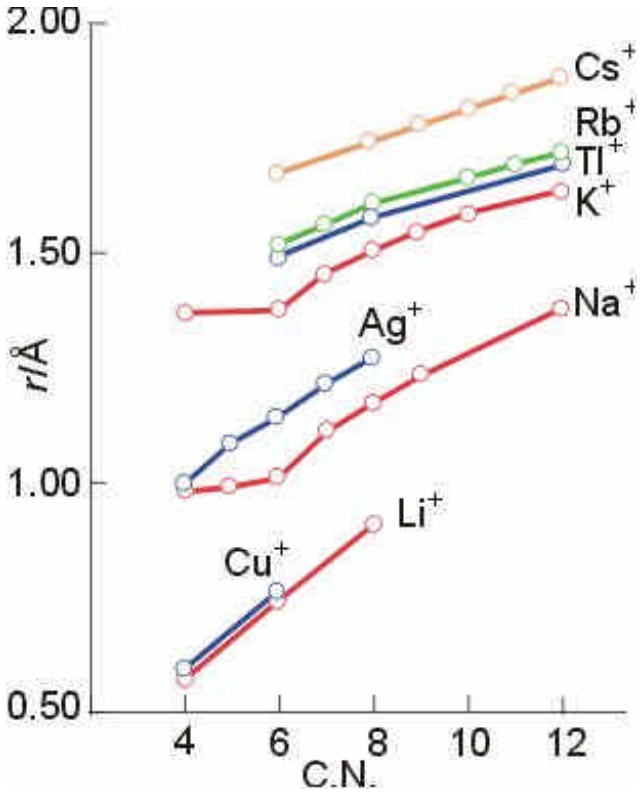


2.1 Basics of Structures
Trends of the ionic radii

- ionic radii increase on going down a group
- radii of equal charge ions decrease across a period

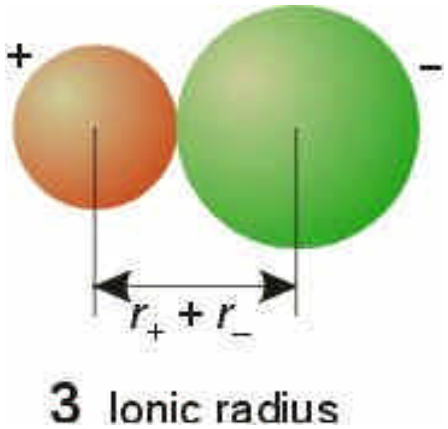
} cf. atomic radii

- ionic radii increase with increasing coordination number (the higher its CN the bigger the ions seems to be !!)
- the 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: $r(Cs^{+}) > r(F^{-})$)



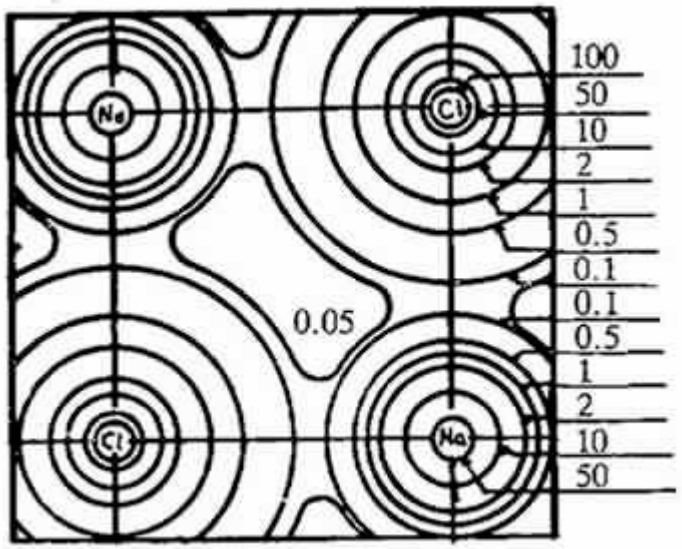
2.1 Basics of Structures
Determination of the ionic radius

Ionic radius = d – r(F, O…)



3 Ionic radius

Structure analyses, most important method: X-ray diffraction

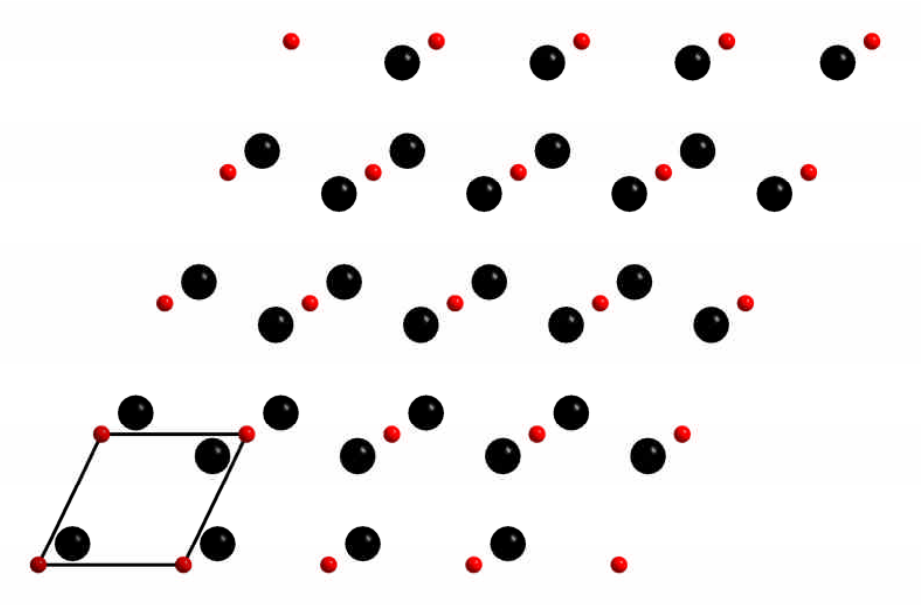


L. Pauling:

- **Radius of one ion is fixed to a reasonable value ($r(O^{2-}) = 140$ pm)**
- **That value is used to compile a set of self consistent values for other ions.**

2.1 Basics of Structures
Structure and lattice – what is the difference?

Example:
structure and lattice
in 2D

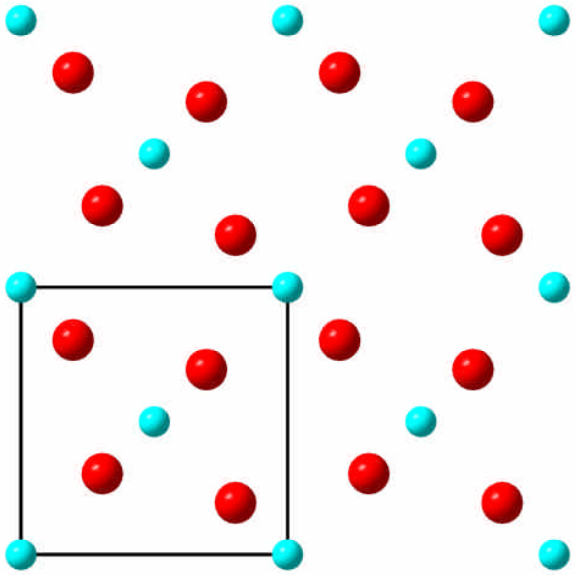


- **Lattice**
  - **pattern of points**
  - **no chemical information, mathematical description**
  - **no atoms, but points and lattice vectors (a, b, c, α, β, γ), unit cell**
- **Motif (characteristic structural feature, atom, group of atoms…)**
- **Structure = Lattice + Motif**
  - **contains chemical information (e. g. environment, bond length…)**
  - **describes the arrangement of atoms**

2.1 Basics of Structures
Unit cell

Unit Cell (interconnection of lattice and structure)

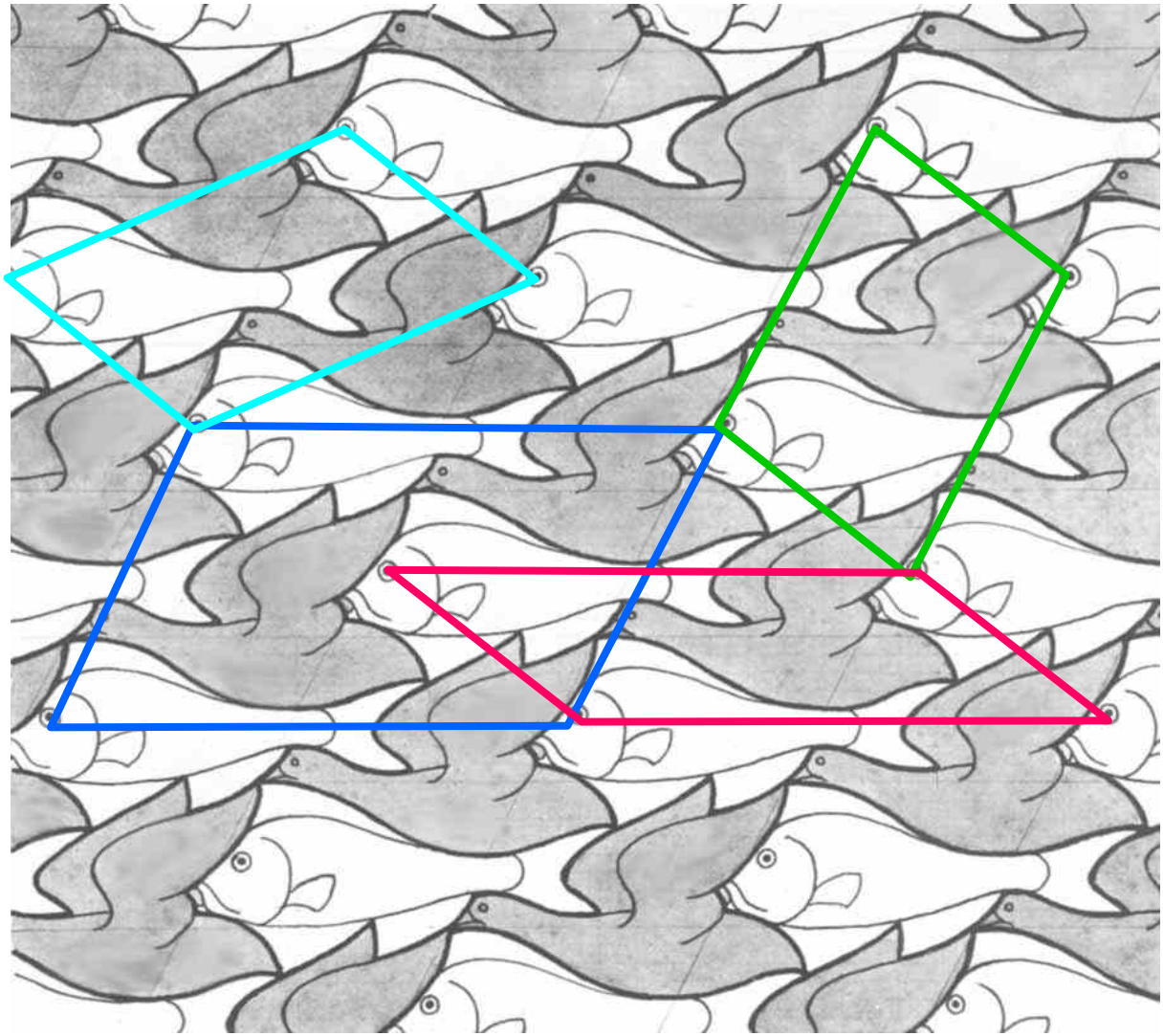
- **an parallel sided region of the lattice from which the entire crystal can be constructed by purely translational displacements**
- **<u>contents of unit cell represents chemical composition</u> (multiples of chemical formula)**
- **primitive cell: simplest cell, contain one lattice point**



2.1 Basics of Structures
Unit cell – which one is correct?

Conventions:

1. Cell edges should, whenever possible, coincide with symmetry axes or reflection planes
2. The smallest possible cell (the reduced cell) which fulfills 1 should be chosen



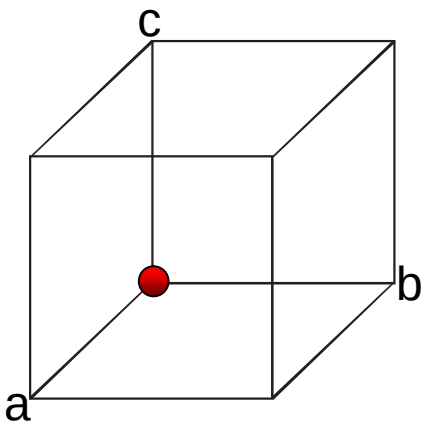
2.1 Basics of Structures
Unit cells and crystal system

- millions of structures but 7 crystal systems
- crystal system = particular restriction concerning the unit cell
- crystal system = unit cell with characteristic symmetry elements (later)

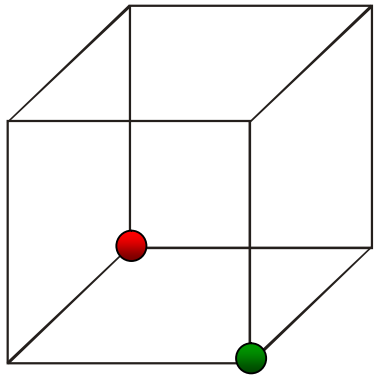
Crystal system	Restrictions axes	Restrictions angles
Triclinic	-	-
Monoclinic	-	$\alpha = \gamma = 90°$
Orthorhombic	-	$\alpha = \beta = \gamma = 90°$
Tetragonal	a = b	$\alpha = \beta = \gamma = 90°$
Trigonal	a = b	$\alpha = \beta = 90°,\ \gamma = 120°$
Hexagonal	a = b	$\alpha = \beta = 90°,\ \gamma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

2.1 Basics of Structures
Indices of directions in space

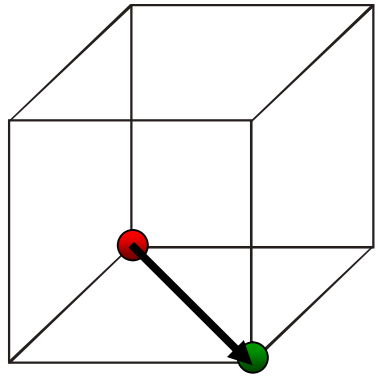
"[110]", square brackets for directions
Procedure in three steps



1. Select 000



2. Mark position of second point

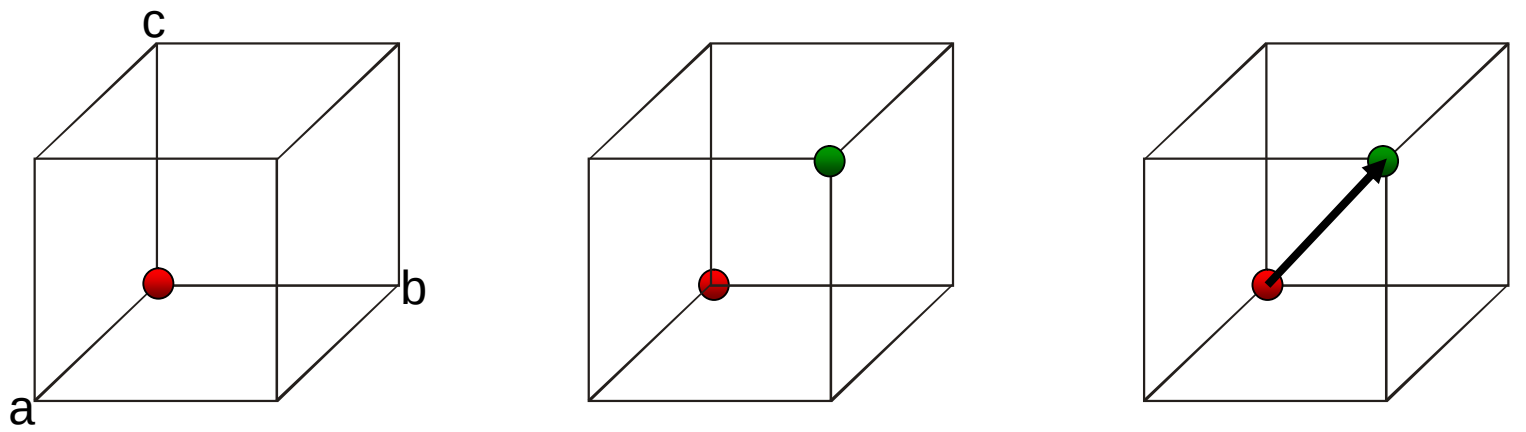


3. Draw vector

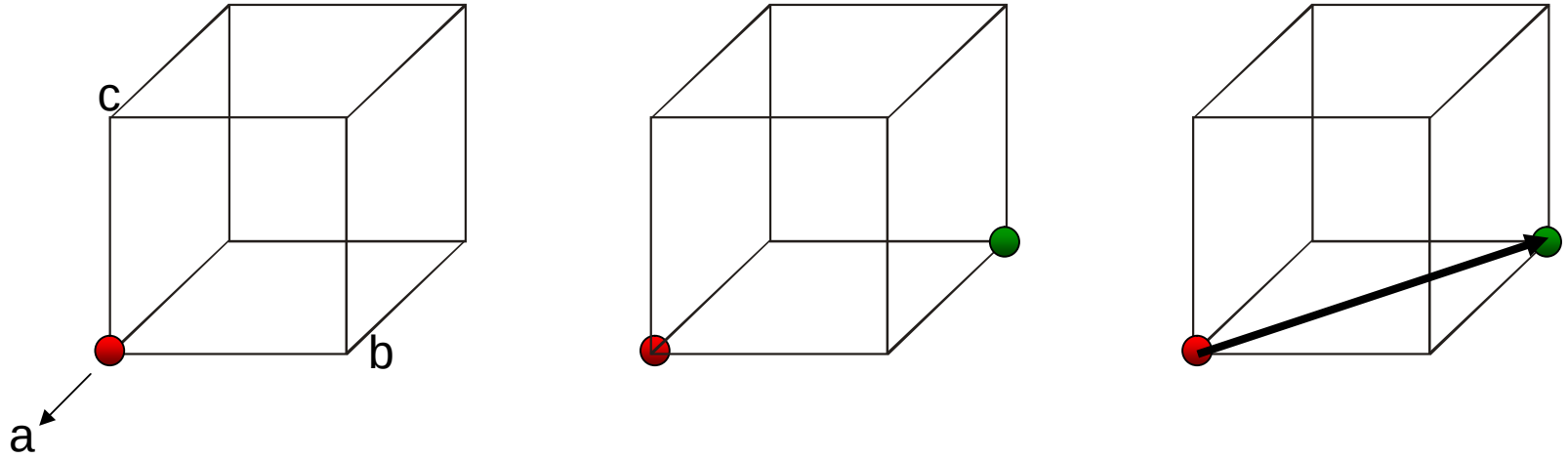
Convention: right-handed coordinate system
- **middle finger: a**
- **forefinger: b**
- **thumb: c**

2.1 Basics of Structures
Indices of directions in space – examples

[111]

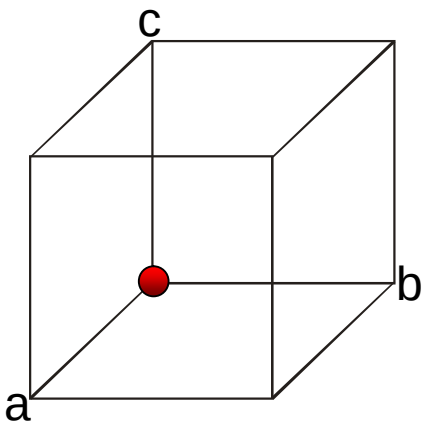


[$\bar{1}$10]

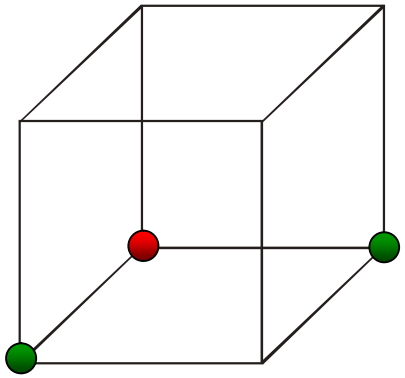


2.1 Basics of Structures
Indices of planes in space

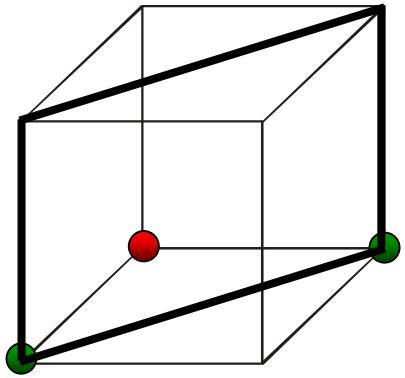
"(110)" <u>round brackets for planes</u>
Procedure in three steps



1. Select 000



2. Mark intercept (1/h 1/k 1/l) of the axes (if possible)

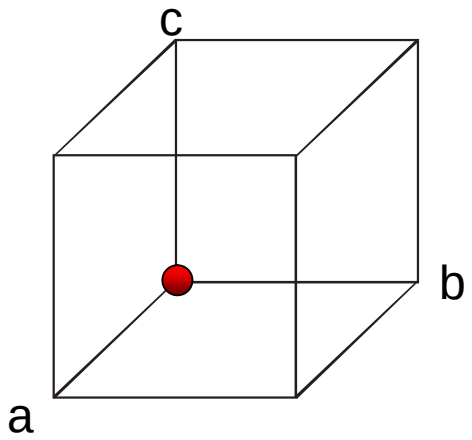


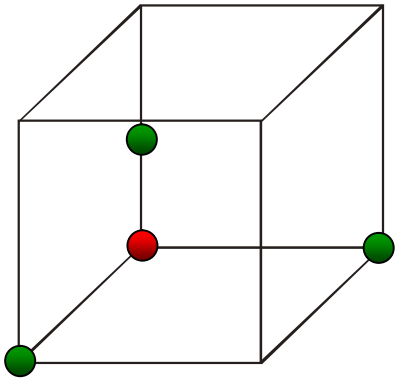
3. Draw plane

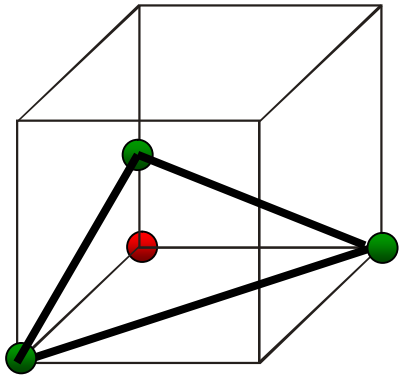
Convention: right-handed coordinate system

