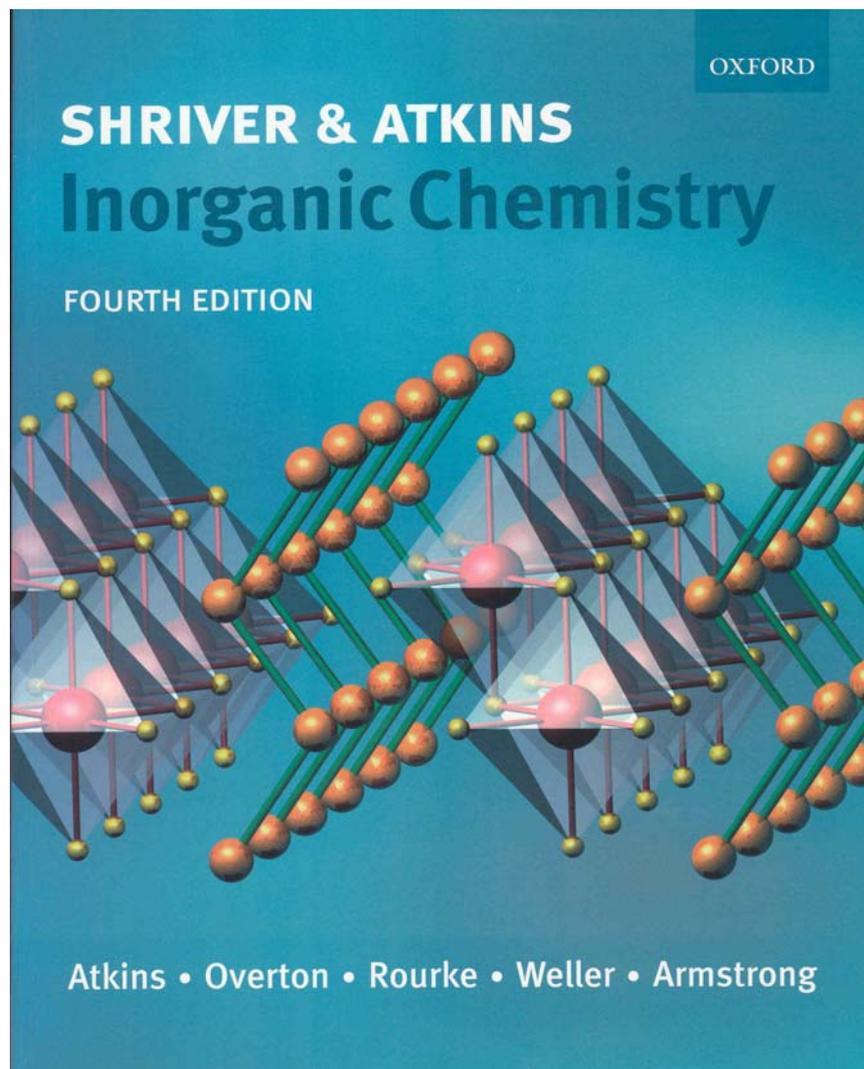# Advanced Inorganic Chemistry
Part 3: Basic Solid State Chemistry

1. Introduction (resources, aspects, classification)

2. Basic structural chemistry (hard sphere packing)

3. Chemical bonding in solids (electrostatic interactions)

4. Chemical preparation of solids (conventional methods)

5. More complex structures

6. Special structures and materials

7. Structure determination methods

1. Introduction: Textbook and other resources

SHRIVER & ATKINS
Inorganic Chemistry

OXFORD

FOURTH EDITION

Atkins • Overton • Rourke • Weller • Armstrong

a) Shriver & Atkins

Ch 3: The structure of simple solids

Ch 6: Physical techniques in Inorganic Chemistry (Diffraction Methods)

Ch 23: Solid State and Materials Chemistry

b) Advanced Inorg. Chemistry

   Part 1: Inorganic Molecules Section Structure Determ. Methods

1. Introduction: Special aspects of solid state chemistry

- Close relationship to solid state physics
- Crystal Chemistry: Structure and symmetry of solids, i.e.
  Size and packing of atoms: close packed structures (high space filling), symmetry groups, crystal systems, unit cells
- Physical methods for the characterization of solids
  - X-ray structure analysis, electron microscopy, NMR …
  - Thermal analysis, spectroscopy, magnetism, conductivity …
- Synthesis
  - HT-synthesis, hydro-/solvothermal synthesis, soft chemistry
  - Crystal growth
  - Chemical Vapor Deposition (CVD)

1. Introduction: Why is the solid state interesting?

**Most elements and compounds are solid at room temperature**

1. Introduction: Classifications of solids (examples)

- <u>Amorphous solids, glasses</u>: short range order (no 3D periodicity)

- <u>Covalent solids</u> (e.g. diamond, boron nitride): extreme hardness

- <u>Ionic solids</u> (e.g. NaCl): defects, dislocations, colour centres …
  ionic conductivity (e.g. α-AgI): dynamical disorder, enhanced
  diffusion of Ag^+ ions in an external field, "solid electrolytes"

- <u>Molecular materials</u> (e.g. Elements, MOFs: **M**etal **O**rganic **F**rameworks,
  fullerides)

- <u>Metals</u> (e.g. Cu): positive temperature coefficient of electrical
  resistivity

- <u>Semiconductors, insulators</u>: band gap, electrical conductivity

- <u>Ionic conductors</u>: ionic conductivity

- <u>Superconductors</u>: "zero resistivity" below T_c

- <u>Magnetic materials</u>: hard and soft magnetic materials

2.1 Basic structural Chemistry: Size of atoms
Approximation: atoms can be treated like spheres

(a) $2r_M$

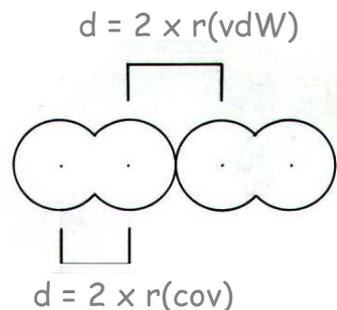(b) r_{cov}

(c) $r_+ + r_-$

d = 2 x r(vdW)

d = 2 x r(cov)
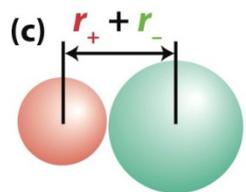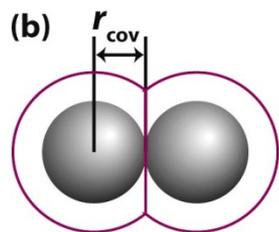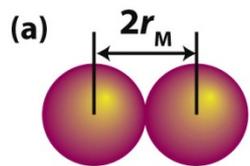
Metallic radius: d/2 in a metal (frequently: CN = 12) in other cases d/2 in elemental modification stable at ambient temperature

Covalent radius: d/2 in a molecule (single bond)

Atomic radii

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

Van der Waals radius between adjacent molecules

2.1 Basic structural Chemistry
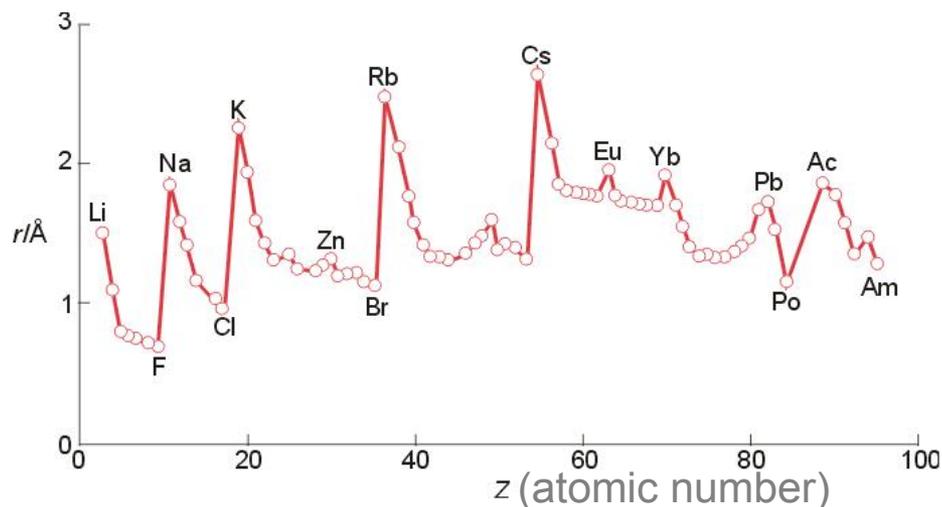## Trends of the atomic radii in the periodic table

1A (1)							8A (18)
H 37							He 31

1A (1)	2A (2)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
H 37							He 31
Li 152	Be 112	B 85	C 77	N 75	O 73	F 72	Ne 71
Na 186	Mg 160	Al 143	Si 118	P 110	S 103	Cl 100	Ar 98
K 227	Ca 197	Ga 135	Ge 122	As 120	Se 119	Br 114	Kr 112
Rb 248	Sr 215	In 167	Sn 140	Sb 140	Te 142	I 133	Xe 131
Cs 265	Ba 222	Tl 170	Pb 146	Bi 150	Po 168	At (140)	Rn (140)
Fr (270)	Ra (220)						

3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	(8)	8B (9)	(10)	1B (11)	2B (12)
Sc 162	Ti 147	V 134	Cr 128	Mn 127	Fe 126	Co 125	Ni 124	Cu 128	Zn 134
Y 180	Zr 160	Nb 146	Mo 139	Tc 136	Ru 134	Rh 134	Pd 137	Ag 144	Cd 151
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)

7

2.1 Basics structural Chemistry: 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	153	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).

La – Lu 187-172

„Lanthanide contraction"

Ga: 122 pm !

Change of ionic radii with coordination number

Table 1.5 Ionic radii, r/pm*

Li$^+$	Be^{2+}	B^{3+}			N^{3-}	O^{2-}	F$^-$
59(4)	27(4)	12(4)			132	135(2)	128(2)
76(6)						138(4)	131(4)
						140(6)	133(6)
						142(8)	
Na$^+$	**Mg^{2+}**	**Al^{3+}**			**P^{3-}**	**S^{2-}**	**Cl$^-$**
99(4)	49(4)	39(4)			212	184(6)	167(6)
102(6)	72(6)	53(6)					
116(8)	89(8)						
K$^+$	**Ca^{2+}**	**Ga^{3+}**			**As^{3-}**	**Se^{2-}**	**Br$^-$**
138(6)	100(6)	62(6)			222	198(6)	196(6)
151(8)	112(8)						
159(10)	128(10)						
160(12)	135(12)						
Rb$^+$	**Sr^{2+}**	**In^{3+}**	**Sn^{2+}**	**Sn^{4+}**		**Te^{2-}**	**I$^-$**
149(6)	116(6)	79(6)	83(6)	74(6)		221(6)	206(6)
160(8)	125(8)	92(8)	93(8)				
173(12)	144(12)						
Cs$^+$	**Ba^{2+}**	**Tl^{3+}**					
167(6)	149(6)	88(6)					
174(8)	156(8)	**Tl$^+$**					
188(12)	175(12)	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

Which polyhedron types represent
the different CN's ?

2.1 Basic structural Chemistry: Trends of the ionic radii

- Ionic radii increase on going down a group

- Radii of equal charge ions decrease across a period, c.f. atomic radii

- Ionic radii increase with increasing coordination number (the higher its CN, the bigger the ions are or seem 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: $r(Cs^+) > r(F^-)$)
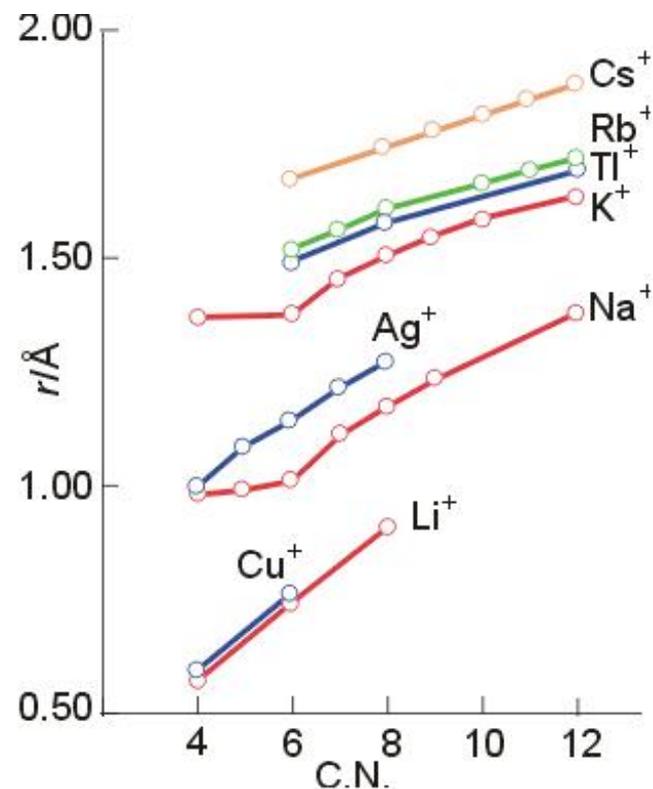
2.1 Basic structural Chemistry: Unit cells

- A 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, contains one lattice point
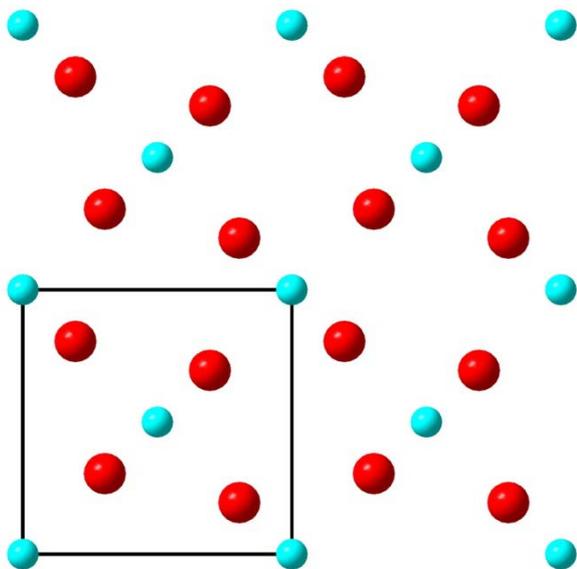
Exercise for students already familiar with basic structure types: Consider the unit cell contents and chemical formula of the structures: NaCl, ZnS (Sphalerite and Wurtzite), NiAs, CaF_2, TiO_2, $CaTiO_3$.

