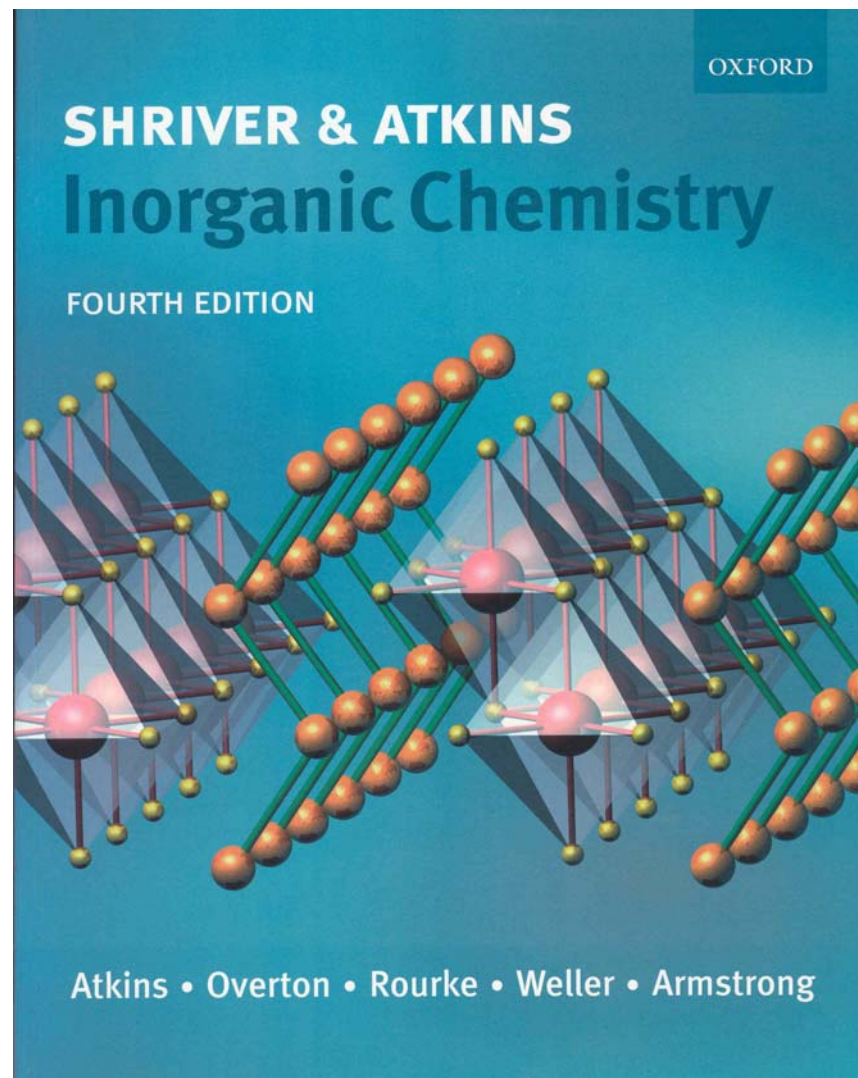


Advanced Inorganic Chemistry (Part 1) Basic Solid State Chemistry WS 07/08

(H.J. Deiseroth)

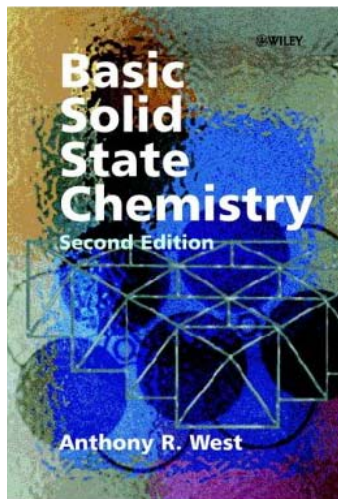
Resources



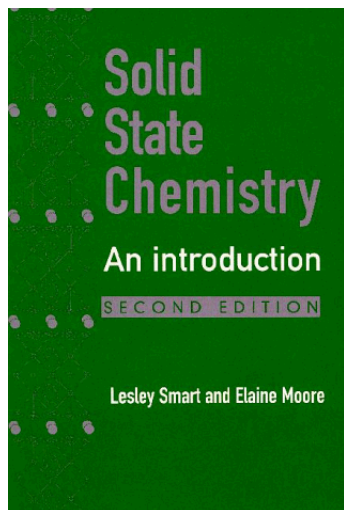
Resources

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

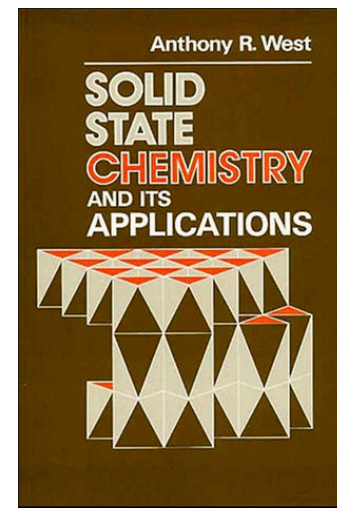
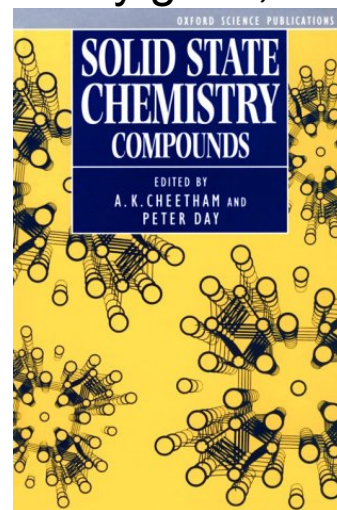
recommendation



german



very good, but not basic level

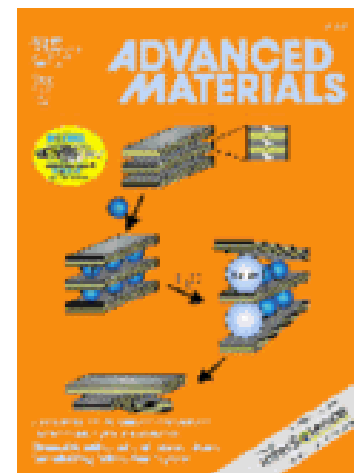
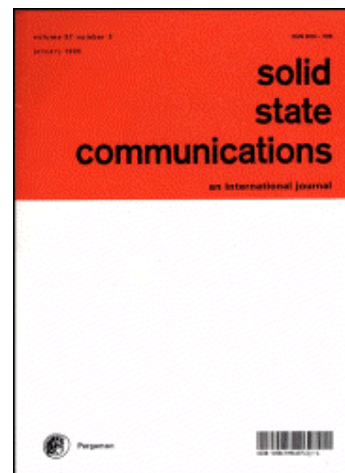
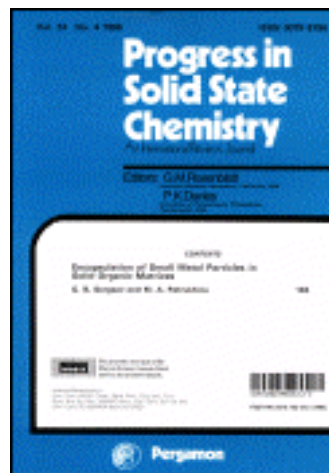
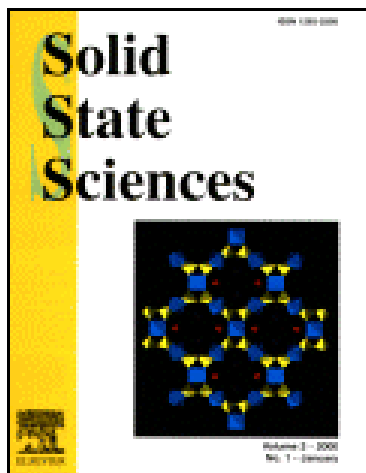


Internet resources

- <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 - 16.10.07

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

2.6 Structure of nanomaterials

} Oxides...

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		

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)

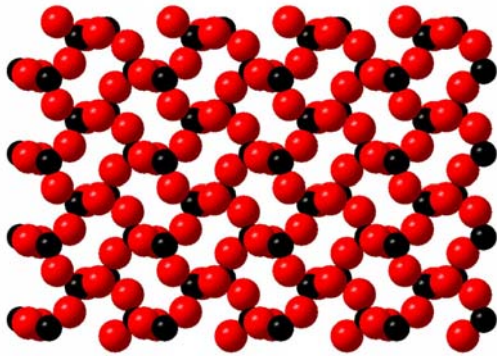
- **Degree of order**
 - crystals: long range order (3D periodicity)
 - amorphous solids, glasses: short range order (no 3D periodicity)
 - crystals with disorder of a partial structure (ionic conductors)
- **Chemical bonding – typical properties**
 - covalent solids (e.g. diamond, boron nitride): extreme 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...
 - defects in solids, point defects, dislocations

2.1 Basics of Structures

Visualization of structures

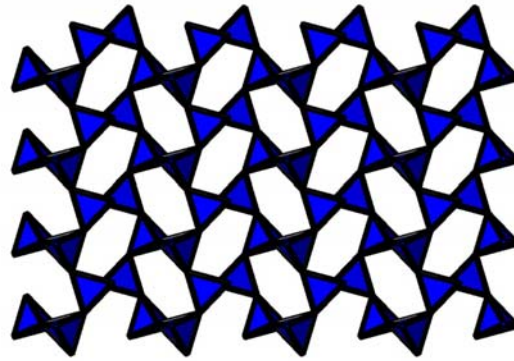
Example: Cristobalite (SiO_2)

Description of packing



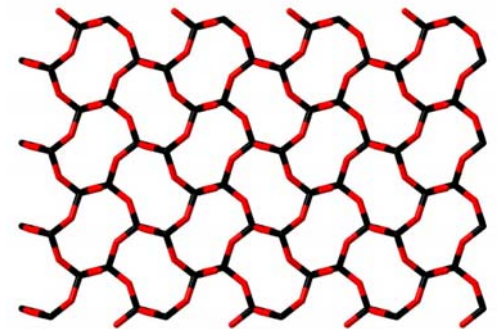
Bragg jun. (1920)
Sphere packing

Description of environment



Pauling (1928)
Polyhedra

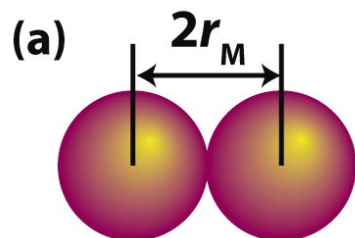
Description of topology



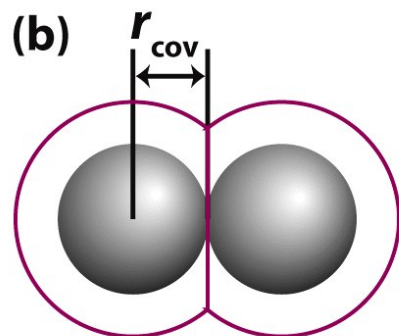
Wells (1954)
3D nets

2.1 Basics of Structures

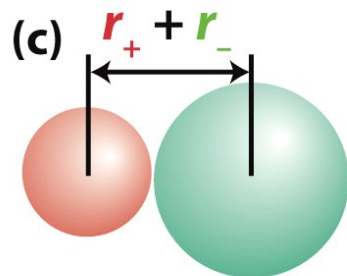
Approximation: atoms can be treated like spheres



Metallic radius: $d/2$ in metal



covalent radius: $d/2$ in molecule (single bond)



ionic radius: reference, e.g. $r(\text{O}^{2-}) = 140 \text{ pm}$ (Shannon for CN = 6)

Figure 1-23

Shriver & Atkins Inorganic Chemistry, Fourth Edition

© 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

2.1 Basics of Structures

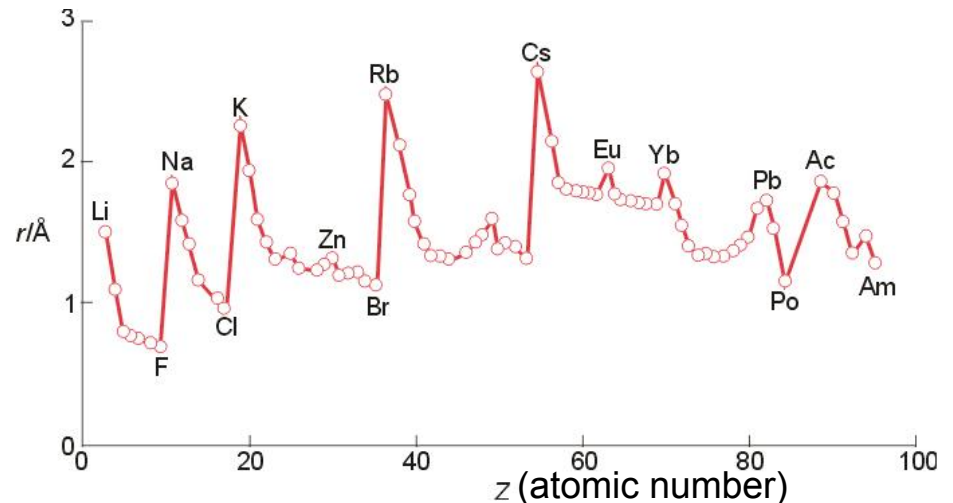
Trends of the atomic radius

	1A (1)								8A (18)
1	H 37 •	2A (2)							He 31 •
2	Li 152 ●	Be 112 ●							
3	Na 186 ●	Mg 160 ●							
4	K 227 ●	Ca 197 ●							
5	Rb 248 ●	Sr 215 ●							
6	Cs 265 ●	Ba 222 ●							
7	Fr (270) ●	Ra (220) ●							

	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	
	B 85 ●	C 77 ●	N 75 ●	O 73 ●	F 72 ●	Ne 71 ●
	Al 143 ●	Si 118 ●	P 110 ●	S 103 ●	Cl 100 ●	Ar 98 ●
	Ga 135 ●	Ge 122 ●	As 120 ●	Se 119 ●	Br 114 ●	Kr 112 ●
	In 167 ●	Sn 140 ●	Sb 140 ●	Te 142 ●	I 133 ●	Xe 131 ●
	Tl 170 ●	Pb 146 ●	Bi 150 ●	Po 168 ●	At (140) ●	Rn (140) ●

	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	(8)	8B (9)	(10)	1B (11)	2B (12)
4	Sc 162 ●	Ti 147 ●	V 134 ●	Cr 128 ●	Mn 127 ●	Fe 126 ●	Co 125 ●	Ni 124 ●	Cu 128 ●	Zn 134 ●
5	Y 180 ●	Zr 160 ●	Nb 146 ●	Mo 139 ●	Tc 136 ●	Ru 134 ●	Rh 134 ●	Pd 137 ●	Ag 144 ●	Cd 151 ●
6	La 187 ●	Hf 159 ●	Ta 146 ●	W 139 ●	Re 137 ●	Os 135 ●	Ir 136 ●	Pt 138 ●	Au 144 ●	Hg 151 ●

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



2.1 Basics of Structures Atomic radii

Table 1.4 Atomic radii, r/pm^*

Li	Be											B	C	N	O	F
157	112											88	77	74	66	64
Na	Mg											Al	Si	P	S	Cl
191	160											143	118	110	104	99
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
235	197	164	147	135	129	137	126	125	125	128	137	155	122	121	117	114
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
250	215	182	160	147	140	135	134	134	137	144	152	167	158	141	137	133
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
272	224	172	159	147	141	137	135	136	139	144	155	171	175	182		

* The values refer to coordination number 12 (see Section 3.2).

Ga: 122 pm !

2.1 Basics of Structures Ionic radii

Table 1.5 Ionic radii, r/pm^*

Li⁺ 59(4) 76(6)	Be²⁺ 27(4)	B³⁺ 12(4)			N³⁻ 132	O²⁻ 135(2) 138(4) 140(6) 142(8)	F⁻ 128(2) 131(4) 133(6)
Na⁺ 99(4) 102(6) 116(8)	Mg²⁺ 49(4) 72(6) 89(8)	Al³⁺ 39(4) 53(6)			P³⁻ 212	S²⁻ 184(6)	Cl⁻ 167(6)
K⁺ 138(6) 151(8) 159(10) 160(12)	Ca²⁺ 100(6) 112(8) 128(10) 135(12)	Ga³⁺ 62(6)			As³⁻ 222	Se²⁻ 198(6)	Br⁻ 196(6)
Rb⁺ 149(6) 160(8) 173(12)	Sr²⁺ 116(6) 125(8) 144(12)	In³⁺ 79(6) 92(8)	Sn²⁺ 83(6) 93(8)	Sn⁴⁺ 74(6)		Te²⁻ 221(6)	I⁻ 206(6)
Cs⁺ 167(6) 174(8) 188(12)	Ba²⁺ 149(6) 156(8) 175(12)	Tl³⁺ 88(6) Tl⁺ 164(6)					

* Numbers in parentheses are the coordination number of the ion. For more values, see *Resource section 1*.