2.1 Basics of Structures
Indices of planes in space – examples

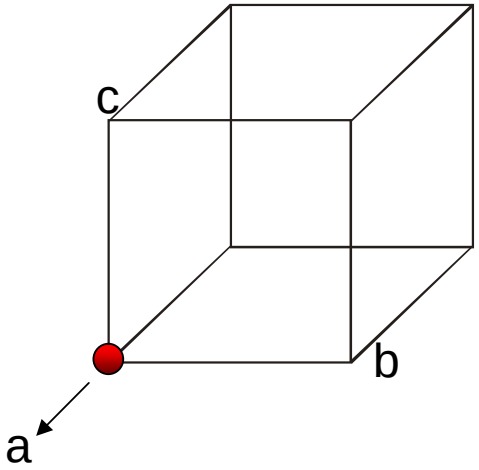
(112)

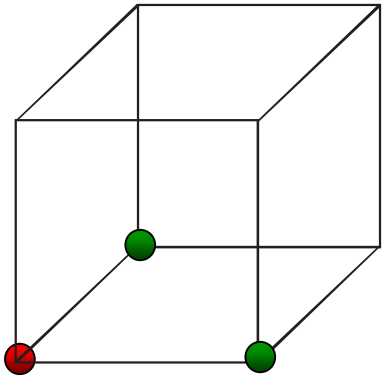


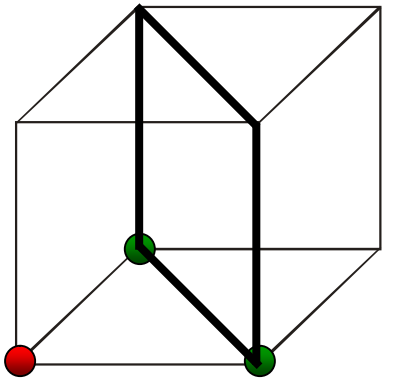




($\bar{1}$10)







2.1 Basics of Structures
Fractional coordinates

- **Rules for marking the position of an atom in a unit cell:**
  - **fractional coordinates are related to directions**
  - **possible values for x, y, z: [0; 1]**
  - **atoms are generated by symmetry elements**
  - **negative values: add 1.0, values > 1.0: substract 1.0 (or multiples)**

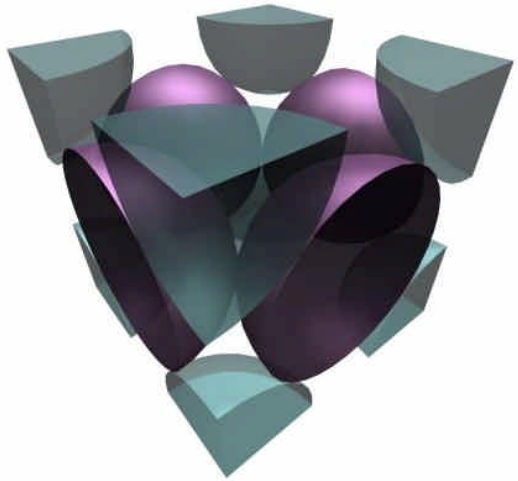
- **Example: Sphalerite (Zincblende)**

factional coordinates

- **Equivalent points are represented by one triplet only**
  - **equivalent by translation**
  - **equivalent by other symmetry elements, later**

2.1 Basics of Structures
Number of atoms per unit cell (Z)

- **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**



Example 1: Sphalerite

number of atoms 1

Example 2: Wurzite

number of atoms 2

- **Wyckoff-notation: number of particular atom per unit cell**

2.1 Basics of Structures
Wyckoff-notation - example

Crystal data

Formula sum	Mg_2SiO_4 (Olivine)
Crystal system	orthorhombic
Space group	*P* b n m (no. 62)
Unit cell dimensions	*a* = 4.75(2) Å, *b* = 10.25(4) Å, *c* = 6.00(2) Å
Z	4

Atomic coordinates

Atom	**Ox.**	**Wyck.**	**x**	**y**	**z**
Mg1	+2	4*a*	0.00000	0.00000	0.00000
Mg2	+2	4*c*	0.00995(600)	0.27734(600)	0.75000
Si1	+4	4*c*	0.07373(500)	0.4043(50)	0.25000
O1	-2	4*c*	0.23242(1000)	0.0918(100)	0.75000
O2	-2	4*c*	0.2793(100)	0.05078(1000)	0.25000
O3	-2	8*d*	0.22266(1000)	0.33594(1000)	0.46289(1000)

2.1 Basics of Structures
Wyckoff-notation and occupancy-factors

Crystal data

Formula sum	$Cu_{0.8}\,In_{2.4}\,Se_4$
Crystal system	tetragonal
Space group	*I* -4 2 m (no. 121)
Unit cell dimensions	*a* = 5.7539(3) Å *c* = 11.519(1) Å
Z	2

Atomic coordinates

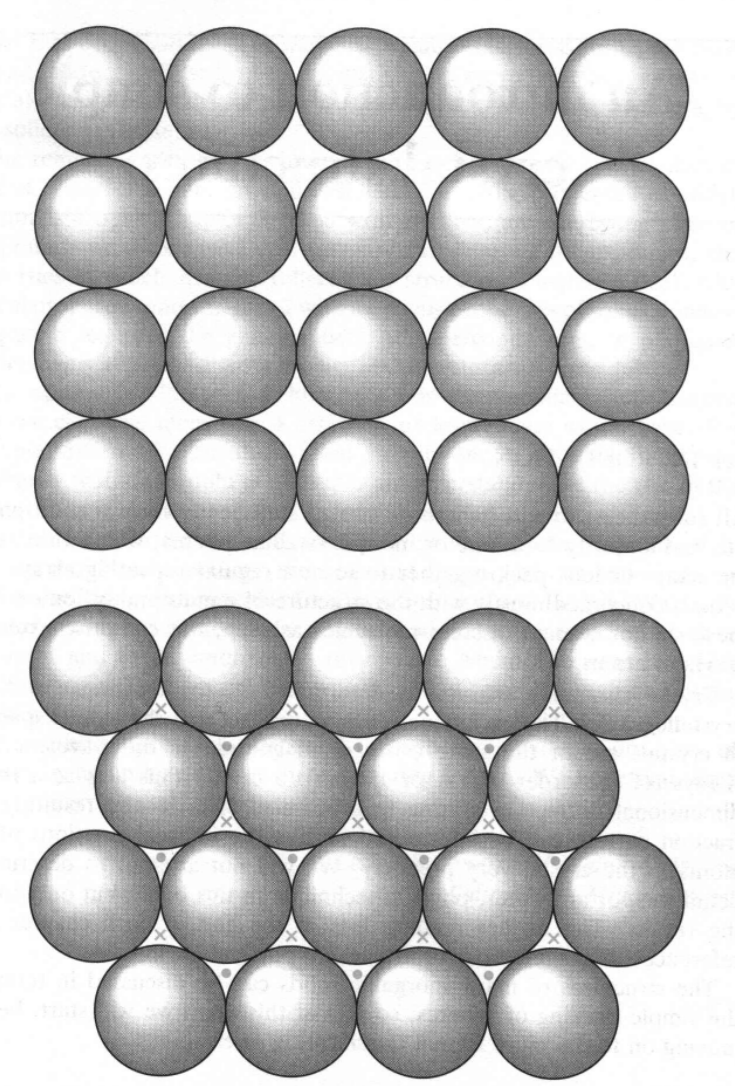
Atom	**Ox.**	**Wyck.**	**Occ.**	**x**	**y**	**z**
Cu1	+1	2*a*	0.8	0	0	0
In1	+3	4*d*	1.0	0	1/2	1/4
In2	+3	2*b*	0.4	0	0	1/2
Se1	-2	8*i*	1.0	1/4	1/4	1/8

- **Occ. factor < 1.0: mixing of atoms and vacancies on the same position**
- **Calculation of the composition: Cu: 2 × 0.8; In: 4 × 1 + 2 × 0.4; Se: 8 × 1**

Summary to 2.1

- Atoms can be treated (and visualized) like spheres
- Different types of radii
- Structure and lattice
- Unit Cell
- 7 crystal sytems
- Indexation of directions and planes
- Fractional coordinates
- Z: number of atoms per unit cell
- Wyckoff-notation and occupancy factors

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



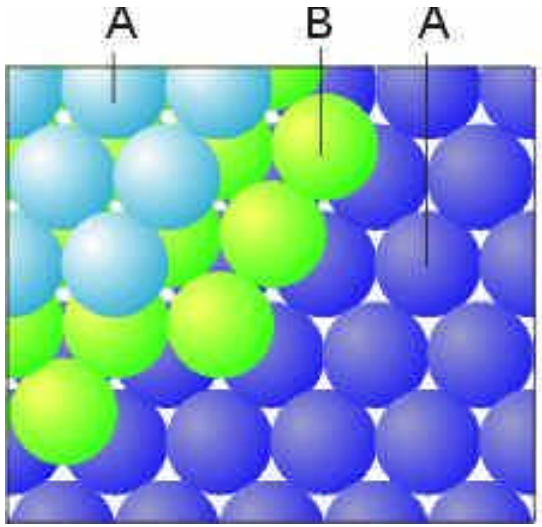
primitive packing
(low space filling)

close packing
(high space filling)

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

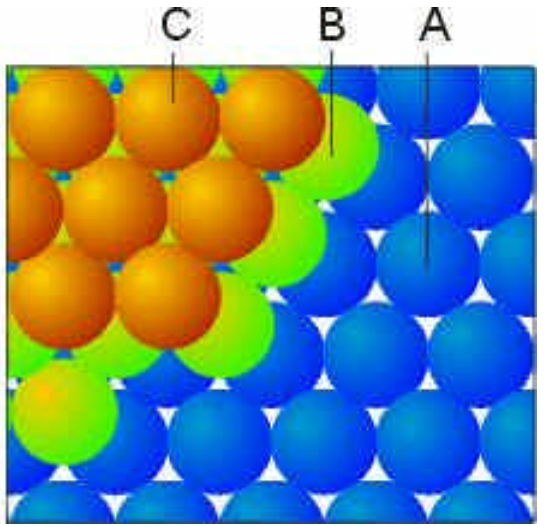
Example 1: HCP

close packed layer
1

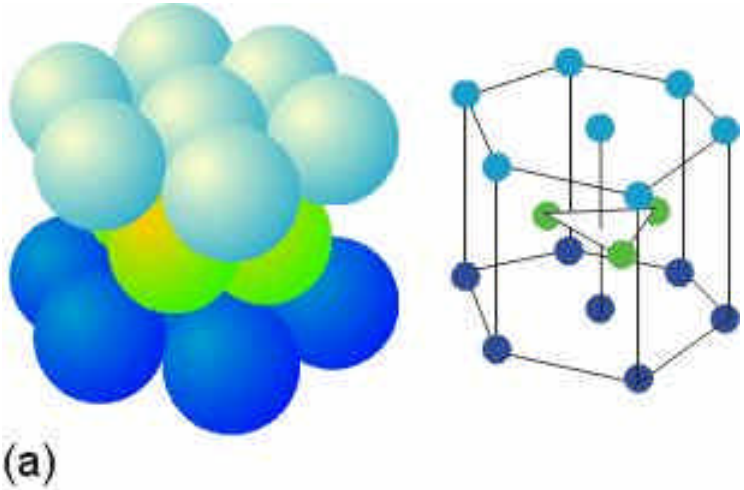


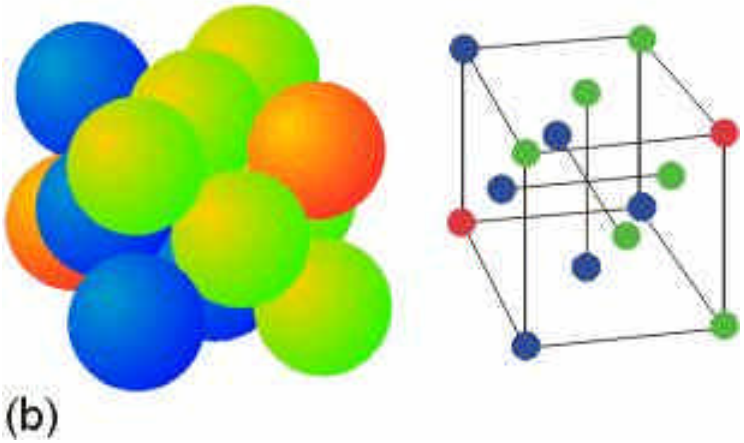
Example 2: CCP

close packed layer
2



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





HCP

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

close packed layer: (001)

anticuboctahedron

space filling = 74%

CN = 12

cuboctahedron

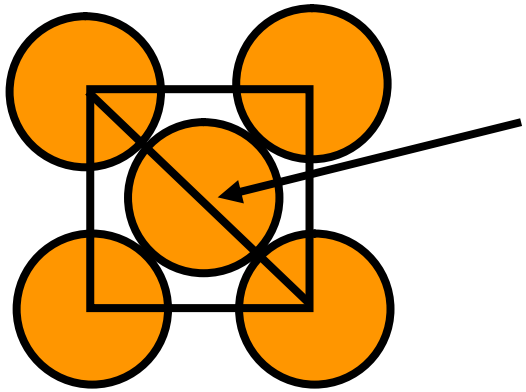
CCP

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

close packed layer: (111)

2.2 Simple close packed structures (metals) Calculation of space filling – example CCP

$$\text{Space filling} = \frac{\text{Volume occupied by atoms (spheres)}}{\text{Volume of the unit cell}}$$



$$4r = \sqrt{2}a$$

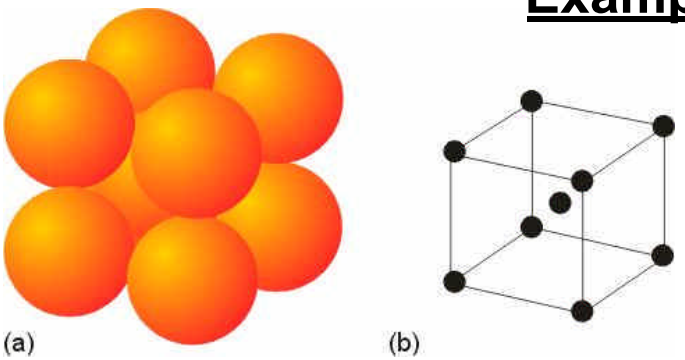
$$V(cell) = a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3$$

$$ZV(sphere) = 4\frac{4}{3}\pi r^3$$

$$spacef. = \left(\frac{4\frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3}\right) = \frac{\sqrt{2}\pi}{6} = 0.74$$

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

Example 2: primitive packing

(α-Po)

space filling = 52%

CN = 6

Example 3: structures of manganese

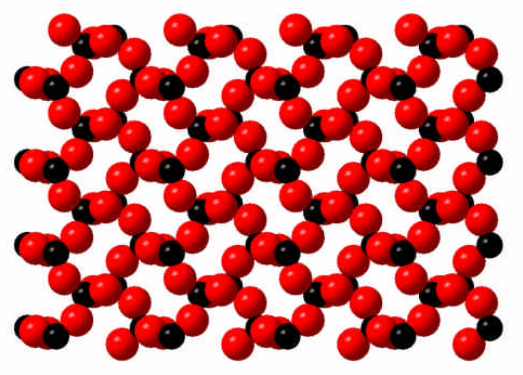
alpha Mn

beta Mn

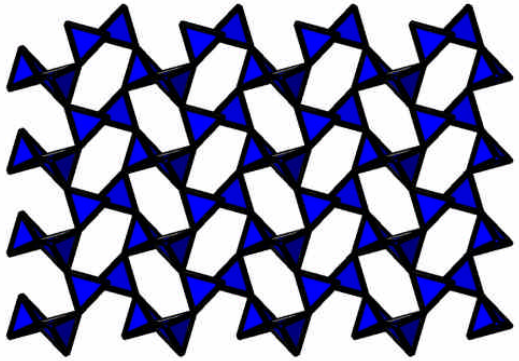
gamma Mn

2.2 Basics of Structures
Visualization of structures - polyhedra

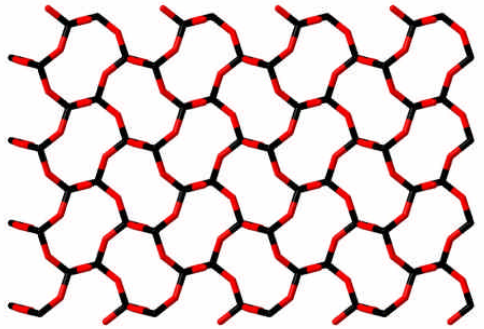
Example: Cristobalite (SiO_2)



Bragg jun. (1920)
Sphere packing

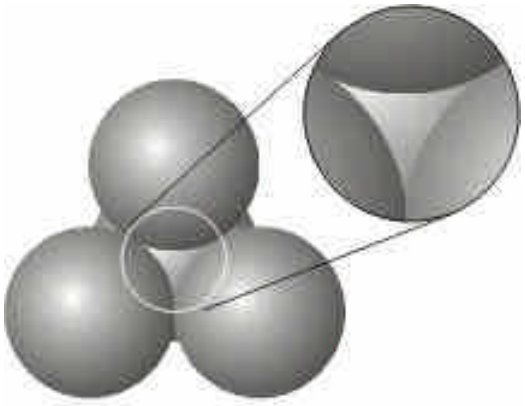


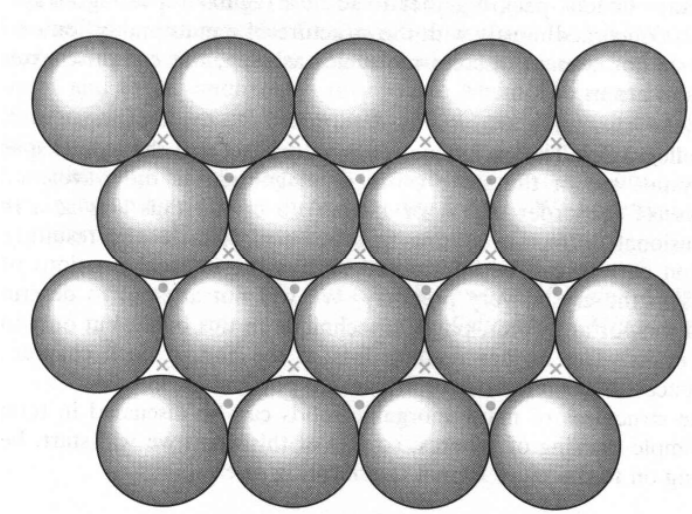
Pauling (1928)
Polyhedra

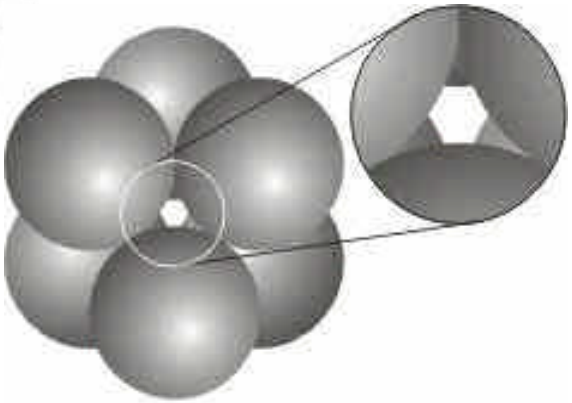


Wells (1954)
3D nets

2.2 Simple close packed structures (metals)
Holes in close packed structures







Tetrahedral hole
TH

Tetrahedron

Octahedral hole
OH

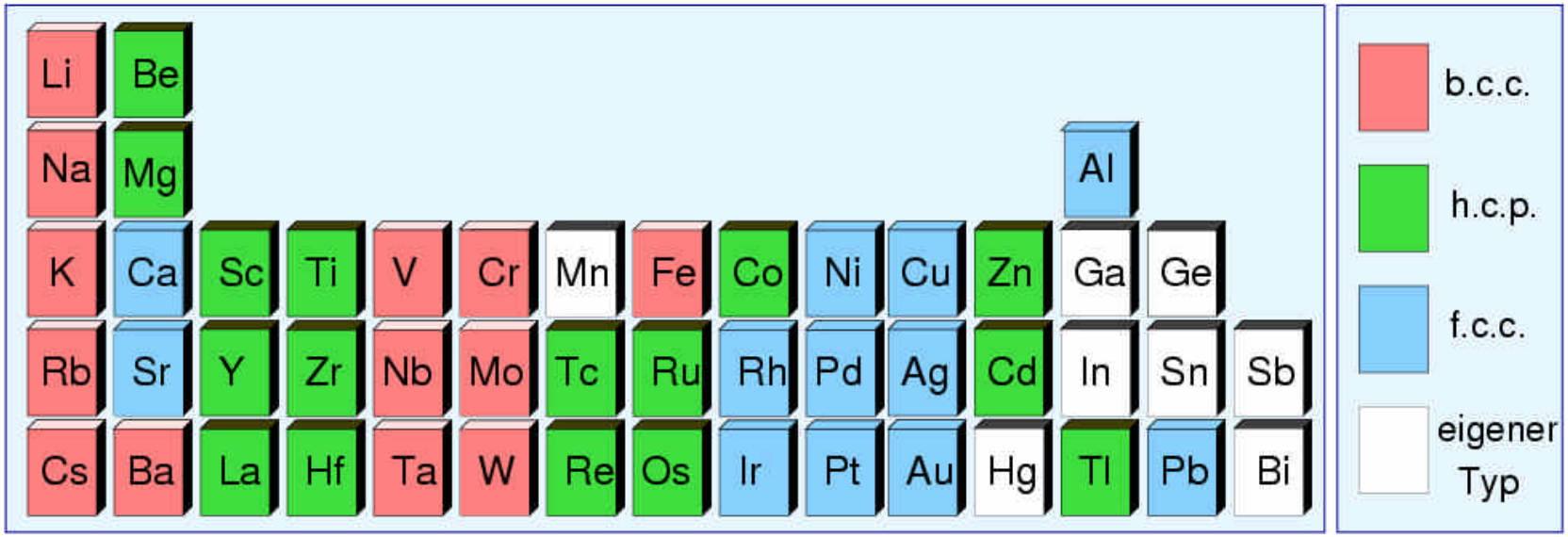
Octahedron

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

	HCP  OH, TH in HCP	CCP  OH, TH in CCP
Number OH/TH	**n/2n**	**n/2n**
Location	**OH: 4 corners, all edges TH: inside unit cell**	**OH: center, all edges TH: center of each octant**
Distances OH/TH	**!very short!**  Connection of tetrahedra, HCP  Connection of octahedra, HCP	**no short distances**