2.1 Basic structural Chemistry:
Unit cells and coordination numbers
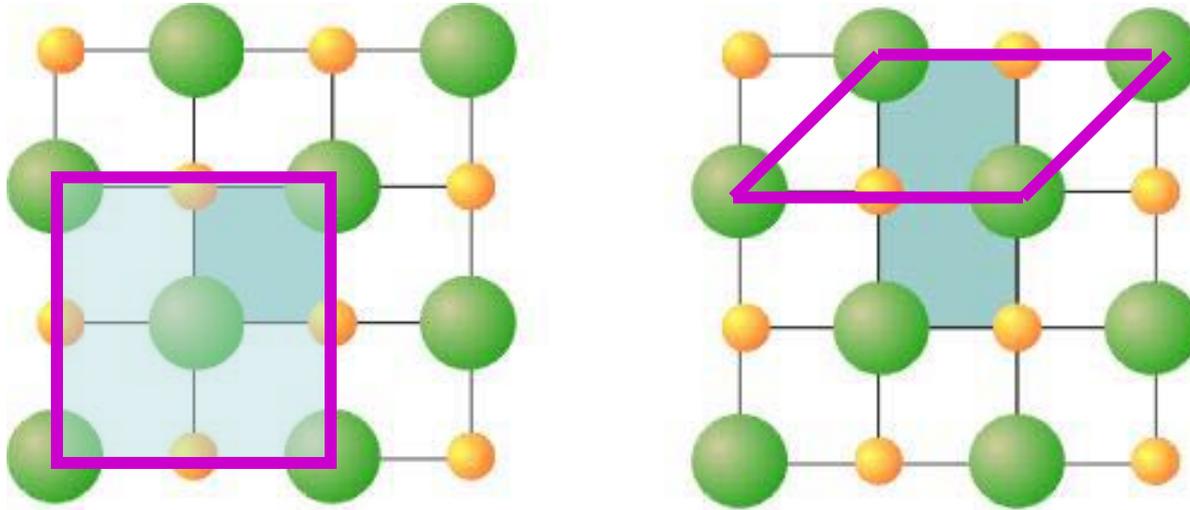
1. **Cell edges should coincide with symmetry axes or reflection planes**

2. **The smallest possible cell which fulfills 1 should be chosen**

Coordination Number (CN): Number of direct neighbours of a given atom („first coordination sphere")

CN 4

Se6
275.5
Se4   242.0   Cu3   243.7
260.0
Se3   Se5

CN 3

Se2
241.6   Cu1   236.9
238.0   Se6
Se3

CN 2

Cu6
237.0   228.5
164°
Se6   Se5
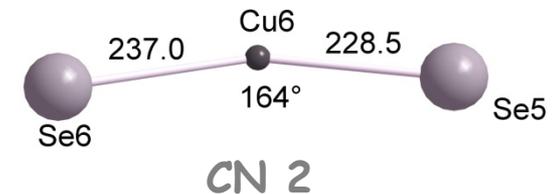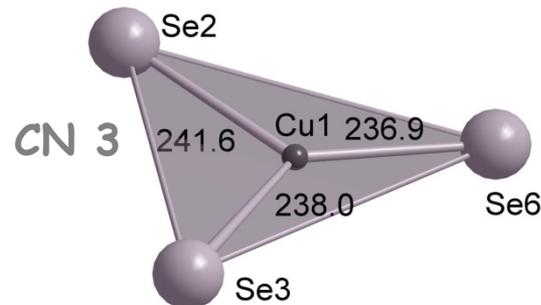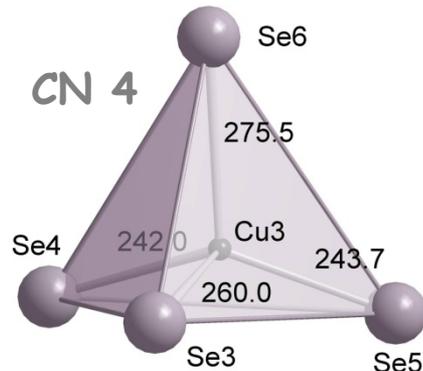
2.1 Basic structural Chemistry
Unit cells and crystal system

Repeat symmetry elements and symmetry operations for molecules and solids !
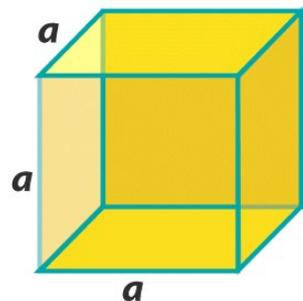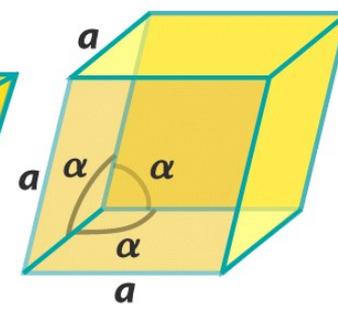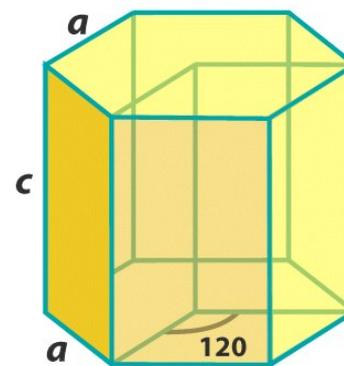

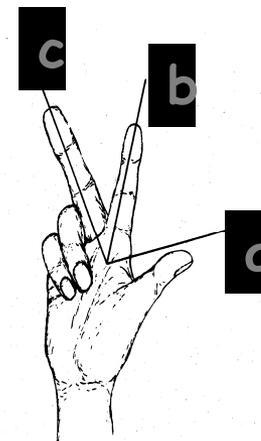Cubic
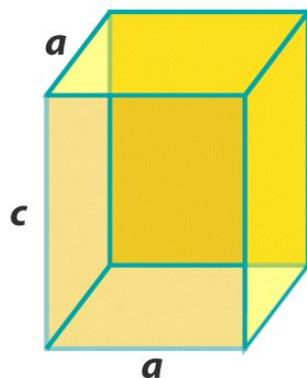
Tetragonal
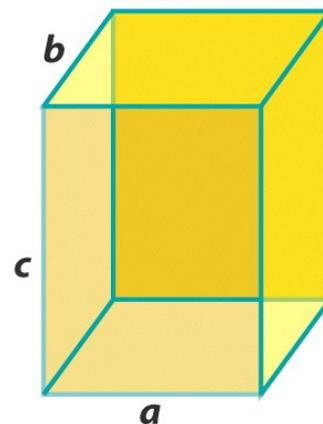
Orthorhombic
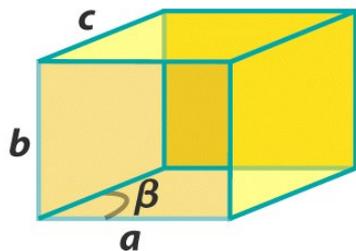
Monoclinic
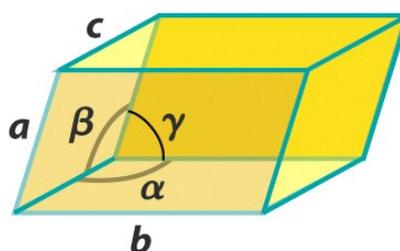
Triclinic

Trigonal

Hexagonal

2.1 Basic structural Chemistry: Fractional coordinates

- Rules for marking the position of an atom in a unit cell:
  - Possible values for x, y, z are $0 < x,y,z < 1$
  - Atoms are generated by symmetry elements ("equivalent atoms")
  - Values < 0: add 1.0, values > 1.0: substract 1.0 (or multiples)
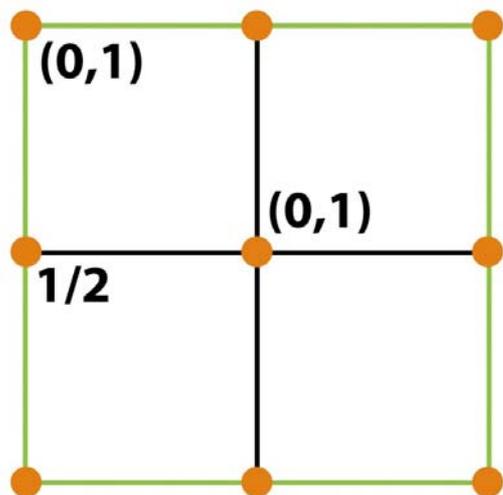 - Equivalent atoms are referenced only once

Figure 3-7
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

Figure 3-8
Shriver & Atkins Inorganic Chemistry, Fourth Edition
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Projection represent. of an fcc unit cell
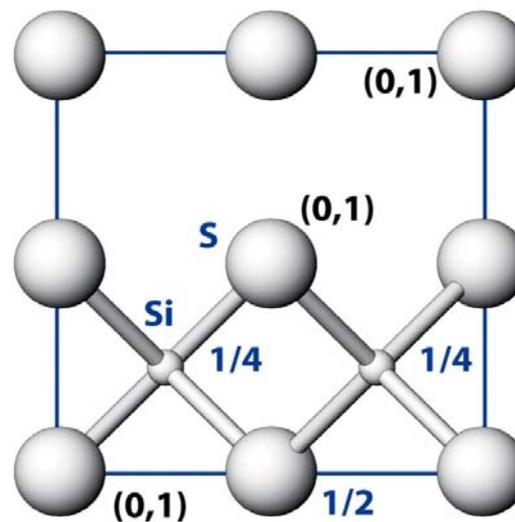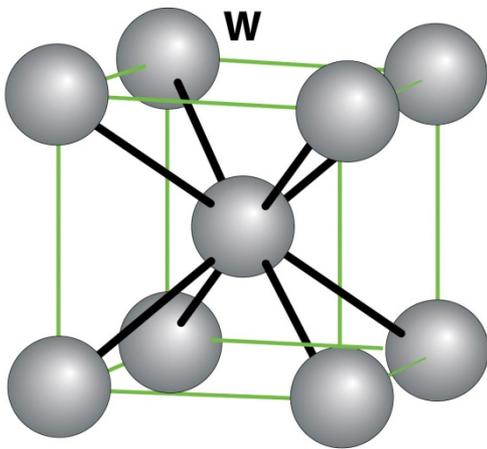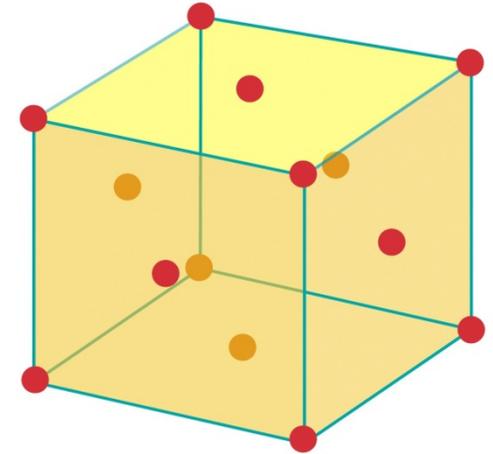with the heights of the lattice points

The structure of silicon sulfide (SiS_2)
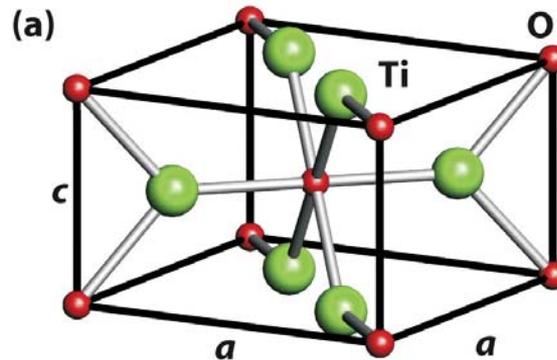with the heights of the atom positions

14

2.1 Basics structural Chemistry
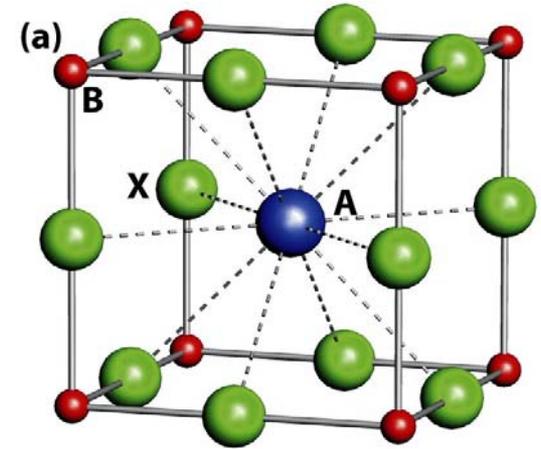## Number of atoms (formula units) per unit cell (Z)

- 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

Structure of metallic W

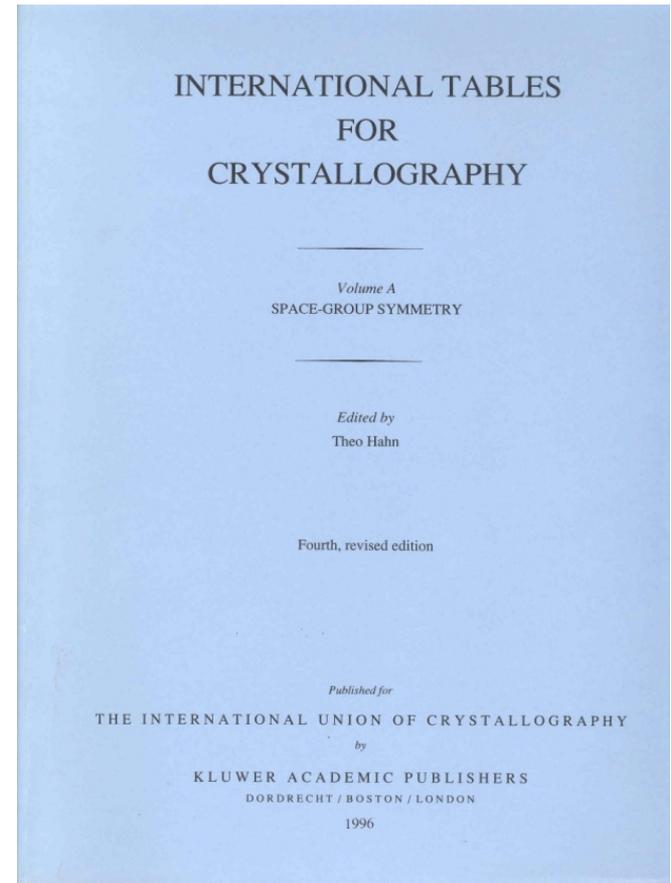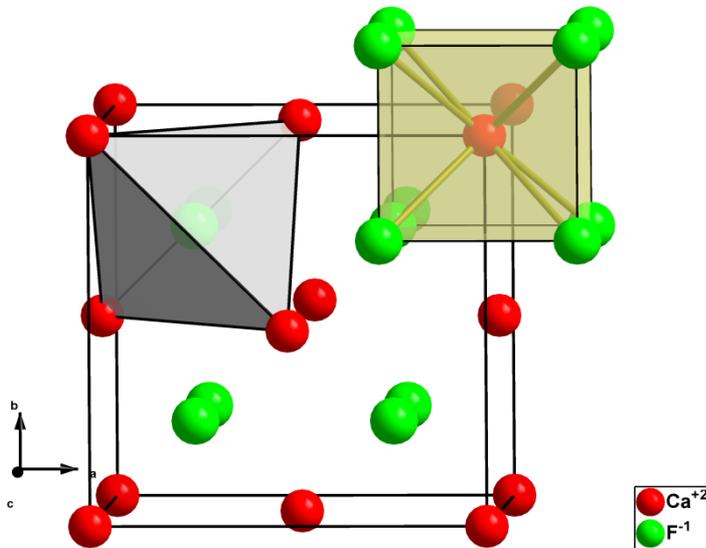Structure of TiO_2

Structure of ABX_3

2.1 Basic structural Chemistry: Wyckoff notation etc.

Crystal data

Formula/crystal system/Space group/Z: CaF_2 (Fluorite)/cubic/***Fm*-3*m*** (no. 225)/4
Lattice constant(s)   : a = 5.4375(1) Å

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
			$\frac{3}{4}$	$\frac{3}{4}$	$\frac{1}{4}$

Structure of CaF_2

2.2 Simple close packed structures (metals):
Close packing of spheres in 2- and 3D

primitive packing (low space filling)

close packing (high space filling)

Figure 3-10a
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

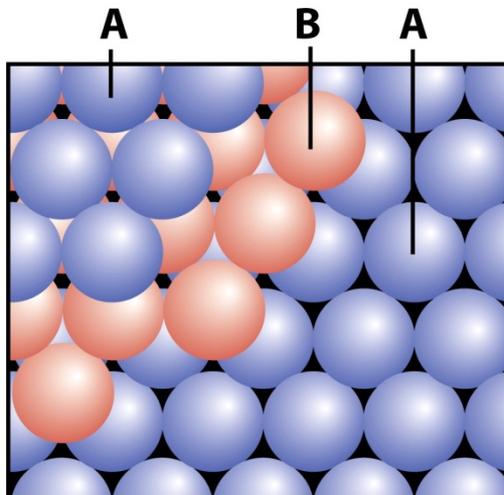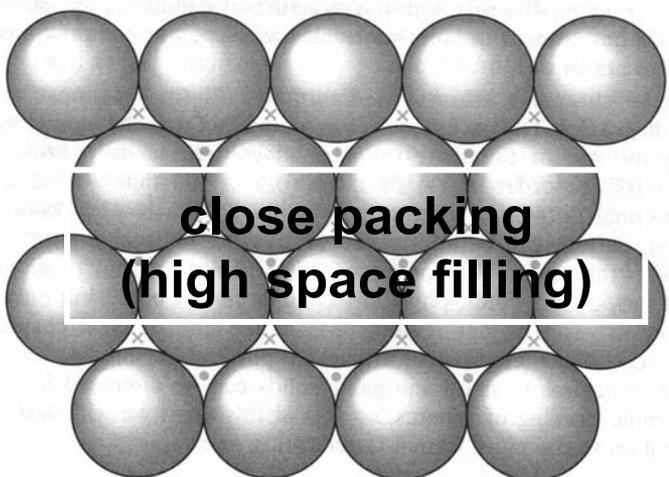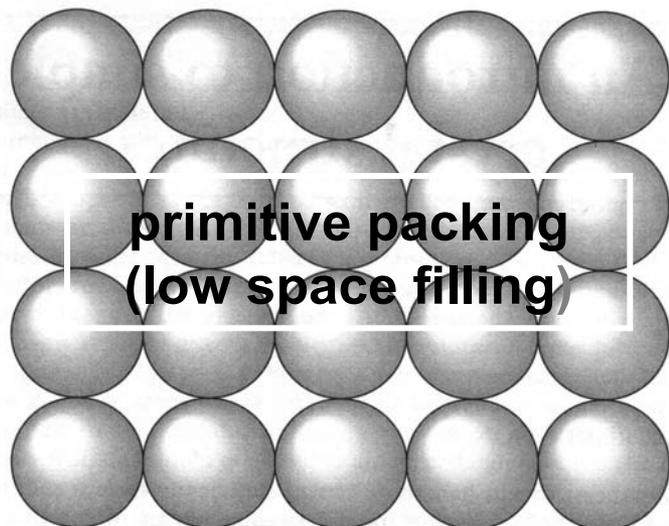**hexagonal close packing (hcp)**