Table 3.3 The variation of radius with coordination number

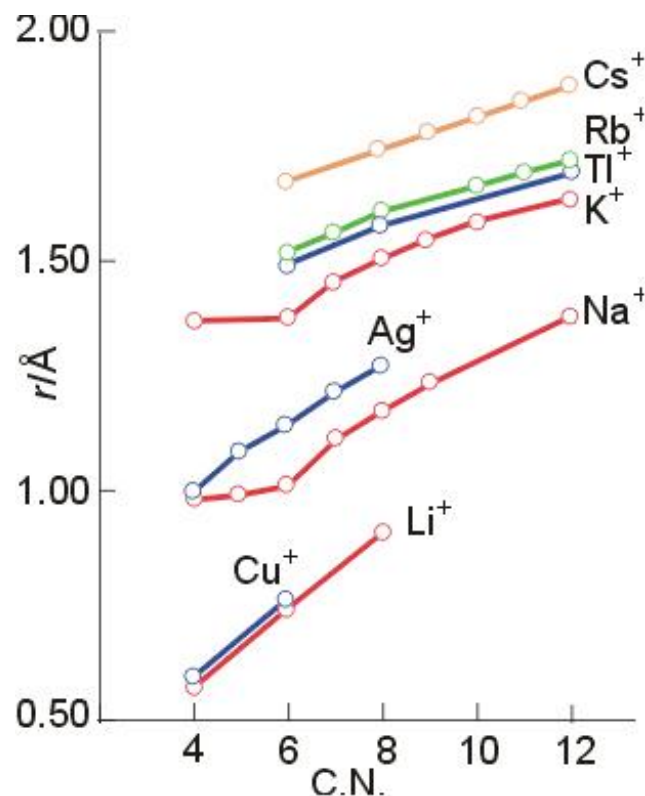
Coordination number	Relative radius
12	1
8	0.97
6	0.96
4	0.88

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
- 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 ($r(\text{Fe}^{2+}) > r(\text{Fe}^{3+})$)
- cations are usually the smaller ions in a cation/anion combination (exception: $r(\text{Cs}^+) > r(\text{F}^-)$)

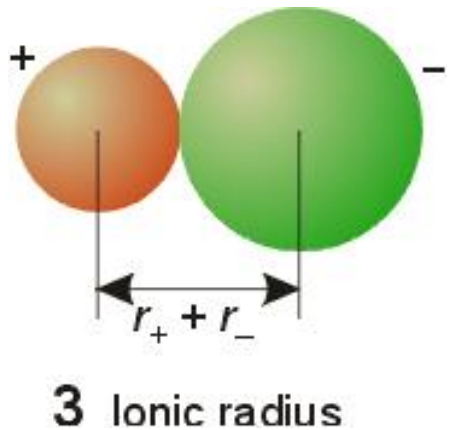
} cf. atomic radii



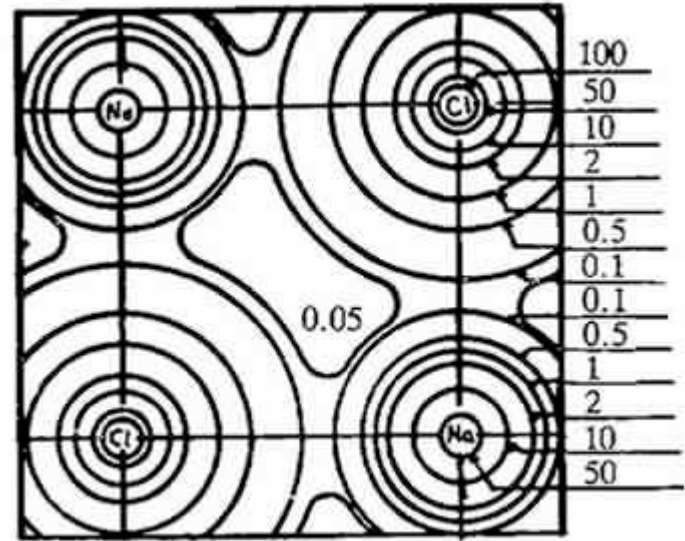
2.1 Basics of Structures

Determination of the ionic radius

Ionic radius = $d - r(\text{F, O...})$



Structure analyses,
most important method:
X-ray diffraction



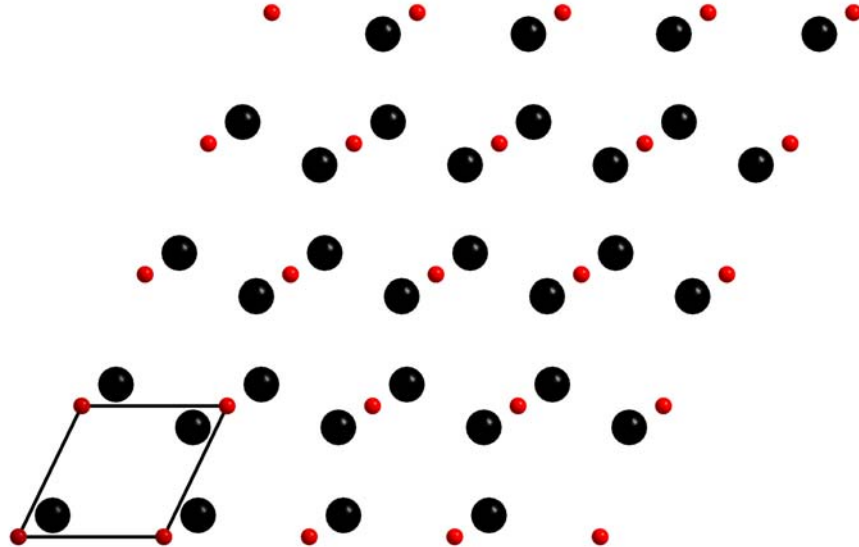
L. Pauling:

- Radius of one ion is fixed to a reasonable value ($r(\text{O}^{2-}) = 140 \text{ pm}$)
- 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**



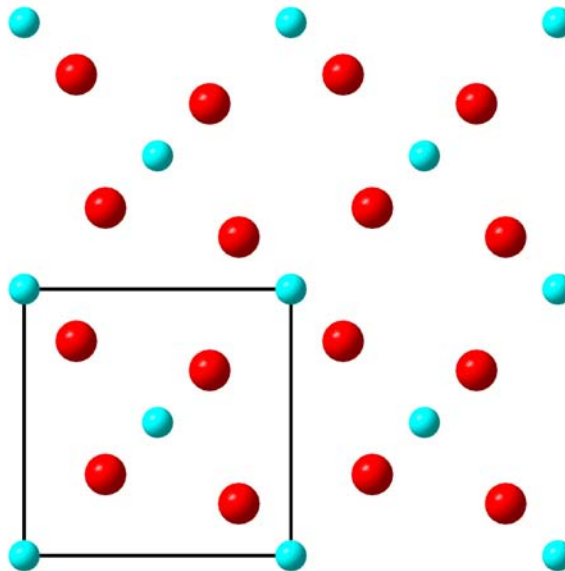
- **Lattice**
 - pattern of points
 - no chemical information, mathematical description
 - no atoms, but points and lattice vectors (a , b , c , α , β , γ), unit cell
- **Motif** (characteristic structural feature, atom, group of atoms...)
- **Structure = Lattice + Motif**
 - contains chemical information (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
- contents of unit cell represents chemical composition
(multiples of chemical formula)
- primitive cell: simplest cell, contain one lattice point



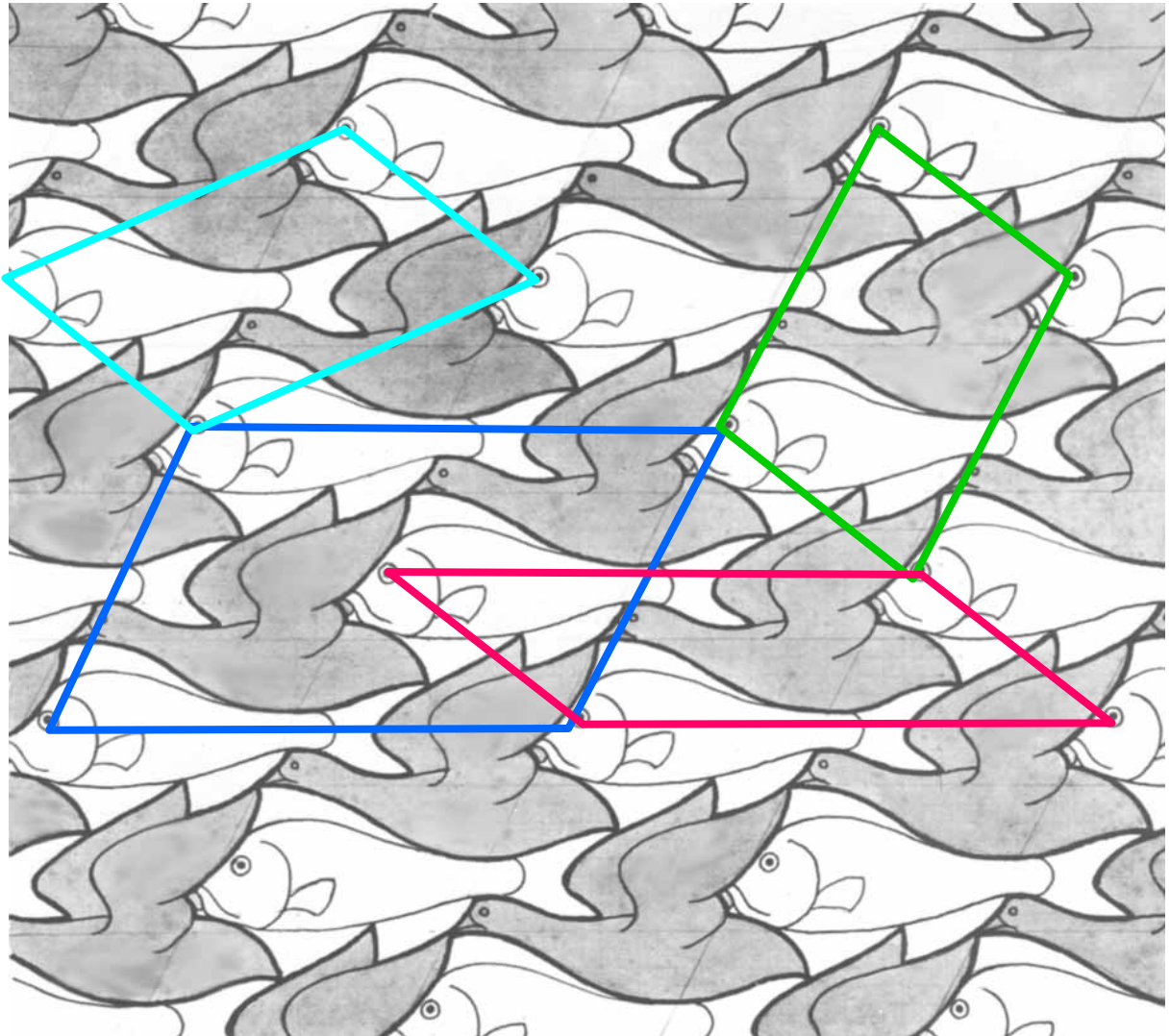
2.1 Basics of Structures

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

M.C. Escher



2.1 Basics of Structures

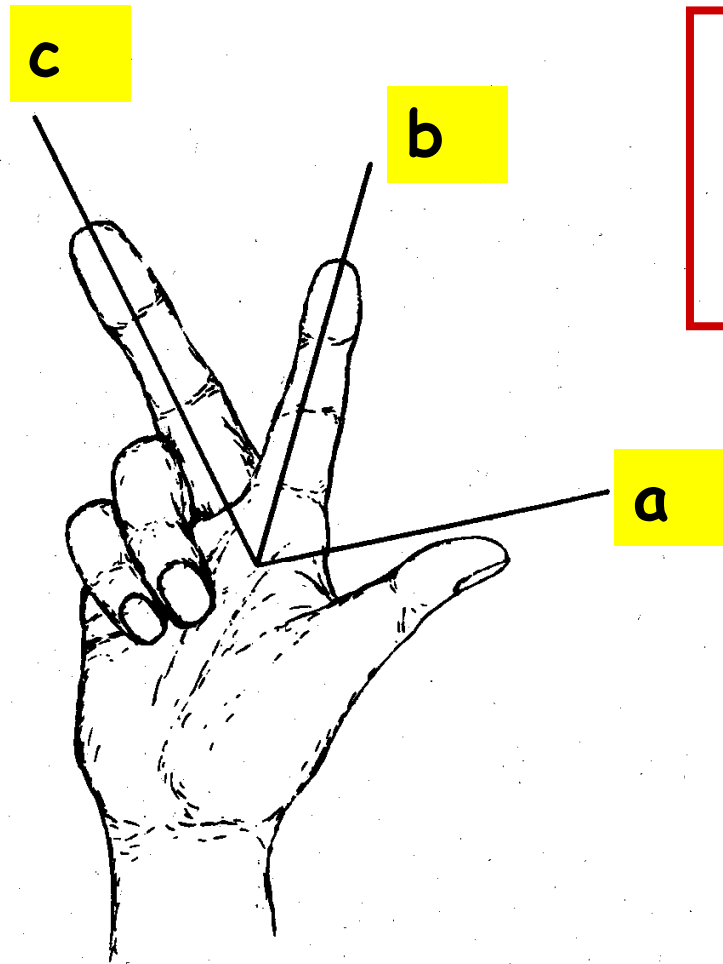
Unit cells and crystal system

- 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	-	$\alpha = \gamma = 90^\circ$
Orthorhombic	-	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b$	$\alpha = \beta = \gamma = 90^\circ$
Trigonal	$a = b$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Hexagonal	$a = b$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$

2.1 Basics of Structures

Unit cells and crystal system: "Right Hand Rule"

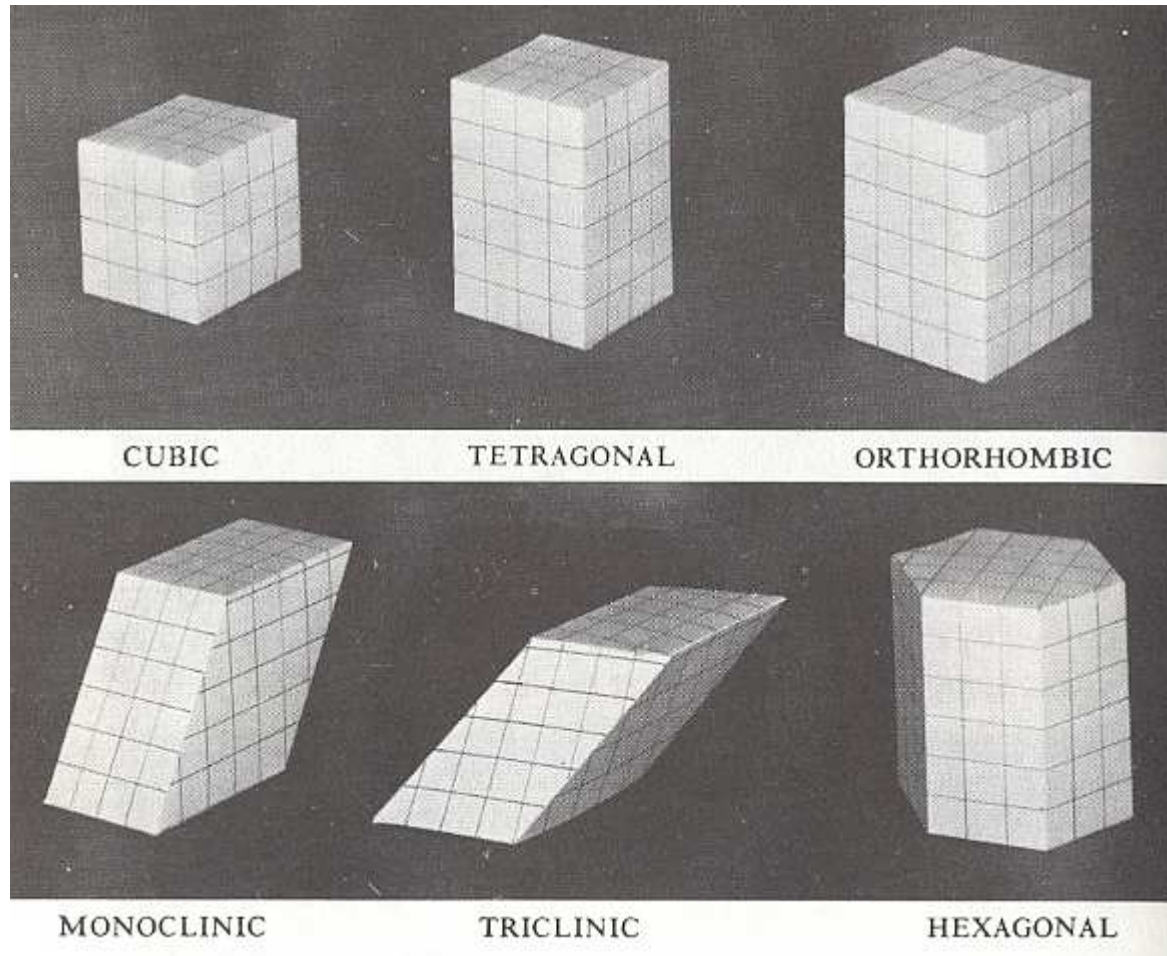


Definition of the directions of the base vectors (a , b , c) that describe the crystal system of the unit cell.

Figure 2.4. Right-hand rule.