Summary to 2.2

- **Concept of close packing (layer sequences, unit cell, space filling)**
- **Structure of metals**



- **Holes in close packed structures**

2.3 Basic structure types
Overview

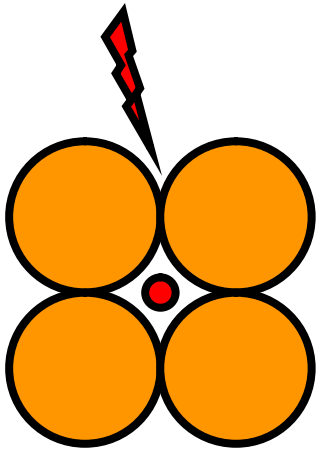
„Basic“: anions form CCP or HCP, cations in OH and/or TH

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! (LATER)	HCP	0 and 2n

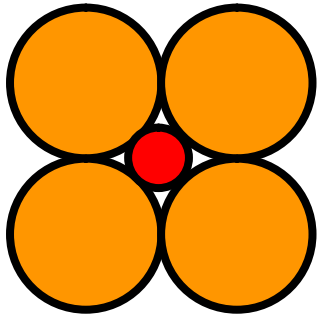
2.3 Basic structure types
Pauling rules: understanding polyhedral structures

(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)

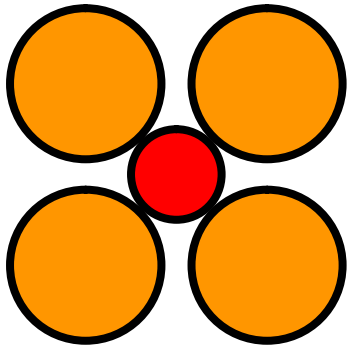
Scenario for radius ratios:



worst case



optimum



low space filling

2.3 Basic structure types
Pauling rules: understanding polyhedral structures

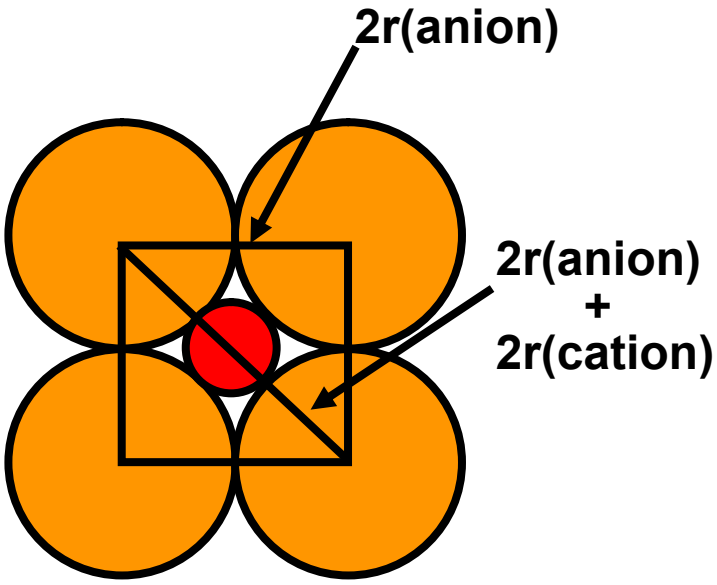
coordination	anion polyhedron	radius ratios	cation
3	triangle	0.15-0.22	C
4	tetrahedron	0.22-0.41	Si, Al
6	octahedron	0.41-0.73	Al, Fe, Mg, Ca
8	cube	0.73-1.00	K, Na
12	close packing (anti)cuboctahedron	1.00	

Example: Octahedron

Radius ratio
:tahedral coordinatic

$$\frac{\sqrt{2}}{1} = \frac{2r(anion) + 2r(cation)}{2r(anion)}$$

$$\sqrt{2} - 1 = \frac{r(cation)}{r(anion)} = 0.414$$



2.3 Basic structure types
Pauling rules: understanding polyhedral structures

(2) Negative and positive local charges should be balanced.
The sum of bond valences $\sum s_{ij}$ should be equal to the oxidation state V_i of ion i: $V_i = \sum s_{ij}$

Example 1-TiO_2 (Rutile)

$CN(Ti^{4+}) = 6$, $CN(O^{2-}) = 3$: $s_{ij}(Ti\text{-}O) = \pm 2/3$

$\sum s_{ij}(Ti) = 4$, $\sum s_{ij}(O) = 2$

Example 2 - GaAs (Sphalerite)

$CN(Ga^{3+}) = 4$, $CN(As^{3-}) = 4$: $s_{ij} = \pm 3/4$

$\sum s_{ij}(Ga) = 3$, $\sum s_{ij}(As) = 3$

Example 3 - $SrTiO_3$ (Perovskite)

$CN(Sr^{2+}) = 12$, $CN(Ti^{4+}) = 6$,
$CN(O^{2-}) = 4(Sr)$ and $2(Ti)$
s_{ij} (Sr-O) = 1/6 , s_{ij} (Ti-O) = 2/3

2.3 Basic structure types
Pauling rules: understanding polyhedral structures

(3) The presence of shared edges, and particularly shared faces decreases the stability of a structure. This is particularly true for cations with large valences and small CN.

(4) In a crystal containing different cations those with large valence and smalll CN do not tend to share polyhedron elements with each other.

(5) The number of chemically different coordination environments for a given ion in a crystal tends to be small.

2.3 Basic structure types
NaCl-type

Crystal data

Formula sum	NaCl
Crystal system	cubic
Space group	*F* m -3 m (no. 225)
Unit cell dimensions	*a* = 5.6250(5) Å
Z	4


NaCl

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Na	+1	4*a*	0	0	0
Cl	-1	4*b*	1/2	1/2	1/2

Structural 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
Bonding in ionic structures – Coulomb interaction

Classic picture of ionic bonding: cations donate electrons to anions thus each species fullfills the octet rule.

i.e. $Na + F \rightarrow Na^+ + F^-$

Interaction between anions and cations: Coulomb interactions.

$$V_{AB} = -A \frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_{AB}} N$$

Coulomb potential of an ion pair

V_{AB}: Coulomb potential (electrostatic potential)
A: Madelung constant (depends on structure type)
z: charge number, e: elementary charge = 1.602×10^{-19}C
ε_o: dielectric constant (vacuum permittivity) = $8.85\times10^{-12}C^2/(Nm^2)$
r_{AB}: shortest distance between cation and anion
N: Avogadro constant = 6.023×10^{23} mol^{-1}

2.3 Basic structure types
Bonding in ionic structures – Coulomb interaction

Calculating the Madelung constant (for NaCl)

$$A = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \ldots$$

First coordination sphere

Second coordination sphere

Third coordination sphere

First term: attraction from the 6 nearest neighbors

Second term: repulsion (opposite sign) from 12 next nearest neighbors

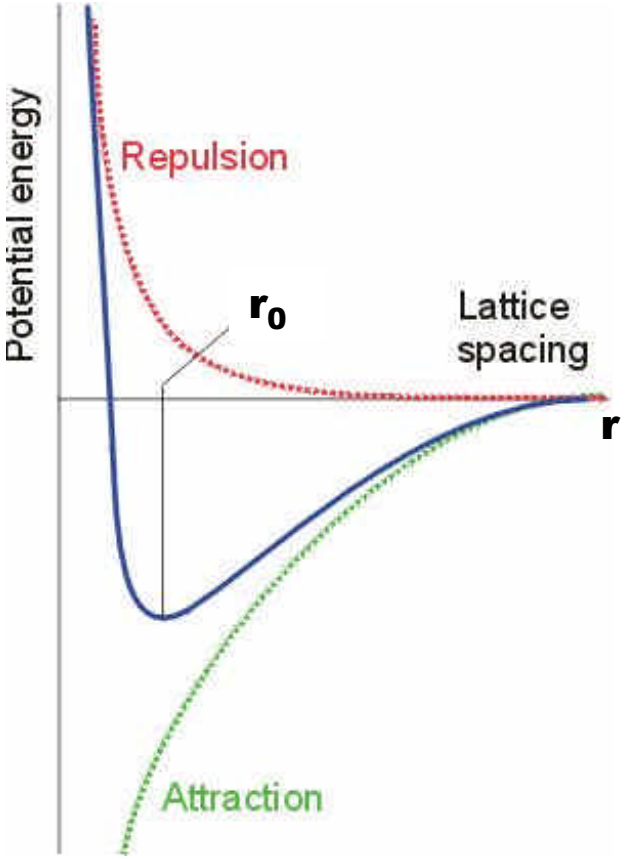
…

A converges to a value of 1.748.

	A	CN
Rock Salt	**1.748**	**6**
CsCl	**1.763**	**8**
Sphalerite	**1.638**	**4**
Fluorite	**5.039**	**8**

2.3 Basic structure types
Bonding in ionic structures - repulsion

Repulsion arising from overlap of electron clouds



Because the electron density of atoms decreases exponentially towards zero at large distances from the nucleus the Born repulsion shows the same behaviour

approximation:

$$V_{Born} = \frac{B}{r^n}$$

B and n are constants for a given atom type; n can be derived from compressibility measurements (~8)

2.3 Basic structure types
Lattice energy of a ionic structure

1) **Set the first derivative of the sum to zero**
2) **Substitute B-parameter of repulsive part**

$$\Delta H_L^0 = Min.(V_{AB} + V_{Born})$$

$$\Delta H_L^0 = -A\frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_0} N\left(1-\frac{1}{n}\right)$$

- **typical values, measured (calculated) [kJ mol^{-1}]:**
  - **NaCl: –772 (-757); CsCl: -652 (-623)**
  - **measured means by Born Haber cycle (later)**
- **fraction of Coulomb interaction at r_0: ~ 90%**
- **missing in our lattice energy calculations:**
  - **zero point energy**
  - **dipole-dipole interaction**
  - **covalent contributions, example: AgCl: -912 (-704)**

2.3 Basic structure types
Sphalerite-type

Crystal data

Formula sum	ZnS
Crystal system	cubic
Space group	*F* -4 3 m (no. 216)
Unit cell dimensions	*a* = 5.3450 Å
Z	4

Layer in sphalerite

Stacking sequence

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Zn1	+2	4*a*	0	0	0
S2	-2	4*c*	1/4	1/4	1/4

Structural and other features:

- **diamond-type structure**
- **50% of tetrahedral holes in CCP filled**
- **connected layers, sequence (S-layers): ABC, polytypes**
- **Zn, S is coordinated by 4 S, (tetrahedra, common corners)**
- **applications of sphalerite-type structures very important (semiconductors: solar cells, transistors, LED, laser…)**

2.3 Basic structure types
Wurzite-type

Crystal data

Formula sum	ZnS
Crystal system	hexagonal
Space group	*P* 6_3 m c (no. 186)
Unit cell dimensions	*a* = 3.8360 Å, *c* = 6.2770 Å
Z	2

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Zn1	+2	*2b*	1/3	2/3	0
S1	-2	*2b*	1/3	2/3	3/8

Stacking sequence

Structural features:

- **connected layers, sequence (S-layers): AB**
- **Zn is coordinated by 4 S (tetrahedra, common corners)**
- **polytypes**

2.3 Basic structure types
CaF_2-type

Crystal data

Formula sum	CaF_2
Crystal system	cubic
Space group	*F* m -3 m (no. 225)
Unit cell dimensions	*a* = 5.4375(1) Å
Z	4

Coordination Ca

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Ca1	+2	4*a*	0	0	0
F1	-1	8*c*	1/4	1/4	1/4

Structural features:

- **all TH of CCP filled**
- **F is coordinated by 4 Ca (tetrahedron)**
- **Ca is coordinated by 8 F (cube)**

2.3 Basic structure types
$CdCl_2$-type

Crystal data

Formula sum	$CdCl_2$
Crystal system	trigonal
Space group	*R* -3 m (no. 166)
Unit cell dimensions	*a* = 6.2300 Å, α = *36*°
Z	1

Stacking sequence

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Cd1	+2	3*a*	0	0	0
Cl1	-1	36*i*	0.25(1)	0.25(1)	0.25(1)

One layer

Structural features:

- **layered structure, sequence (Cl-layers): ABC**
- **Cd is coordinated octahedrally by 6 Cl (via six common edges)**
- **polytypes**

2.3 Basic structure types
CdI_2-type

Crystal data

Formula sum	CdI_2
Crystal system	trigonal
Space group	*P* -3 m 1 (no. 164)
Unit cell dimensions	*a* = 4.2500 Å, *c* = 6.8500 Å
Z	1

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Cd1	+2	1*a*	0	0	0
I1	-1	2*d*	1/3	2/3	1/4

Stacking sequence

Structural features:

- **layered structure, sequence (I-layers): AB**
- **Cd is coordinated octahedrally by 6 I (via six common edges)**
- **polytypes**

2.3 Basic structure types
Intercalation of layered compounds

- **Reversible intercalation of atoms between the layers of a layered compound**
- **Host-guest interactions, structure-property relations**

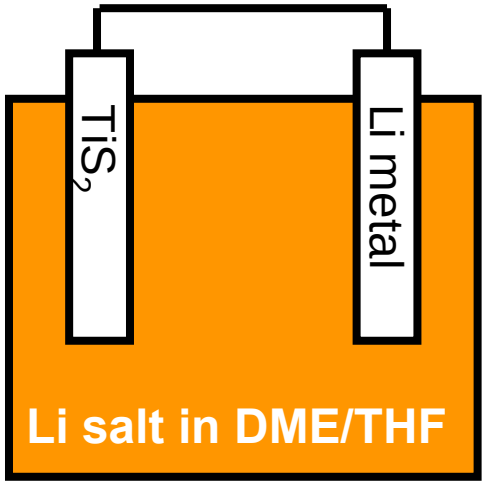
<u>Example 1</u>: Graphite

- **Electron donors (alkali metals, e. g. KC_8)**
- **Electron acceptors (NO_3^-, Br_2, AsF_5...)**
- **Properties: Increase of interlayer spacing, color change, increase of conductivity, change of electronic structure**

<u>Example 2</u>: TiS_2 (CdI_2-type)

- **Electron donors (alkali metals, copper, organic amines)**
- **Application: Li-TiS_2-battery**

$$xLi\ (metal) \rightarrow xLi^+(solv) + xe^-$$
$$xLi^+(solv) + TiS_2 + xe^- \rightarrow Li_xTiS_2(s)$$



2.3 Basic structure types
Li_3Bi-type

Crystal data

Formula sum	Li_3Bi
Crystal system	cubic
Space group	*F* m -3 m (no. 225)
Unit cell dimensions	*a* = 6.7080 Å
Z	4


Unit cell

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Bi1	+0	4*a*	0	0	0
Li1	+0	4*b*	1/2	1/2	1/2
Li2	+0	8*c*	1/4	1/4	1/4

Structural features:

- **all holes of CCP filled by Li**
- **not many examples of this structure type**

2.3 Basic structure types
NiAs-type

Crystal data

Formula sum	NiAs
Crystal system	hexagonal
Space group	*P* 63/m m c (no. 194)
Unit cell dimensions	*a* = 3.619(1) Å, *c* = 5.025(1) Å
Z	2

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Ni1	+3	2*a*	0	0	0
As1	-3	2*c*	1/3	2/3	1/4

Octahedra

Trigonal prisms

Octahedron and trig. prism

Structural features:

- **all OH of HCP filled**
- **Ni is coordinated by 6 As (octahedron)**
- **metal-metal-bonding (common faces of the octahedra)**
- **As is coordinated by 6 Ni (trigonal prism)**
- **type ≠ antitype**

Summary to 2.3

- **Pauling rules**
- **Lattice energy calculations of ionic structures**
- **Structures of basis structure types:**

  NaCl, ZnS, CaF_2, $CdCl_2$, CdI_2, Li_3Bi, NiAs

2.4 More complex structures
Introduction

“More complex”:

- **deviations from close packing of anions**
- **no close packing of anions**
- **cations in simple (highly symmetrical) polyhedra**
- **other species besides tetrahedra and octahedra**
- **complex interconnection of the polyhedra**

2.4 More complex structures
Oxides: Rutile (TiO_2)

Crystal data

Formula sum	TiO_2
Crystal system	tetragonal
Space group	*P* 4_2/m n m (no. 136)
Unit cell dimensions	*a* = 4.5937 Å, *c* = 2.9587 Å
Z	2

Octahedra in Rutile

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z	
Ti1	+4	2*a*	0	0	0	
O1	-2	4*f*	0.30469(9)	0.30469(9)		0

Structural features:

- **no HCP arrangement of O (CN(O,O) = 11)**
- **mixed corner and edge sharing of TiO_6-octahedra**
- **columns of trans edge sharing TiO_6-octahedra, connected by common corners**
- **many structural variants**
- **application: pigment**

2.4 More complex structures
Oxides: ReO_3

Crystal data

Formula sum	ReO_3
Crystal system	cubic
Space group	*P* m -3 m (no. 221)
Unit cell dimensions	*a* = 3.7504(1) Å
Z 1	

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Re1	+6	1*a*	0	0	0
O1	-2	3*d*	1/2	0	0


Unit cell

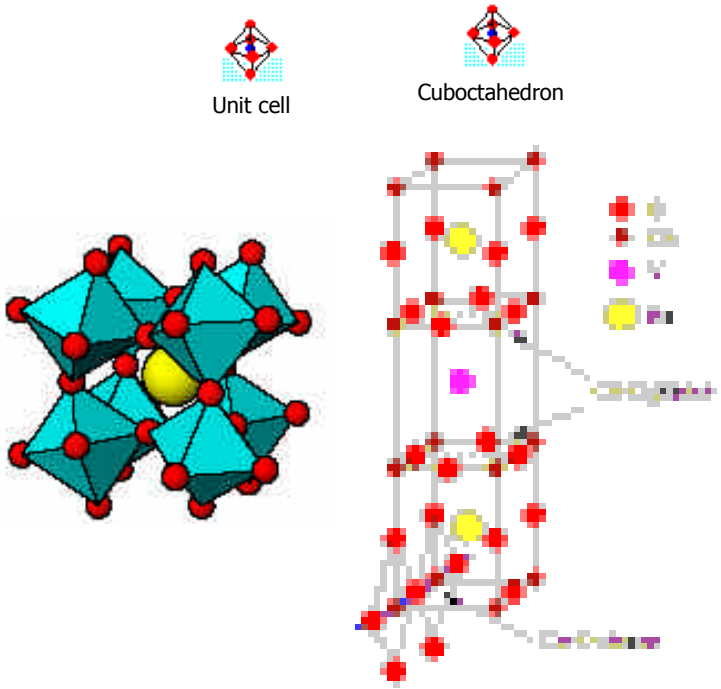
Structural features:

- **no close packing (CN (O,O) = 8)**
- **ReO_6 octahedra connected by six common corners**
- **large cavity in the center of the unit cell**
- **filled phase (A_xWO_3 tungsten bronze)**

2.4 More complex structures
Oxides: undistorted perovskite ($SrTiO_3$)

Crystal data

Formula sum	$SrTiO_3$
Crystal system	cubic
Space group	*P* m -3 m (no. 221)
Unit cell dimensions	*a* = 3.9034(5) Å
Z	1



Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Sr1	+2	1*a*	0	0	0
Ti1	+4	1*b*	1/2	1/2	1/2
O1	-2	3*c*	0	1/2	1/2

Structural features:

- **filled ReO_3 phase, CN (Ca) = 12 (cuboctaehdron), CN (Ti) = 6 (octahedron)**
- **many distorted variants (even the mineral $CaTiO_3$!)**
- **many defect variants (HT-superconductors, $YBa_2Cu_3O_{7-x}$)**
- **hexagonal variants and polytyps**

2.4 More complex structures
Oxides: Spinel ($MgAl_2O_4$)

Crystal data

Formula sum	$MgAl_2O_4$
Crystal system	cubic
Space group	*F* d -3 m (no. 227)
Unit cell dimensions	*a* = 8.0625(7) Å
Z	8

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Mg1	+2	8*a*	0	0	0
Al1	+3	16*d*	5/8	5/8	5/8
O1	-2	32*e*	0.38672	0.38672	0.38672

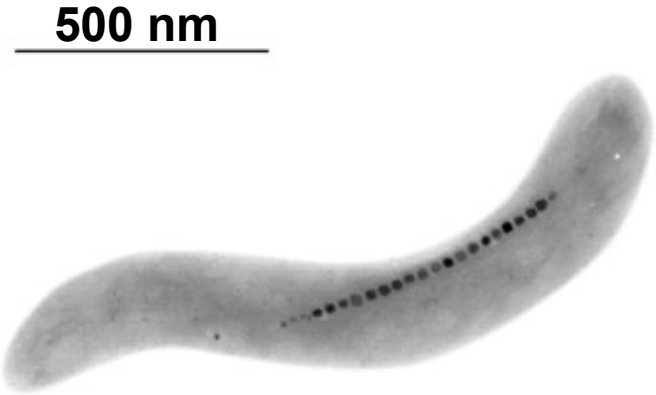
Diamond Document

Diamond Document

Structural features:

- **distorted CCP of O**
- **Mg in tetrahedral holes (25%), no connection of tetrahedra**
- **Al in octahedral holes (50%), common edges**
- **Inverse spinel structures $Mg_{TH}Al_{2OH}O_4 \rightarrow In_{TH}(Mg, In)_{OH}O_4$**
- **Application: ferrites (magnetic materials)**