Figure 3-10b
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
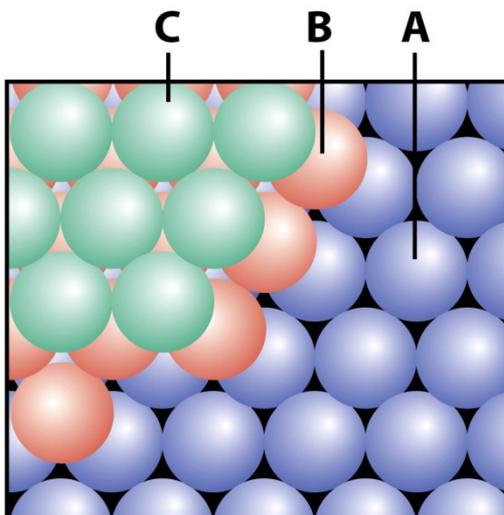
Cubic close packing (ccp, fcc)

2.2 Simple close packed structures (metals):
Close packing of spheres in 2- and 3D

Space filling P = 74%, CN = 12

hcp

ccp (fcc)
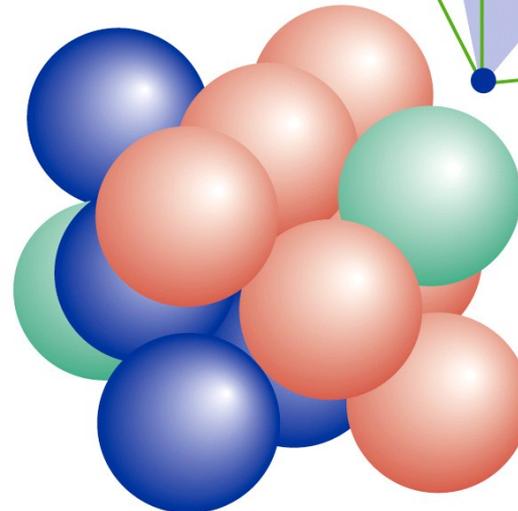
Figure 3.11

(Be, Mg, Zn, Cd, Ti, Zr, Ru ...)   **(Cu, Ag, Au, Al, Ni, Pd, Pt...)**

2.2 Simple close packed structures (metals)
Typical coordination polyhedra of atoms
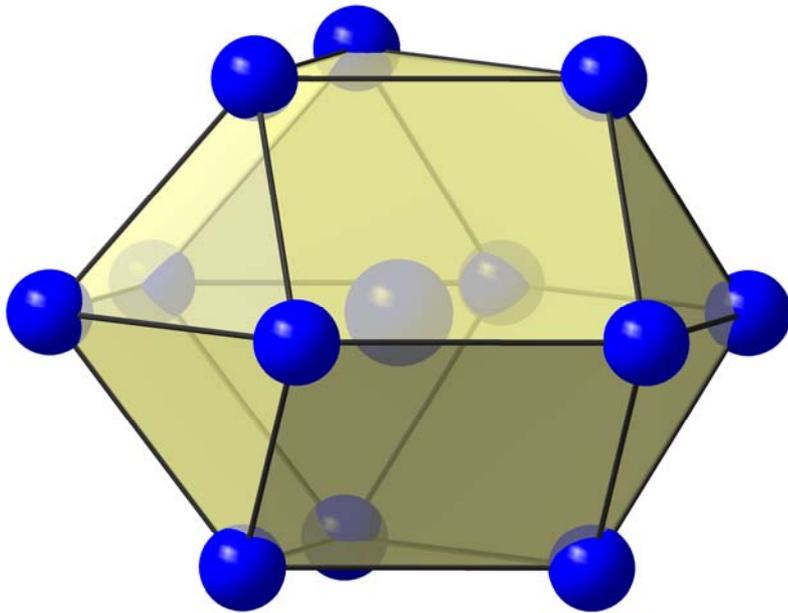
| Hexagonal close packed structure hcp (CN: 12): anti-cuboctahedron | Cubic close packed structure ccp (fcc) (CN: 12): cuboctahedron |
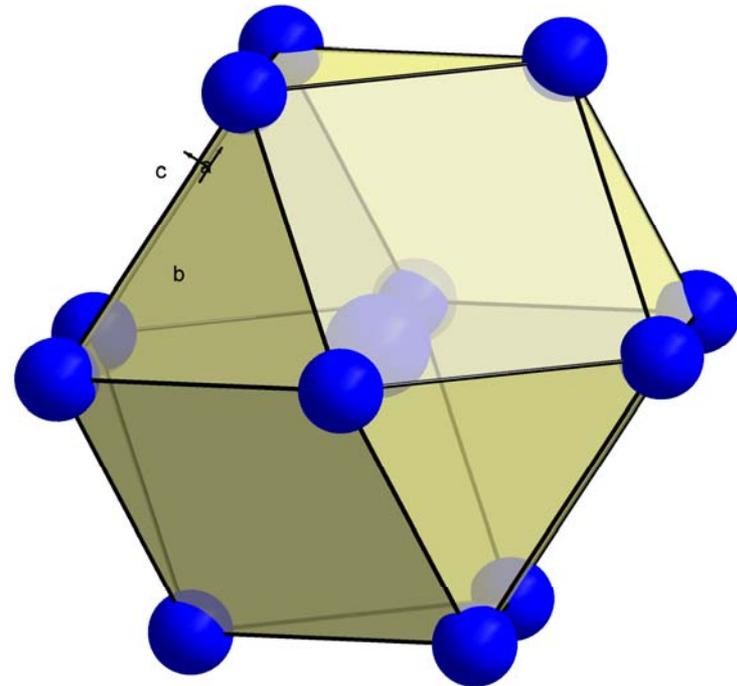
2.2 Simple close packed structures
The crystal structure of C_{60} !!
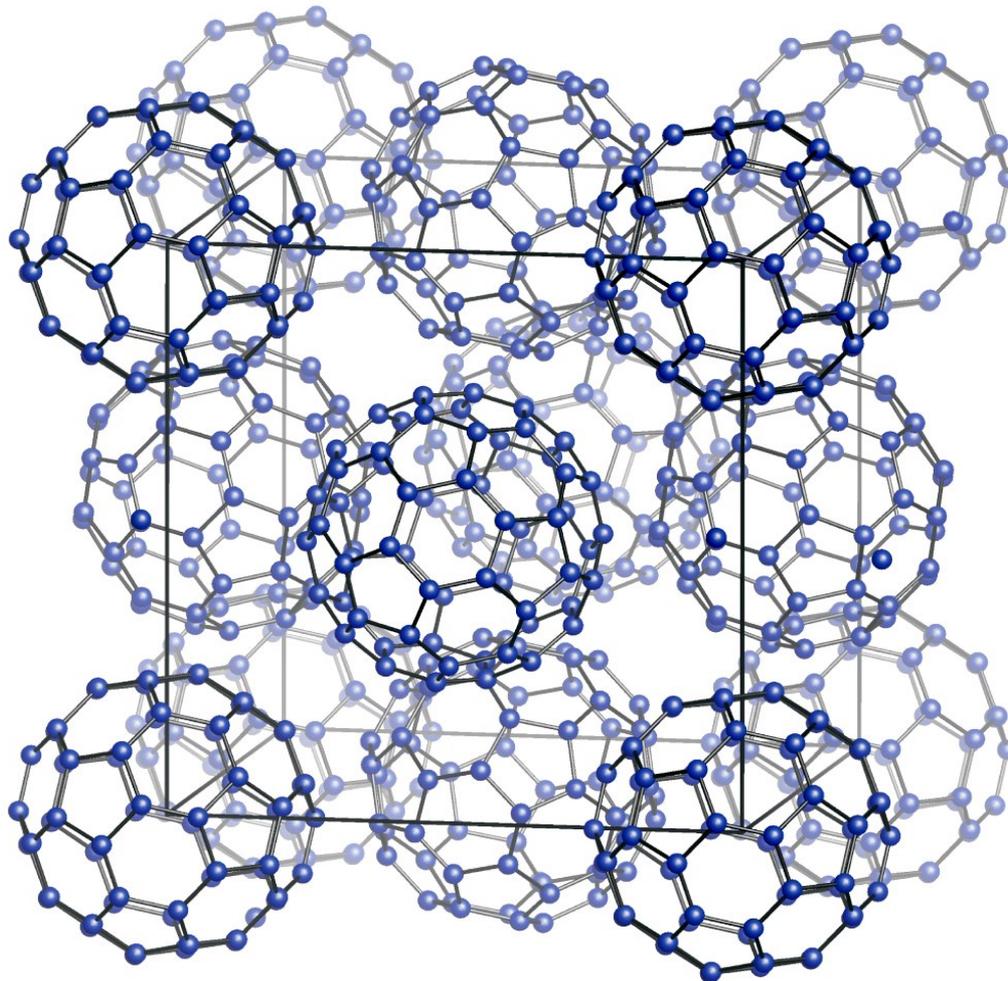
2.2 Simple close packed structures (metals)
Other types of sphere packings

(a)

(b)
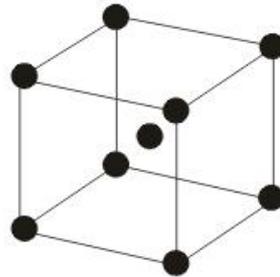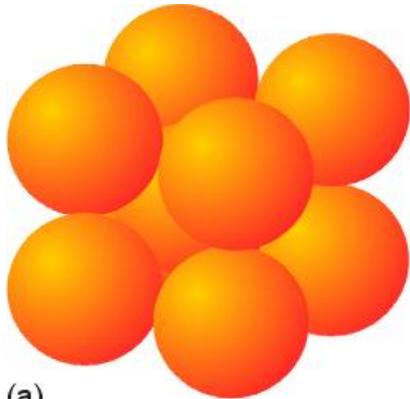
**Body centered cubic, bcc
(Fe, Cr, Mo, W, Ta, Ba ...)**

Space filling = **68%**

CN = **8**
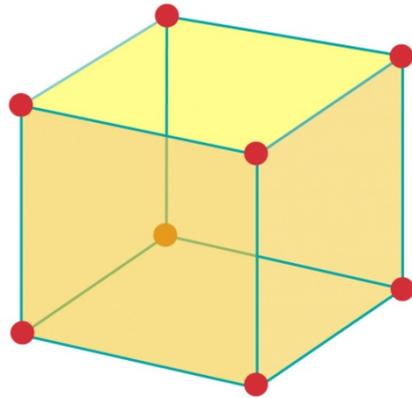
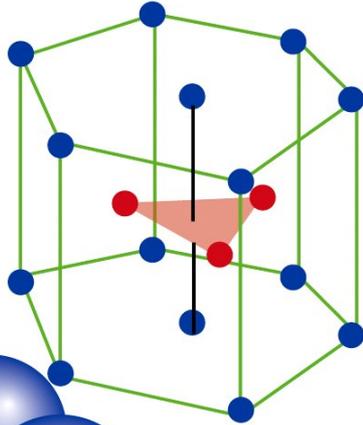**Primitive packing**

space filling = **52%**

CN = **6**

(α-Po)

Figure 3-3
Shriver & Atkins Inorganic Chemistry, Fourth Edition
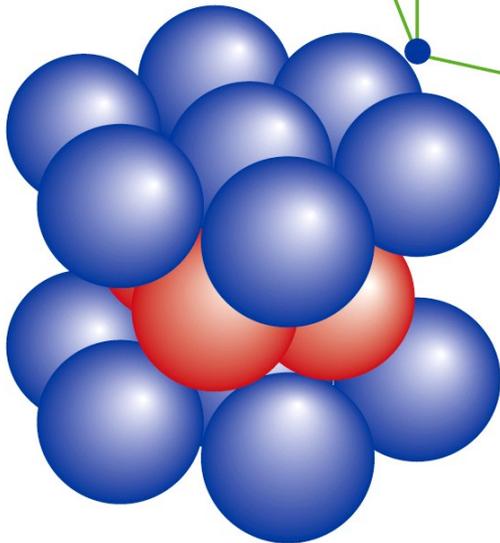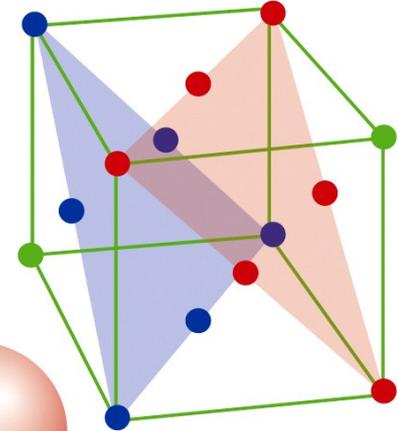© 2006 by D. F. Shriver, P. W. Atkins, T.L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

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

Space filling = $\dfrac{\text{Volume occupied by atoms (spheres)}}{\text{Volume of the unit cell}}$
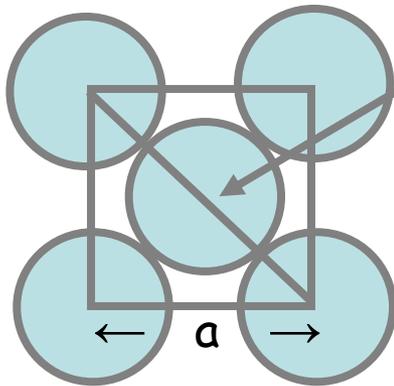
$$4r = \sqrt{2}a$$

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

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

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

2.2 Simple close packed structures (elements)
What structures are built by the elements?

Inform **yourself** about important elemental structures that do **not** fit into the concept of close packing of spheres: B, C (3-5 modifications), Si, Ge, Sn, P (white, black, red), As, Sb, S, Se, Te, I

2.2 Simple close packed structures
Holes in close packed structures
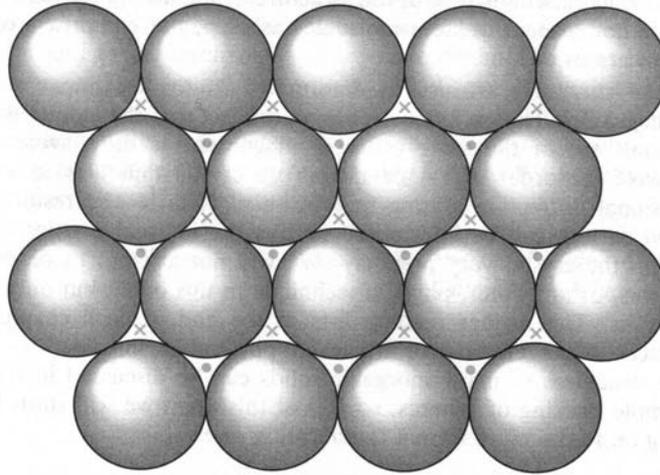
Trigonal holes
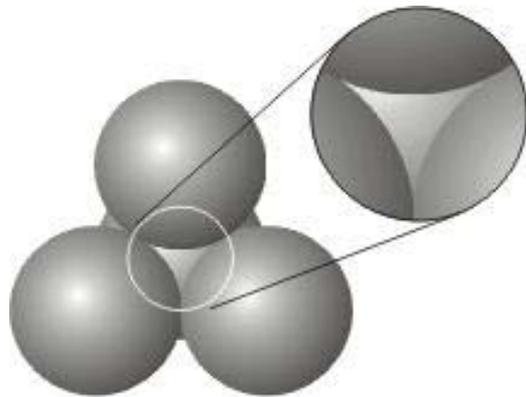
Tetrahedral hole TH
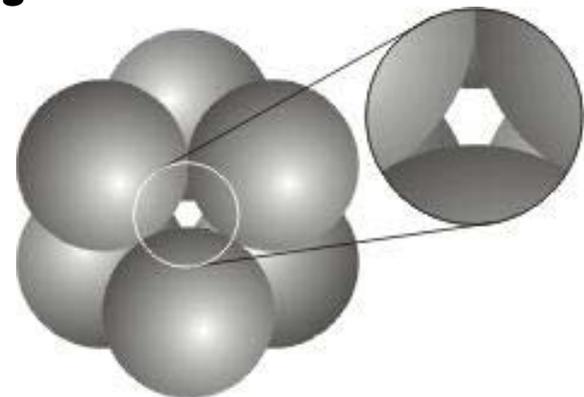
Octahedral hole OH

2.2 Simple close packed structures
Octahedral holes in close packed structures

ccp (fcc)

hcp
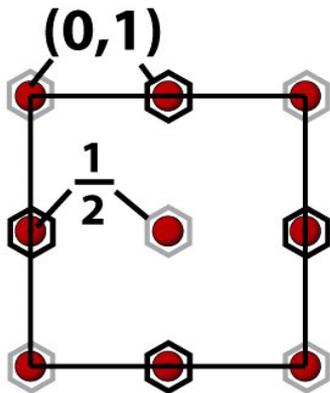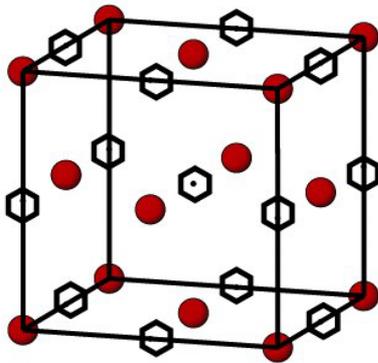
A close packing contains as many octahedral holes as close packed atoms.