2.1 Basics of Structures

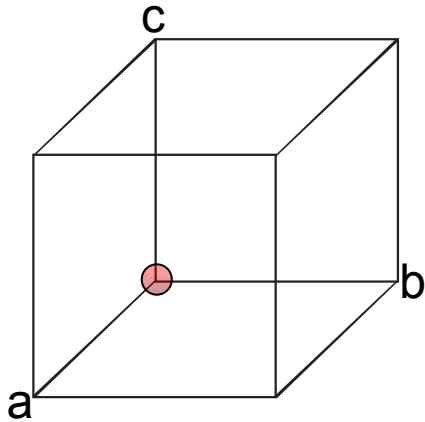
Unit cells and crystal system



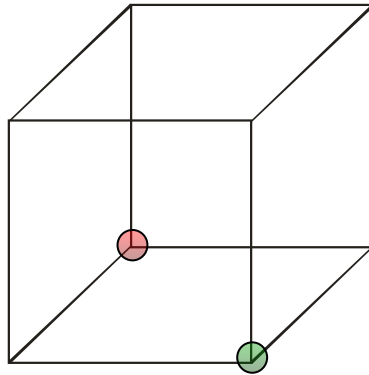
2.1 Basics of Structures

Indices of directions in space

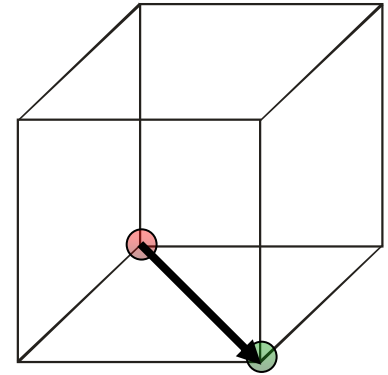
“ $[110]$ ”, square brackets for directions
Procedure in three steps



1. Select 000



2. Mark position of second point



3. Draw vector

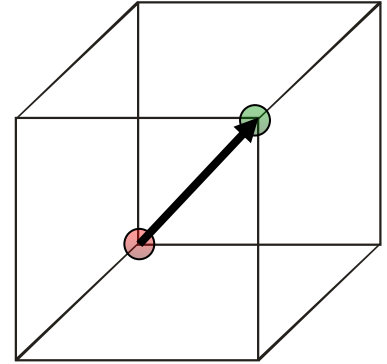
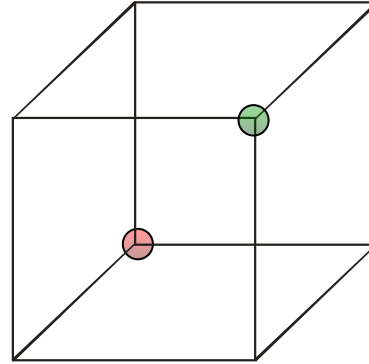
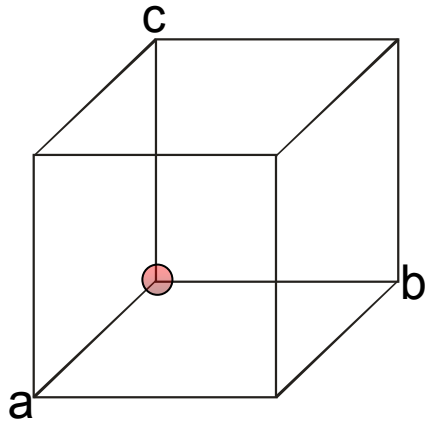
Convention: right-handed coordinate system

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

2.1 Basics of Structures

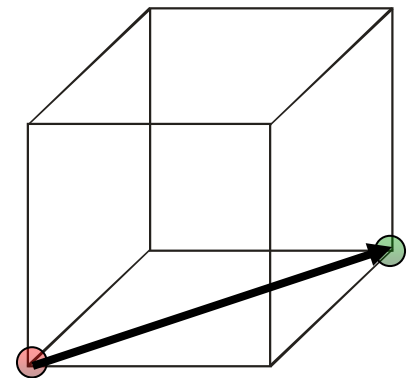
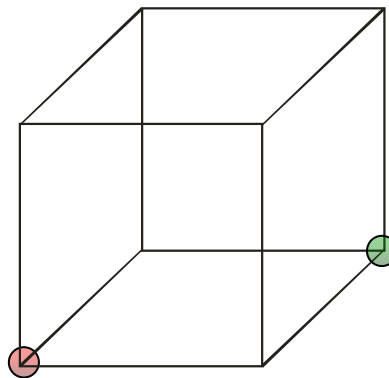
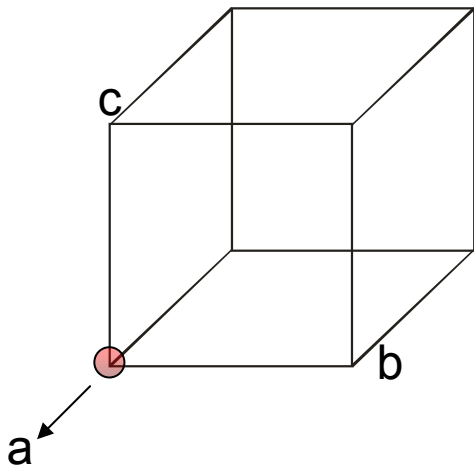
Indices of directions in space - examples

[111]



brackets

$[\bar{1}10]$

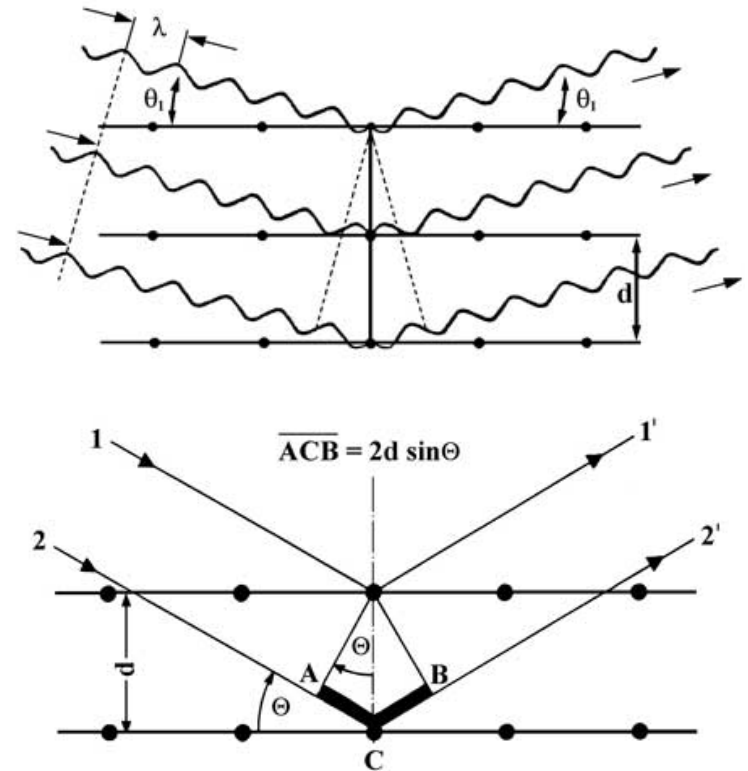
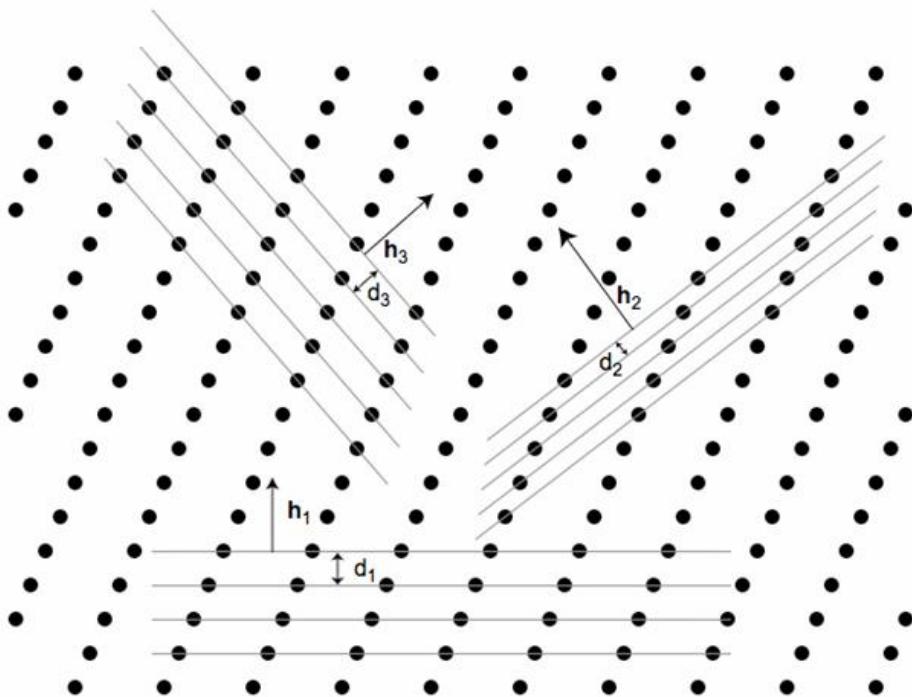


2.1 Basics of Structures

Indices of planes in space

Why are they important ?

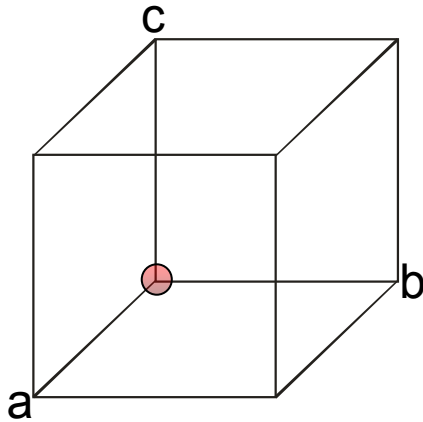
Bragg equation:
 $n \lambda = 2d \sin\theta$



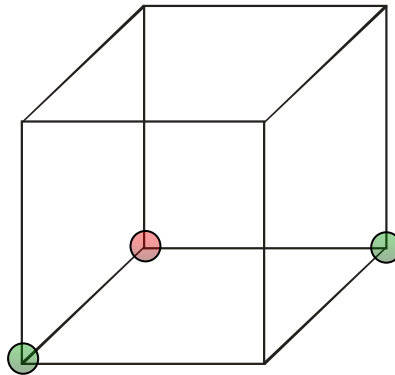
2.1 Basics of Structures

Indices of planes in space

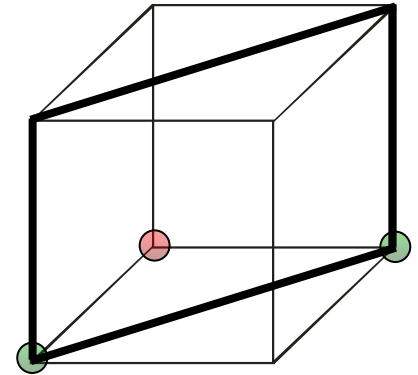
“(110)” round brackets for planes
Procedure in three steps



1. Select 000



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



3. Draw plane

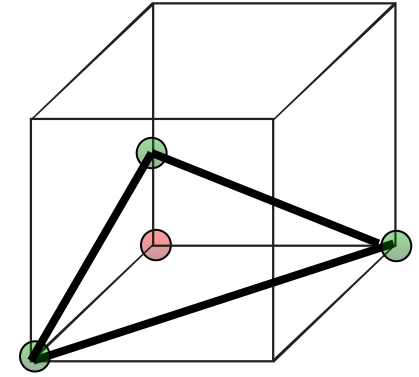
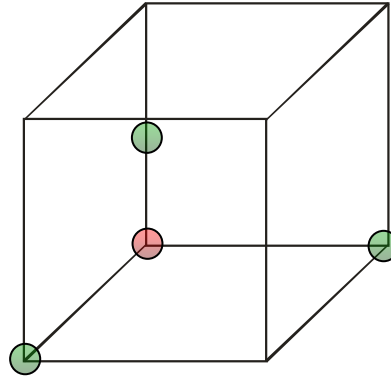
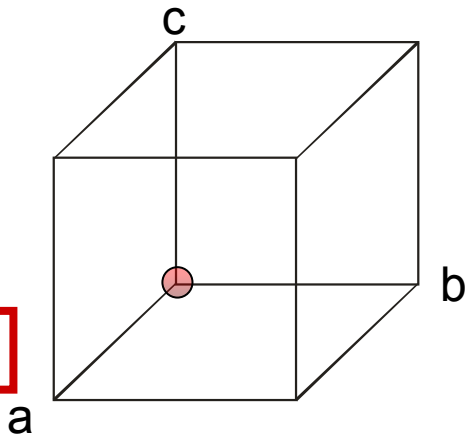
Convention: right-handed coordinate system

2.1 Basics of Structures

Indices of planes in space - examples

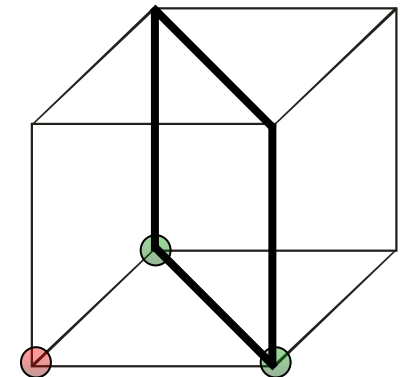
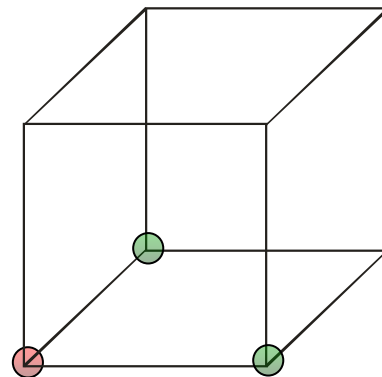
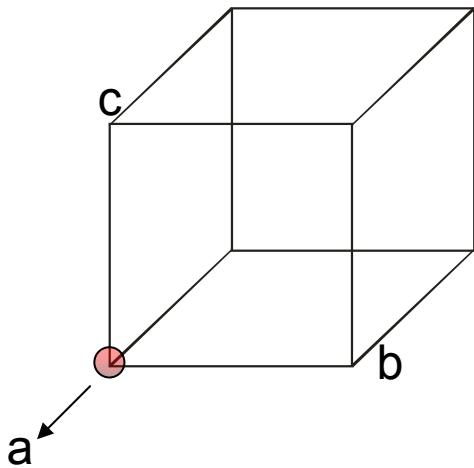
(112)

parentheses



Inverse of axis intercept !

($\bar{1}$ 10)



2.1 Basics of Structures

Fractional coordinates

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

- **Example: Sphalerite (Zincblende)**



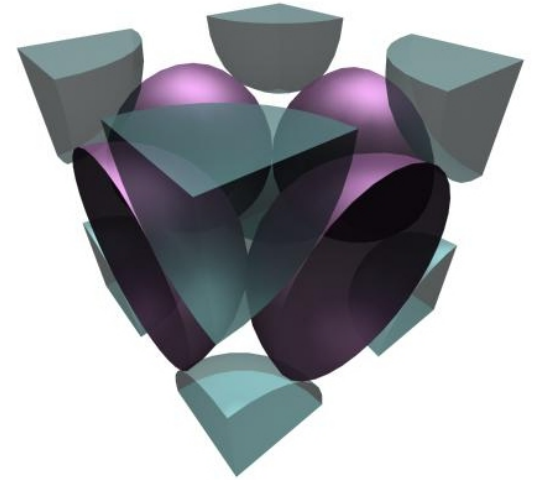
- **Equivalent points are represented by one triplet only**
 - equivalent by translation
 - equivalent by other symmetry elements, later

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 atoms per unit cell**

2.1 Basics of Structures

Wyckoff-notation - example

Crystal data

Formula sum	Mg ₂ SiO ₄ (Olivine)
Crystal system	orthorhombic
Space group	<i>P</i> b n m (no. 62)
Unit cell dimensions	<i>a</i> = 4.75(2) Å, <i>b</i> = 10.25(4) Å, <i>c</i> = 6.00(2) Å
<i>Z</i>	4

Atomic coordinates

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

2.1 Basics of Structures

Wyckoff-notation and occupancy-factors

Crystal data

Formula sum	$\text{Cu}_{0.8} \text{In}_{2.4} \text{Se}_4$
Crystal system	tetragonal
Space group	$I-42m$ (no. 121)
Unit cell dimensions	$a = 5.7539(3) \text{ \AA}$ $c = 11.519(1) \text{ \AA}$
Z	2

Atomic coordinates

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

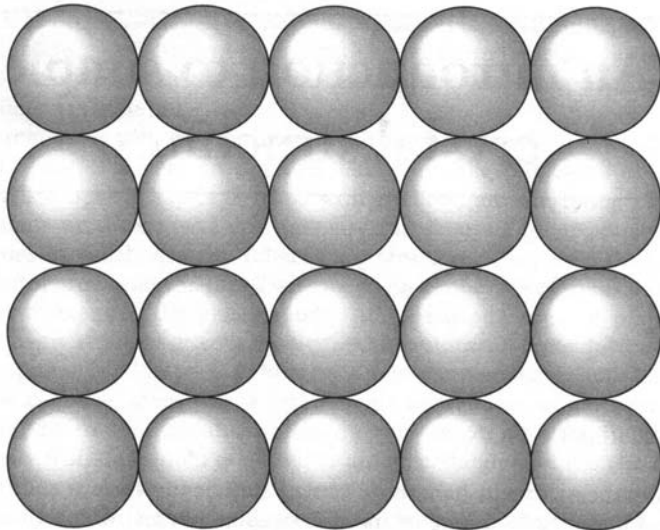
- Occ. factor < 1.0 : mixing of atoms and vacancies on the same position
- Calculation of the composition: Cu: 2×0.8 ; In: $4 \times 1 + 2 \times 0.4$; Se: 8×1

Summary to 2.1

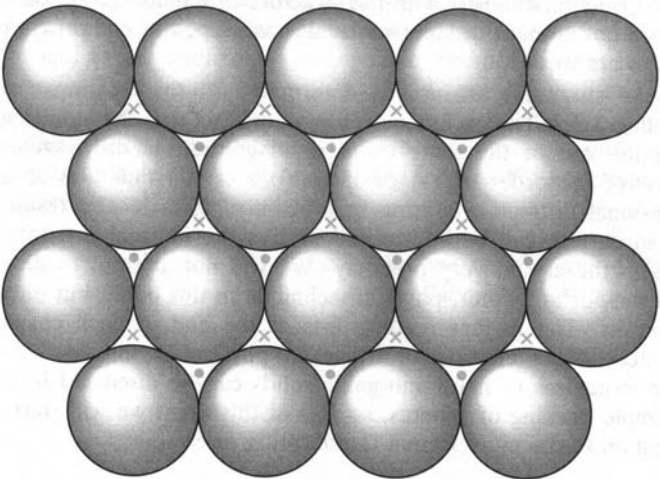
- **Atoms can be treated (and visualized) like spheres**
- **Different types of radii**
- **Structure and lattice**
- **Unit Cell**
- **7 crystal systems**
- **Indexation of directions and planes**
- **Fractional coordinates**
- **Z: number of atoms per unit cell**
- **Wyckoff-notation and occupancy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