2.4 More complex structures
Oxides: Spinel (Fe_3O_4)



Magnetospirillum

Ocher

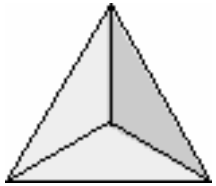
Summary to 2.4

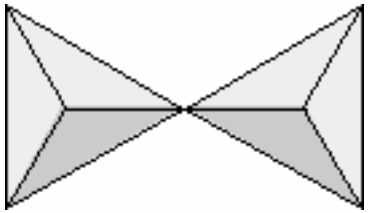
- More complex structures
- Rutile
- ReO_3
- Perovskite and structural variations
- Spinel and structural variations

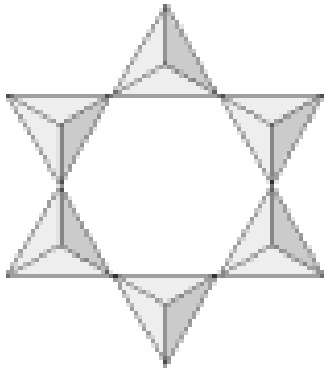
2.5 Complex structures
Oxides: Silicates- overview 1

From simple building units to complex structures

Structural features:
- fundamental building unit: SiO_4 tetrahedron
- isolated tetrahedra or connection via common corners
- MO_6 octahedra , MO_4 tetrahedra (M = Fe, Al, Co, Ni…)







Nesosilicates

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

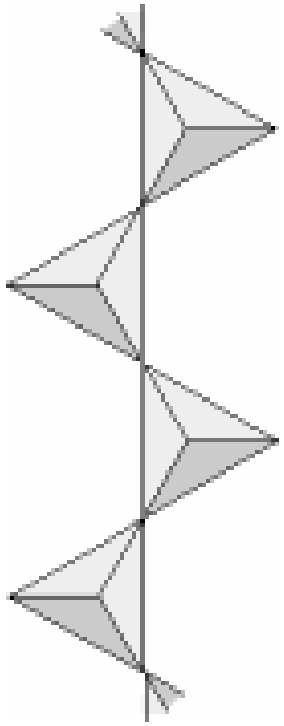
Sorosilicates

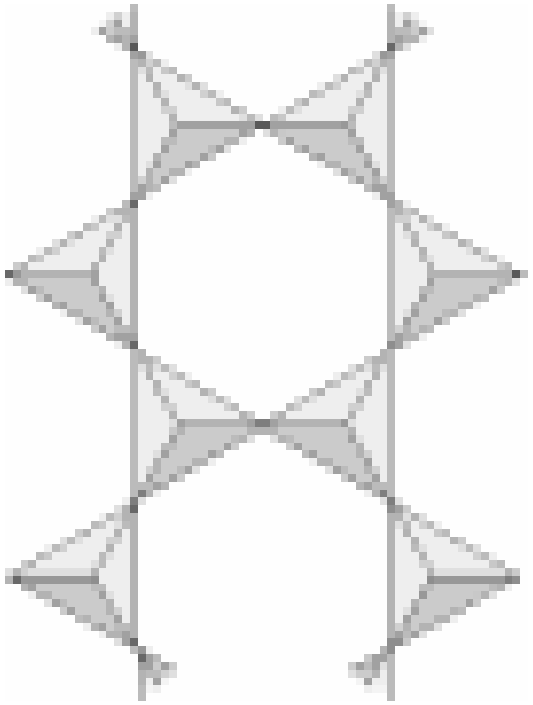
$Si_2O_7^{6-}$
Thortveitite: $(Sc,Y)_2Si_2O_7$

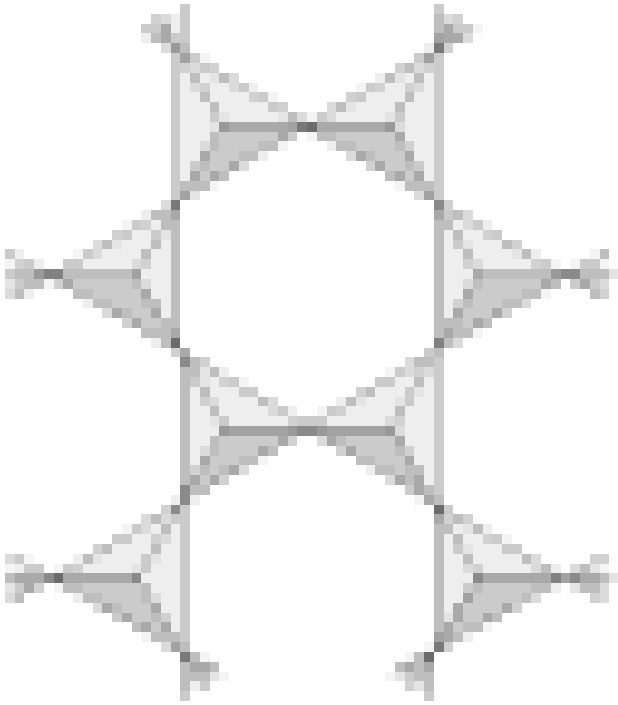
Cyclosilicates

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

2.5 Complex structures
Oxides: Silicates- overview 2







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: $K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$

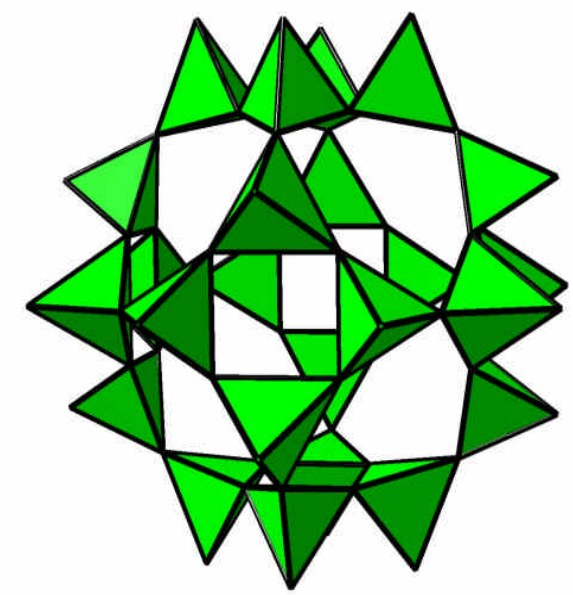
2.5 Complex structures
Oxides: Silicates- overview 3

Tectosilicates

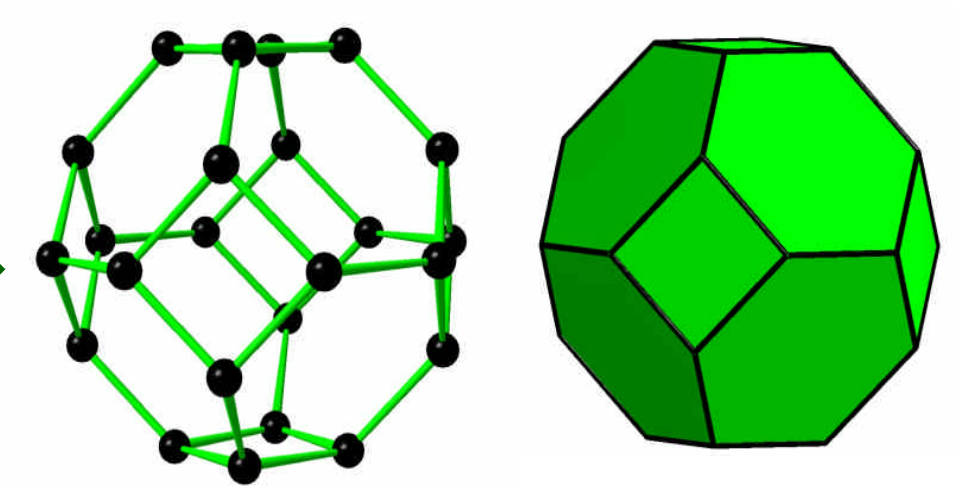
SiO_2

Faujasite: $Ca_{28}Al_{57}Si_{135}O_{384}$

β-cage

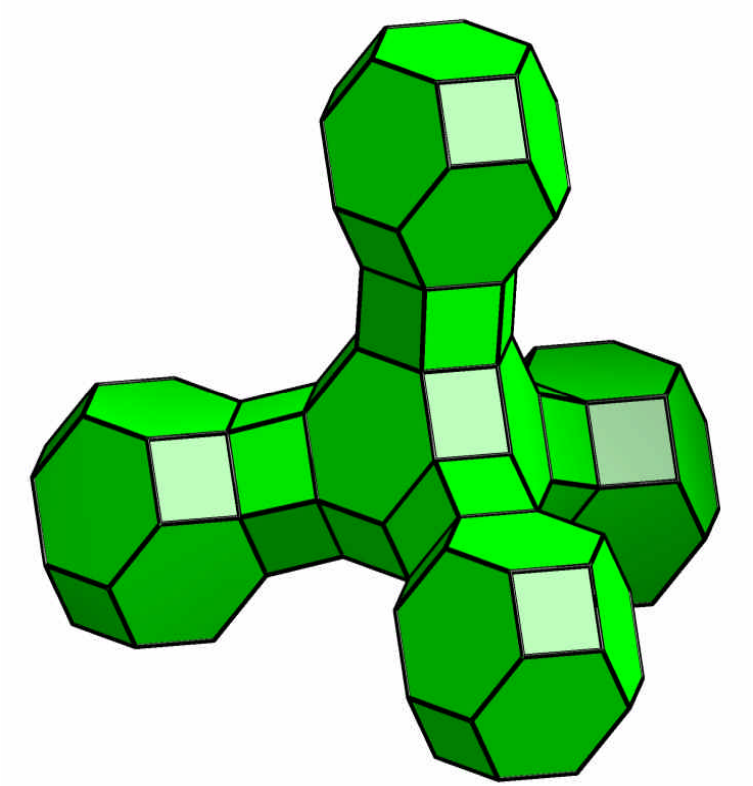


T-Atom-representation

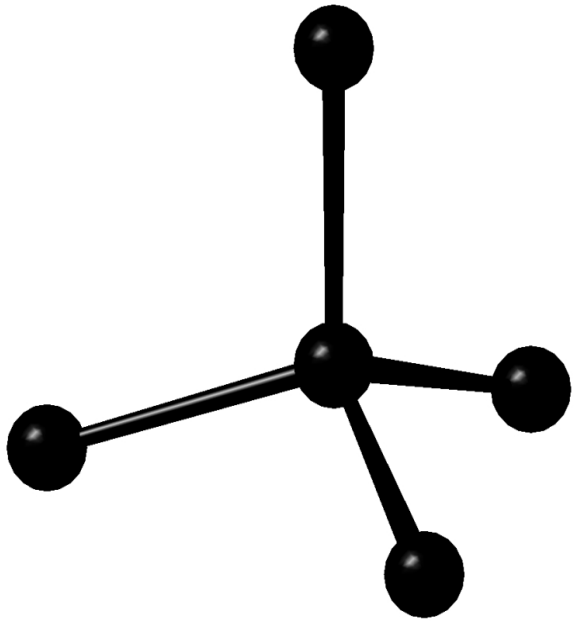


2.5 Complex structures
Concept for visualization of topology

T-Atom representation



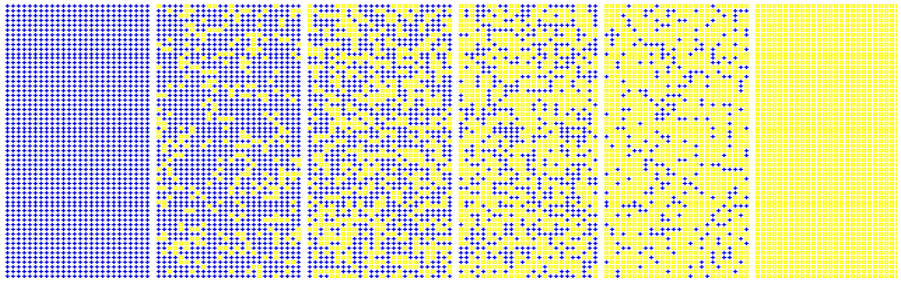
3D-Nets: edge + vertex



2.5 Complex structures
Intermetallics- overview

Solid solutions: Example: Rb_xCs_{1-x} BCC-structure, disordered

- chemically related
- small difference of electronegativity
- similar number of valence electrons
- similar atomic radius
- (high temperature)

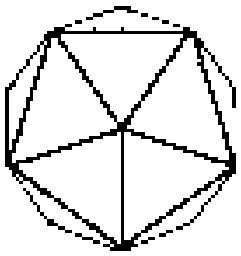


Ordered structures: from complex building units to complex structures

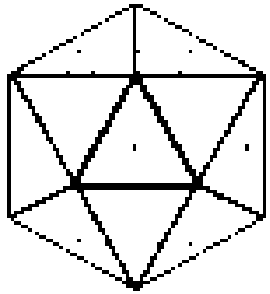
Rule: complex structures

Exception:
simple structures

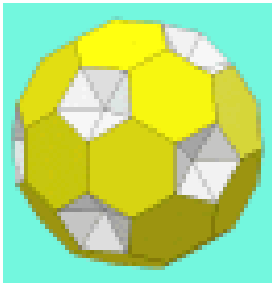
CuZn



CN 12



CN 16



2.5 Complex structures
Intermetallics- Hume-Rothery-phases

Trend 1:
Intermetallics with a defined relation between structure and VEC (Valence Electron Concentration)

Number (N) of valence electrons (empirical rules):
0: Fe, Co, Ni, Pt, Pd; 1: Cu, Ag, Au
2: Be, Mg, Zn, Cd; 3: Al; 4: Si, Ge, Sn; 5: Sb
VEC = N(val. electr) / N(atoms) (both per formula unit)

VEC	3/2	3/2	3/2	21/13	7/4
Structure	CuZn	β-Mn	HCP	γ-Brass	HCP
Example	Cu_3Al CoAl NiIn	Cu_5Si Ag_3Al $CoZn_3$	Cu_3Ga Ag_3In Au_5Sn	Cu_5Zn_8 Cu_9Al_4 $Cu_{31}Si_8$	$CuZn_3$ Cu_3Sn Ag_3Sn

2.5 Complex structures
Intermetallics- Laves-phases

Trend 2:
Intermetallics with a high space filling (71%)
Typical radius ratio: 1:1.225

Structure	$MgCu_2$	$MgZn_2$	$MgNi_2$
Example	$TiCr_2$ $AgBe_2$ $CeAl_2$	$BaMg_2$ $FeBe_2$ WFe_2	FeB_2 $TaCo_2$ $ZrFe_2$

2.5 Complex structures
Zintl-phases- overview

Experimental observation:
element 1 + element 2 → compound (liquid ammonia)
element 1: alkali, alkaline-earth, rare-earth metals
element 2 (examples): Ga-Tl, Si-Pb, As-Bi…

Properties of the compounds:
- **salt like structures, colored**
- **soluble clusters in liquid ammonia**
- **semiconductors**
- **fixed composition, valence compounds**

} **Characteristics of Zintl phases**

The Zintl-rule („8-N-rule“)

- **The structure of the anions follows the octet rule**
- **The number of bonds of each anion is 8-N (N = number of electrons of the anion)**
- **The anions adopt structures related to the elements of group N**

2.5 Complex structures
Zintl-phases- examples

- 8-N = 0, N = 8: Mg_2Si: Si^{4-}, isolated atoms (noble gases: HCP or CCP)
- 8-N = 1, N = 7: Sr_2P_2: P^-, dimers (halogene)
- 8-N = 2, N = 6: CaSi: Si^{2-}, chains or rings (chalcogene)
- 8-N = 3, N = 5: $CaSi_2$: Si^-, sheets or 3D nets (pnicogene, black phosphorous)
- 8-N = 4, N = 4: NaTl: Tl^-, 3D framework of tetrahedra (tetrel, diamond)

Example: Ba_3Si_4

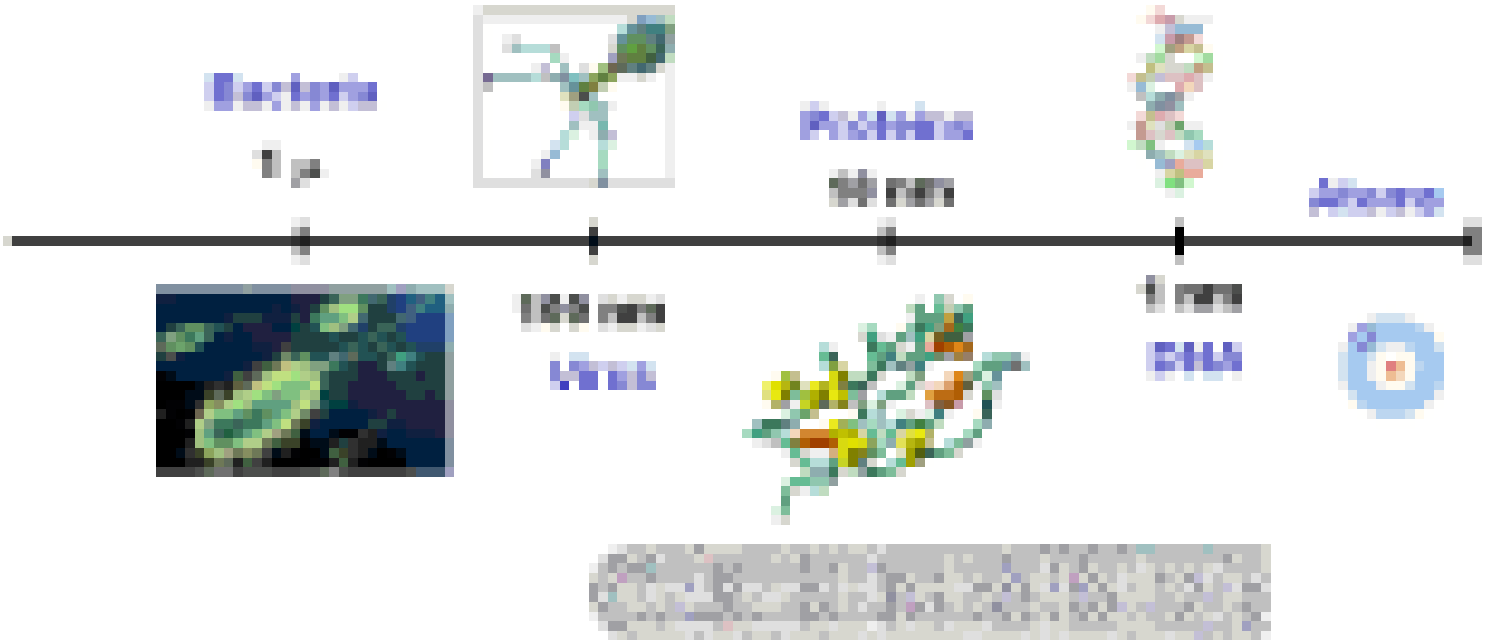
Ba3Si4

Summary to 2.5

- Complex structures
- Silicates (six structure families, complex framework of tetrahedra)
- Intermetallics (complex framework of complex polyhedra)
- Simple Zintl-phases

2.6 Structure of nanomaterials
What is nano?

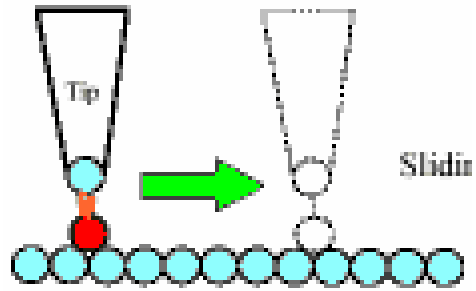
Definition: at least one dimension < 100 nm

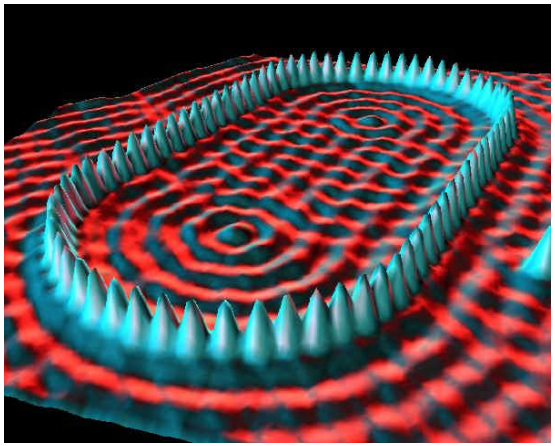


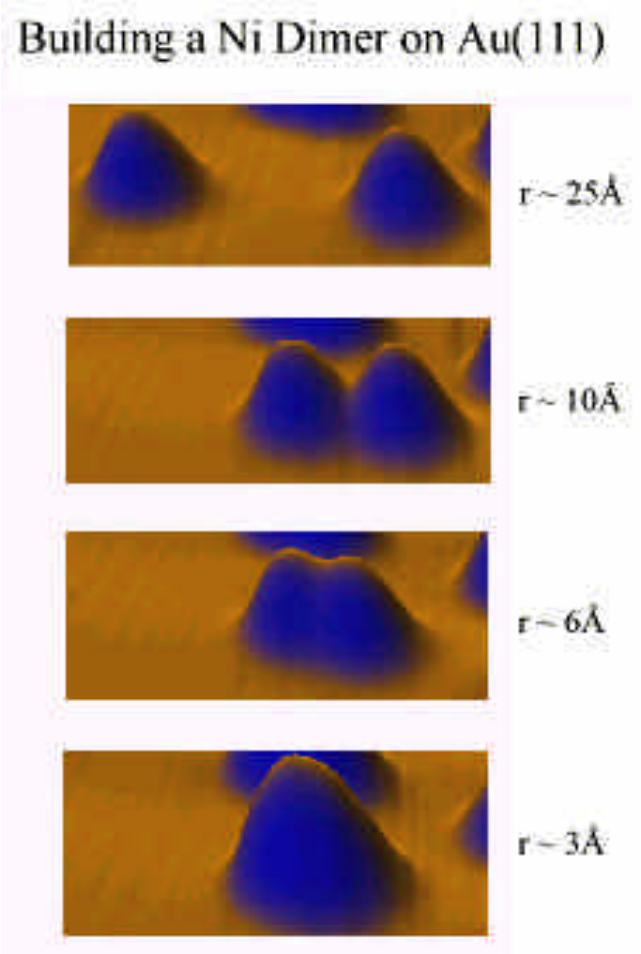
Nanotube

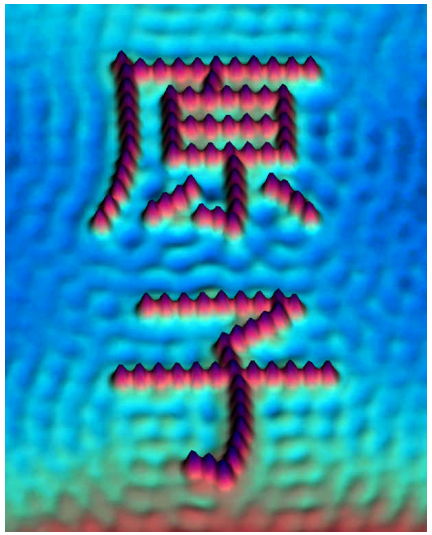
2.6 Structure of nanomaterials
Physical approaches to nanostructures