$(0,1)$

$\frac{1}{2}$

$\left(\frac{1}{4}, \frac{3}{4}\right)$

$\frac{1}{2}$

$(0,1)$
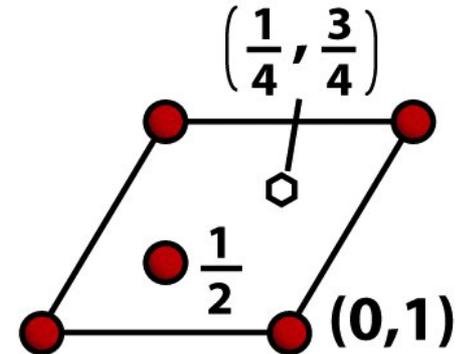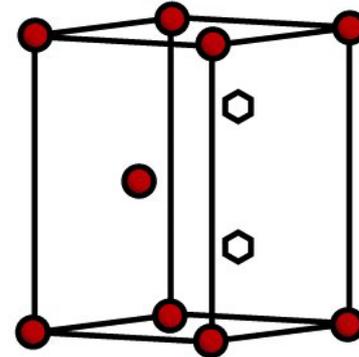
2.2 Simple close packed structures
Tetrahedral holes in close packed structures

ccp (fcc)

hcp
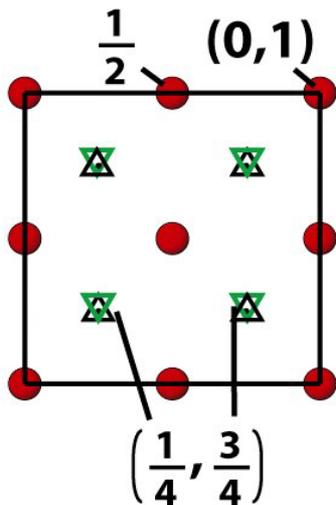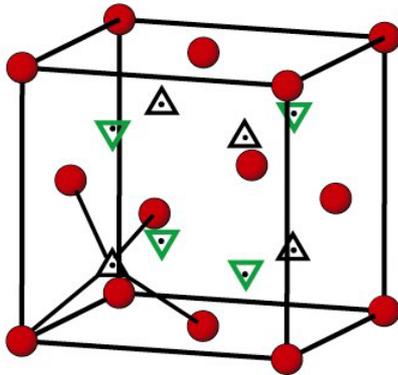
A close packing contains twice as many tetrahedral holes as close packed atoms.

$\frac{1}{2}$ (0,1)

$\left(\frac{1}{4}, \frac{3}{4}\right)$

$\left(\frac{1}{8}, \frac{7}{8}\right)$ $\frac{1}{2}$ $\left(\frac{3}{8}, \frac{5}{8}\right)$

(0,1)
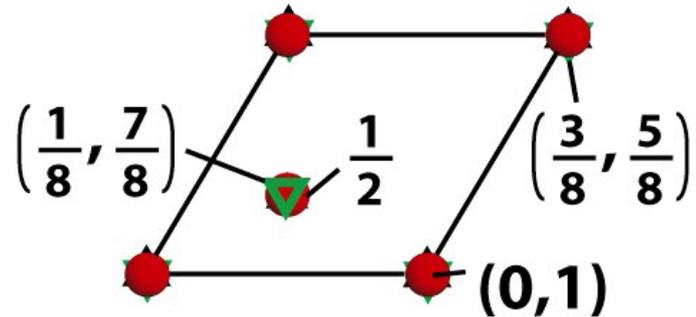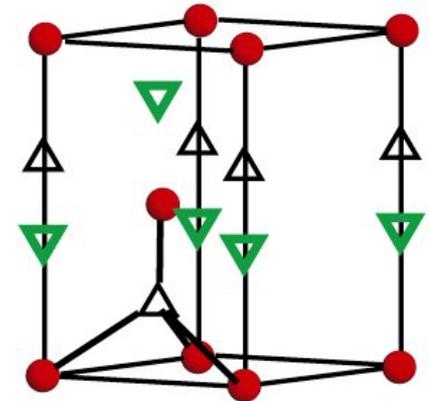
2.2 Simple close packed structures
Structure types derived from close packing by systematic filling of holes

Structure type (underlined: close packed atom type)	Examples	Packing	Holes filled
Na$\underline{Cl}$	AgCl, BaS, CaO, CeSe, GdN, NaF, **Na$_3$BiO$_4$,** V$_7$C$_8$	CCP	All octahedra by Na
Ni$\underline{As}$	TiS, CoS, CoSb, AuSn	HCP	All octahedra by Ni
$\underline{Ca}$F$_2$	CdF$_2$, CeO$_2$, **Li$_2$O**, Rb$_2$O, SrCl$_2$, ThO$_2$, ZrO$_2$, AuIn$_2$	CCP	All tetrahedra by F
Cd$\underline{Cl}_2$	MgCl$_2$, MnCl$_2$, FeCl$_2$, Cs$_2$O, CoCl$_2$	CCP	1/2 octahedra by Cd
Cd$\underline{I}_2$	MgBr$_2$, PbI$_2$, SnS$_2$, Mg(OH)$_2$, Cd(OH)$_2$, Ag$_2$F	HCP	1/2 octahedra by Cd
Sphalerite (Zn$\underline{S}$)	AgI, BeTe, CdS, CuI, GaAs, GaP, HgS, InAs, ZnTe	CCP	1/2 tetrahedra by Zn
Wurzite (Zn$\underline{S}$)	AlN, BeO, ZnO, CdS (HT)	HCP	1/2 tetrahedra by Zn
Li$_3\underline{Bi}$	Li$_3$Au	CCP	All octah. and tetrahedra by Li

2.2 Simple close packed structures
1st Pauling rule

(1) In most cases 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
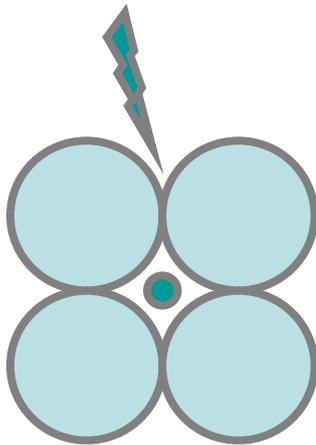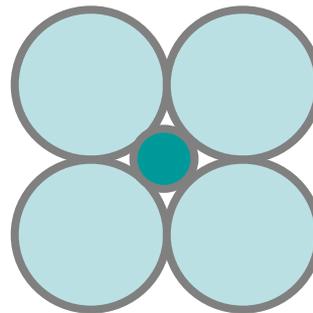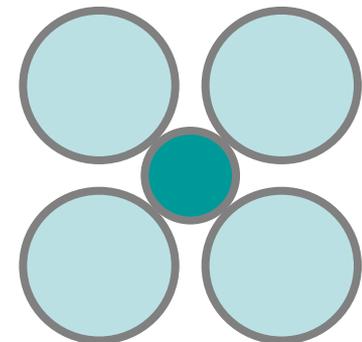
worst case   optimum   low space filling

2.2 Simple close packed structures
Ideal radius ratios for different types of coordination

CN	Polyhedron	radius ratios
3	triangle	0.15-0.22
4	tetrahedron	0.22-0.41
6	octahedron	0.41-0.73
8	cube	0.73-1.00
12	(anti)cuboctahedron	1.00

Example: Octahedron

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

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

2r(anion)

2r(anion) + 2r(cation)

1
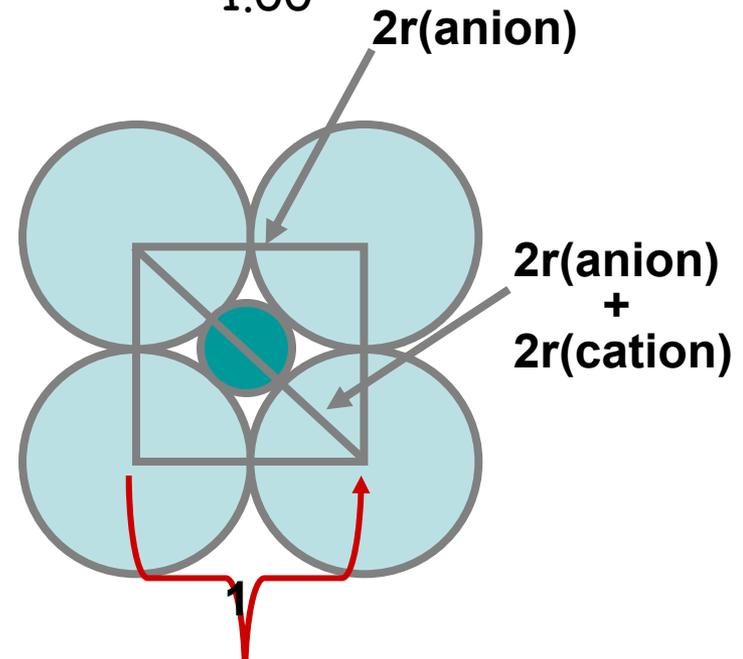
2.3 Basic structure types: NaCl-type

Crystal data

Formula sum	NaCl
Crystal system	cubic
Space group	$F\,m\,\text{-}3\,m$ (no. 225)
Unit cell dimensions	$a = 5.6250(5)$ Å
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

(a)

Figure 3-28
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Structural features:
- **All octahedral holes of CCP filled**
- **Na is coordinated by 6 Cl, Cl is coordinated by 6 Na**
- **One $NaCl_6$-octaherdon is connected to 12 $NaCl_6$-octahedra via common edges (how many via common corners and faces ?)**

2.3 Basic structure types: Sphalerite-type

Crystal data

Formula sum	ZnS
Crystal system	cubic
Space group	$F\,\bar{4}\,3\,m$ (no. 216)
Unit cell dimensions	a = 5.3450 Å
Z	4

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
S	- 2	4a	0	0	0
Zn	+2	4c	1/4	1/4	1/4

(a)

Figure 3-32
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Structural and other features:
- **Diamond-type structure**
- **50% of tetrahedral holes in CCP filled**
- **Zn is coordinated by 4 S, (tetrahedra, common corners)**
  (how is S coordinated by Zn ?)
- **Applications of sphalerite-type structures are important**
  (semiconductors: solar cells, transistors, LED…)

1

2.3 Basic structure types: Wurzite-type

Crystal data

Formula sum	ZnS
Crystal system	hexagonal
Space group	$P6_3mc$ (no. 186)
Unit cell dimensions	$a = 3.8360$ Å, $c = 6.2770$ Å
Z	2

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Zn	+2	2b	1/3	2/3	0
(dto., gen. by 2_1			2/3	1/3	1/2)
S	- 2	2b	1/3	2/3	3/8
(dto., gen. by 2_1			2/3	1/3	7/8)
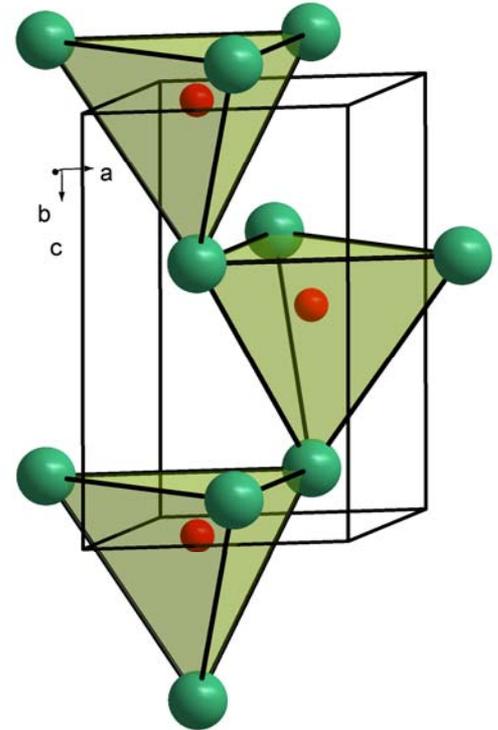
Structural features:
- **50% of tetrahedral holes in HCP filled**
- **Sequence (S-layers): AB**
- **Zn is coordinated by 4 S (tetrahedra, common corners)**
- **(how is S coordinated by Zn?)**

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

Atomic coordinates

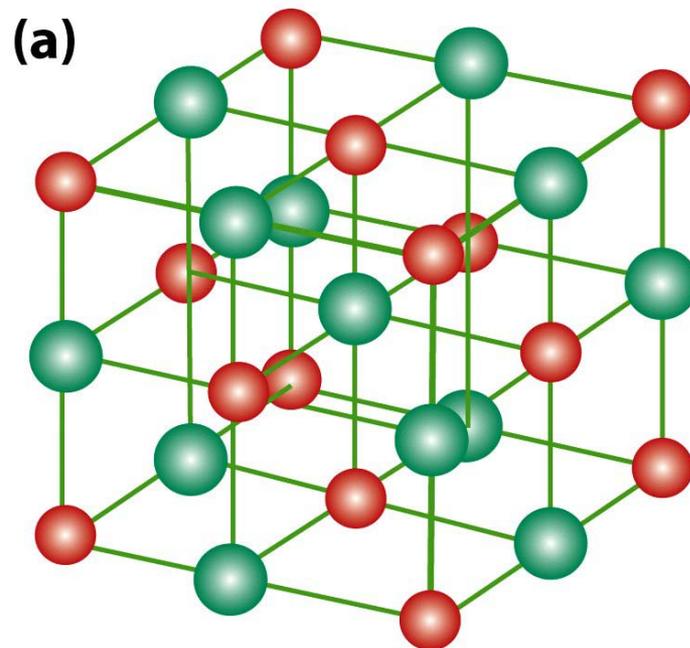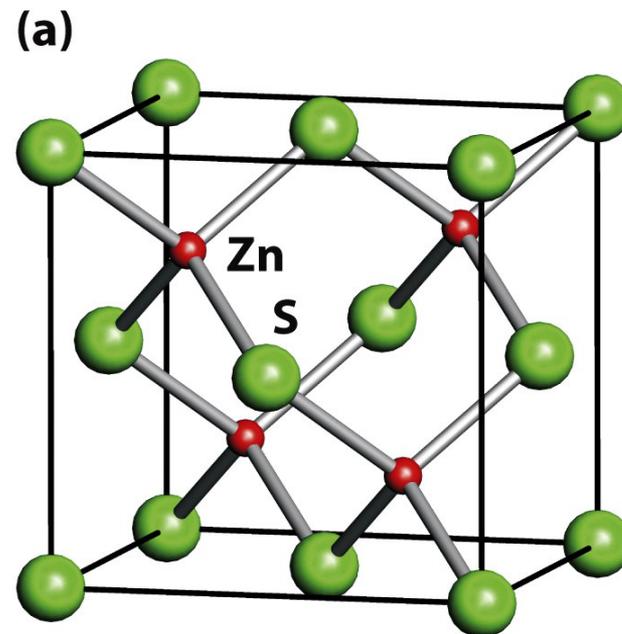| Atom	Ox.	Wyck.	x	y	z
Ca	+2	4*a*	0	0	0
F	- 1	8*c*	1/4	1/4	1/4
(dto., gen. by -1			3/4	3/4	3/4)