2.2 Simple close packed structures (metals)

Close packing in 2D



**primitive packing
(low space filling)**

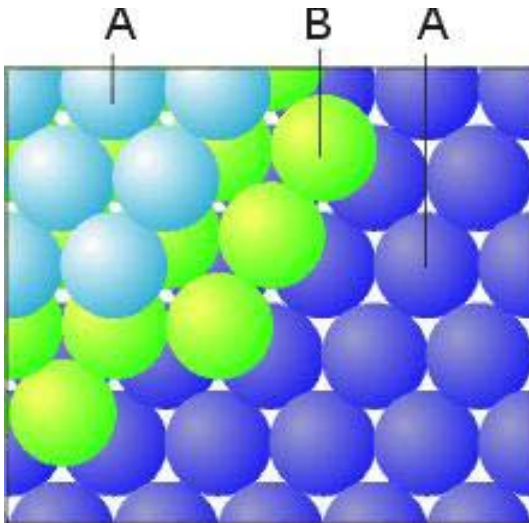


**close packing
(high space filling)**

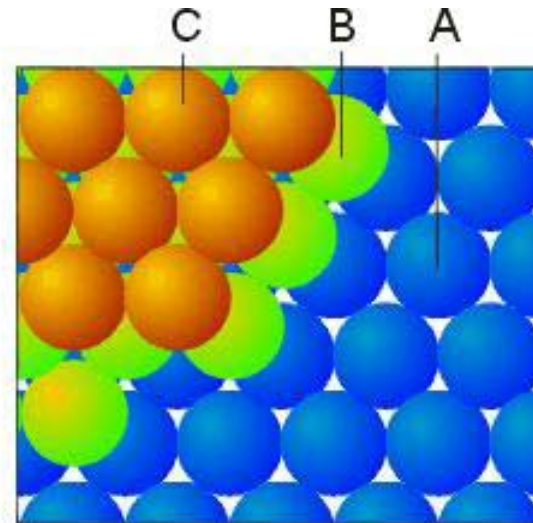
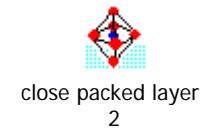
2.2 Simple close packed structures (metals)

Close packing in 3D

Example 1: HCP

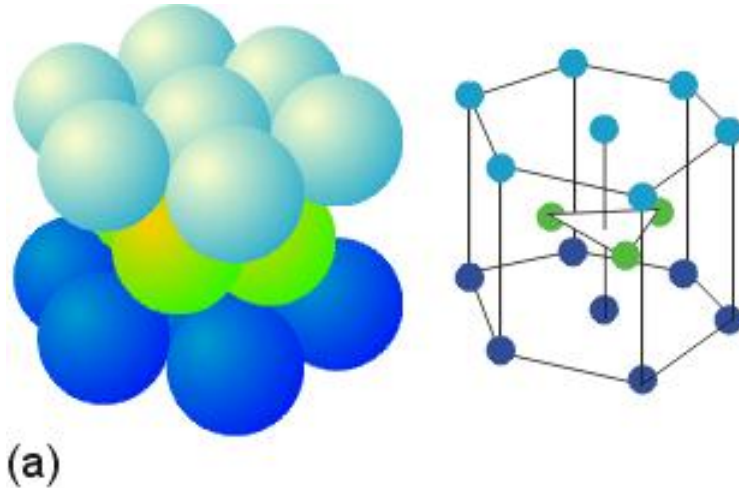


Example 2: CCP



2.2 Simple close packed structures (metals)

Unit cells of HCP and CCP



HCP

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

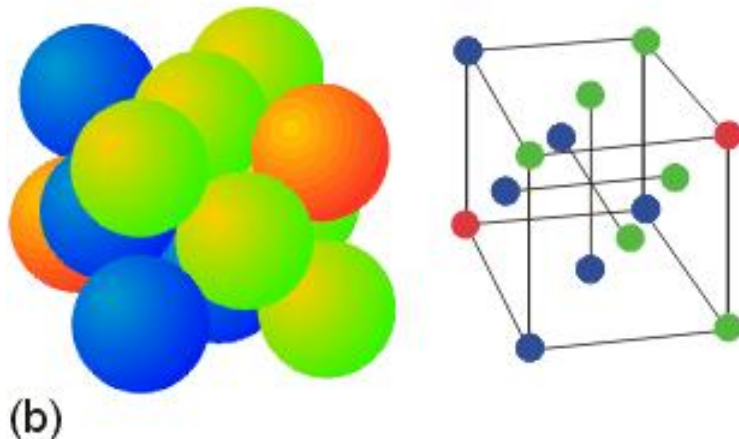
close packed layer: (001)



anticyuboctahedron

space filling = 74%

CN = 12



CCP

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

close packed layer: (111)

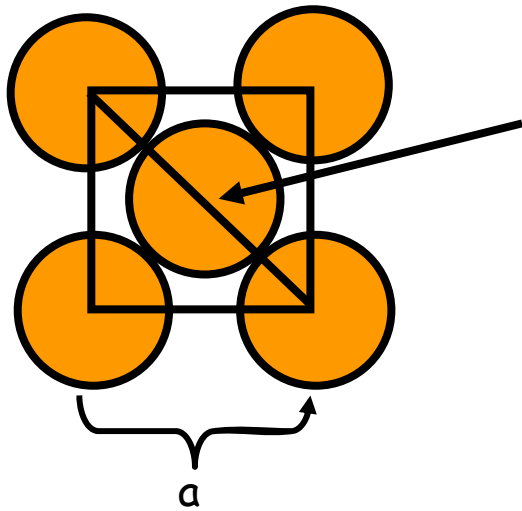


cuboctahedron

2.2 Simple close packed structures (metals)

Calculation of space filling - example CCP

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



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

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

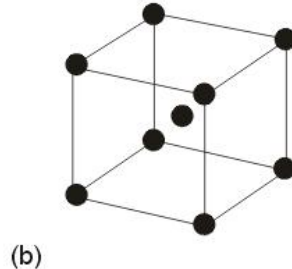
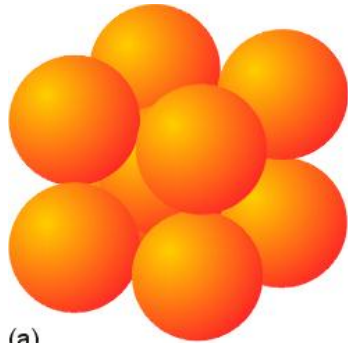
$$ZV(\text{sphere}) = 4 \frac{4}{3} \pi r^3$$

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

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%

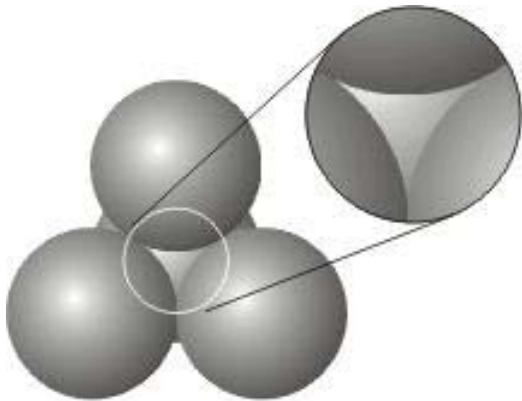
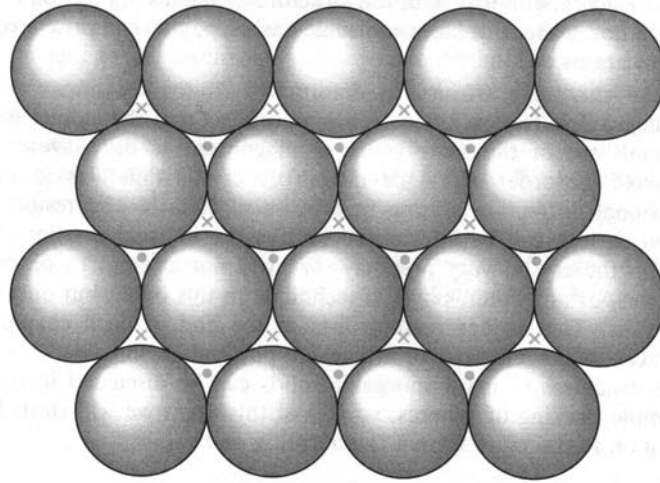
CN = 6

Example 3: structures of manganese



2.2 Simple close packed structures (metals)

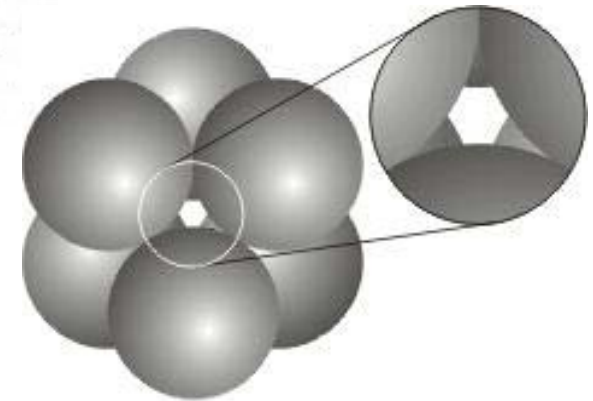
Holes in close packed structures



Tetrahedral hole
TH



Tetrahedron



Octahedral hole
OH



Octahedron

2.2 Simple close packed structures (metals)

Properties of OH and TH in HCP and CCP



**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!

no short distances



Summary to 2.2

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

Periodic table showing crystal structures for elements. Legend: b.c.c. (red), h.c.p. (green), f.c.c. (blue), eigener Typ (white).

Row	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8	Column 9	Column 10	Column 11	Column 12	Column 13	Column 14	Column 15	Column 16
1	Li (b.c.c.)	Be (h.c.p.)														
2	Na (b.c.c.)	Mg (h.c.p.)											Al (f.c.c.)			
3	K (b.c.c.)	Ca (f.c.c.)	Sc (h.c.p.)	Ti (h.c.p.)	V (b.c.c.)	Cr (b.c.c.)	Mn (eigener Typ)	Fe (b.c.c.)	Co (h.c.p.)	Ni (f.c.c.)	Cu (f.c.c.)	Zn (h.c.p.)	Ga (eigener Typ)	Ge (eigener Typ)		
4	Rb (b.c.c.)	Sr (f.c.c.)	Y (h.c.p.)	Zr (h.c.p.)	Nb (b.c.c.)	Mo (b.c.c.)	Tc (h.c.p.)	Ru (h.c.p.)	Rh (f.c.c.)	Pd (f.c.c.)	Ag (f.c.c.)	Cd (h.c.p.)	In (eigener Typ)	Sn (eigener Typ)	Sb (eigener Typ)	
5	Cs (b.c.c.)	Ba (b.c.c.)	La (h.c.p.)	Hf (h.c.p.)	Ta (b.c.c.)	W (b.c.c.)	Re (h.c.p.)	Os (h.c.p.)	Ir (f.c.c.)	Pt (f.c.c.)	Au (f.c.c.)	Hg (eigener Typ)	Tl (h.c.p.)	Pb (f.c.c.)	Bi (eigener Typ)	

- **Holes in close packed structures**

2.3 Basic structure types

Overview

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

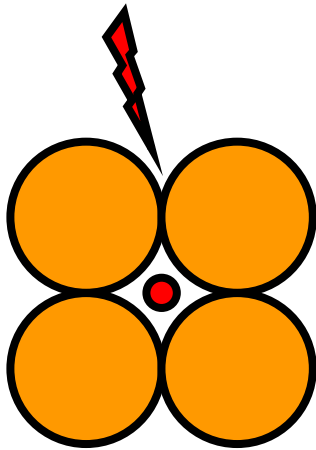
Structure type	Examples	Packing	Holes filled OH and TH
NaCl	AgCl, BaS, CaO, CeSe, GdN, NaF, Na₃BiO₄ , V₇C₈	CCP	n and 0n
NiAs	TiS, CoS, CoSb, AuSn	HCP	n and 0n
CaF ₂	CdF ₂ , CeO ₂ , Li₂O , Rb ₂ O, SrCl ₂ , ThO ₂ , ZrO ₂ , AuIn ₂	CCP	0 and 2n
CdCl ₂	MgCl ₂ , MnCl ₂ , FeCl ₂ , Cs ₂ O, CoCl ₂	CCP	0.5n and 0
CdI ₂	MgBr ₂ , PbI ₂ , SnS ₂ , Mg(OH) ₂ , Cd(OH) ₂ , Ag ₂ F	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 ₃ Bi	Li ₃ Au	CCP	n and 2n

2.3 Basic structure types

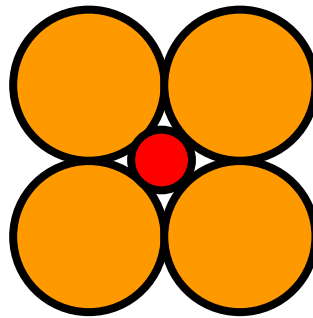
Pauling rules: understanding polyhedral structures

(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: $r(\text{cation})/r(\text{anion})$

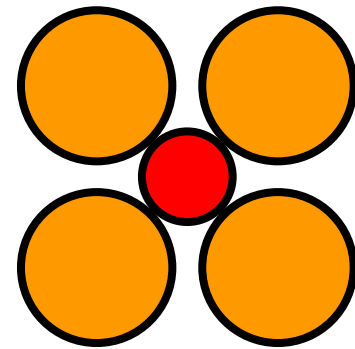
Scenario for radius ratios:



worst case



optimum



low space filling

2.3 Basic structure types

Pauling rules: understanding polyhedral structures

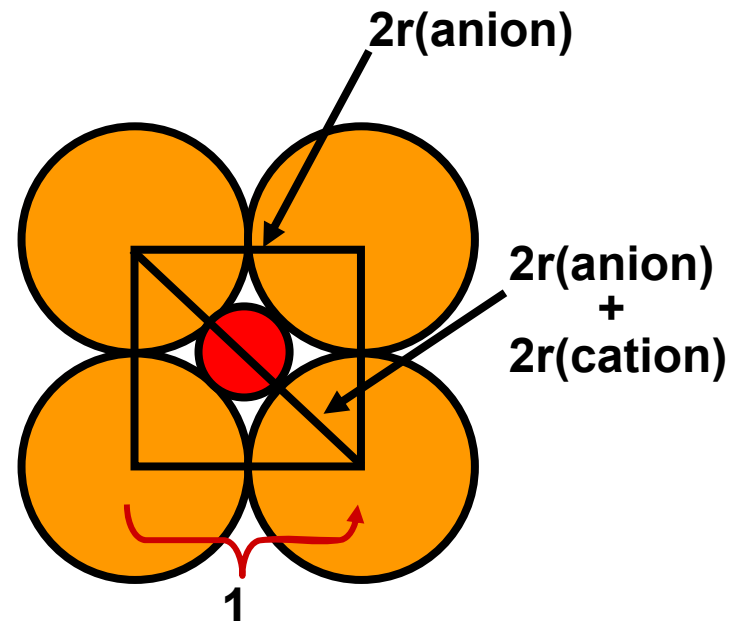
□ coordination	anion polyhedron	radius ratios	cation
3	triangle	0.15-0.22	C
4	tetrahedron	0.22-0.41	Si, Al
6	octahedron	0.41-0.73	Al, Fe, Mg, Ca
8	cube	0.73-1.00	K, Na
12	close packing (anti)cuboctahedron	1.00	

Example: Octahedron



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

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



Exercises

1. Discuss and explain the different types of atomic radii that can be used to describe crystal structures.
2. Assume the lattice constants of the following rock salt type structures to be 545 pm (MgSe), 591 pm (CaSe), 623 pm (SrSe) and 662 pm (BaSe). Calculate the cation radii. To determine the Se^{2-} radius, assume that the Se^{2-} ions are in direct contact in MgSe.
3. Assume WC to crystallize in the rock salt structure. Describe the mutual coordination of W and C.
4. How many neighbours (Cl^- and/or Na^+ !) has a Na^+ ion in NaCl in its (a) first (Cl^-), (b) second (Na^+) and (c) third (Cl^-) coordination sphere?
5. The element Ta is bcc and has an atomic radius of 0.143 nm at 20 °C. Calculate a value for its lattice constants in Å.
6. The element W crystallizes in the bcc structure with lattice constants 3.16 Å. Calculate a value for its atomic radius in nm.
7. Calculate a value for the density of fcc Nickel from its lattice constant $a=0.352$ nm and its atomic mass of 58.71 g/mol.
8. Calculate the enlargement factor of surface if you grind a 1 cm³ cube of a solid material into smaller cubes with an edge length of 100 μm.
9. Sketch the principle properties of the fluorite structure.
10. Make suggestions for possible structure types of a crystalline solid with the general chemical composition AB_2 .

2.3 Basic structure types

Pauling rules: understanding polyhedral structures

(1) 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)

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

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

Example 2 - GaAs (Sphalerite)

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

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

Example 3 - SrTiO_3 (Perovskite)

$$\text{CN}(\text{Sr}^{2+}) = 12, \text{CN}(\text{Ti}^{4+}) = 6,$$

$$\text{CN}(\text{O}^{2-}) = 4(\text{Sr}) \text{ and } 2(\text{Ti})$$

$$s_{ij}(\text{Sr-O}) = 1/6, s_{ij}(\text{Ti-O}) = 2/3$$

2.3 Basic structure types

Pauling rules: understanding polyhedral structures

(2) 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.