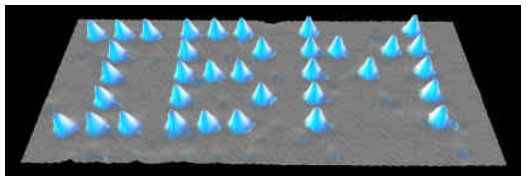
Atom manipulation







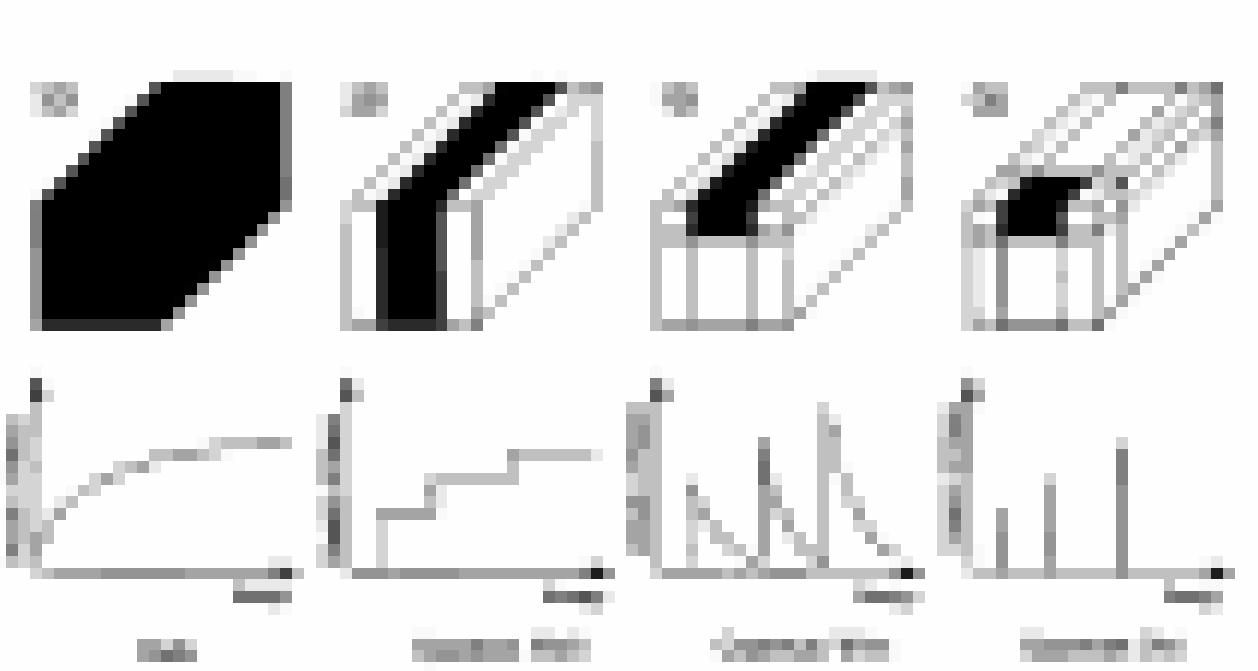




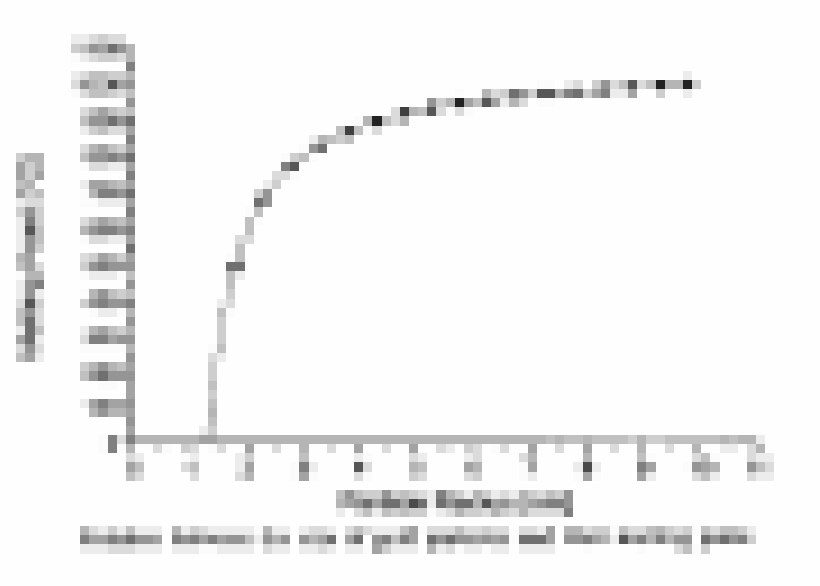
Building a Ni Dimer on Au(111)

2.6 Structure of nanomaterials
Why nano? – what is the difference to micro?

Electronic structure (simple illustration, details later)



2.6 Structure of nanomaterials
Why nano? – fundamental properties

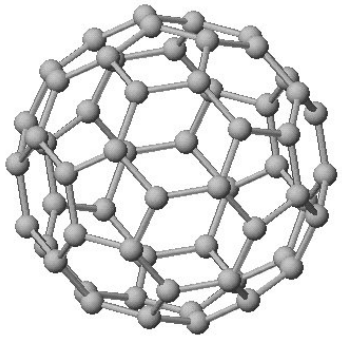


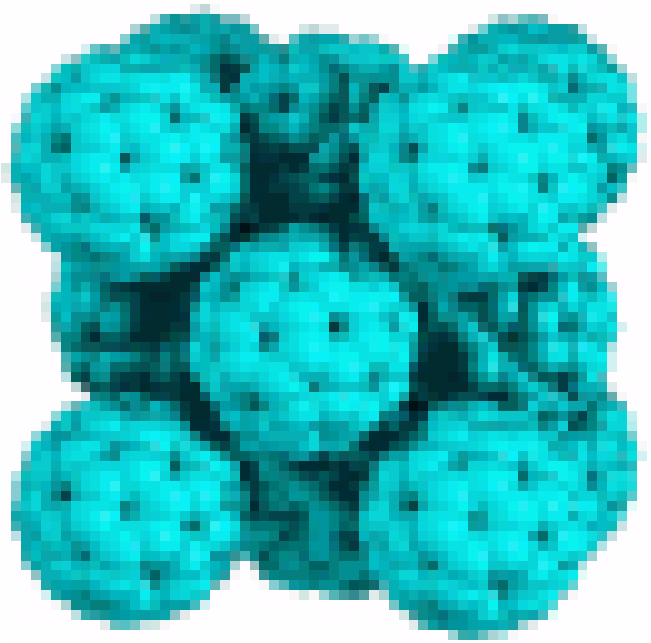
CdS-colloids, different particle sizes

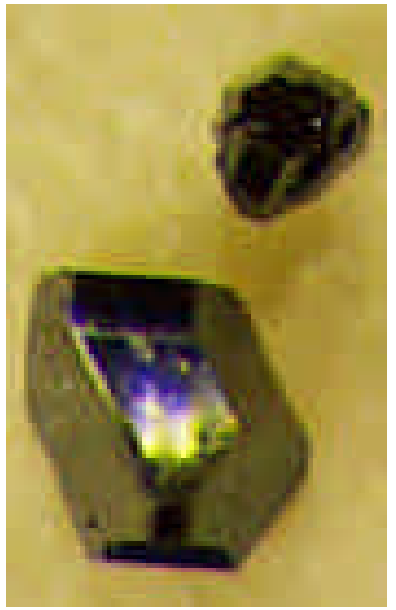
- melting point: structure dominated by small CN (e.g. 9 instead of 12)
- magnetism (increasing spin interactions with decreasing particle size)
- optical properties (example: nano-Au, purple of cassius)
- conductivity (deviations from the Ohm‘s law)

Vision of nano: design of properties by designing the size of objects „wavefunction engineering“ and not the chemistry of the objects

2.6 Structure of nanomaterials
Structures containing large entities - fullerenes







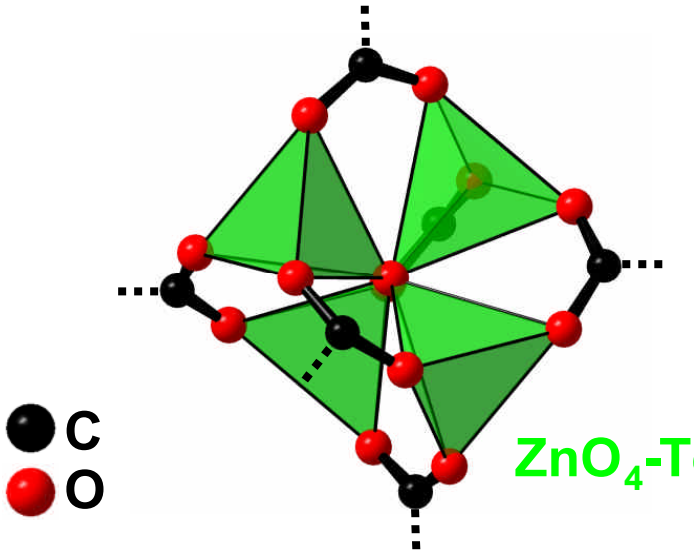
Chemistry of fullerenes

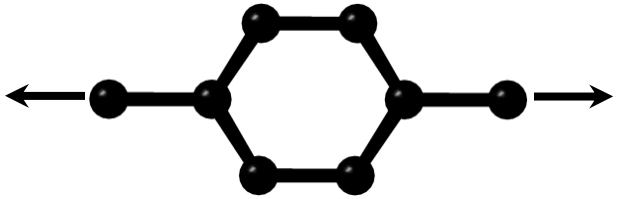
- Synthesis: vaporization of carbon
- ion implantation in C60 cage
- partial filling of OH by alkali or rare earth metals (fullerides)
- several chemical modifications

2.6 Structure of nanomaterials
Structures containing large holes - MOF

MOF = Metal organic framework

Synthesis: Diffusion of Zn(II)salts in organic acids
simple chemistry (precipitation) – remarkable results



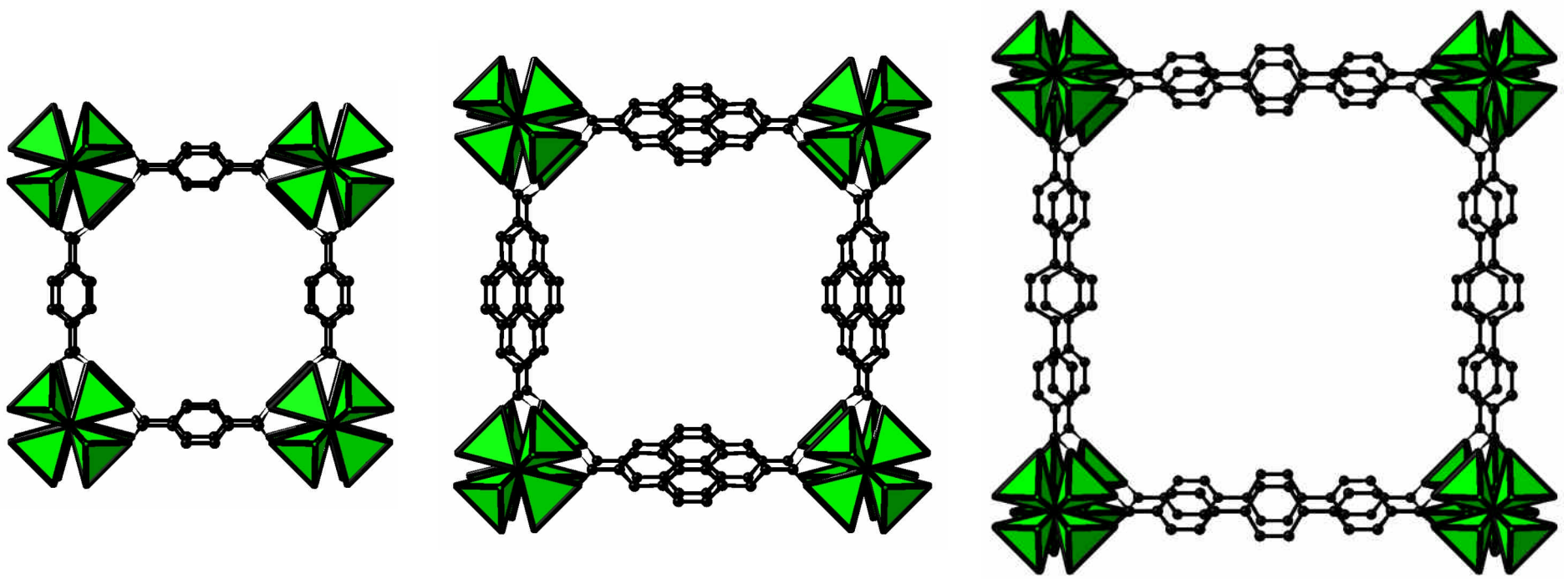


Secundary buiding unit

Organic linker

2.6 Structure of nanomaterials
Structures containing large holes - MOF

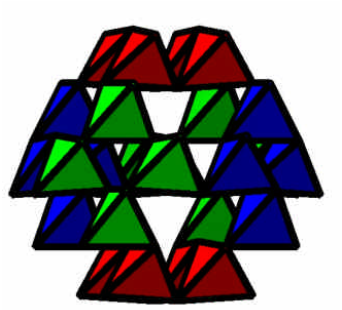
MOF = Metal organic framework



Unique structural features

- principle of scaling
- highly crystalline materials
- lowest density of crystalline matter, up to 0.21 g/cm^3
- ab initio design of materials

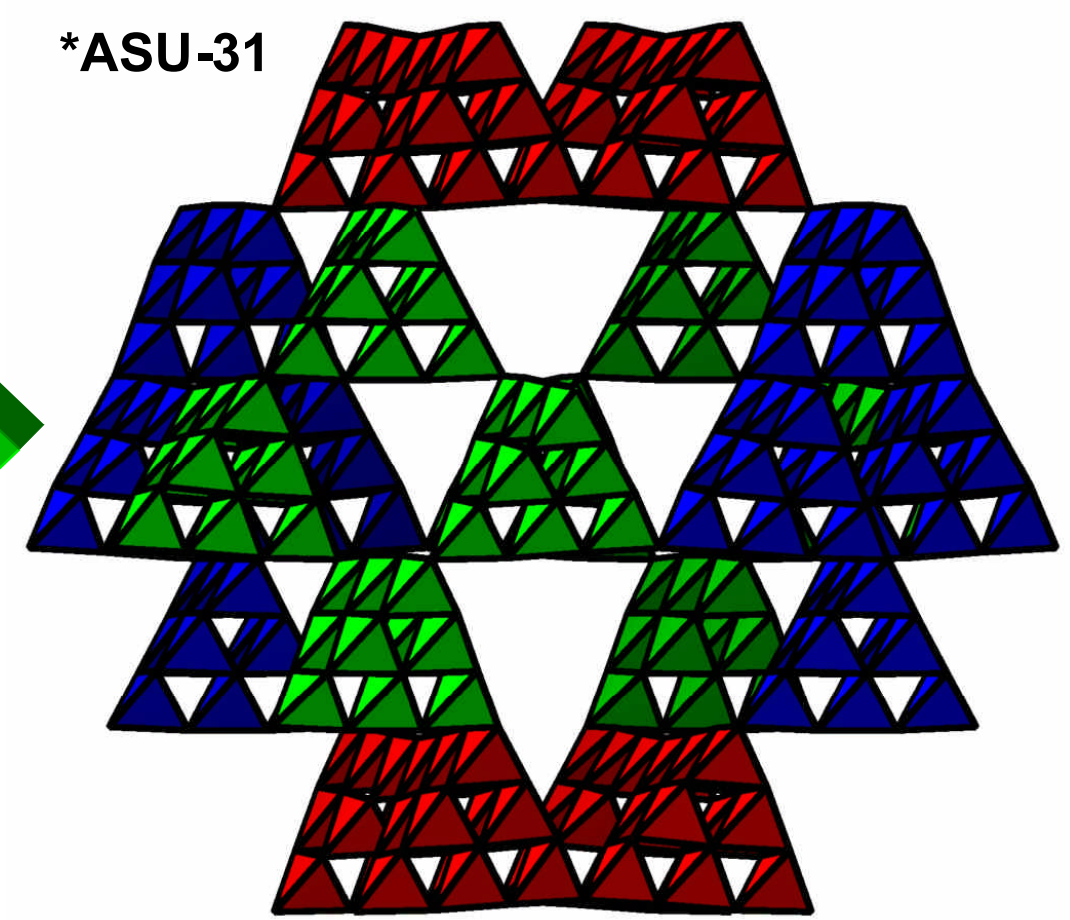
2.6 Structure of nanomaterials
Structures containing large holes – new materials



Solalite-type topology

Scaling

*ASU-31

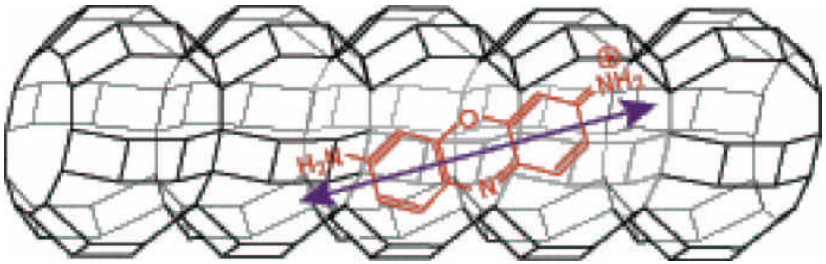


Sodalite-type topology

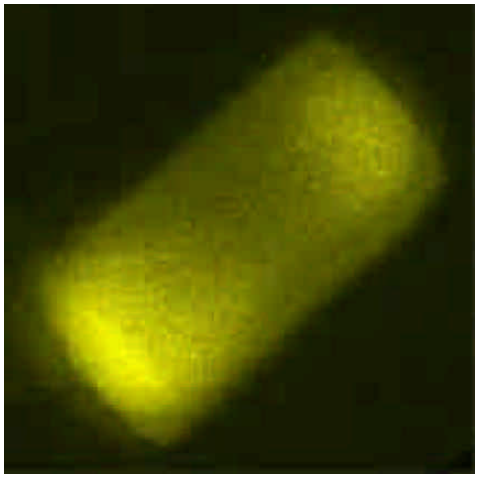
*Arizona State University

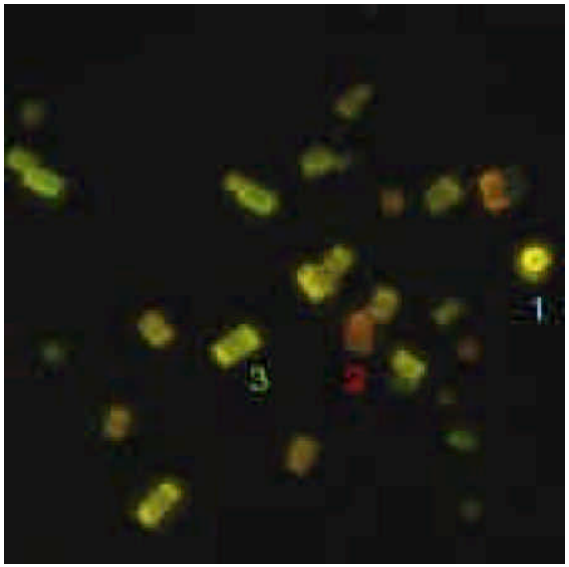
2.6 Structure of nanomaterials
Structures containing channels - Zeolites

Composite materials, e. g. dyes in zeolite crystals



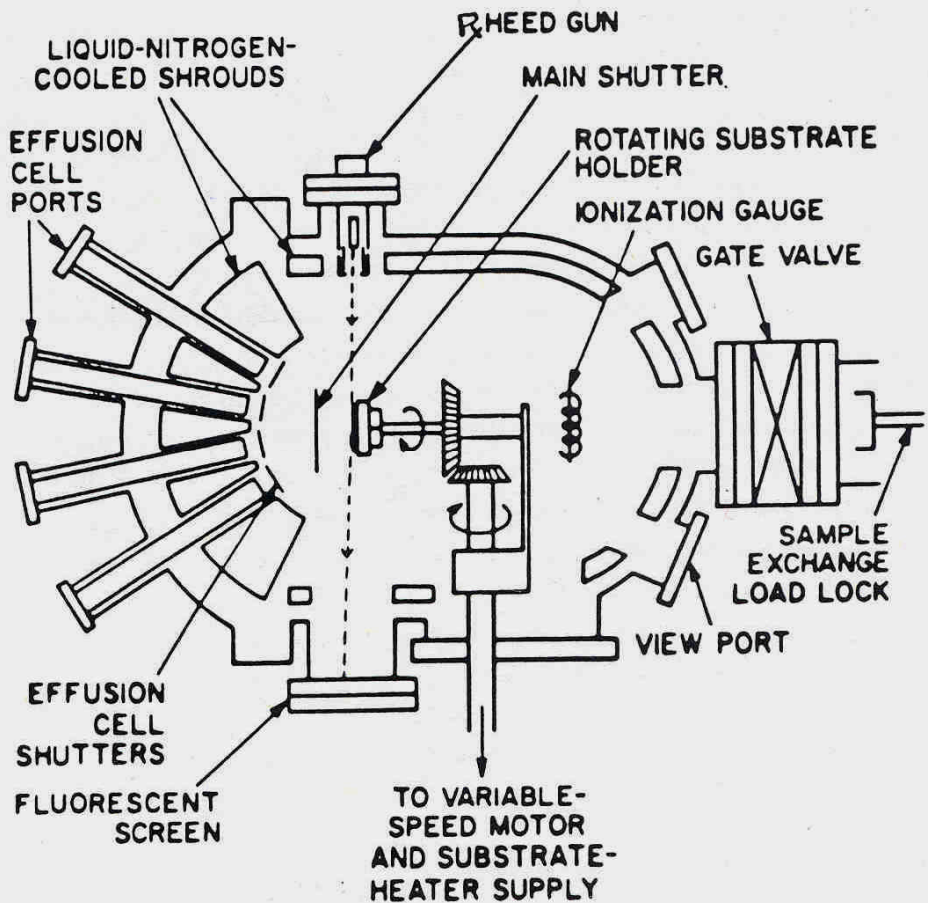
- dyes are highly persistent
- interactions of dye molecules (use as antennas)