Figure 3-33
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Structural features:
- **All TH of CCP filled**
- **F is coordinated by 4 Ca (tetrahedron)**
- **(how is Ca coordinated by F?)**

2.3 Basic structure types: $CdCl_2$-type

Crystal data

Formula sum	$CdCl_2$
Crystal system	trigonal
Space group	$R\,\text{-}3\,m$ (no. 166)
Unit cell dimensions	a = 6.23 Å, $\alpha = 36°$
Z	1

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Cd	+2	1a	0	0	0
Cl	-1	2c	0.25(1)	0.25(1)	0.25(1)
(dto., gen. by -1			0.75(1)	0.75(1)	0.75(1))
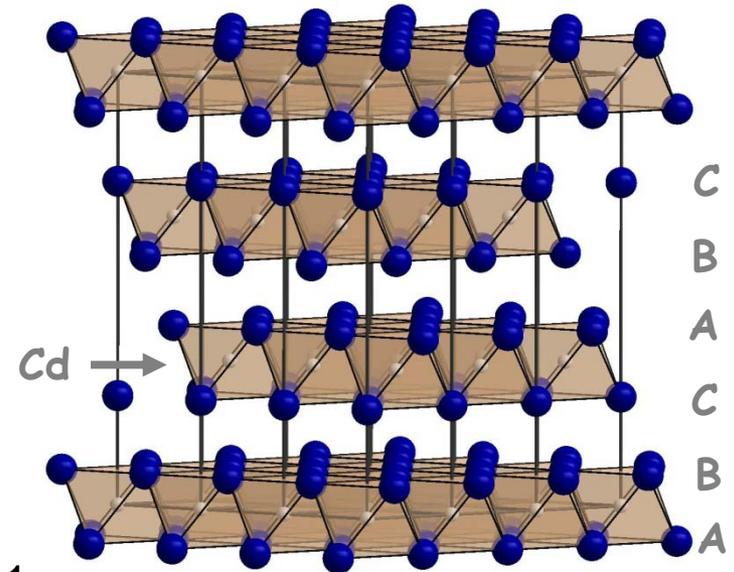
Structural features:
- **Layered structure, sequence (Cl-layers): ABC**
- **Cd is coordinated octahedrally by 6 Cl (via six common edges)**
- **(how is Cl coordinated by Cd?)**
- **Polytypes**

2.3 Basic structure types: CdI_2-type

Crystal data

Formula sum	CdI_2
Crystal system	trigonal
Space group	$P\,\text{-}3\,m\,1$ (no. 164)
Unit cell dimensions	a = 4.24 Å, c = 6.86 Å
Z	1

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Cd	+2	1a	0	0	0
I	- 1	2d	1/3	2/3	0.249
(dto., gen. by -1			2/3	1/3	0.751)
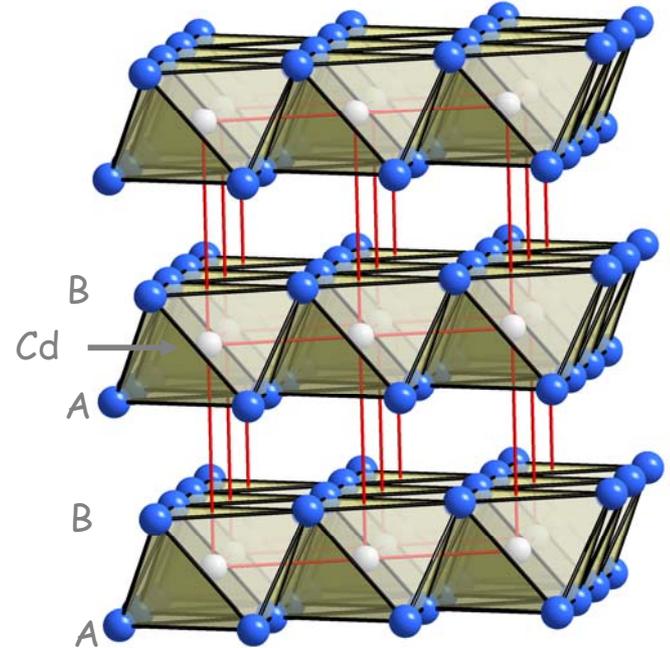
Structural features:
- **Layered structure, sequence (I-layers): AB**
- **Cd is coordinated octahedrally by 6 I (via six common edges)**
- **(how is I coordinated by Cd?)**
- **Polytypes**

2.3 Basic structure types: NiAs-type

Crystal data

Formula sum	NiAs
Crystal system	hexagonal
Space group	$P6_3/mmc$ (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
Ni	+3	2a	0	0	0
(dto., gen. by -1			0	0	1/2)
As	- 3	2c	1/3	2/3	1/4
(dto., gen. by -1			2/3	1/3	3/4)

(a)

Ni
As

(b)

1/2
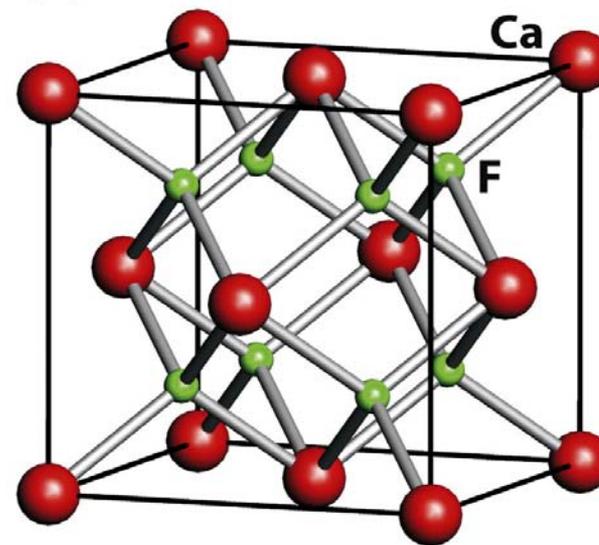
$\left(\frac{1}{4},\frac{3}{4}\right)$ (0,1)

(c)

Figure 3-35
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Structural features:
- **All OH of HCP filled**
- **Ni is coordinated by 6 As (octahedron)**
- **Metal-metal-bonding (common faces of the octahedra)**
- **(how is As coordinated by Ni?)**
- **Type ≠ antitype**

36

3. Chemical bonding in solids

Bonding models and theories of solids must account for basic properties as:

- Type, stability and distribution of crystal structures

- Mechanism and temperature dependence of the electrical conductivity of insulators, semiconductors, metals and alloys

- Lustre of metals, thermal conductivity and color of solids, ductility and malleability of metals ...

Useful models and theories are e.g.:
- Radius ratio and Pauling rules (ionic solids)
- Concept of lattice enthalpy (ionic solids)
- Band model (various types of solids)
- Kitaigorodskii's packing theory (molecular solids)

3.1 Bond valence, Radius ratio and Pauling rules

- Ionic structures consist of charged, elastic and polarizable speres.

- They are arranged so that cations are surrounded by anions and vice versa, and are held together by electrostatic forces.

- To maximize the electrostatic attraction (the lattice energy), coordination numbers are as high as possible, provided that neighbouring ions of opposite charge are in contact.

- Next nearest anion-anion and cation-cation interactions are repulsive, leading to structures of high symmetry with maximized volumes → attraction vs repulsion!

- The valence of an ion is equal to the sum of the electrostatic bond strengths between it and adjacent ions of opposite charge.

3.2 Lattice enthalpy of ionic solids

The <u>lattice enthalpy</u> is the standard molar enthalpy change for the following process:

$$M^+_{(gas)} + X^-_{(gas)} \rightarrow MX_{(solid)} \quad \Delta H_L: \textbf{ lattice enthalpy}$$

Because the formation of a solid from a „gas of ions" is always <u>exothermic</u> lattice enthalpies (defined in this way !!) are usually negative numbers.

If entropy considerations are neglected the <u>most stable crystal structure</u> of a given compound is the one with the <u>highest lattice enthalpy.</u>

ΔH_L can be derived from a simple electrostatic model or the Born-Haber cycle

3.2 Lattice enthalpy determined by the <u>Born-Haber cycle</u>

After Hess (and the 1. set of thermodynamics) reaction enthalpy is independent of the reaction path. For the formation of an ionic solid MX this means:
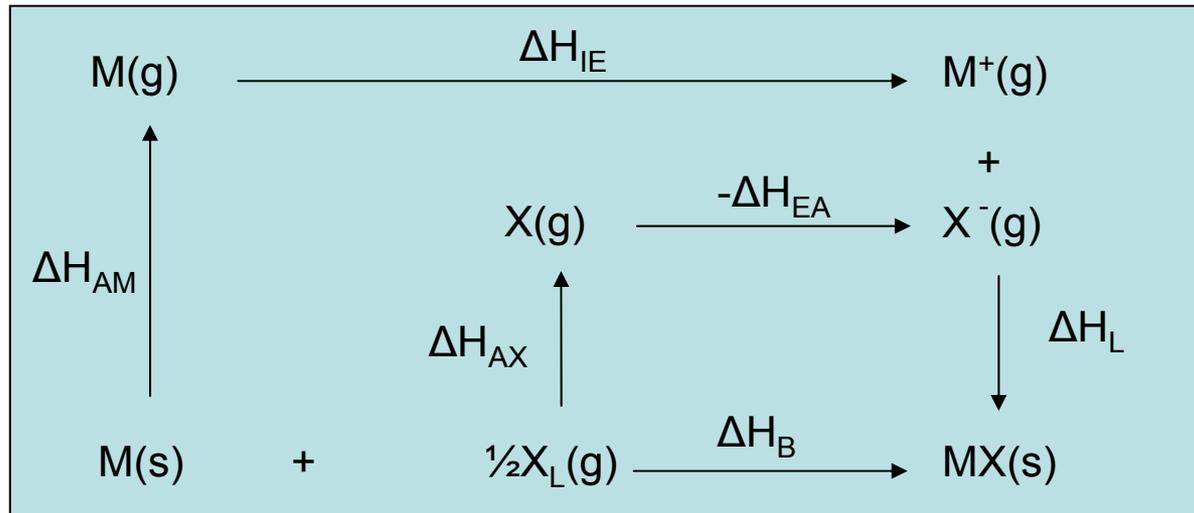
with: $\Delta H_B = \Delta H_{AM} + \Delta H_{AX} + \Delta H_{IE} - \Delta H_{EA} + \Delta H_L$

ΔH_{AM} and ΔH_{AX}: enthalpy of atomisation to gas of M and X ($\sim$ enthalpy of sublimation for M and ½ of the enthalpy of dissoziation for X_2)
ΔH_{IE} and ΔH_{EA}: enthalpy of ionisation of M and electron affinity of X ($-\Delta H_{EA} = \Delta H_{IA}$)
ΔH_B and ΔHL: enthalpy of formation and lattice enthalpy

3.2 Lattice enthalpy determined by the <u>Born-Haber cycle</u>

K$^+$(g) + e$^-$(g) + Cl(g)

dissozation
122
K$^+$(g) + e$^-$(g)
+$\frac{1}{2}$Cl$_2$(g)

electron affinity
−355

ionisation
425

K$^+$(g) + Cl$^-$(g)

K(g) + $\frac{1}{2}$Cl$_2$(g)

subli-mation **89**

lattice enthalpy
x

K(s) + $\frac{1}{2}$Cl$_2$(g)

438

inverse enthalpy of formation

KCl(s)
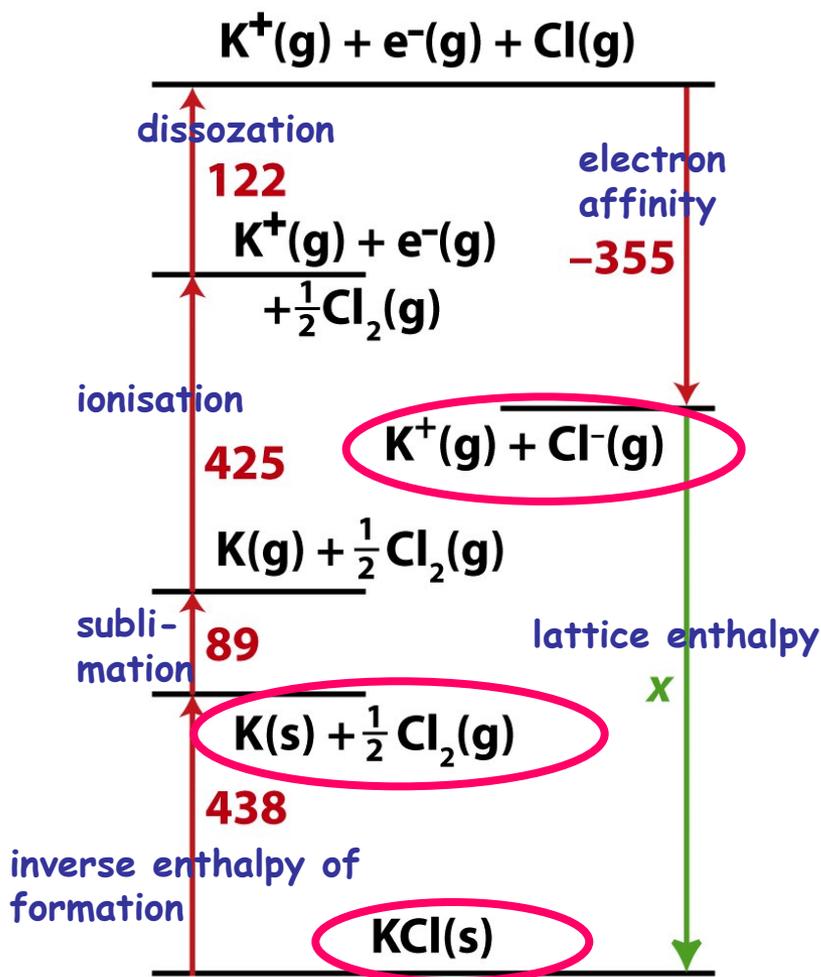
A **Born-Haber diagram** for KCl

(all enthalpies: kJ mol^{-1} for <u>normal conditions</u> → standard enthalpies)

Standard enthalpies of
- sublimation, ΔH_{Ax}: +89 (K)
- ionization, ΔH_{IE}: +425 (K)
- dissoziation, ΔH_{AM}: +244 (Cl$_2$)
- electron affinity, $-\Delta H_{EA}$: -355 (Cl)
- lattice enthalpy, ΔH_L: -x = -719
- enthalpy of formation, ΔH_B: -438 (for KCl)

The harder the ions, the higher ΔH_B

3.3 Calculation of lattice enthalpies

$$\Delta H_L^0 = V_{AB} + V_{Born}$$

V_{AB} = Coulomb (electrostatic) interaction between <u>all</u> cations and anions treated as <u>point charges</u> (Madelung part of lattice enthalpy („MAPLE")

V_{Born} = Repulsion due to the overlap of electron clouds (Born repulsion)

3.3 Calculation of lattice enthalpies (MAPLE)

Coulombic contributions to lattice enthalpies, MADELUNG Part of Lattice Enthalpy, atoms treated as <u>point charges</u>)

$$V_{AB} = -A \; N_A \; \left(\frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_{AB}} \right)$$