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

(4) 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	$Fm\bar{3}m$ (no. 225)
Unit cell dimensions	$a = 5.6250(5) \text{ \AA}$
Z	4

Atomic coordinates

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



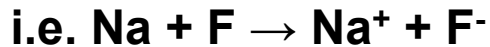
Structural features:

- all octahedral holes of CCP filled, type = antitype
- Na is coordinated by 6 Cl, Cl is coordinated by 6 Na
- One NaCl_6 -octahedron is coordinated by 12 NaCl_6 -octahedra
- Connection of octahedra by common edges

2.3 Basic structure types

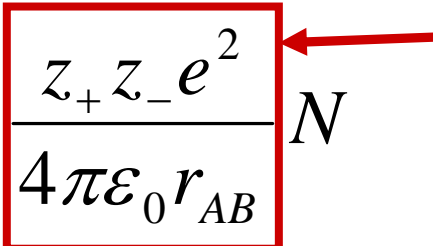
Bonding in ionic structures – Coulomb interaction

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



Interaction between anions and cations: Coulomb interactions.

$$V_{AB} = -A \frac{z_+ z_- e^2}{4\pi\epsilon_0 r_{AB}} N$$

 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 = $1.602 \times 10^{-19} \text{C}$

ϵ_0 : dielectric constant (vacuum permittivity) = $8.85 \times 10^{-12} \text{C}^2/(\text{Nm}^2)$

r_{AB} : shortest distance between cation and anion

N: Avogadro constant = $6.023 \times 10^{23} \text{mol}^{-1}$

2.3 Basic structure types

Bonding in ionic structures – Coulomb interaction

Calculating the Madelung constant (for NaCl)

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

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.

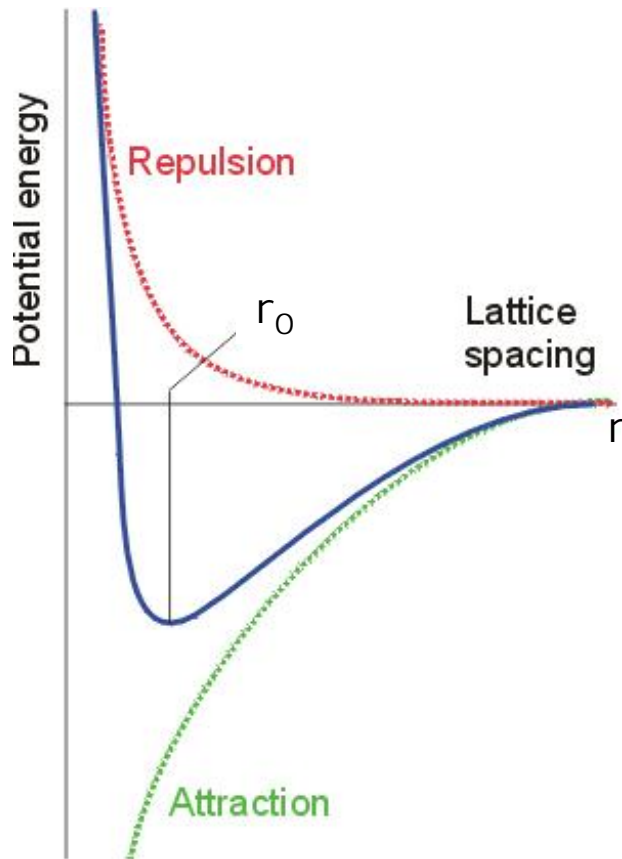


	A	CN
Rock Salt	1.748	6
CsCl	1.763	8
Sphalerite	1.638	4
Fluorite	5.039	8

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 an ionic structure

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

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

$$\Delta H_L^0 = -A \frac{z_+ z_- e^2}{4\pi\epsilon_0 r_0} N \left(1 - \frac{1}{n}\right)$$

- **typical values, measured (calculated) [kJ mol⁻¹]:**
 - NaCl: -772 (-757); CsCl: -652 (-623)
 - measured means “calculated” 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	$F\bar{4}3m$ (no. 216)
Unit cell dimensions	$a = 5.3450 \text{ \AA}$
Z	4



Layer in sphalerite



Stacking sequence

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Zn1	+2	4a	0	0	0
S2	-2	4c	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	$P6_3mc$ (no. 186)
Unit cell dimensions	$a = 3.8360 \text{ \AA}$, $c = 6.2770 \text{ \AA}$
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

CaF₂-type

Crystal data

Formula sum	CaF ₂
Crystal system	cubic
Space group	<i>Fm</i> -3 <i>m</i> (no. 225)
Unit cell dimensions	<i>a</i> = 5.4375(1) Å
<i>Z</i>	4

Atomic coordinates

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



Coordination Ca

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	$R\bar{3}m$ (no. 166)
Unit cell dimensions	$a = 6.2300 \text{ \AA}$, $\alpha = 36^\circ$
Z	1

Atomic coordinates

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



Stacking sequence



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

CdI₂-type

Crystal data

Formula sum	CdI ₂
Crystal system	trigonal
Space group	<i>P</i> -3 m 1 (no. 164)
Unit cell dimensions	<i>a</i> = 4.2500 Å, <i>c</i> = 6.8500 Å
<i>Z</i>	1

Atomic coordinates

Atom	Ox.	Wyck.	<i>x</i>	<i>y</i>	<i>z</i>
Cd1	+2	1 <i>a</i>	0	0	0
I1	-1	2 <i>d</i>	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

NiAs-type

Crystal data

Formula sum	NiAs
Crystal system	hexagonal
Space group	$P 63/m m c$ (no. 194)
Unit cell dimensions	$a = 3.619(1) \text{ \AA}$, $c = 5.025(1) \text{ \AA}$
Z	2

Atomic coordinates

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



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 \neq antitype

2.3 Basic structure types

Intercalation of layered compounds

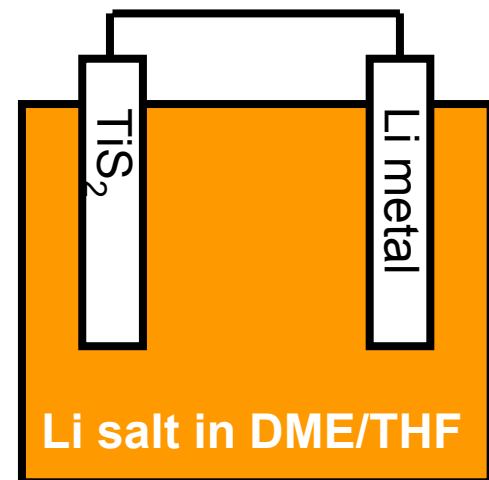
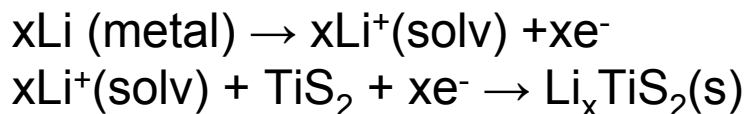
- Reversible intercalation of atoms between the layers of a layered compound
- Host-guest interactions, structure-property relations

Example 1: 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

Example 2: TiS_2 (CdI_2 -type)

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

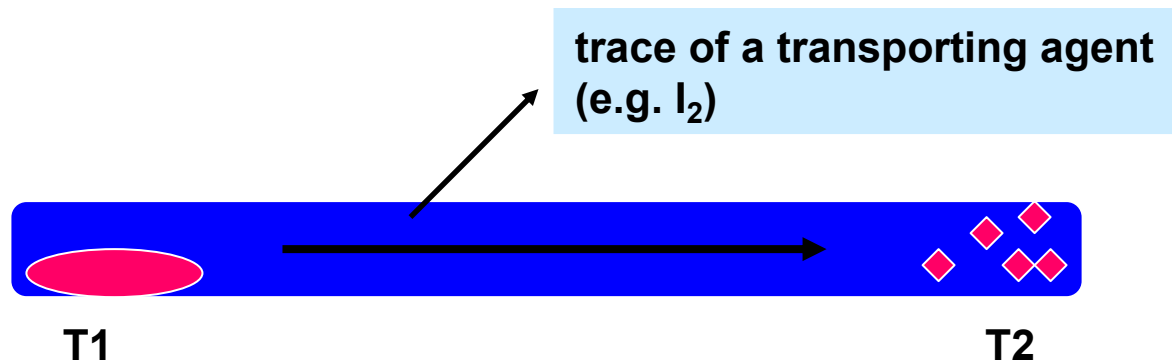


2.3 Conventional chemical preparation methods

Chemical Transport: A solid is dissolved in the gas phase at one place ($T=T_1$) by reaction with a transporting agent (e.g. I_2). At another place ($T=T_2$) the solid is condensed again.

Whether $T_1 < T_2$ or $T_1 > T_2$ depends on the thermochemical balance of the reaction !

Transport can proceed from higher to lower or from lower to higher temperature



Main application: purification and crystallisation of solids

2.3 Growth of big single crystals (e.g. Si)

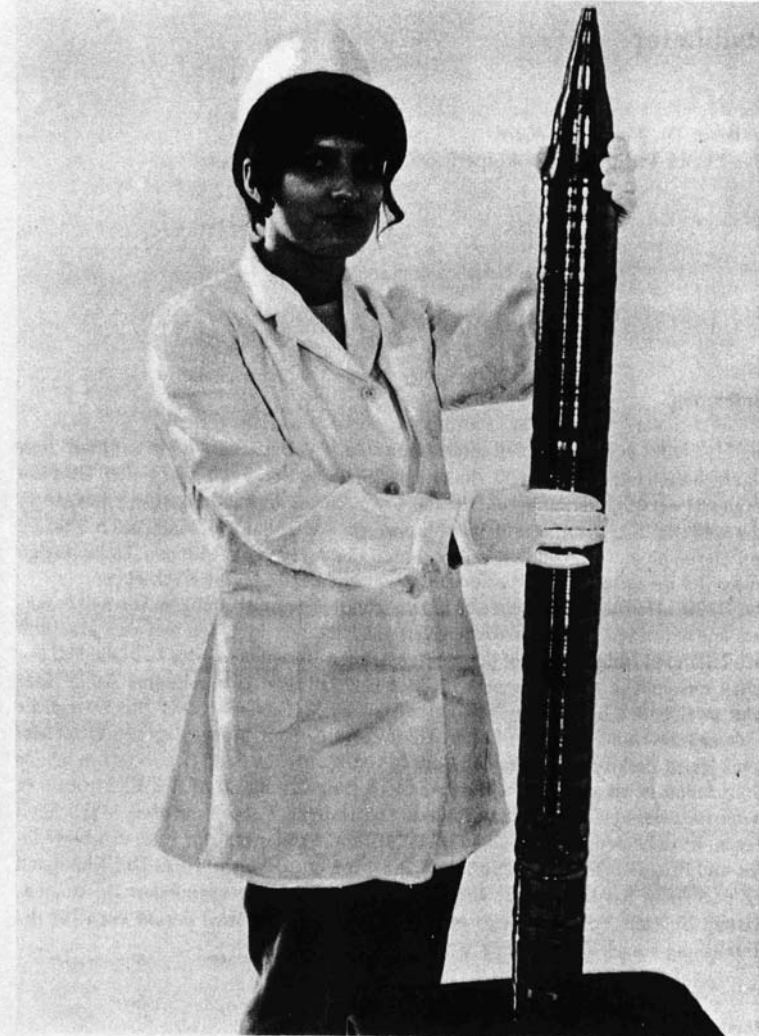
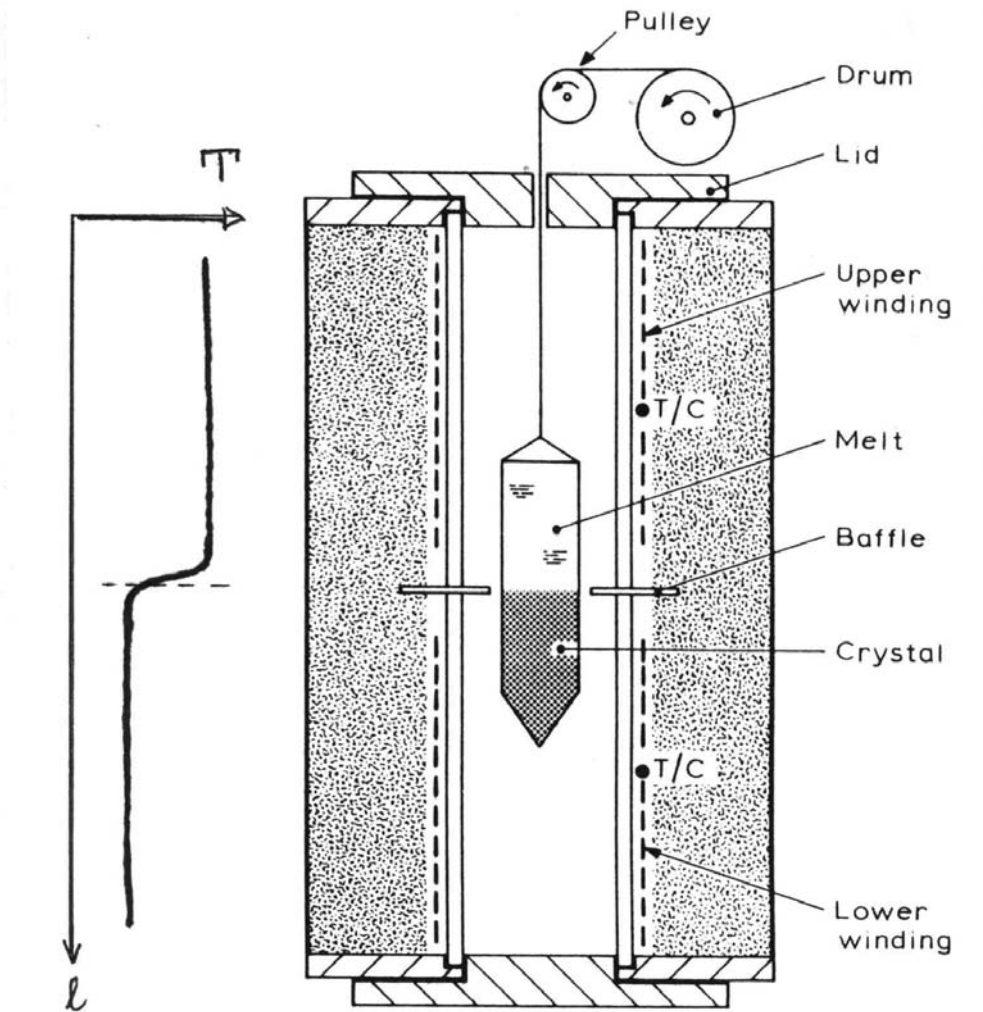


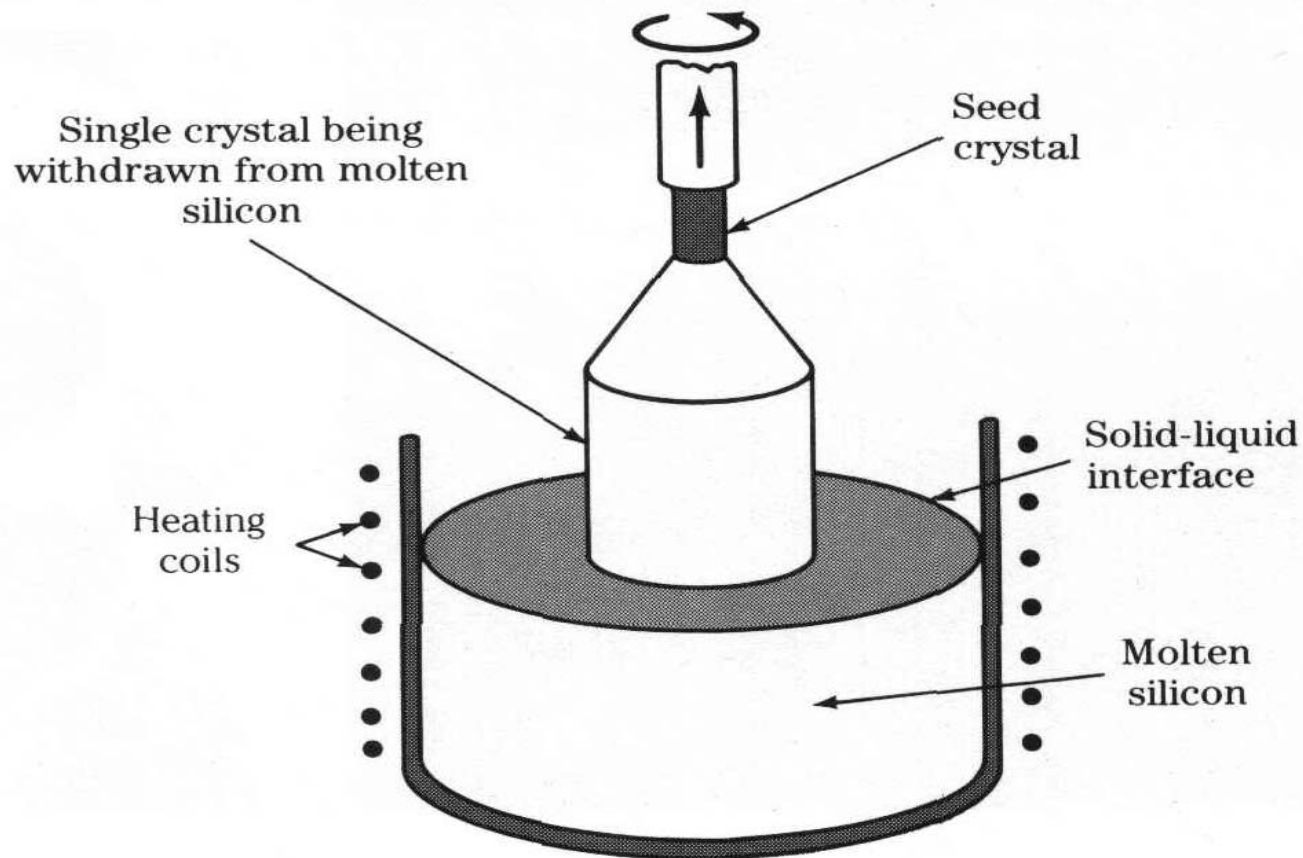
Abb. 1: Großer Silizium-Einkristall mit hoher Perfektion des Kristallbaus und extremer chemischer Reinheit. (Werkfoto der Wacker-Chemitronic, Burghausen; ich danke Dr. E. Lutz für dieses Bild.)