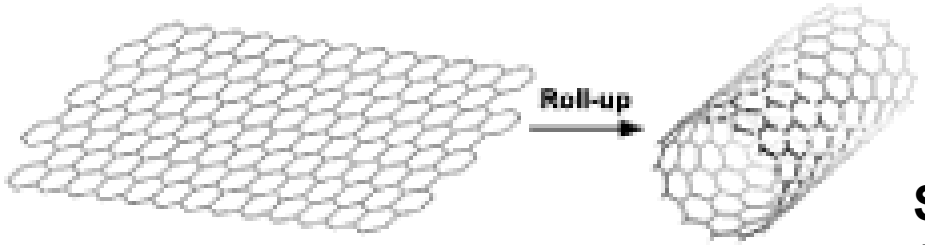


2.6 Structure of nanomaterials
0D nanomaterials – synthesis by MBE

- substrate wafers transferred to high vacuum growth chamber
- elements kept in effusion cells at high temperatures
- shutters over cells open to release vaporized elements, which deposit on sample
- temperature of each K-Cell controls the rate of deposition of that element (Ga, In, Al, etc.)
- precise control over temperatures and shutters allows very thin layers to be grown (~1 ML/sec)
- RHEED patterns indicate surface morphology (Reflection High Energy Electron Diffraction)



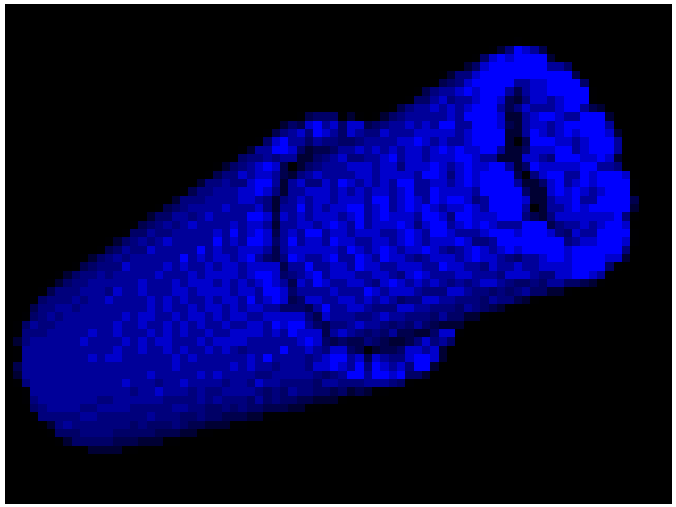
2.6 Structure of nanomaterials
1D nanomaterials – Carbon nanotubes



Graphene sheet

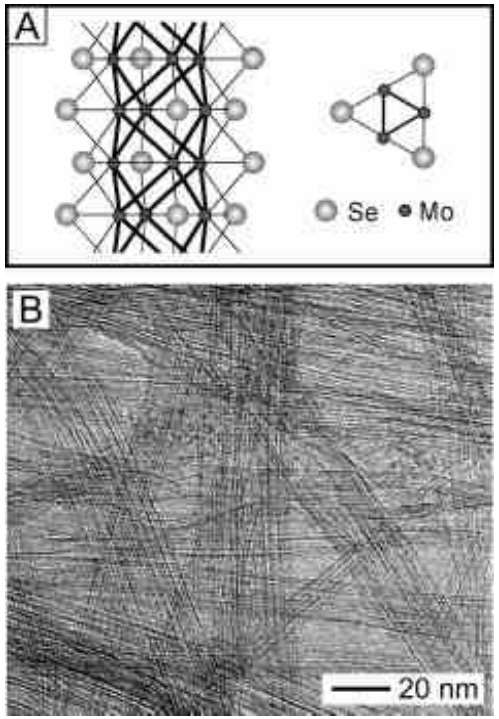
Single walled carbon nanotube (SWCNT)

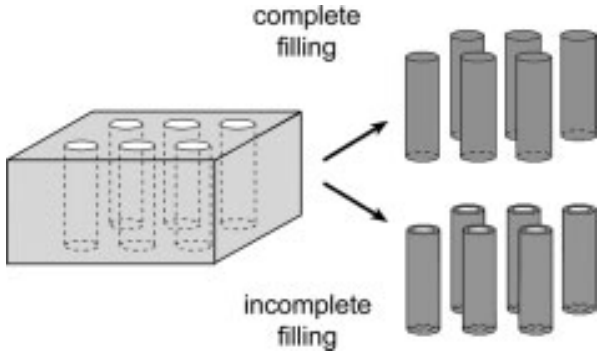
- multiwalled carbon nanotubes (MWCNT)
- different conformations: different conductivity
- electron emission (field emission)
- remarkable mechanical properties
- hydrogen adsorption
- easy electrolyte contact
- polymer strengthening
- transistor components
- drug or chemical storage



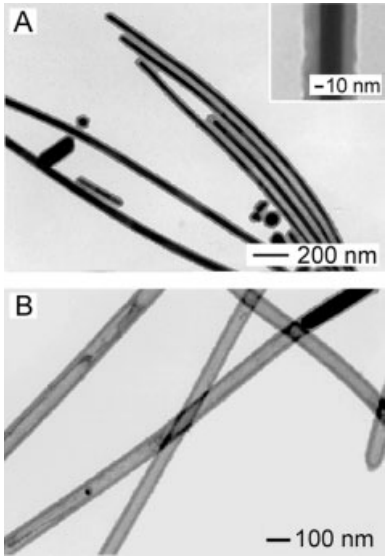
2.6 Structure of nanomaterials
1D nanomaterials – occurrence and synthesis

Misfit of layers
nanorolls (asbestos etc.)

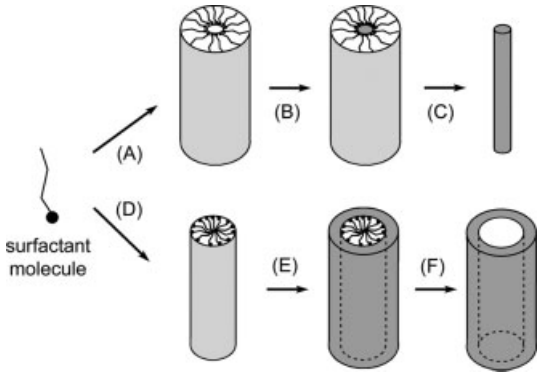




Templates
nanorods, nanotubes



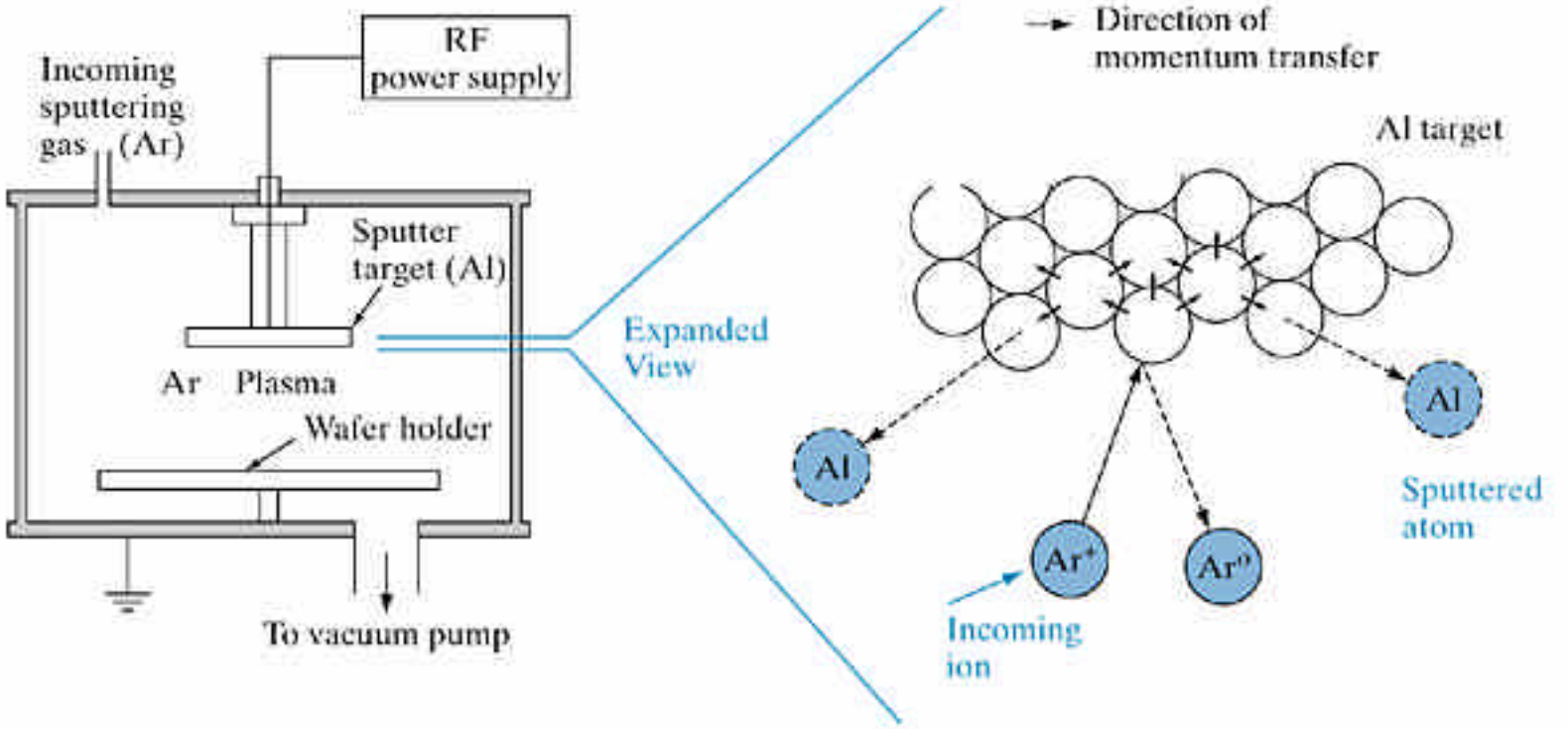
highly anisotropic
crystal structures
(Se, Te, $LiMo_3Se_3$)



Self assembley
nanorods, nanotubes

2.6 Structure of nanomaterials
2D nanomaterials - synthesis

- **Sputtering**
  - **originally a method to clean surfaces**
  - **Ar^+-ions are accelerated in an electrical field and „hit“ the target**
  - **consequence: surface atoms are removed from the surface**
  - **application: SEM, getter-pump (UHV devices)**

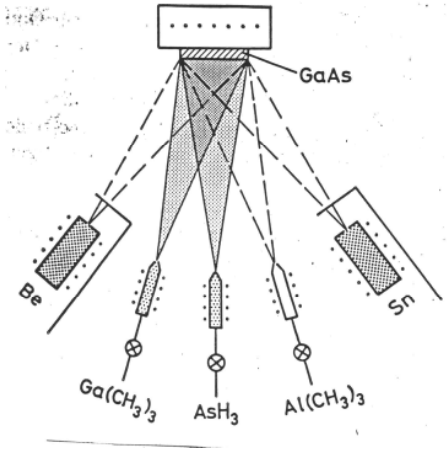


2.6 Structure of nanomaterials
2D nanomaterials - synthesis

- **Epitaxy:**
  - **thin orientated layers of similar crystal structures**
  - **e.g. InAs: a=603,6 pm on GaAs: a=565,4 pm, both sphalerite structures**

- **CVD (Chemical Vapour Deposition)**
  - **decomposition of molecules in the gas phase by electron beam or laser**
  - **deposition on suitable substrates**
  - **e.g. fabrication of LEDs with GaP and $GaAs_{1-x}P_x$, epitaxial layers are produced by thermal decomposition of compounds like AsH_3, $AsCl_3$, PH_3, PCl_3, ...**

- **MBE**

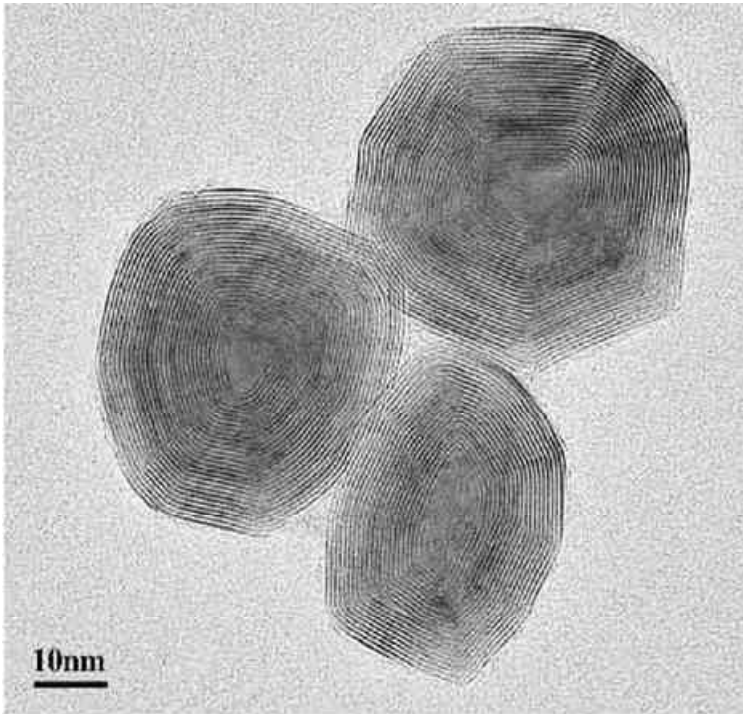


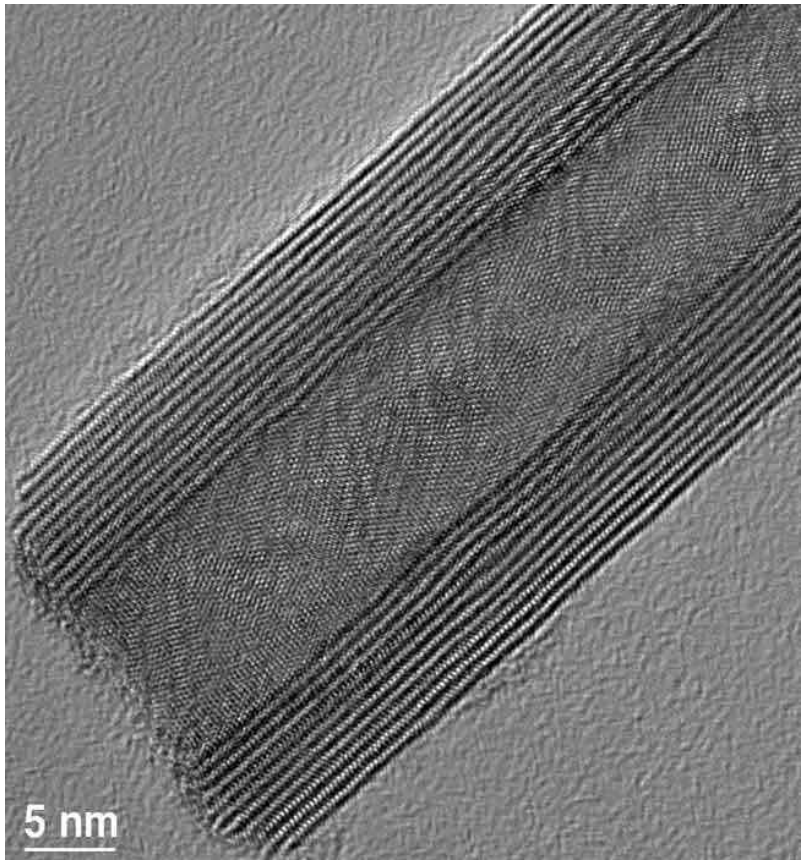
Production of a $Ga_{1-x}Al_xAs$ on GaAs by the MBE process

2.6 Structure of nanomaterials
Chemical approaches to nanomaterials

R. Tenne

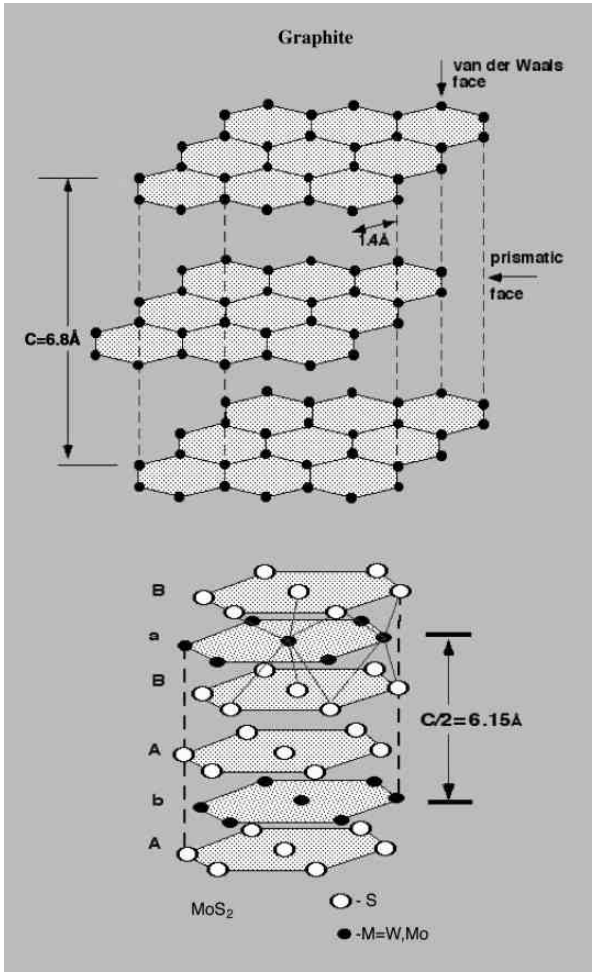
Inorganic fullerenes

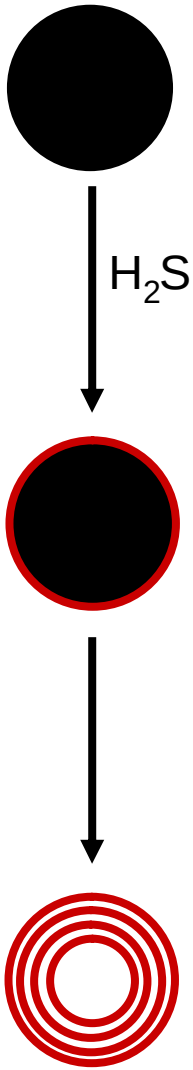




Inorganic nanotubes

2.6 Structure of nanomaterials
Hollow inorganic structures – how does it work?





compact MoO_2 nanoparticle

compact MoO_2 nanoparticle covered with a few layers of MoS_2
consequence: isolated particles

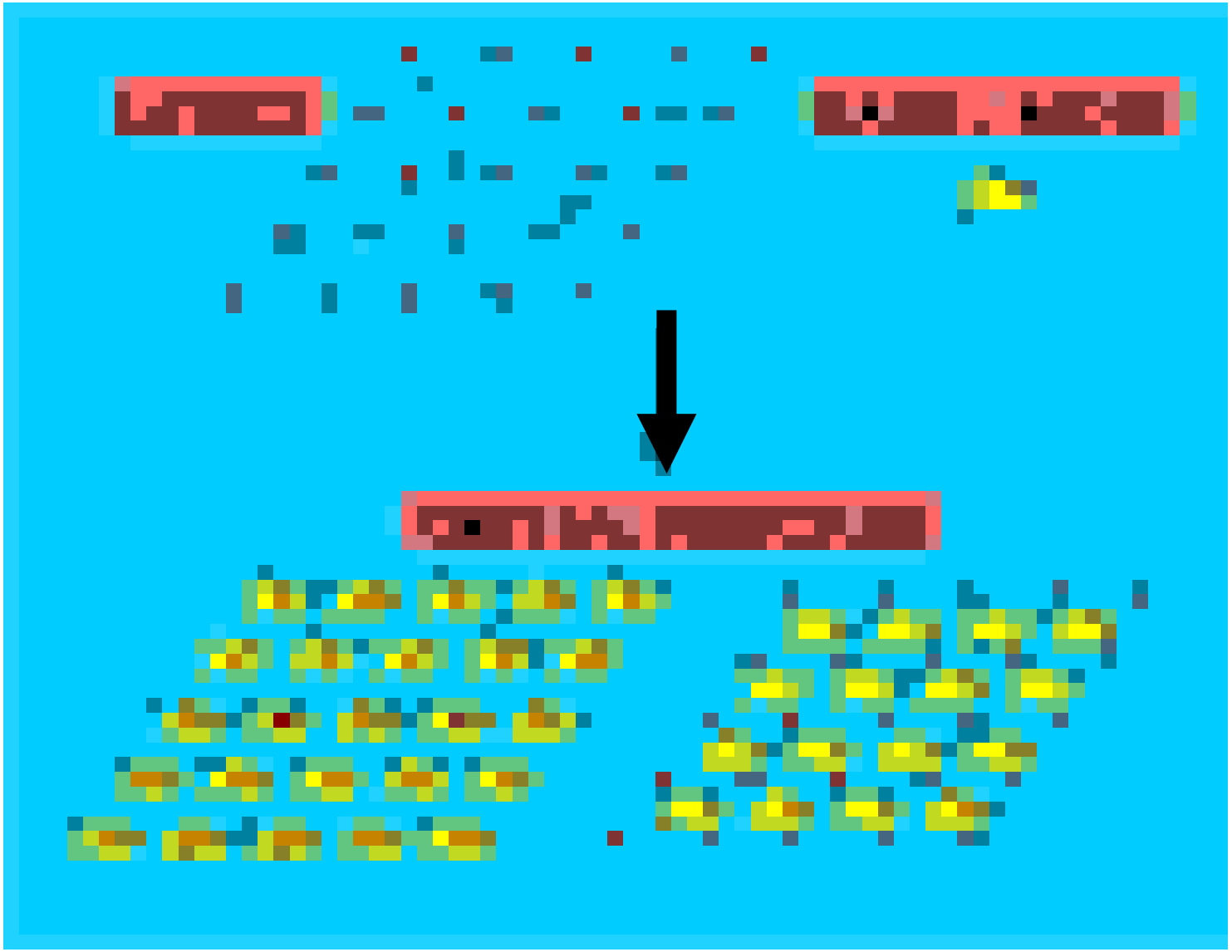
diffusion controlled reaction
density of MoS2 lower than MoO2
consequence: hollow particle