Coulomb potential of an ion pair

V_{AB}: Coulomb potential (electrostatic potential)
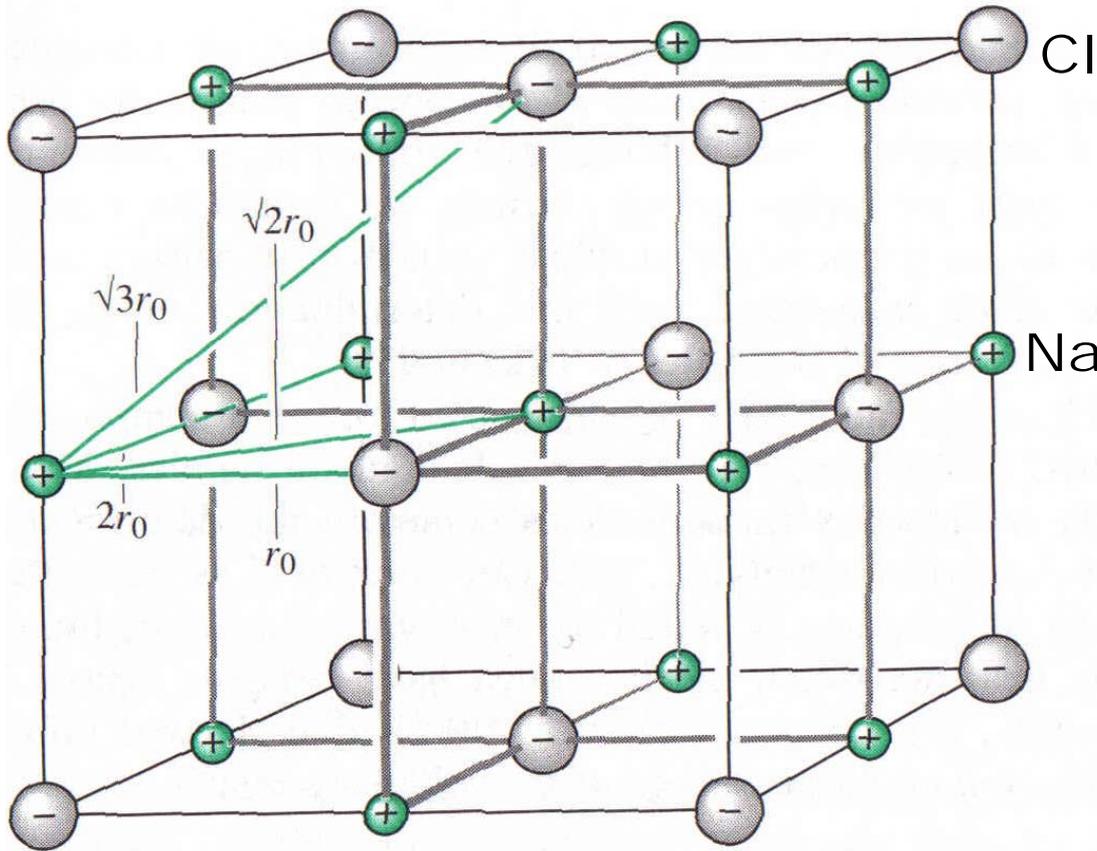A: <u>Madelung constant</u> (depends on structure type)
N_A: Avogadro constant
z: charge number
e: elementary charge
ε_0:   dielectric constant (vacuum permittivity)
r_{AB}: shortest distance between cation and anion

3.3 Calculation of the Madelung constant

typical for 3D ionic solids:
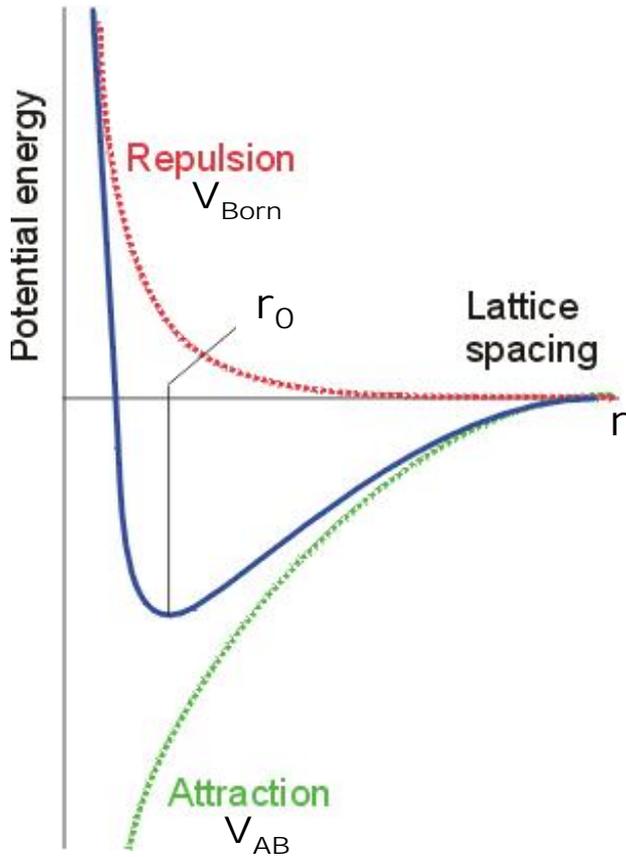Coulomb attraction _and_ repulsion

Madelung constants:

CsCl: 1.763
NaCl: 1.748
ZnS: 1.641 (wurtzite)
ZnS: 1.638 (sphalerite)
ion pair: 1.0000 (!)

$$A = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} \ldots$$

= 1.748... (NaCl)
(infinite summation)

3.3 Born repulsion (V_{Born})

(Repulsion arising from <u>overlap of electron clouds</u> since atoms do not behave as point charges)

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

approximation:

$$V_{Born} = \frac{B}{r_{AB}^{n}} N_A$$

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

45

3.3 Total lattice enthalpy
(Coulomb interaction <u>and</u> Born repulsion)
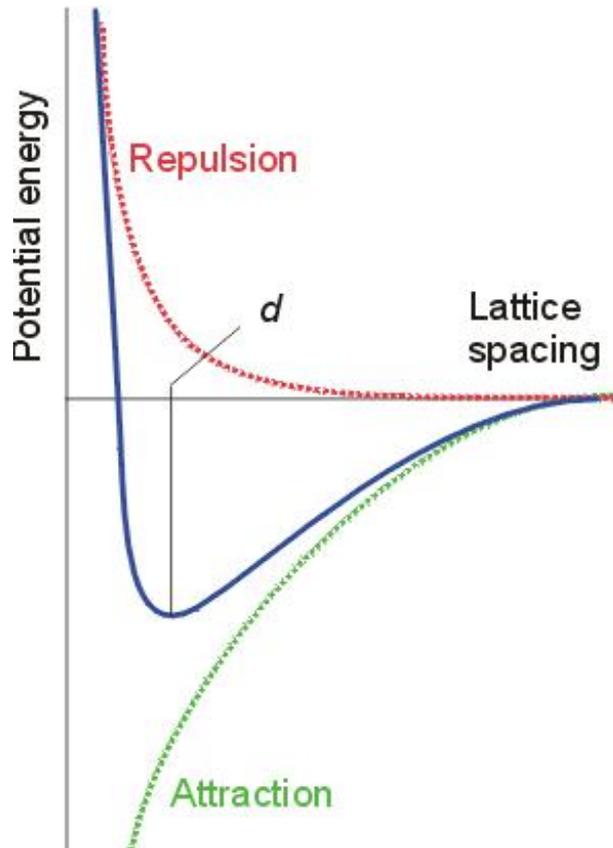
$$\Delta H_L^0 = V_{AB} + V_{Born}$$

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

$$V_{Born} = \frac{B}{r_{AB}^{\,n}}\,N_A$$

3.3 Total lattice enthalpy
(Coulomb interaction <u>and</u> Born repulsion)

$$\Delta H_L^0 = V_{AB} + V_{Born}$$

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

$$V_{Born} = \frac{B}{r_{AB}^{\,n}}\,N_A$$

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

(set first derivative of the sum to zero)

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

3.3 Total lattice enthalpy
(Coulomb interaction <u>and</u> Born repulsion)

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

$$\Delta \mathrm{H}_L^0 = -A \frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_0} N_A (1 - \frac{1}{n})$$

Lattice enthalpies (kJ mol^{-1}) by Born-Haber cyle and (calculated)
NaCl: –772 (-757); CsCl: -652 (-623) …

Applications of lattice enthalpy calculations:
$\rightarrow$ lattice enthalpies and stabilities of „non existent"
   compounds and calculations of electron affinity
   data (see next transparencies)
$\rightarrow$ Solubility of salts in water (see Shriver-Atkins)

3.3 Lattice enthalpy (Calculation for NaCl)

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

$\varepsilon_0 = 8.854 \times 10^{-12}$ C^2/Jm; $e = 1.602 \times 10^{-19}$ C; $N_A = 6.023 \times 10^{23}$ mol^{-1}

$A = 1.748$; $r_0 = 2.8 \times 10^{-10}$ m; $n = 8$ (Born exponent)

$1/4\pi\varepsilon_0 = 8.99 \times 10^9$ Jm/C^2 $e^2 N_A = 1.542 \times 10^{-14}$ C^2/mol

ΔH_L = -1.386 $\times$ 10^{-5} $\times$ A/r_0 $\times$ (1-1/n) Jmol^{-1} (for univalent ions !)

Dimensions: $(C^2 \, Jm)/(C^2 \, m \, mol) = J/mol$

NaCl: $\Delta H_L'$ = - 865 kJ mol^{-1} (only MAPLE)
          $\Delta H_L''$ = - 757 kJ mol^{-1} (including Born repulsion)
          ΔHL = - 772 kJ mol-1 (measured)

Please note that covalent contributions are not included in the calculations, e.g.
NaCl: –772 (-757); CsCl: -652 (-623) for the measured (calculated) values.

3.3 Lattice enthalpy
Comparison of theoretical and experimental (Born-Haber cycle) lattice enthalpies for some rocksalt structures

	$\Delta H_L^{calc} /$ $(kJ\ mol^{-1})$	$\Delta H_L^{exp} /$ $(kJ\ mol^{-1})$	$(\Delta H_L^{exp} - \Delta H_L^{calc}) /$ $(kJ\ mol^{-1})$
LiF	1029	1030	6
LiCl	834	853	19
LiBr	788	807	19
LiI	730	757	27
AgF	920	953	33
AgCl	832	903	71
AgBr	815	895	80
AgI	777	882	105

Table 3-9
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The harder the ions the higher ΔH_L and the lower the differences
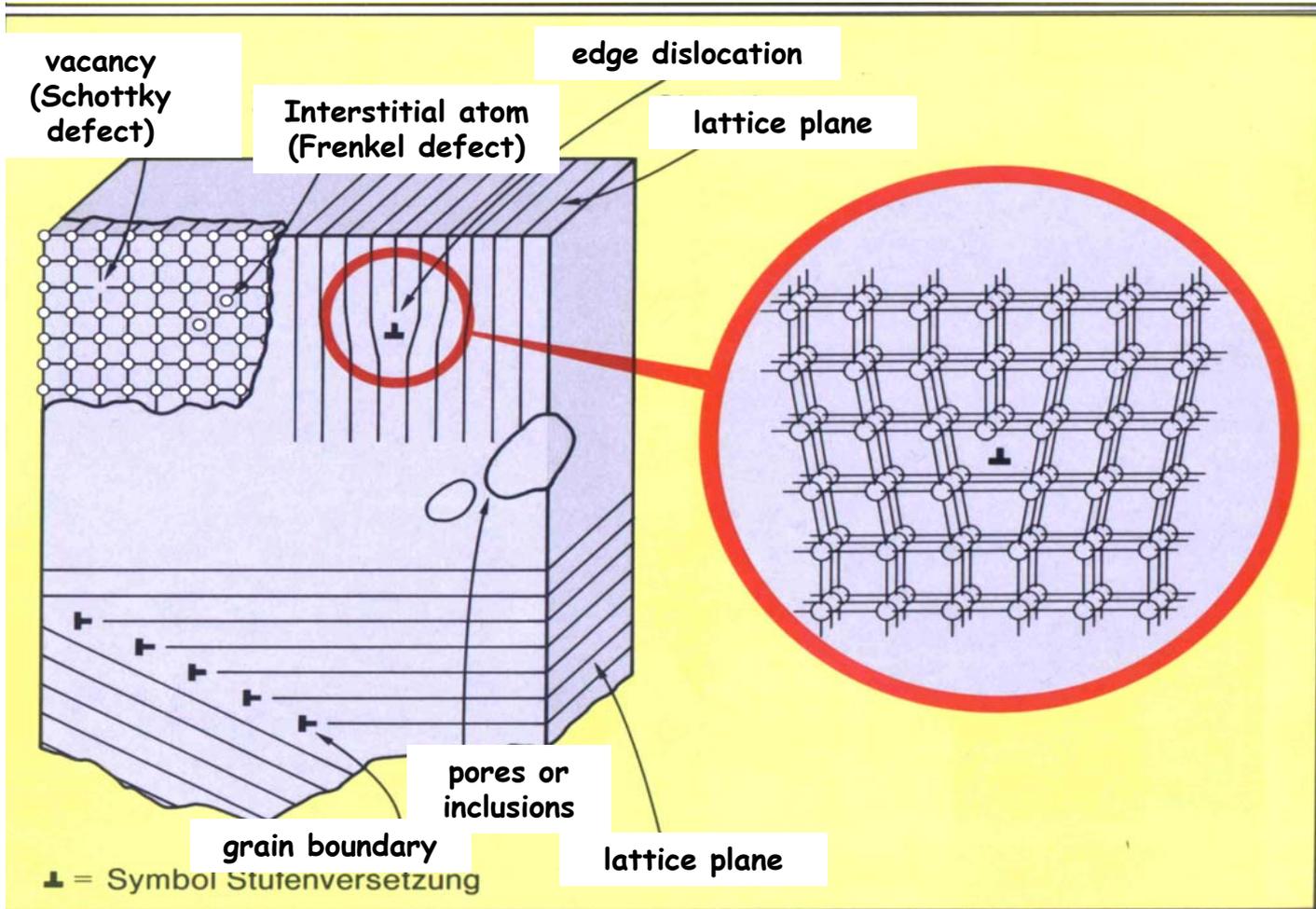
4. Chemical preparation of solids

Possible reaction paths between two solid grains A and B are

Gas phase diffusion   **Interface diffusion**

Volume diffusion   **Surface diffusion**
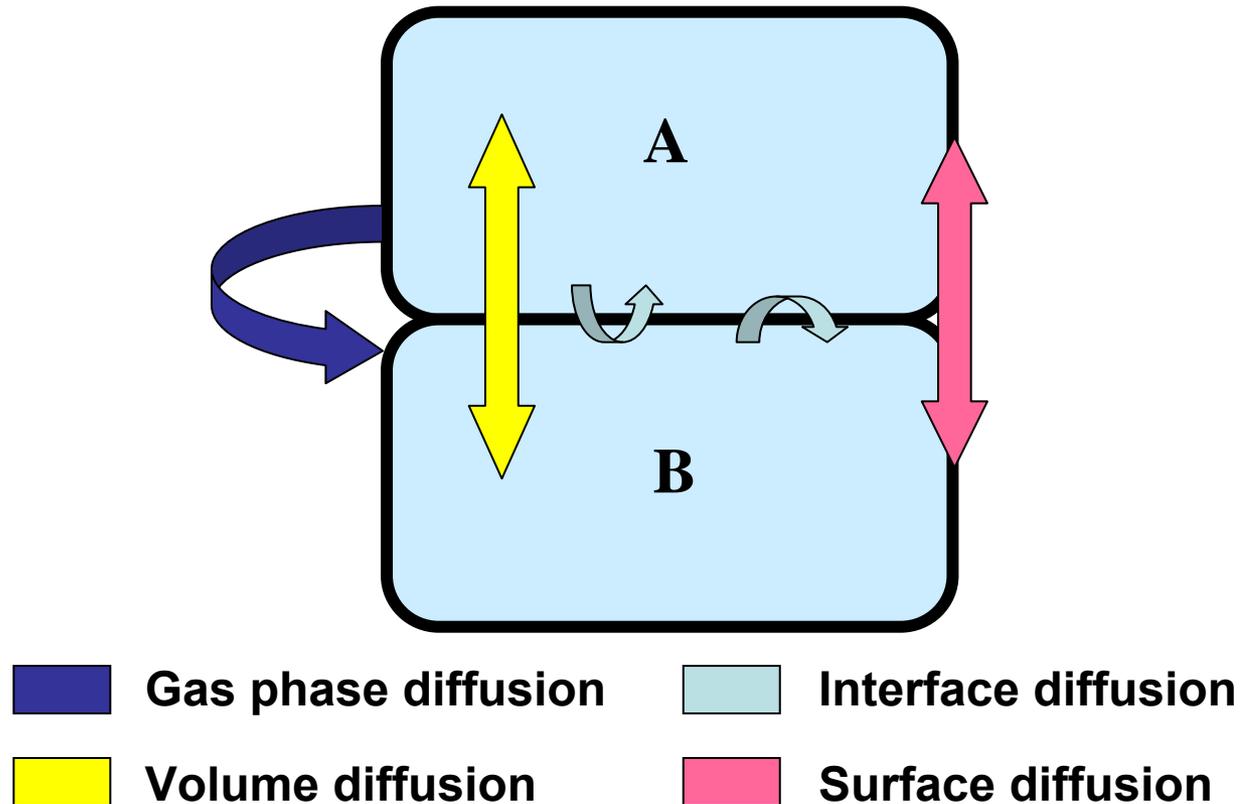
For solid state reactions, the real structure, i.e. defects (imperfections) of (crystalline) solids are important.