2.3 Growth of single crystals: Bridgman-Stockbarger-process (moving temperature gradient)



2.3 Czochralski process: Si (!)

- a rotating seed crystal is raised slowly from a melt with equal composition



2.3 Zone melting

- a small slice of the sample is molten and moved continuously along the sample
- impurities normally dissolve preferably in the melt
(!! icebergs in salt water don't contain any salt !!)
- segregation coefficient k :
$$k = c_{\text{solid}}/c_{\text{liquid}}$$

(c : concentration of an impurity)

only impurities with $k < 1$ can be removed by zone melting !!

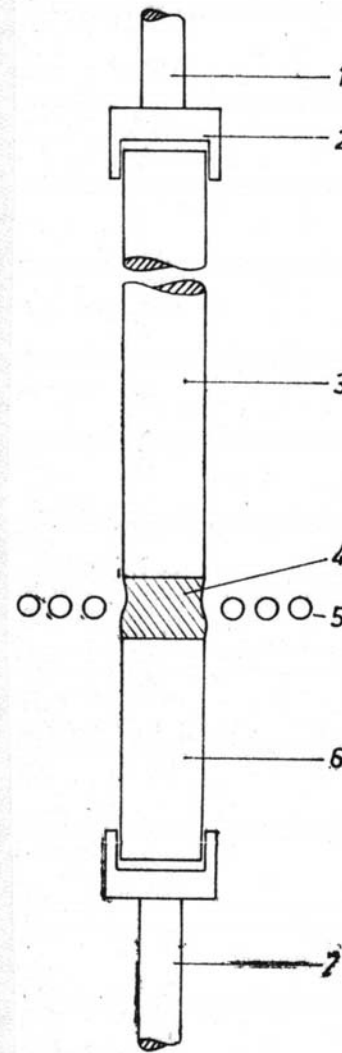


Bild 6.13. Prinzip der Einkristallherstellung nach dem tiegelfreien Zonenschmelzen (floating zone technique)

- 1 Ziehstange
- 2 Stabhalterung
- 3 polykristalliner Ausgangsstab
- 4 Schmelzzone
- 5 wassergekühlter Induktor
- 6 Einkristallkeim
- 7 Keimhalter

2.3 Hydrothermal synthesis

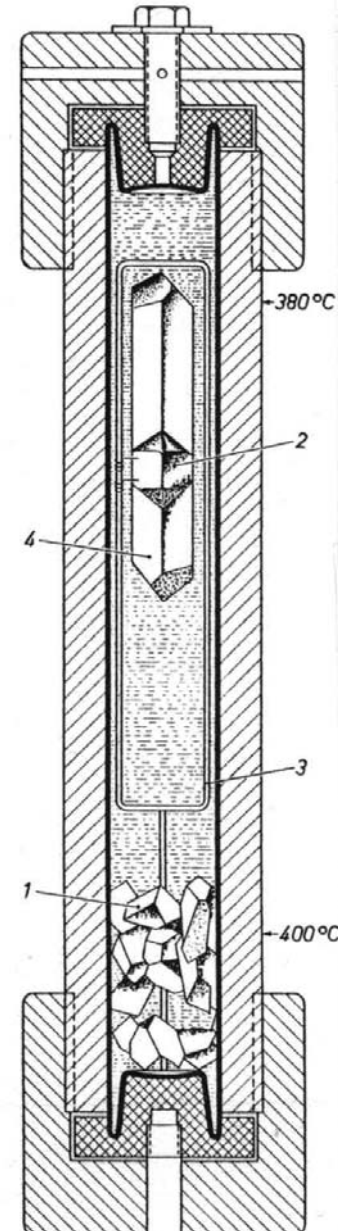
Chemical transport in supercritical aqueous solution (H_2O : $T_k = 374\text{ }^\circ\text{C}$, $p_k = 217,7\text{ atm}$)

Autoclave for the growth of SiO_2 single crystals (\rightarrow quartz)

1500 bar, T- gradient $400 \rightarrow 380\text{ }^\circ\text{C}$

1: nutrient (powder), 2: seed crystal,
3: mechanical fixing of crystal
4: product crystal

Lit.: Die Rolle der Hydrothermalsynthese in der präparativen Chemie, A. Rabenau, Angew. Chem. 97 (1985) 1017



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	$a = 4.5937 \text{ \AA}$, $c = 2.9587 \text{ \AA}$
Z	2



Atomic coordinates

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

Structural features:

- no HCP arrangement of O ($\text{CN}(\text{O},\text{O}) = 11$)
- 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	$Pm\bar{3}m$ (no. 221)
Unit cell dimensions	$a = 3.7504(1) \text{ \AA}$
Z	1

Atomic coordinates

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



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

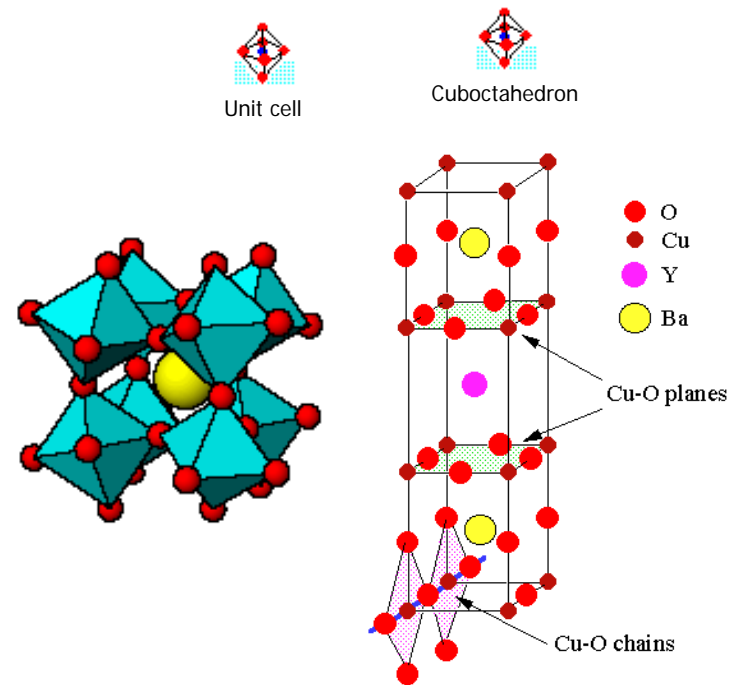
Oxides: undistorted perovskite (SrTiO_3)

Crystal data

Formula sum	SrTiO_3
Crystal system	cubic
Space group	$Pm\bar{3}m$ (no. 221)
Unit cell dimensions	$a = 3.9034(5) \text{ \AA}$
Z	1

Atomic coordinates

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



Structural features:

- filled ReO_3 phase, CN (Ca) = 12 (cuboctahedron), CN (Ti) = 6 (octahedron)
- many distorted variants (even the mineral CaTiO_3 !)
- many defect variants (HT-superconductors, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$)
- hexagonal variants and polytyps

2.4 More complex structures

Oxides: Spinel (MgAl_2O_4 , Fe_3O_4)

Crystal data

Formula sum	MgAl_2O_4
Crystal system	cubic
Space group	$Fd\bar{3}m$ (no. 227)
Unit cell dimensions	$a = 8.0625(7) \text{ \AA}$
Z	8

ICSD database: ~100.000
inorganic crystal structures

Atomic coordinates

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



Diamond Document



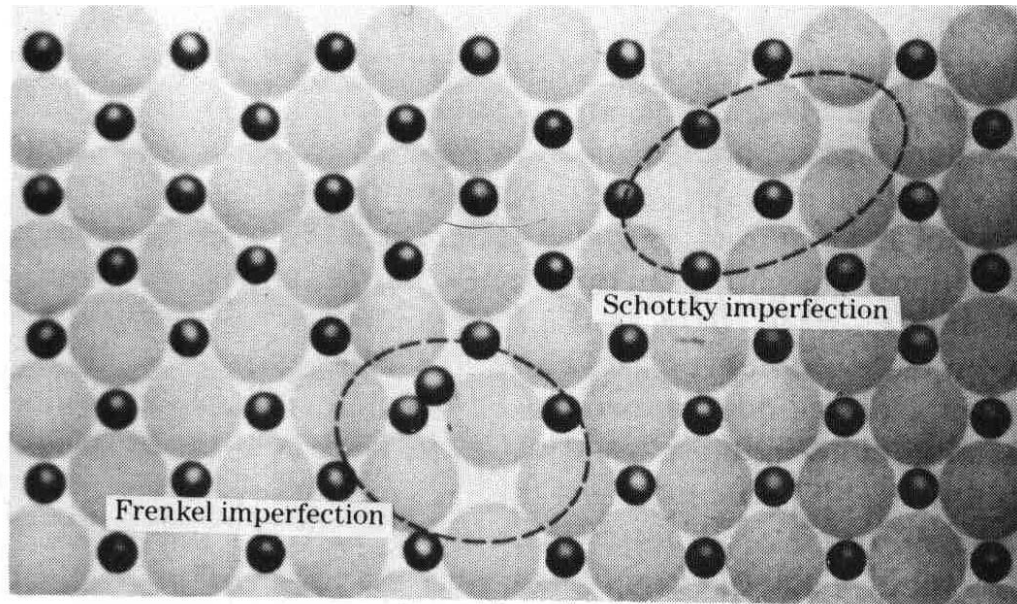
Diamond Document

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 $\text{Mg}_{\text{TH}}\text{Al}_{2\text{OH}}\text{O}_4 \rightarrow \text{In}_{\text{TH}}(\text{Mg}, \text{In})_{\text{OH}}\text{O}_4$
- Application: ferrites (magnetic materials)

2.4 Point defects (imperfections) in solids

Defects are of paramount importance for the diffusion of ions (atoms) in solids



Schottky-imperfection: vacancy, missing ions moved to the surface (can be cations or anions)

Frenkel-imperfection: vacancy, missing ions on interstitial positions (cations only)

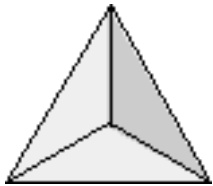
2.5 Complex structures

Oxides: Silicates- overview 1

From simple building units to complex structures

Structural features:

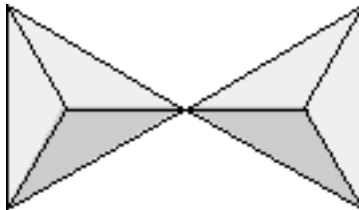
- fundamental building unit: SiO_4 tetrahedron
- isolated tetrahedra or connection via common corners
- MO_6 octahedra , MO_4 tetrahedra (M = Fe, Al, Co, Ni...)



Nesosilicates



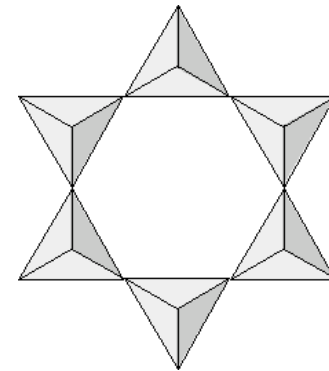
Olivine: $(\text{Mg,Fe})_2\text{SiO}_4$



Sorosilicates



Thortveitite: $(\text{Sc,Y})_2\text{Si}_2\text{O}_7$



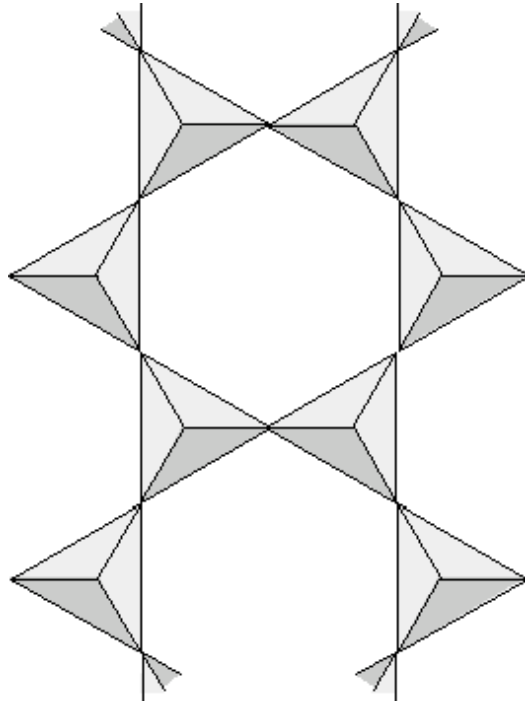
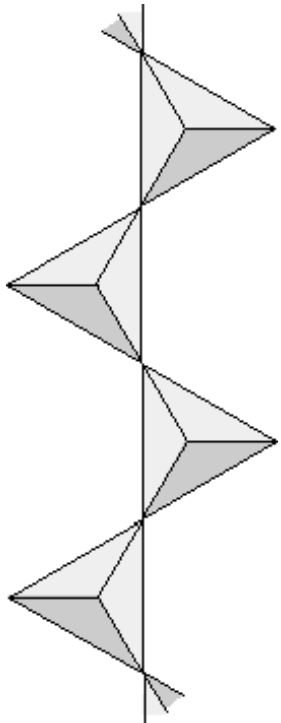
Cyclosilicates



Beryl: $\text{Be}_3\text{Si}_6\text{O}_{18}$

2.5 Complex structures

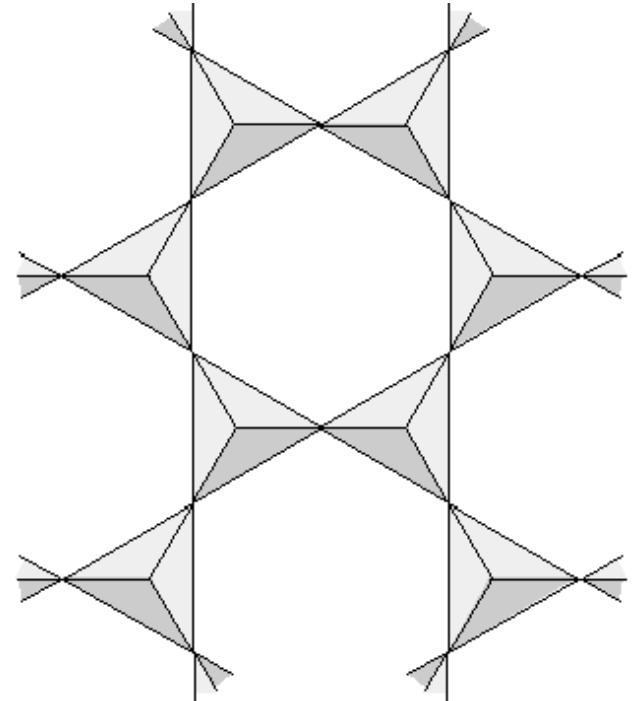
Oxides: Silicates- overview 2



Inosilicates

single chain: SiO_3^{2-}
Pyroxene: $(\text{Mg,Fe})\text{SiO}_3$

double chain: $\text{Si}_4\text{O}_{11}^{6-}$
Tremolite:
 $\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$



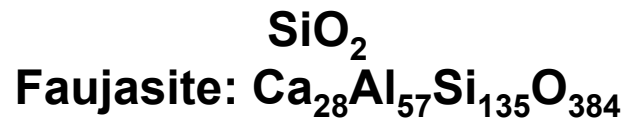
Phyllosilicates

$\text{Si}_2\text{O}_5^{2-}$
Biotite: $\text{K}(\text{Mg,Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$

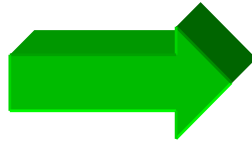
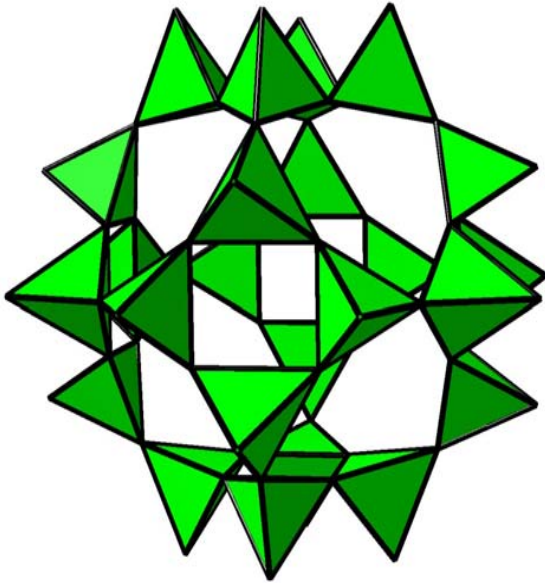
2.5 Complex structures

Oxides: Silicates- overview 3

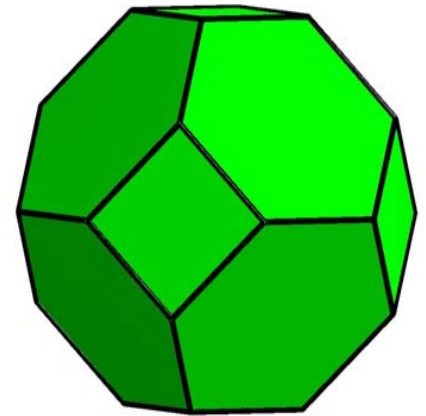
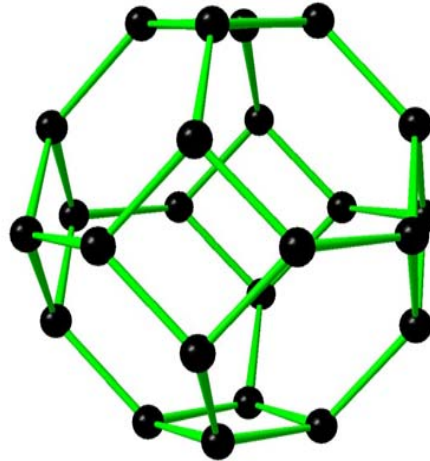
Tectosilicates