Summary to 2.6

- nanomaterials of different dimensionality
- unique properties of small objects
- 0D
- 1D
- 2D
- chemical approaches to nanoparticles

Exercises

2.1 Basics of Structures
Structure and lattice – what is the difference?



2.1 Basics of Structures
Structure and lattice – full description

Crystal data

Formula sum C
Crystal system trigonal
Space group *R* -3 m (no. 166)

Structure

Unit cell dimensions *a, b, c* = 3.6350 Å, α = 39.49 °

Lattice

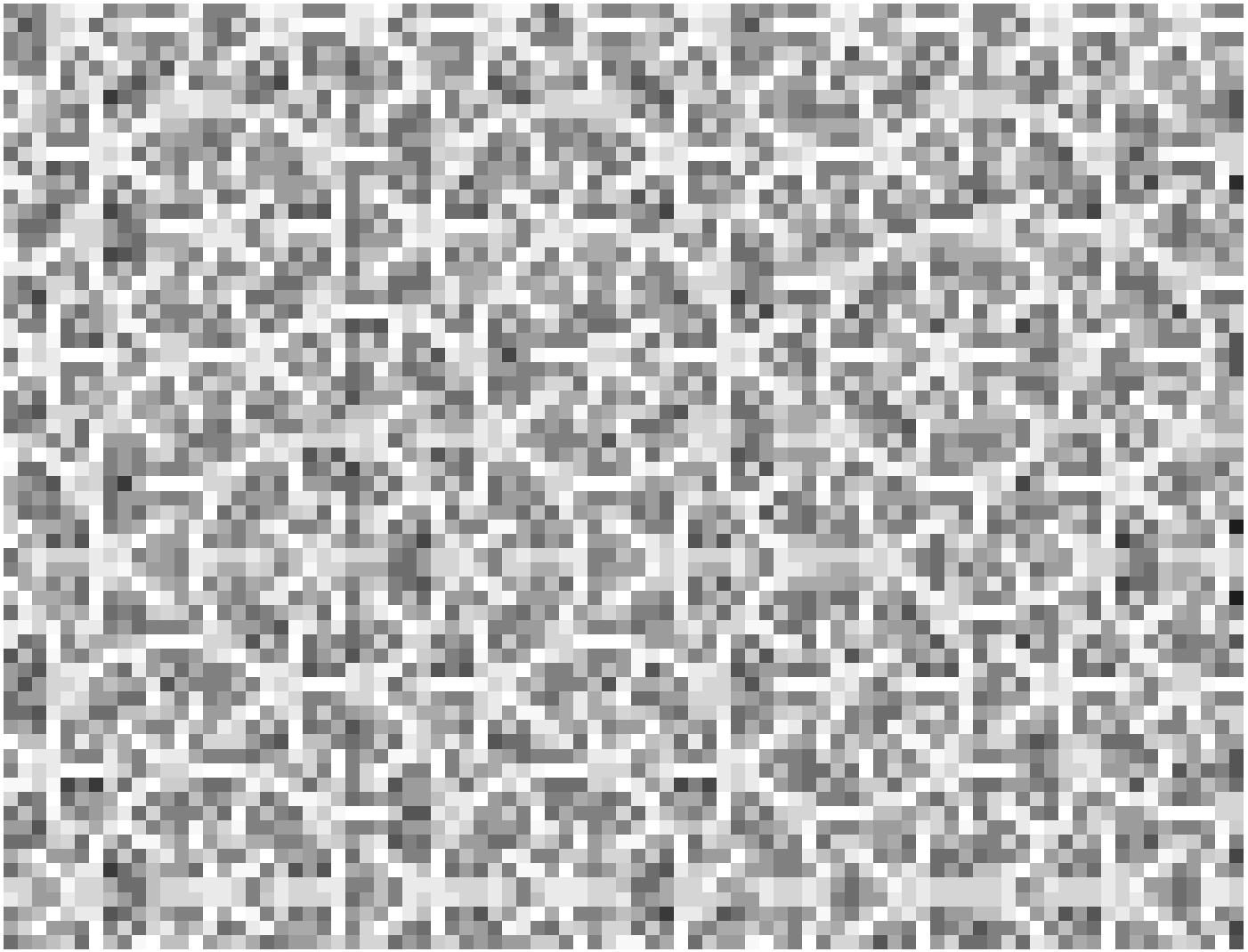
Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
C	+0	*2c*	0.164	0.164	0.164

Structure

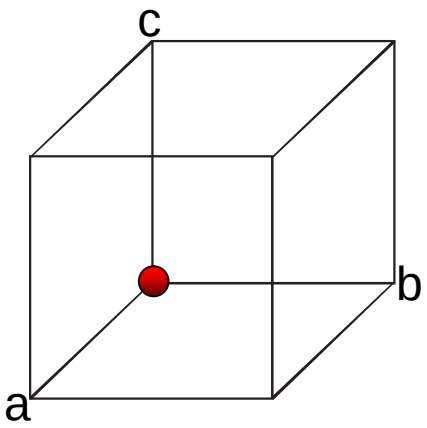
2.1 Basics of Structures
Determine the unit cell of the following pattern

2.1 Basics of Structures
Structures without translational symmetry

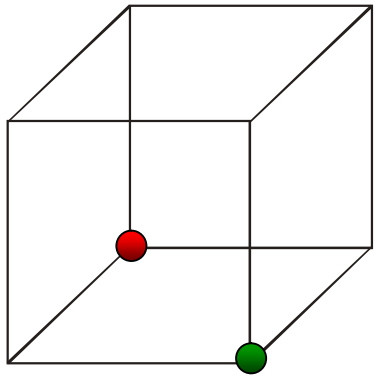


2.1 Basics of Structures
Indices of directions in space

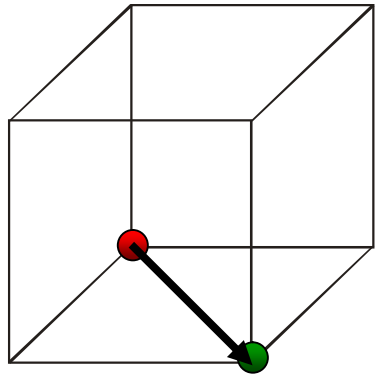
“[110]”
Procedure in three steps



1. Select 000



2. Mark position of second point



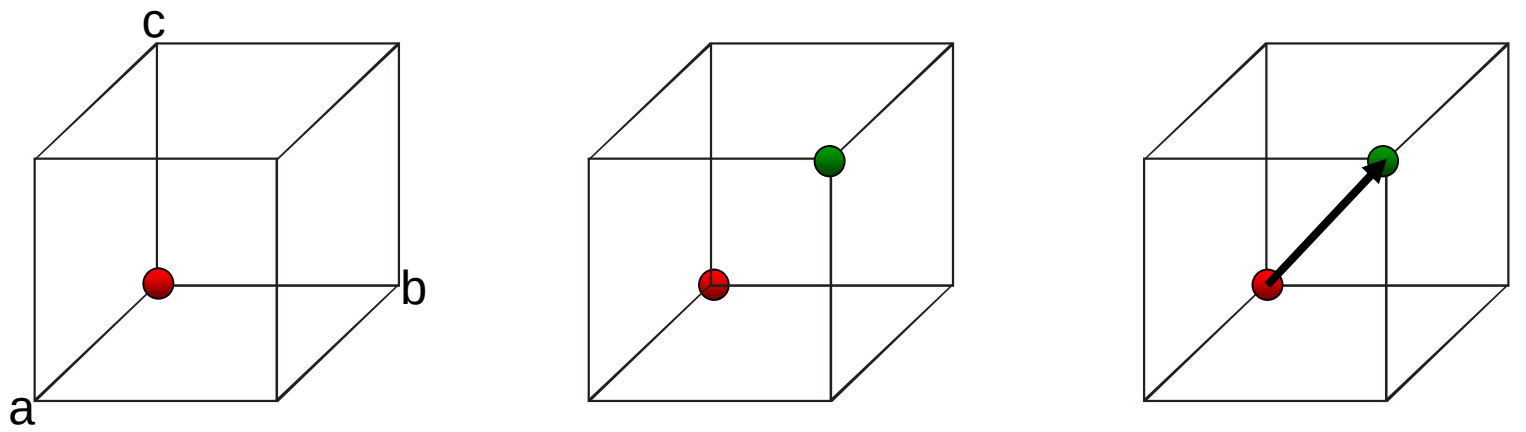
3. Draw vector

Convention: right-handed coordinate system

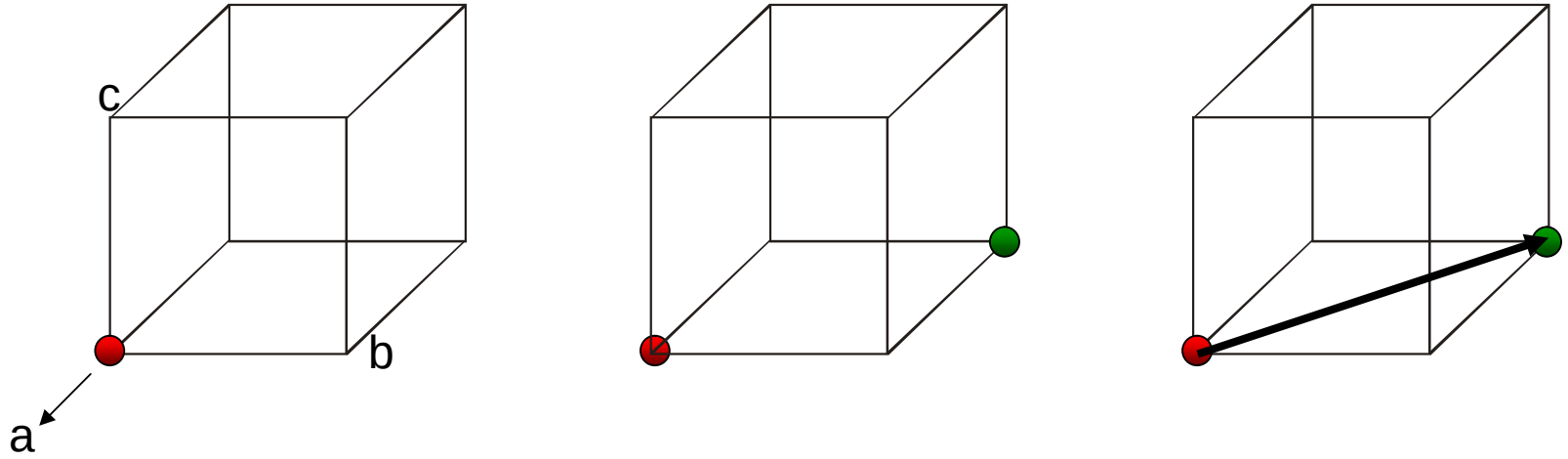
- **middle finger: a**
- **forefinger: b**
- **thumb: c**

2.1 Basics of Structures
Indices of directions in space – examples 1

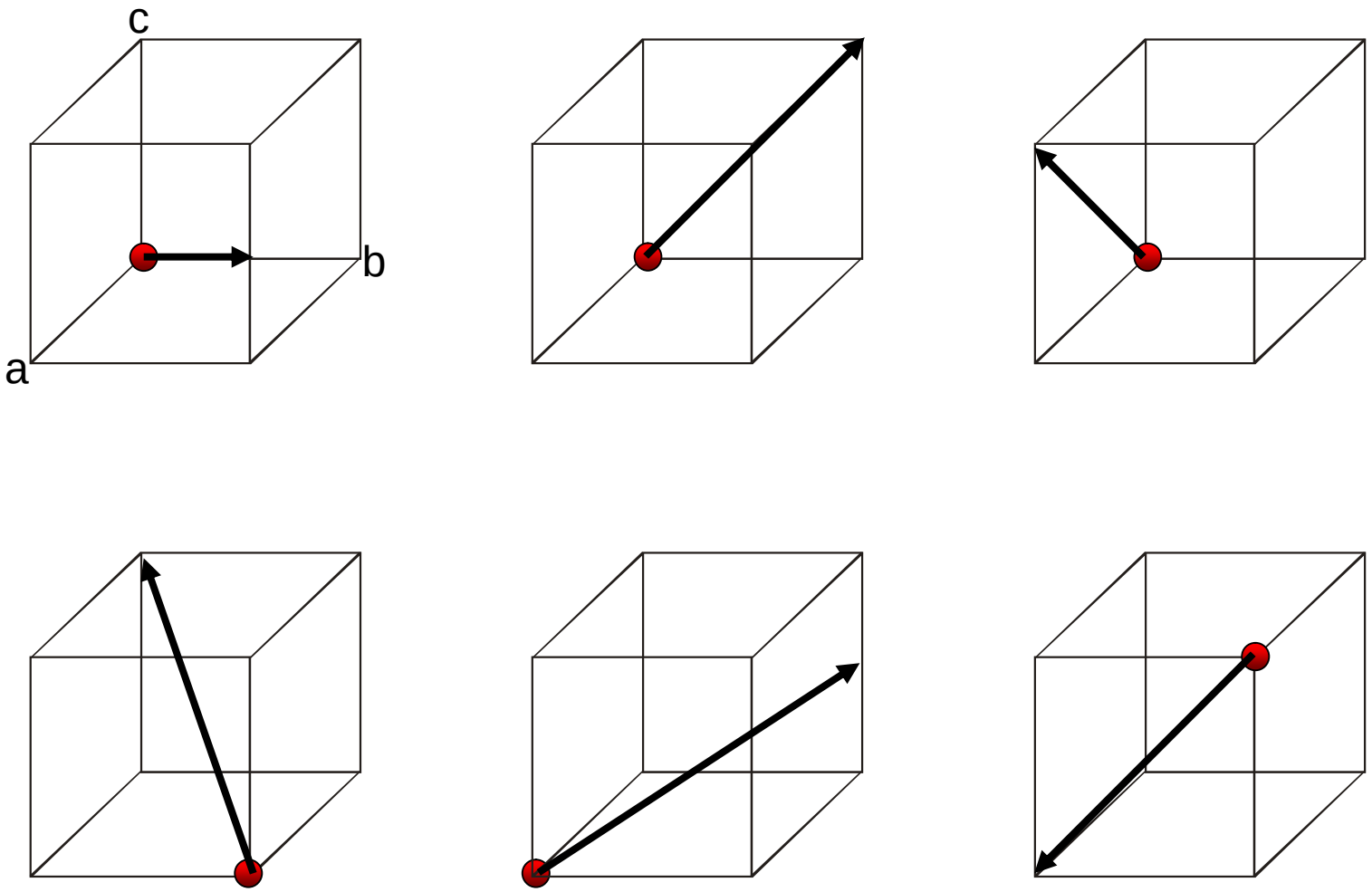
[111]



[$\bar{1}$10]

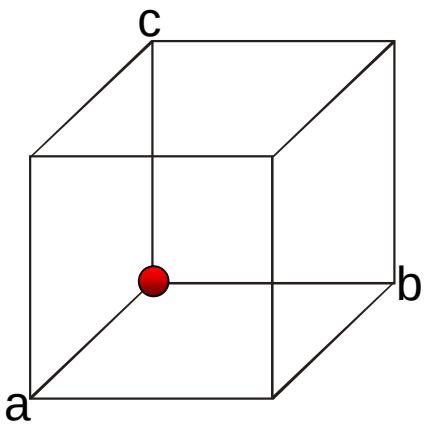


2.1 Basics of Structures
Indices of directions in space – examples 2

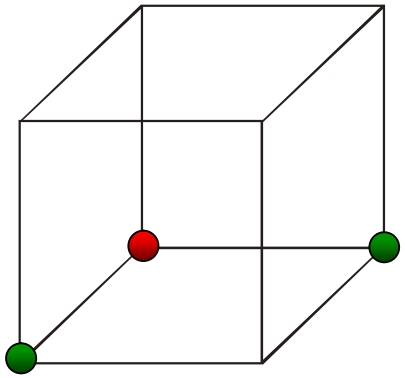


2.1 Basics of Structures
Indices of planes in space

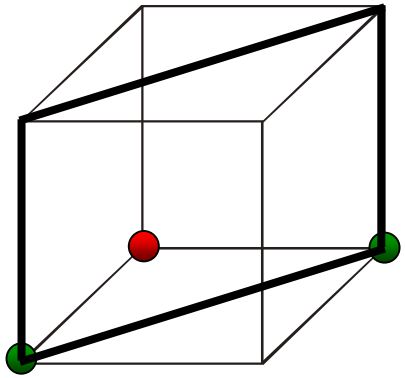
“(110)”
Procedure in three steps



1. Select 000



2. Mark intercept of the axes (if possible)

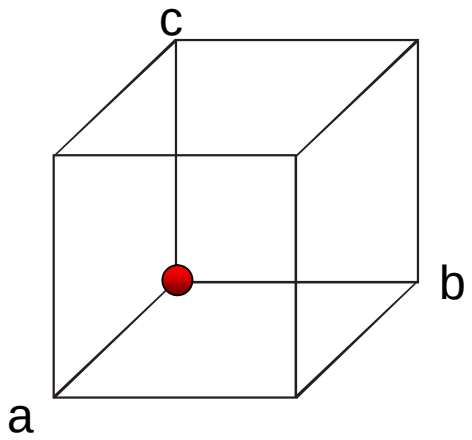


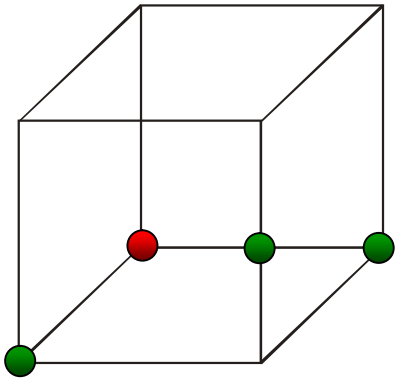
3. Draw plane

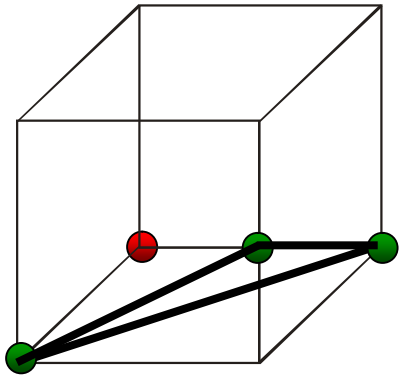
Convention: right-handed coordinate system

2.1 Basics of Structures
Indices of planes in space – examples 1

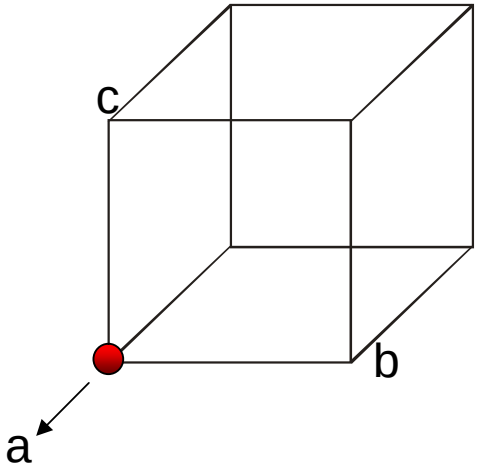
(112)