4. Chemical preparation of solids
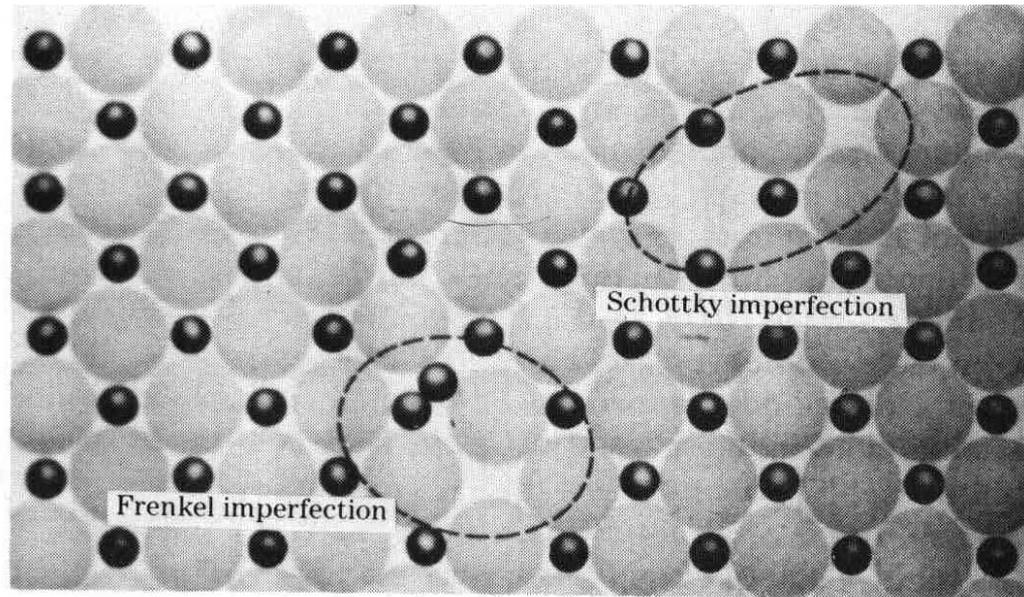## Real structure (defects, imperfections) of crystals

vacancy (Schottky defect)

Interstitial atom (Frenkel defect)

edge dislocation

lattice plane

pores or inclusions

grain boundary

lattice plane

⊥ = Symbol Stufenversetzung

4. Chemical preparation of solids
Point defects (imperfections) in solids

Schottky imperfection

Frenkel imperfection

<u>Schottky defects:</u> vacancies, missing ions move to the surface (can be cations or anions)

<u>Frenkel defects:</u> vacancies, missing ions on interstitial positions (cations only)

Defects are formed spontaneously (10^5 to 10^{20} per cm^{-1} at 400 K) and are of paramount importance for the diffusion of ions and atoms in solids.

4. Chemical preparation of solids

Because of the small diffusion coefficients of ions or atoms in a solid at room temperature (10^{-13} to 10^{-6} cm^2 s^{-1}), special preparation methods and high temperatures are necessary.

4. Conventional chemical preparation methods

Conventional preparation methods in solid state chemistry are:

1 Chemical transport reaction

2 Bridgman-Stockbarger process

3 Floating zone melting process

4 Czochralski process

5 Verneuil process

6 Hydro(solvo)thermal synthesis

7 Chemical Vapor Deposition (CVD)

4.1 Chemical transport reaction

Chemical Transport: A solid is dissolved in the gas phase at one place (with T=T1).
By reaction with a transporting agent (e.g. I_2) it is condensed again at another place (with T=T2).

Trace of a transporting agent (e.g. I_2)

T1

T2

T1

T2
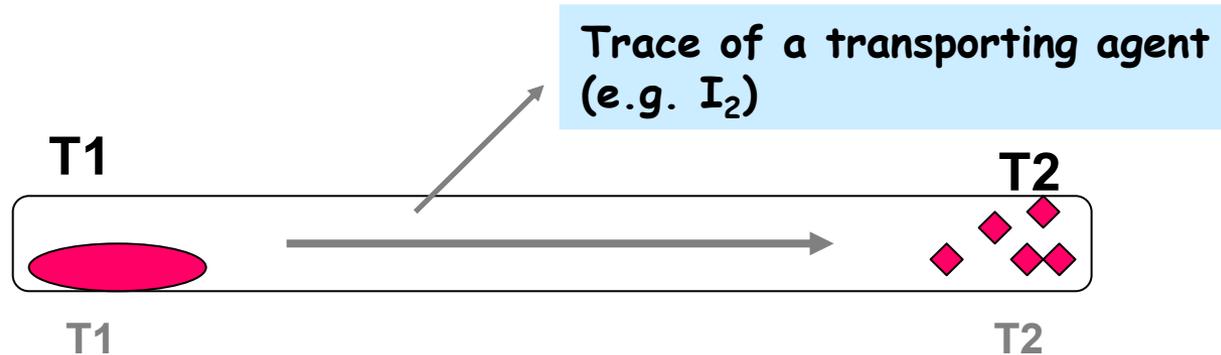
Whether T1 < T2 or T1 > T2 depends on the thermochemical balance of the reaction (remember: Le Chatelier principle?) ! Transport can proceed from higher to lower or from lower to higher temperature.

4.1 Chemical transport reaction

Transport direction

$$hot \rightarrow cold \qquad or \qquad cold \rightarrow hot$$

depends on the enthalpy of the transport reaction

$$A_{(solid)} + B_{(gas)} \leftrightarrow AB_{(gas)} + \Delta H$$
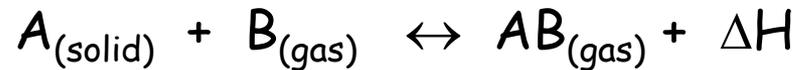
$\Delta H > 0$ (endothermic): hot $\rightarrow$ cold $\qquad$ $\Delta H < 0$ (exothermic): cold $\rightarrow$ hot

Some examples for transport reactions:

$$T1/T2 \,/^oC$$

$$W + 3Cl_2 \leftrightarrow WCl_6 \qquad 400/1400 \quad (exo)$$
$$Ni + 4CO \leftrightarrow Ni(CO)_4 \qquad 50/190 \quad (exo)$$

$$2Al + AlCl_3 \leftrightarrow 3\ AlCl \qquad 1000/600 \quad (endo)$$
$$4Al + Al_2S_3 \leftrightarrow 3Al_2S \qquad 1000/900 \quad (endo)$$
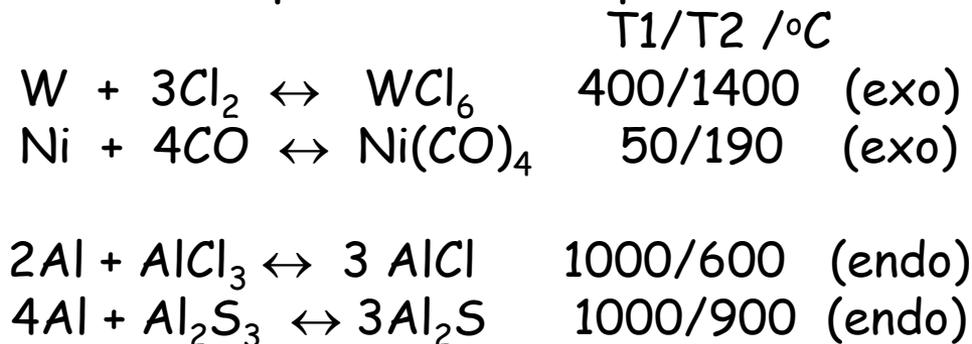
Main application: Purification and crystallisation of solids
small crystals (~ mm size)

4.2 Growth of single crystals:
Bridgman-Stockbarger process (moving temperature gradient)
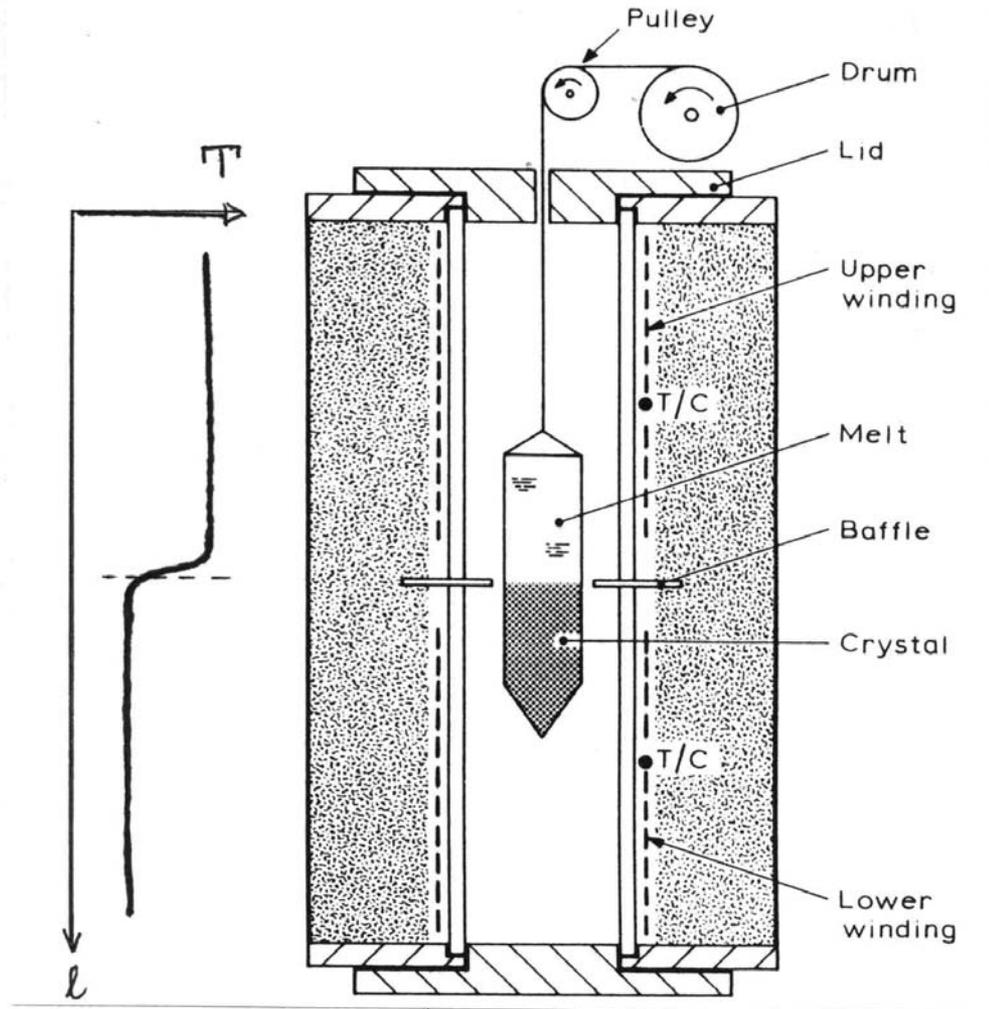
4.3 Zone melting (floating zone refinement)

- A small slice of a rod shaped sample is molten, moved continuously along the rod and shifted to its end

- Impurities normally dissolve preferably in the melt provided (segregation coefficient)
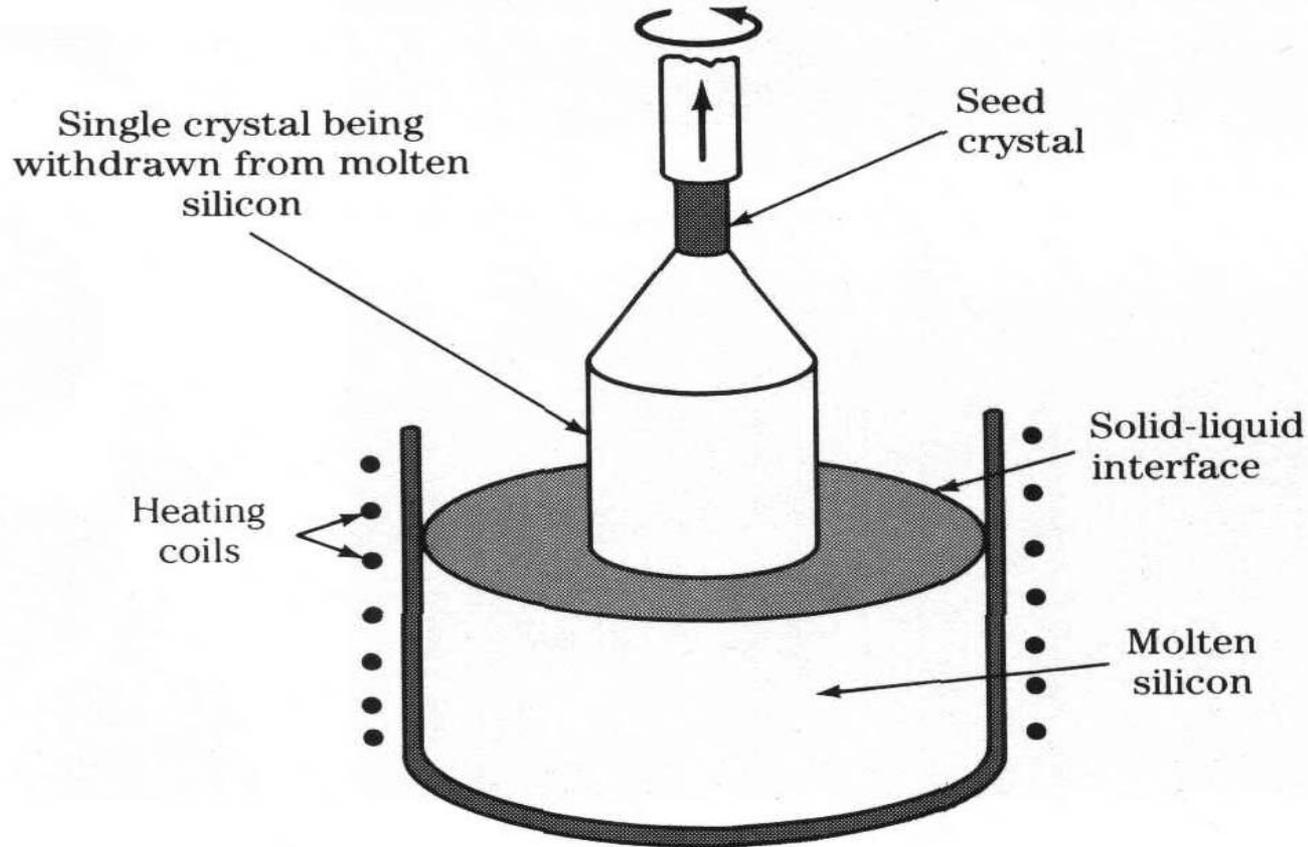
$$k = c_{solid}/c_{liquid}$$

c: concentration of an impurity

<u>Only impurities with k < 1 can be removed by zone melting !!</u>

Bild 6.13. Prinzip der Einkristallherstellung nach dem tiegelfreien Zonen-schmelzen (floating zone technique)

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

4.4 Czochralski process: Si (!)

Single crystal being withdrawn from molten silicon

Seed crystal

Heating coils

Solid-liquid interface

Molten silicon
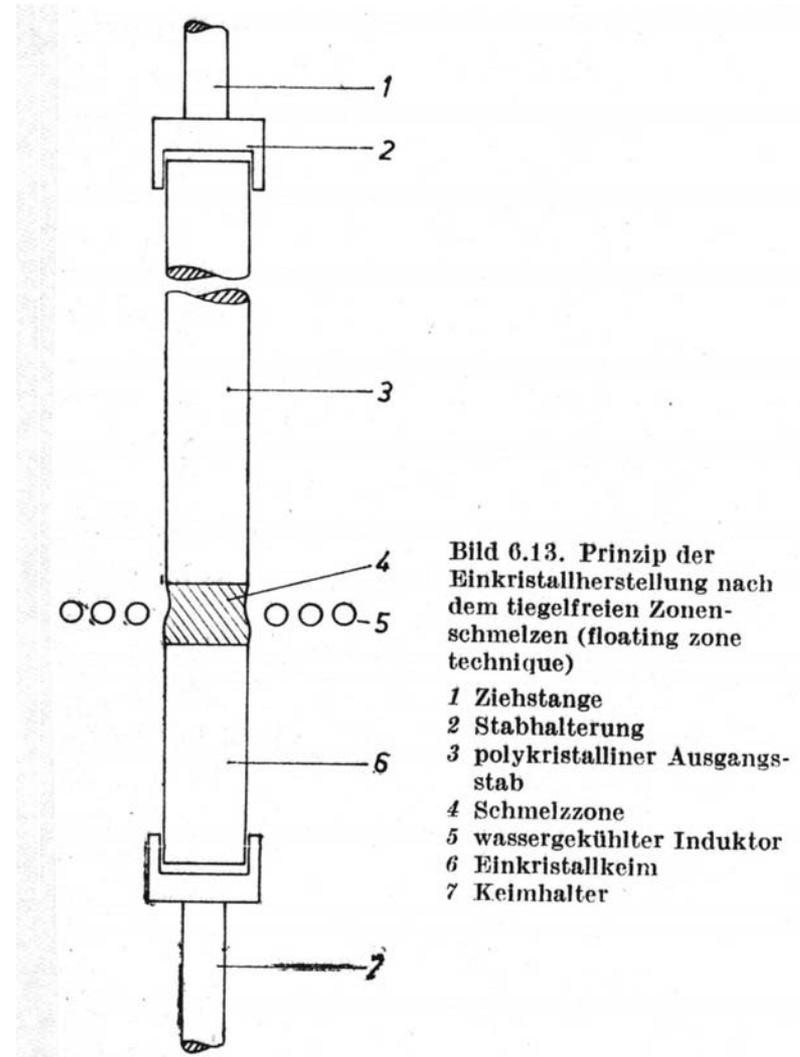
A rotating seed crystal (e.g. Si) is raised slowly from a melt of equal composition (which is rotated in the opposite direction)

4.4 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.)