β -cage



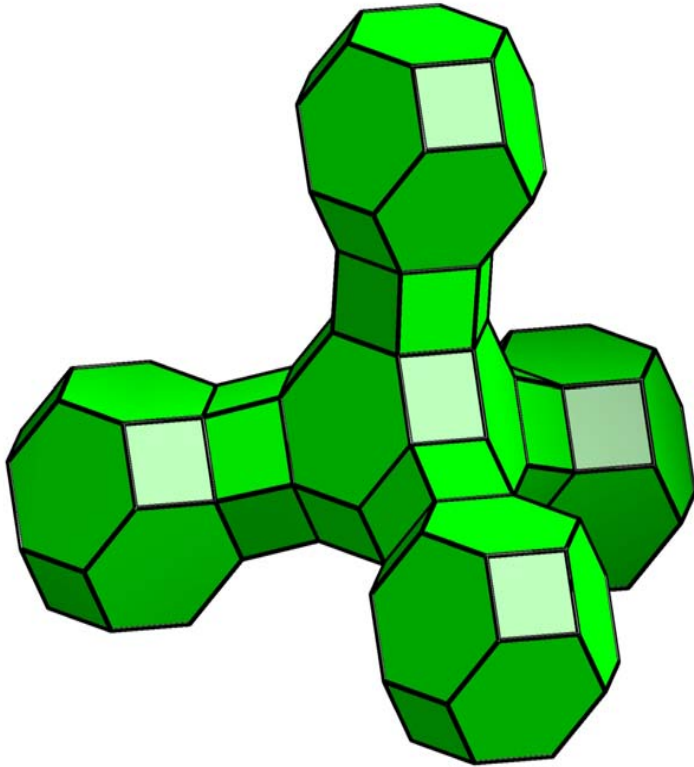
T-Atom-representation



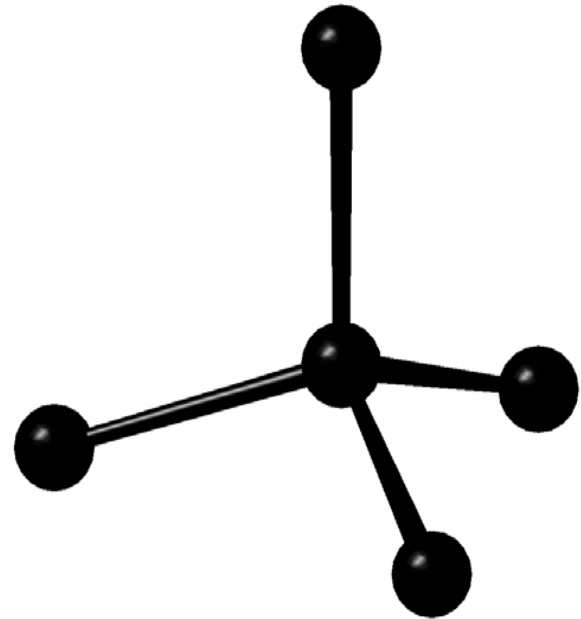
2.5 Complex structures

Concept for visualization of topology

T-Atom representation



3D-Nets: edge + vertex

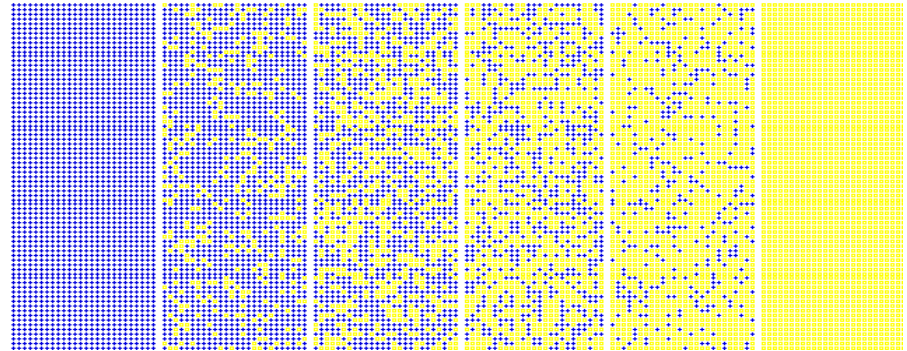


2.5 Complex structures

Intermetallics- overview

Solid solutions: Example: $\text{Rb}_x\text{Cs}_{1-x}$ BCC-structure, disordered

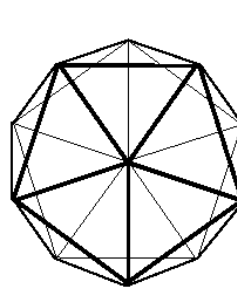
- chemically related
- small difference of electronegativity
- similar number of valence electrons
- similar atomic radius
- (high temperature)



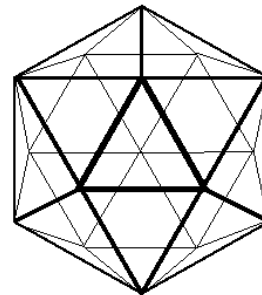
Ordered structures: from complex building units to complex structures

Rule: complex structures

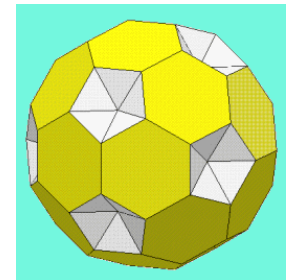
**Exception:
simple structures**



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 = $N(\text{val. electr}) / N(\text{atoms})$ (both per formula unit)

VEC	3/2	3/2	3/2	21/13	7/4
Structure	CuZn	β-Mn	HCP	γ-Brass	HCP
Example	Cu₃Al	Cu₅Si	Cu₃Ga	Cu₅Zn₈	CuZn₃

2.5 Complex structures

Intermetallics- Laves-phases

Trend 2:

Intermetallics with a high space filling (71%)

Typical radius ratio: 1:1.225

Structure	MgCu₂	MgZn₂	MgNi₂
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 (electropositive)

element 2: Ga-Tl, Si-Pb, As-Bi... (less electropositive)

e.g. Na^+Tl^- , $\text{Ca}^{2+}\text{Si}^{2-}$...

Properties of the compounds:

- deeply colored
- soluble clusters in liquid ammonia
- 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 valence 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)
- $8-N = 4$, $N = 4$: NaTi : Ti^- , 3D framework of tetrahedra (tetrel, diamond)

Example: Ba_3Si_4



2.6 Basic Magnetochemistry

The magnetic moment of a single atom (μ)

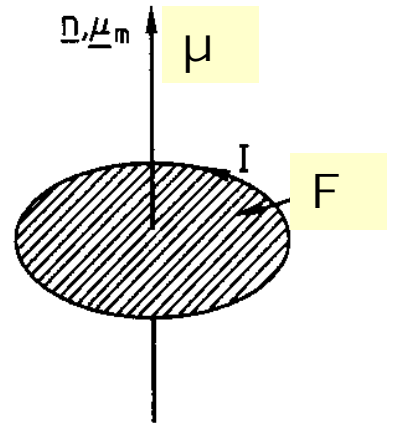
(μ is a vector !)

$\mu = i F [\text{Am}^2]$, circular current i , aerea F

$$\mu_B = eh/4\pi m_e = 0,9274 \cdot 10^{-27} \text{ Am}^2$$

(h : Planck constant, m_e : electron mass)

μ_B : „Bohr magneton“ (smallest quantity of a magnetic moment)



→ for one unpaired electron in an atom:

$$\mu^s = 1,73 \mu_B$$

2.6 Basic Magnetochemistry

→ The magnetic moment of an atom has two components a spin component („spinmoment“) and an orbital component („orbital moment“).

→ Frequently the orbital moment is supressed („spin-only-magnetism“, e.g. coordination compounds of 3d elements)

Magnetisation M and susceptibility χ

$$M = (\sum \mu)/V$$

$\sum \mu$: sum of all magnetic moments μ in a given volume V ,
dimension: $[Am^2/m^3 = A/m]$

The actual magnetization of a given sample is composed of the „intrinsic“ magnetization (susceptibility χ) and an external field H :

$$M = H \chi \quad (\chi: \text{suszeptibility})$$

2.6 Magnetochemistry

There are three types of susceptibilities:

χ_v : dimensionless (volume susceptibility)

χ_g : $[\text{cm}^3/\text{g}]$ (gramm susceptibility)

χ_m : $[\text{cm}^3/\text{mol}]$ (molar susceptibility)

!!!! χ_m is used normally in chemistry !!!!

Frequently: $\chi = f(H) \rightarrow \text{complications !!}$

2.6 Magnetochemistry

Diamagnetism

- external field is weakened
- atoms/ions/molecules with closed shells

$$-10^{-4} < \chi_m < -10^{-2} \text{ cm}^3/\text{mol} \quad (\text{negative sign})$$

Paramagnetism

- external field is strengthened
- atoms/ions/molecules with open shells/unpaired electrons

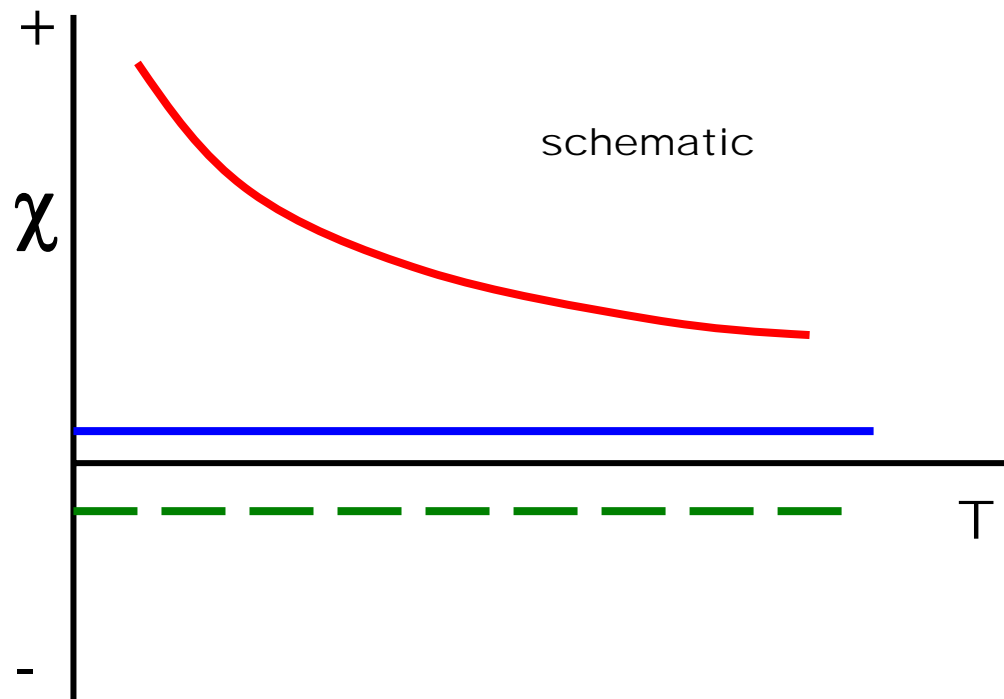
$$+10^{-4} < \chi_m < 10^{-1} \text{ cm}^3/\text{mol}$$

→ diamagnetism (core electrons) + paramagnetism (valence electrons)

2.6 Temperature dependence of the magnetic susceptibility

General:

- | | |
|--------------------------|--|
| 1.) Diamagnetism: | independent of temperature (metals and non-metals) |
| 2.) Paramagnetism: | Curie- or Curie-Weiss-law (non-metals) |
| 3.) Pauli-Paramagnetism: | independent of temperature (metals) |



2.6 Curie- und Curie-Weiss-law for paramagnetic samples

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

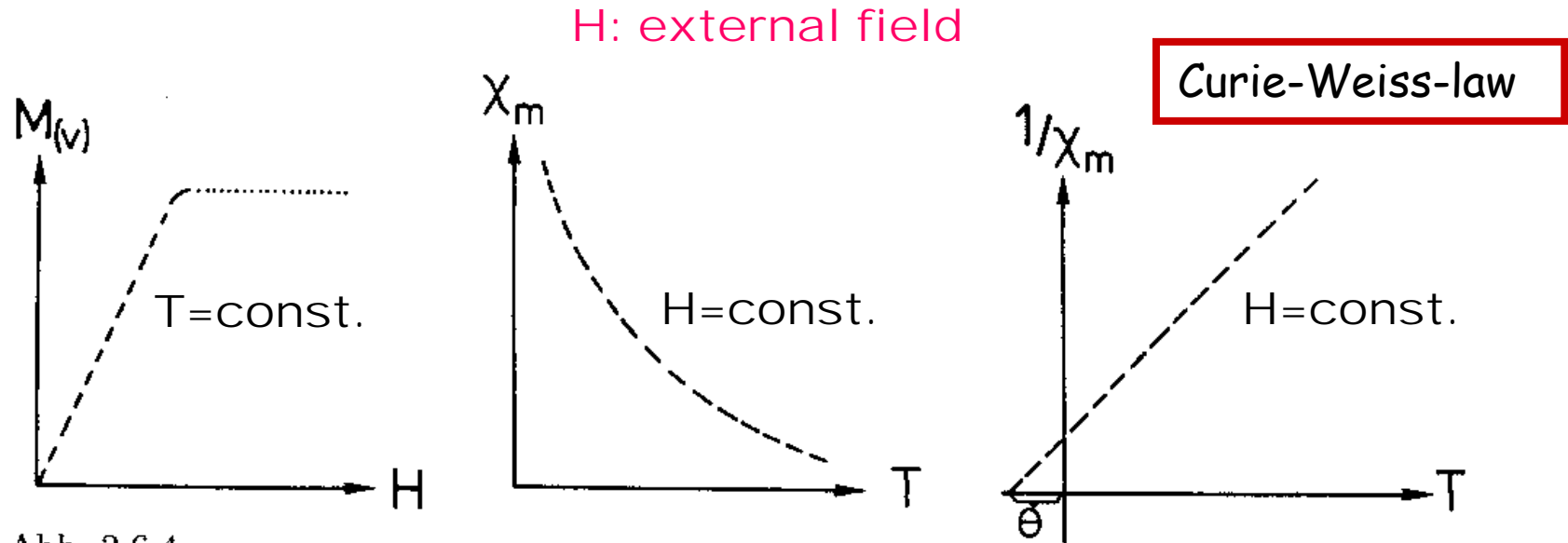


Abb. 2.6.4

$M_{(v)} = f(H)$, $\chi_m = f(T)$ und $\frac{1}{\chi_m} = f(T)$ für paramagnetische Stoffe

2.6 Different types of collective magnetism in a solid due to coupling of magnetic moments



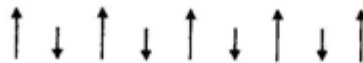
Paramagnetism



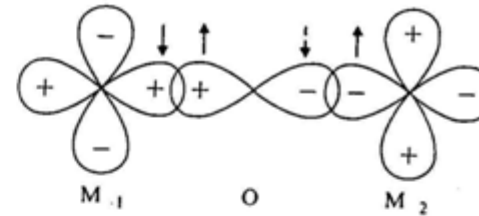
Ferromagnetism



Antiferromagnetism

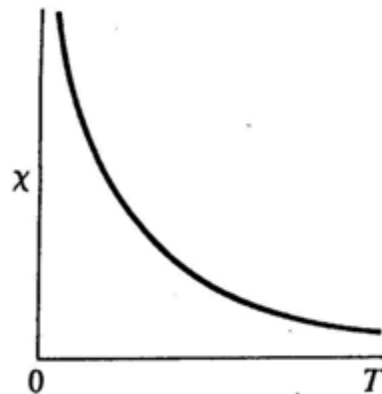


Ferrimagnetism



super exchange
(Superaustausch)

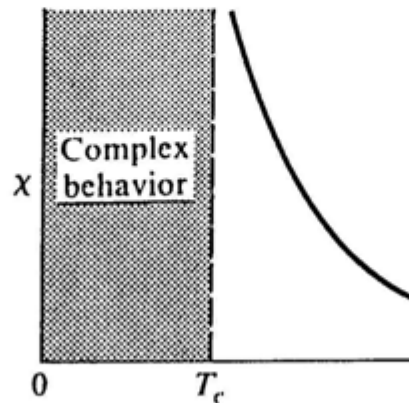
Paramagnetism



$$\chi = \frac{C}{T}$$

Curie law

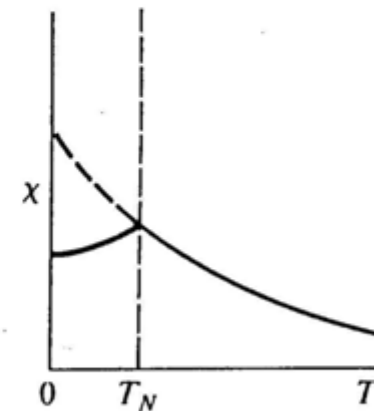
Ferromagnetism and
Ferrimagnetism



$$\chi = \frac{C}{T - T_c}$$

Curie-Weiss law
($T > T_c$)