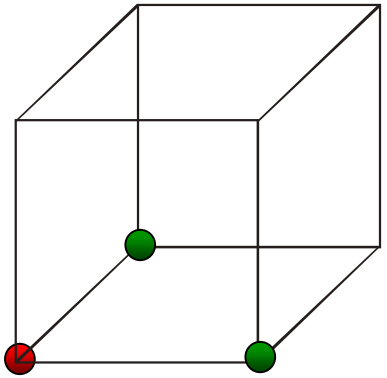


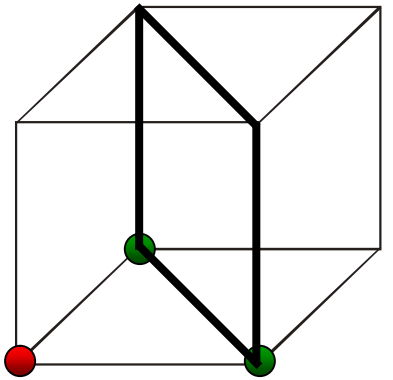




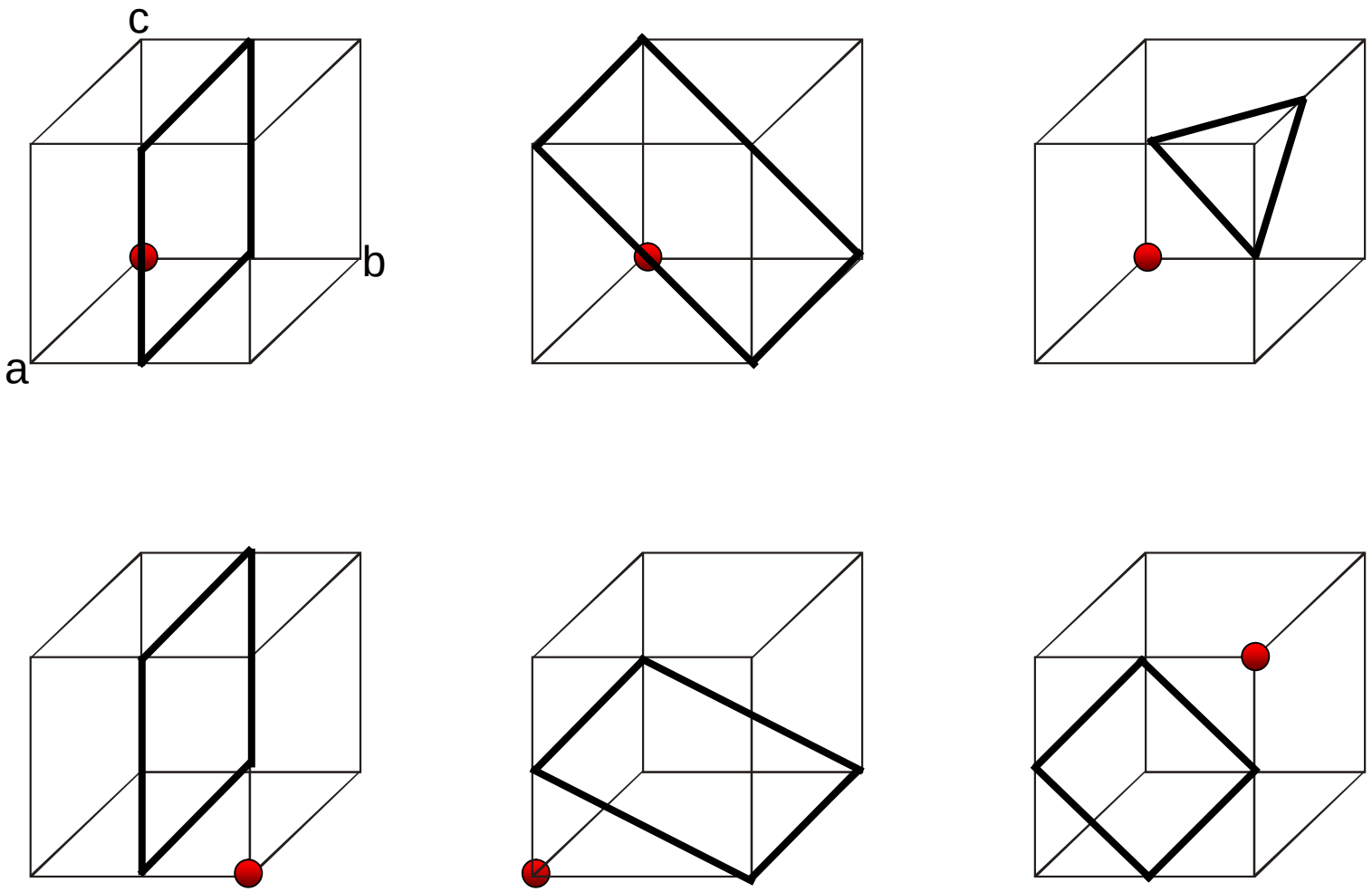
($\bar{1}$10)



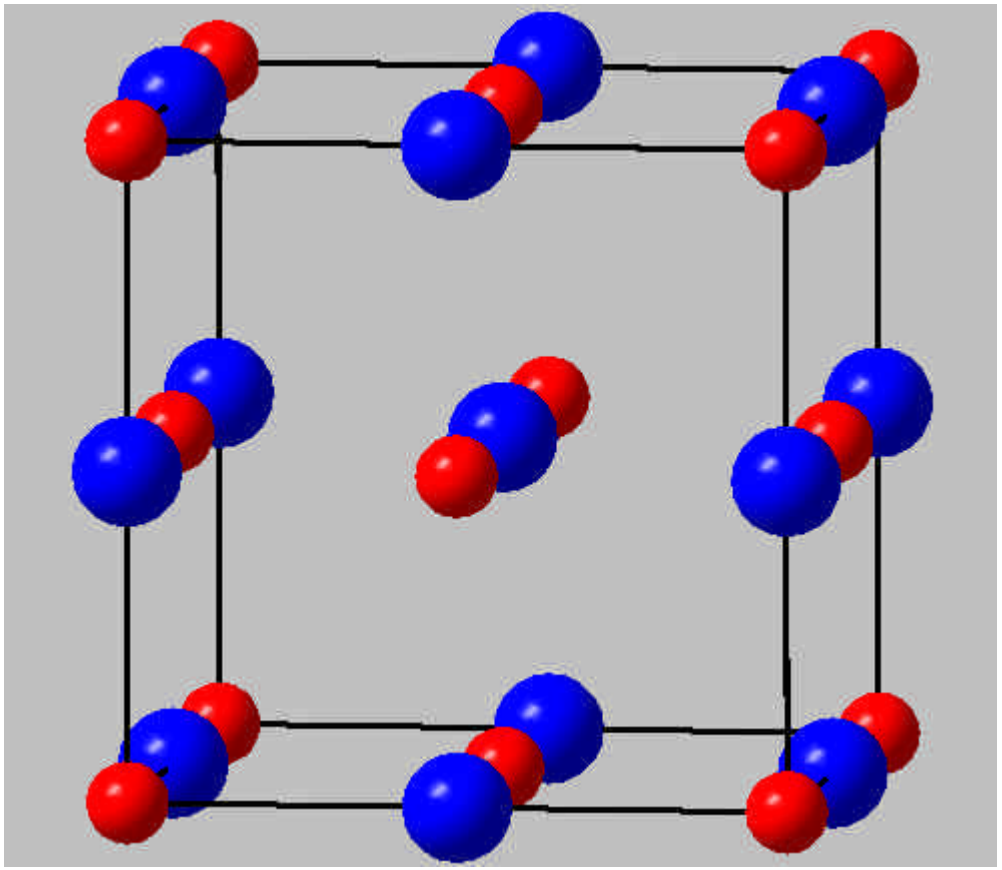




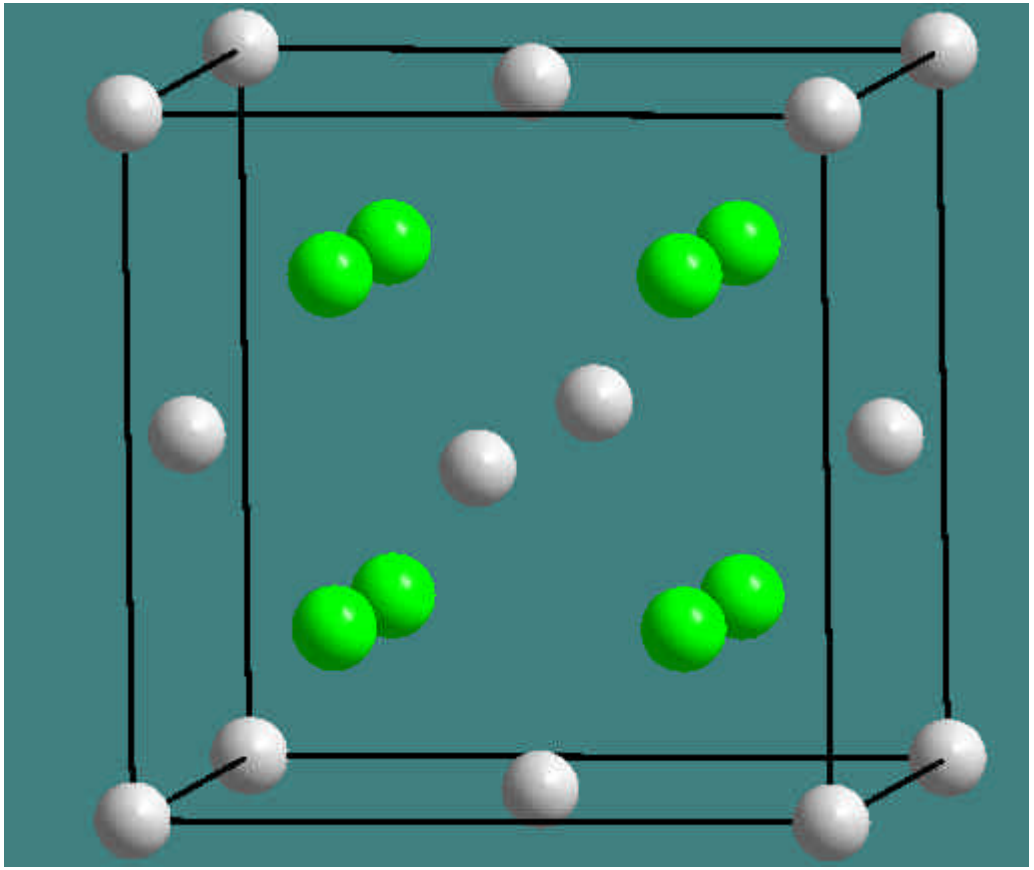
2.1 Basics of Structures
Indices of planes in space – examples 2



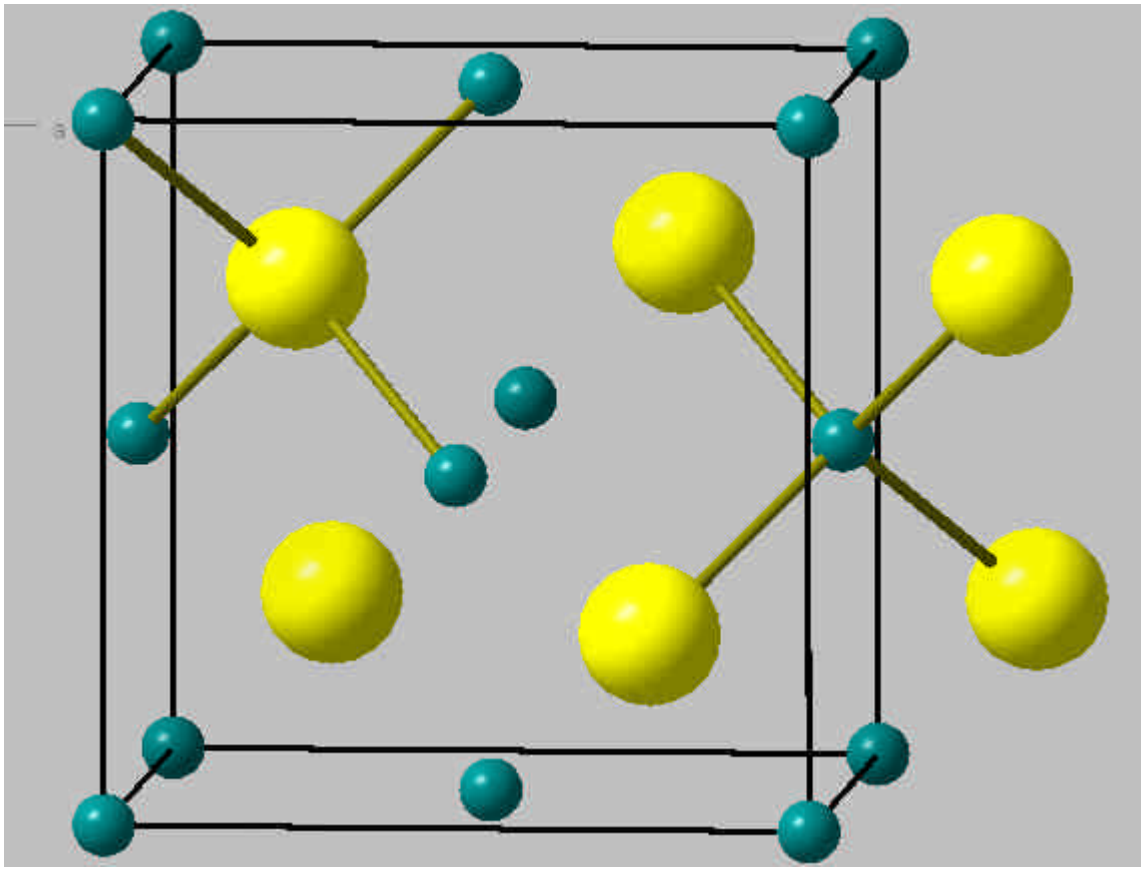
2.1 Basics of Structures
Determine the fractional coordinates and Z



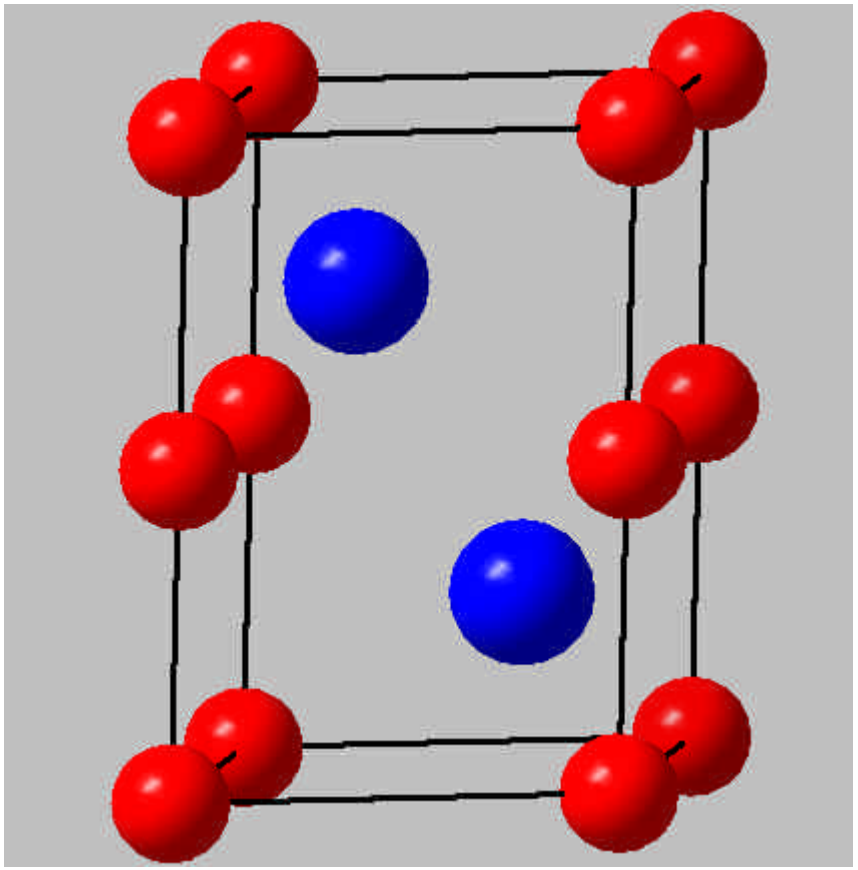
2.1 Basics of Structures
Determine the fractional coordinates and Z



2.1 Basics of Structures
Determine the fractional coordinates and Z



2.1 Basics of Structures
Determine the fractional coordinates and Z



2.1 Basics of Structures
How many Zr,Si and O atoms are in one unit cell?

Crystal data

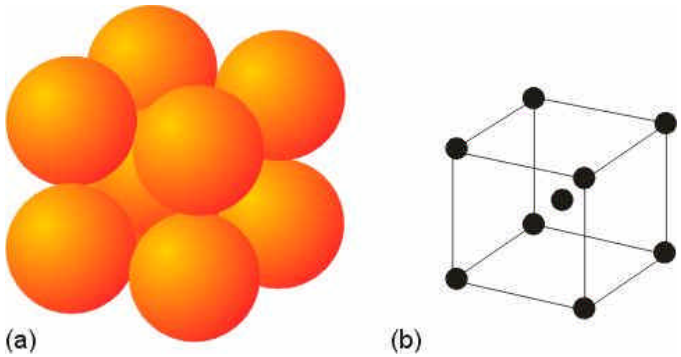
Formula sum	$ZrSiO_4$
Crystal system	tetragonal
Space group	*I* 41/a m d (no. 141)
Unit cell dimensions	*a* = 6.625(6) Å *c* = 6.0313(70) Å
Cell volume	267.00(46) Å3

Atomic coordinates

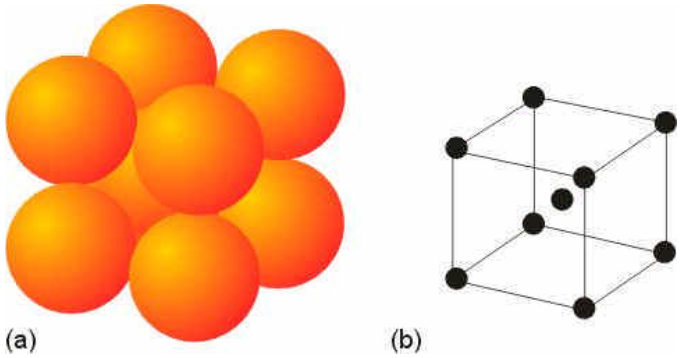
Atom	**Ox.**	**Wyck.**	**x**	**y**	**z**	
O1	-2	16*h*	0	0.06592(10)		0.19922(70)
Zr1	+4	4*a*	0	3/4	1/8	
Si1	+4	4*b*	0	1/4	3/8	

2.2 Simple close packed structures (metals) Calculation of space filling – example BCC

$$\text{Space filling} = \frac{\text{Volume occupied by atoms (spheres)}}{\text{Volume of the unit cell}}$$



2.3 Basic structure types
Calculate the radius ratio for a cubic coordination



2.3 Basic structure types
Pauling rules: understanding polyhedral structures

Example 4 – $Al_2O_3*2SiO_2*2H_2O$ (Kaolinite)

$CN(Al^{3+}) = 6$, $CN(Si^{4+}) = 4$, sij (Al-O) = 1/2 , sij (Si-O) = 1

CN(O1) = 2(Al), CN(O2) = 2(Al) + 1(Si), CN(O3) = 2

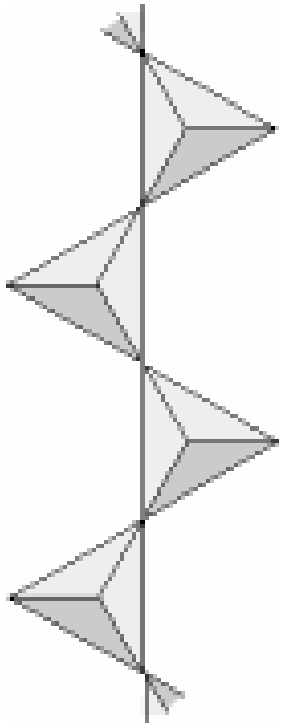
$\sum$sij (O1) = 1 (!!!), $\sum$ sij (O2) = 2, $\sum$ sij (O3) = 2. Consequence: O1 is OH !!!

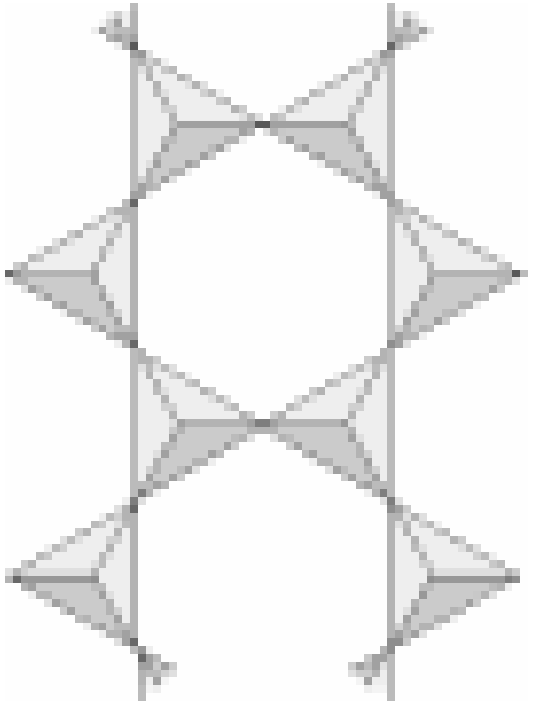
Example 5 – Determine possible coordination spheres of O in Na_3BiO_4

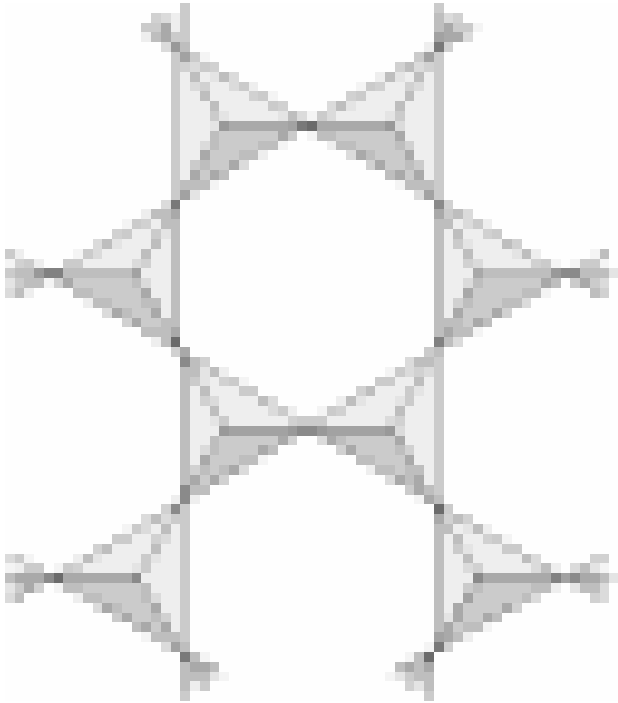
- rock salt type structure CN(O) = 6, CN(cations) = 6, O^{2-}, Na^{+}, Bi^{5+}.
- ONa_6 with charge: -2 + 6/6 = -1
- ONa_5Bi with charge: -2 + 5/6 + 5/6 = -1/3
- ONa_4Bi_2 with charge: -2 + 4/6 + 10/6 = +1/3
- ONa_3Bi_3 with charge: -2 + 3/6 + 15/6 = +1
- Composition and frequency of octahedra:

$O(Na_5Bi)/6 + O(Na_4Bi_2)/6 = O_2Na_{9/6}Bi_{3/6} = O_4Na_3Bi$

2.5 Complex structures
Determine the formula of the characteristic units







2.5 Complex structures
Any suggestions for the anionic partial structure?

$CaSi_2$

KSnAs

$KSnSb_2$

LiGaSn