Antiferromagnetism



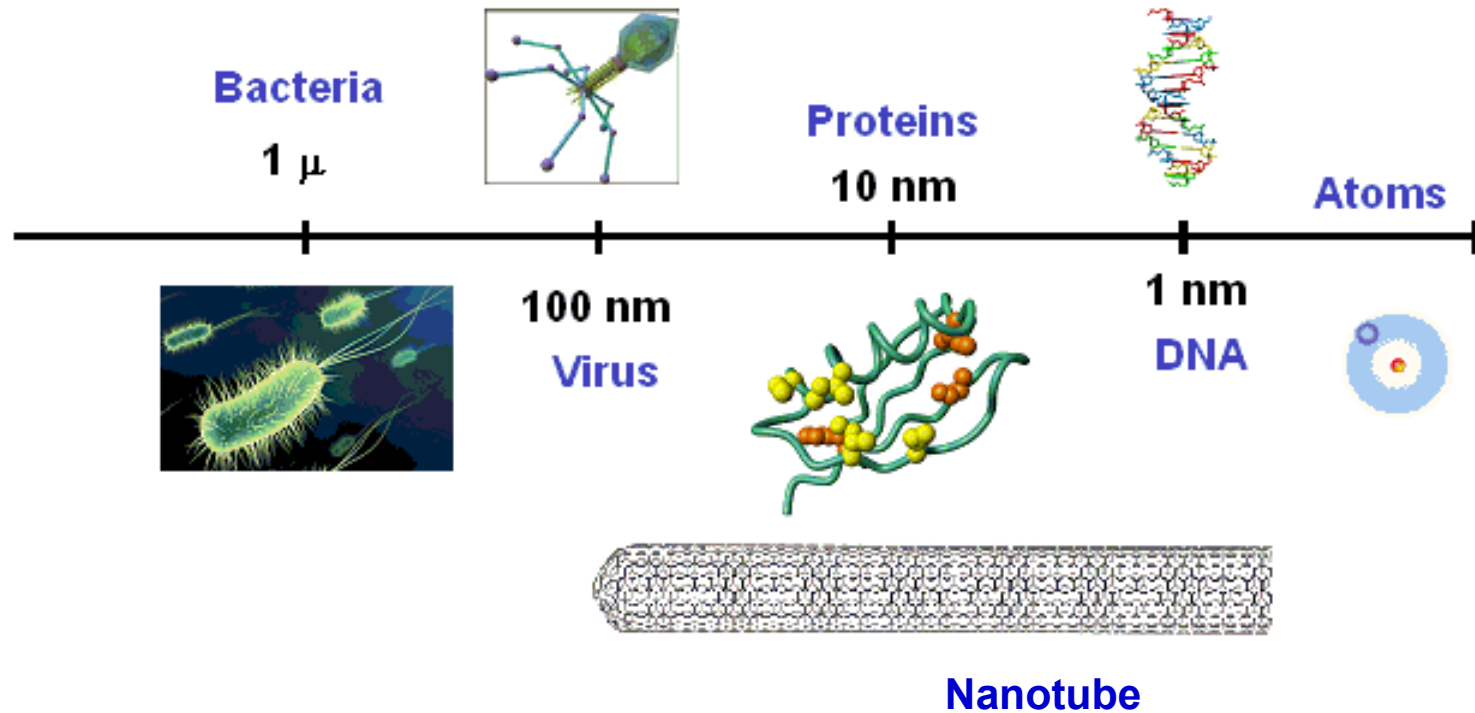
$$\chi = \frac{C}{T + \theta}$$

($T > T_N$)

2.7 Structure of nanomaterials

What is nano?

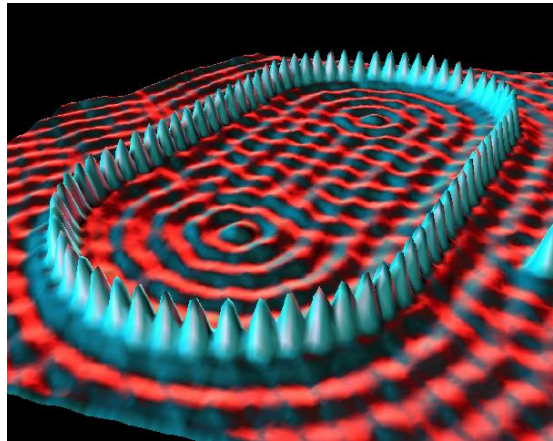
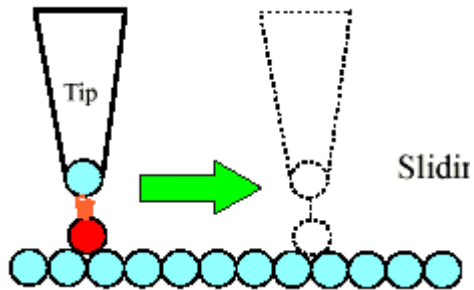
Definition: at least one dimension $< 100\text{ nm}$



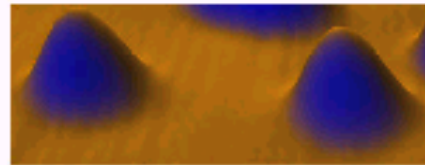
2.7 Structure of nanomaterials

Physical approaches to nanostructures

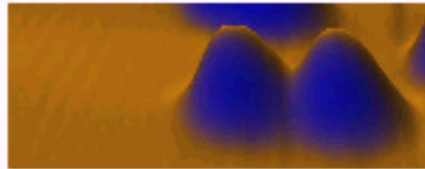
Atom manipulation



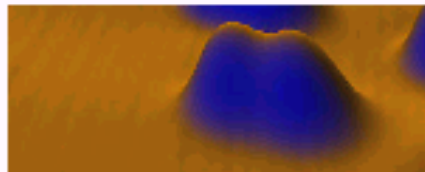
Building a Ni Dimer on Au(111)



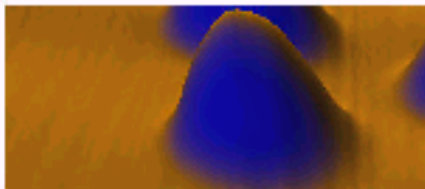
$r \sim 25\text{\AA}$



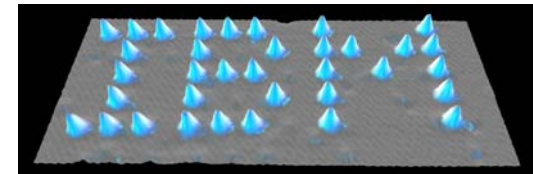
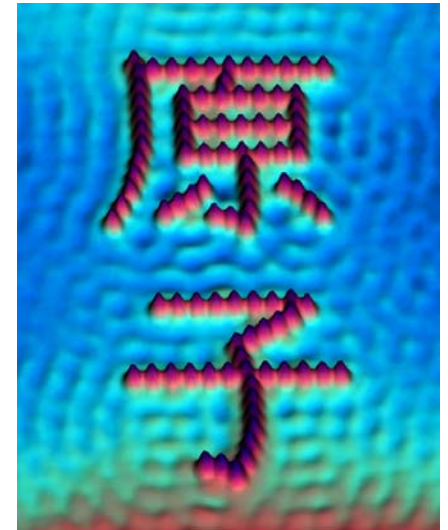
$r \sim 10\text{\AA}$



$r \sim 6\text{\AA}$



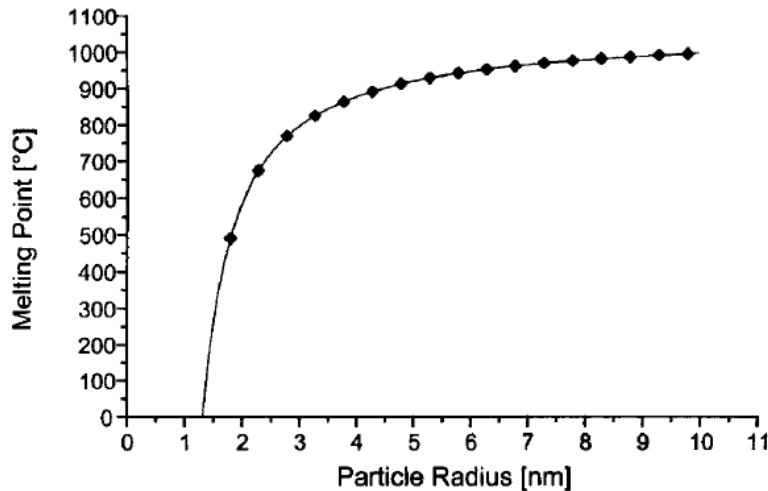
$r \sim 3\text{\AA}$



Building a Ni Dimer on Au(111)

2.7 Structure of nanomaterials

Why nano? – fundamental properties



Relation between the size of gold particles and their melting point.



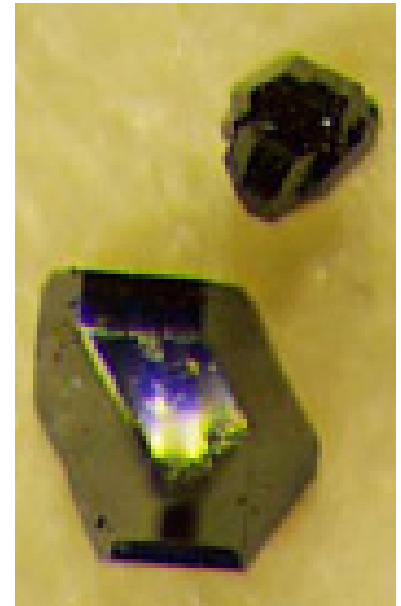
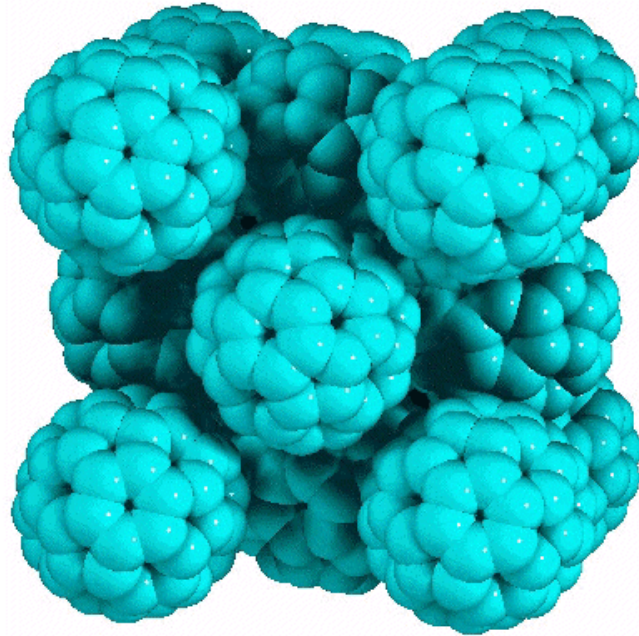
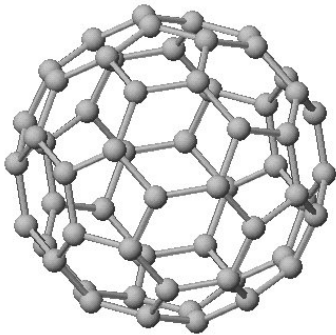
CdS-colloids, different particle sizes

- **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

2.7 Structure of nanomaterials

Structures containing large entities - fullerenes

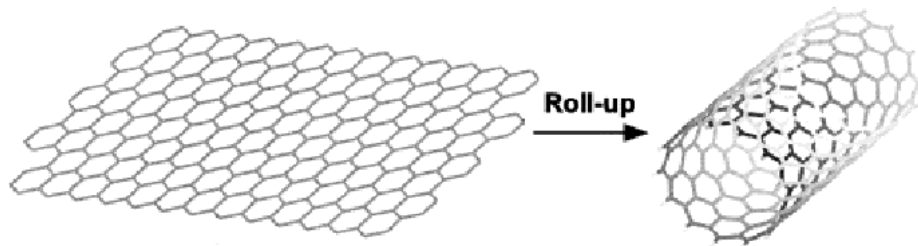


Chemistry of fullerenes

- Synthesis: vaporization of carbon
- ion implantation **in** C₆₀ cage
- fullerides: e.g. $A_3C_{60} \rightarrow (A^+)_3(C_{60})^{3-}$
- numerous chemical modifications

2.7 Structure of nanomaterials

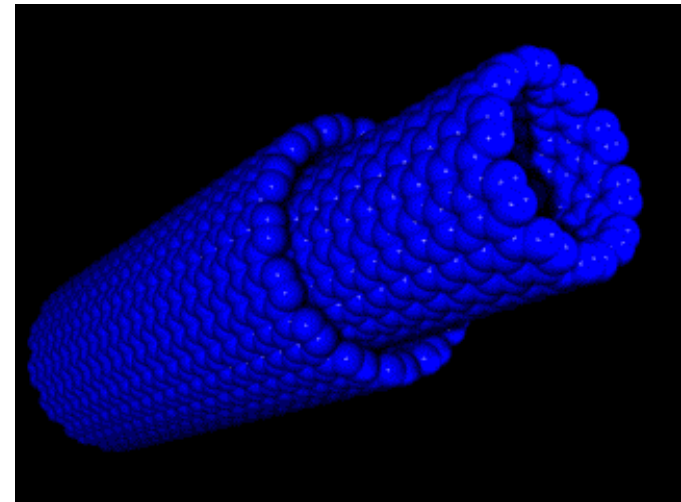
1D nanomaterials - Carbon nanotubes



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

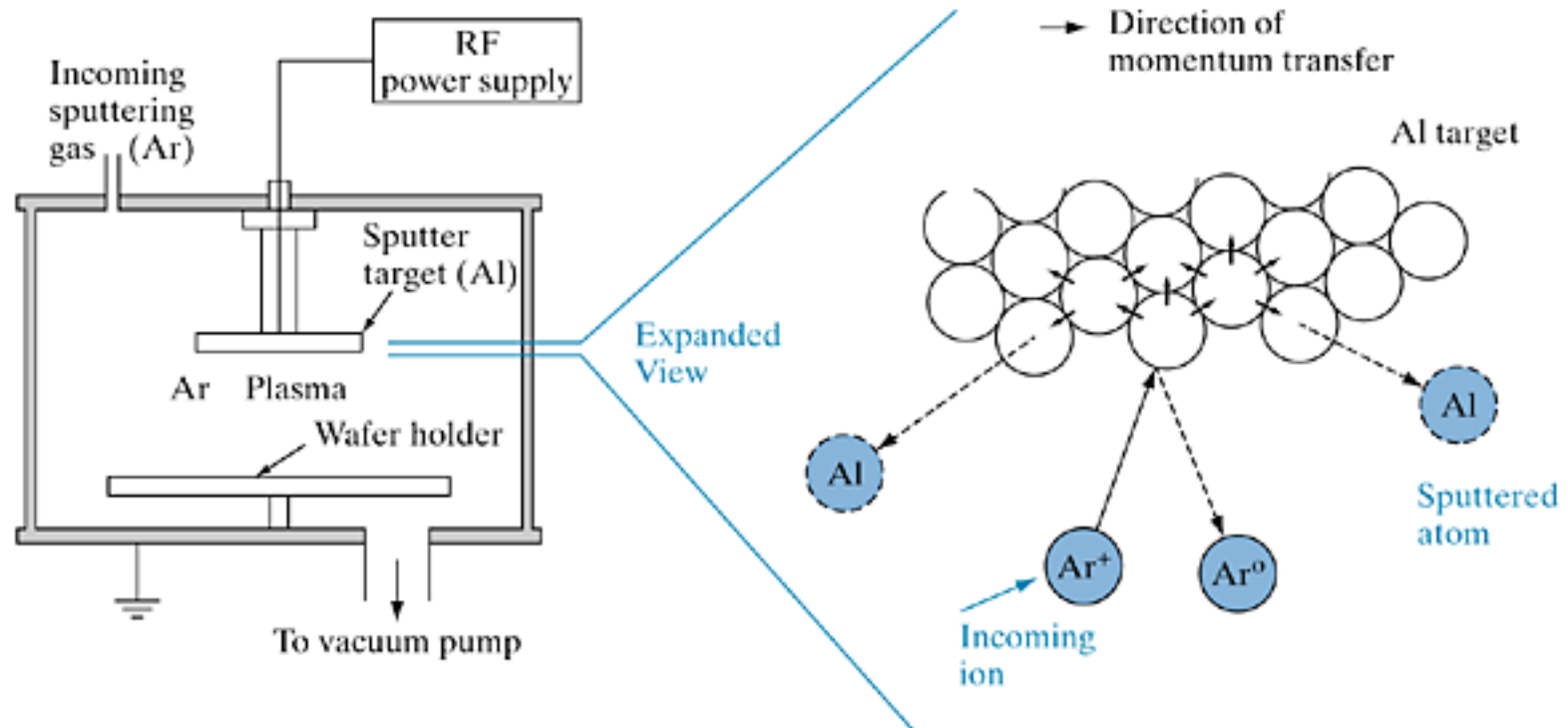


2.7 Structure of nanomaterials

2D nanomaterials - synthesis

- **Sputtering**

- Ar^+ -ions are accelerated in an electrical field and „hit“ the target
- consequence: surface atoms are removed from the surface
- applications: reactive sputtering, surface cleaning ...



2.7 Structure of nanomaterials

2D nanomaterials - synthesis

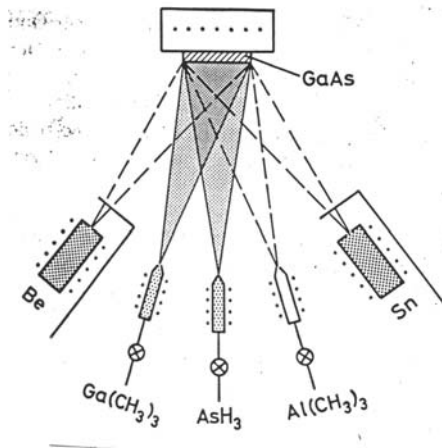
- **Epitaxy:**

- 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 $\text{GaAs}_{1-x}\text{P}_x$,
epitaxial layers are produced by thermal decomposition
of compounds like AsH_3 , AsCl_3 , PH_3 , PCl_3 , ...

- **MBE**



Production of a $\text{Ga}_{1-x}\text{Al}_x\text{As}$
on GaAs by the MBE process

2.7 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 effusion 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)