4.5 Groth of single crystals: Verneuil process

- Preferably for high melting oxides (T > 2000 K)

- Powdered sample is blown into an oxyhydrogen gas burner

Synthetic corundum crystals obtained by the Verneuile process
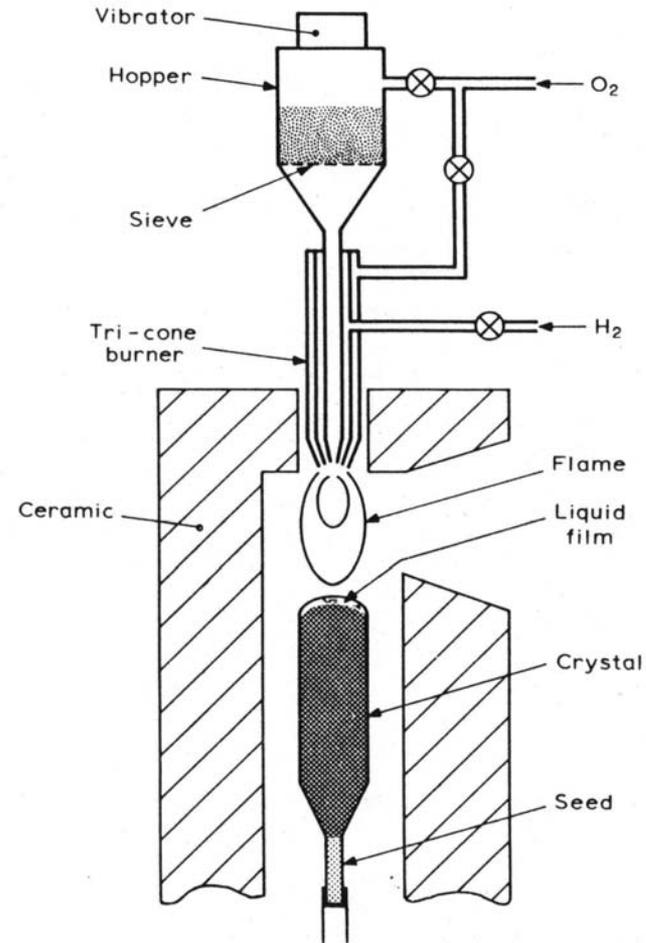
Figure 5.1 A system for the Verneuil growth of oxidic materials. Note that the burner is composed of three coaxial tubes. Some workers use more tubes, and there are also designs using many small parallel tubes. With these it is possible to produce wider flames, and by having independent controls on various sets of tubes it is possible to optimize the heat input to give a nearly flat growth face on a large crystal.

4.6 Hydrothermal synthesis

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

Autoclave for the growth of <u>SiO_2 single crystals ($\rightarrow$ quartz)</u>

1500 bar, T- gradient 400 $\rightarrow$380 ^{o}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
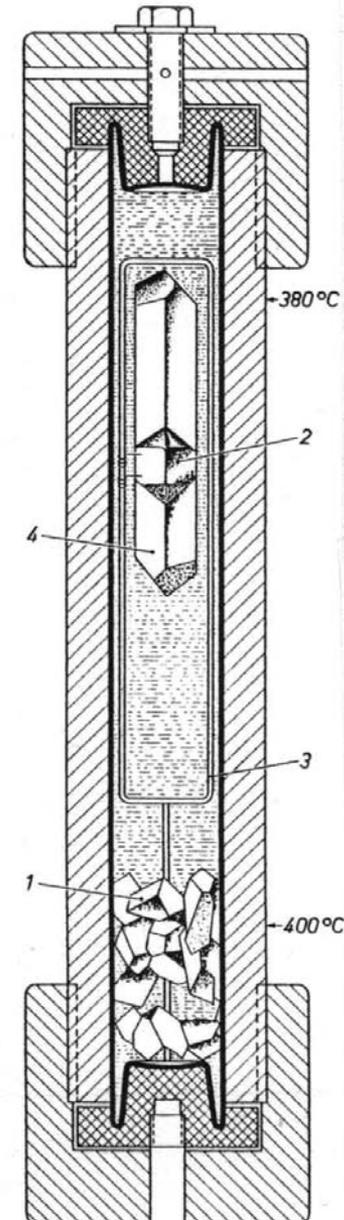
4.7 Preparation of nanomaterials
2D nanomaterials – synthesis (CVD)

CVD (Chemical Vapor Deposition): General term for a variety of methods to deposit a range of solid materials on a target by decomposition of suitable gas phase precursor compounds. $\rightarrow$ semiconducing, ceramic, electrooptic etc materials.
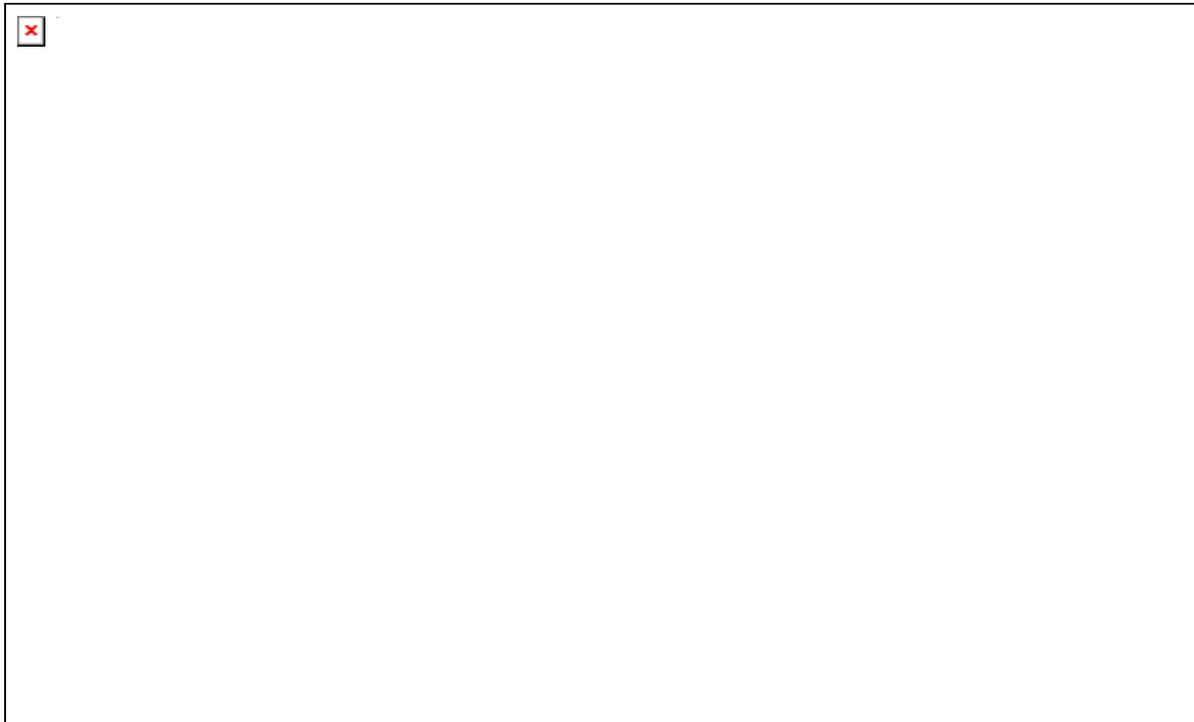
5.1 More complex structures: Rutile (TiO$_2$)

Crystal data

Formula sum	TiO$_2$
Crystal system	tetragonal
Space group	$P4_2/mnm$ (no. 136)
Unit cell dimensions	$a = 4.5937$ Å, $c = 2.9587$ Å
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)	
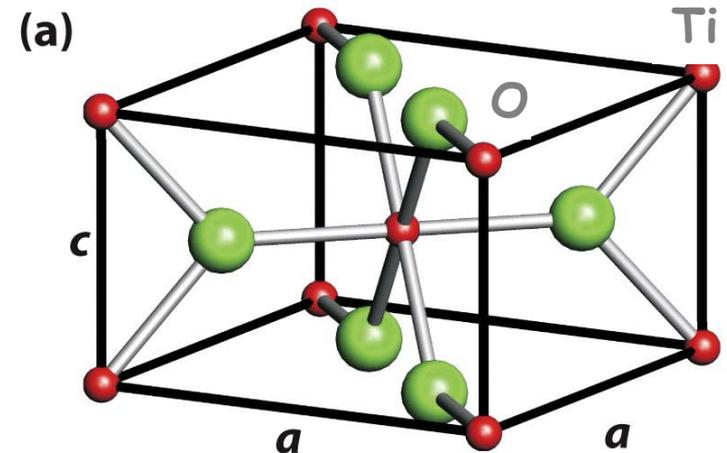
Structural features:
- hcp arrangement of O, 1/2 of OH filled with Ti
- mixed corner and edge sharing of TiO$_6$-octahedra
- columns of trans edge sharing TiO$_6$-octahedra, connected by common corners
- important application: white pigment

65

5.2 More complex structures: 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
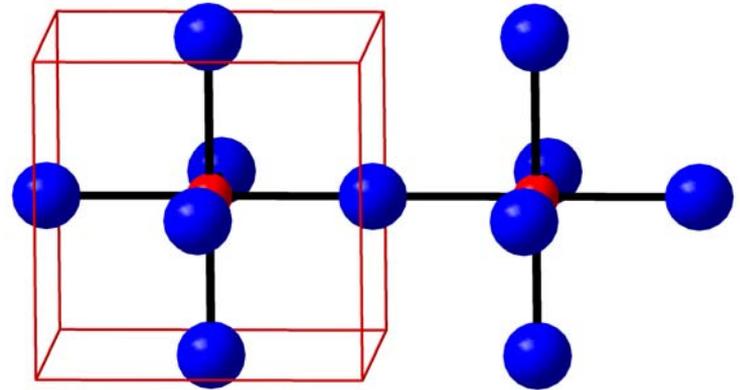
Structural features:
- **not a close packing (ccp of O and vacancies)**
- **ReO$_6$ octahedra connected by six common corners**
- **large cavities at 0,0,0 …**
- **fractional filling in 0,0,0 (A$_{1-x}$WO$_3$ tungsten bronze)**

5.3 More complex structures: 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
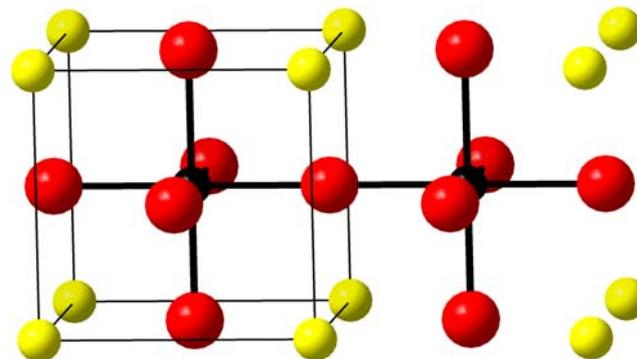
Atomic coordinates

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
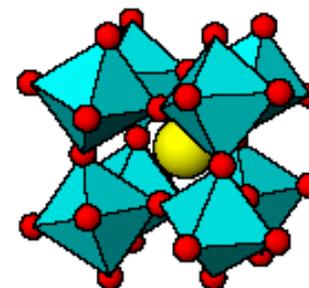
Structural features:
- **filled ReO$_3$ phase, CN (Sr) = 12 (cuboctahedron), CN (Ti) = 6 (octahedron)**
- **many distorted (non-cubic) variants**
- **many defect variants (HT-superconductors, YBa$_2$Cu$_3$O$_{7-x}$)**
- **hexagonal variants and polytyps**

5.4 More complex structures: Spinel ($MgAl_2O_4$, Fe_3O_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	8a	0	0	0
Al1	+3	16d	5/8	5/8	5/8
O1	-2	32e	0.38672	0.38672	0.3867
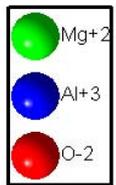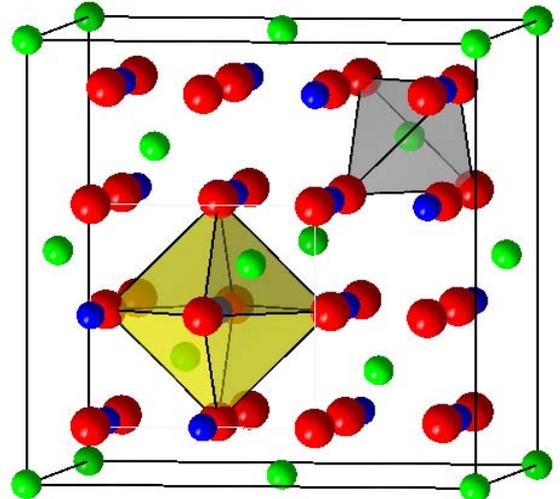
Structural features:
- distorted CCP of O
- Mg in tetrahedral holes (25%)
- Al in octahedral holes (50%)
- Inverse spinel structures $Mg_{TH}Al_{2OH}O_4 \rightarrow In_{TH}(Mg, In)_{OH}O_4$
- Application: ferrites (magnetic materials)

68

6.1 Special structures and materials: Silicates

Structural features:
- **fundamental building unit: SiO$_4$ tetrahedron**
- **isolated tetrahedra or connection via common corners**
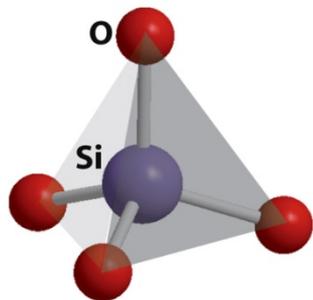
14 $[SiO_4]^{4-}$

Structure 13-14
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
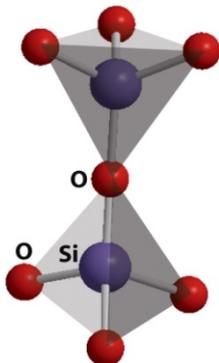
15 $[Si_2O_7]^{6-}$

Structure 13-15
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
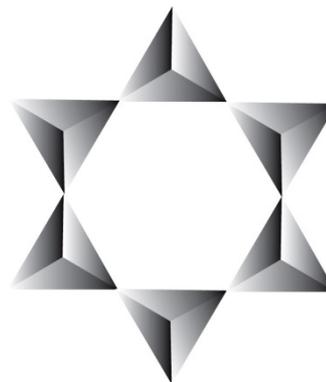
16 $[Si_6O_{18}]^{12-}$

Structure 13-16
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

Cyclosilicate

$[Si_6O_{12/1}O_{12/2}]$
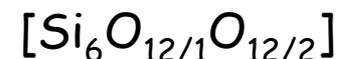
17 $[SiO_3]_n$

Structure 13-17
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

Chainsilicate

$SiO_{2/1}O_{2/2}$

6.1 Special structures and materials: Silicates

Figure 13-14
Shriver & Atkins Inorganic Chemistry, Fourth Edition
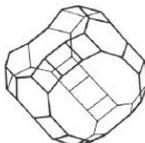© 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong
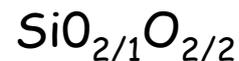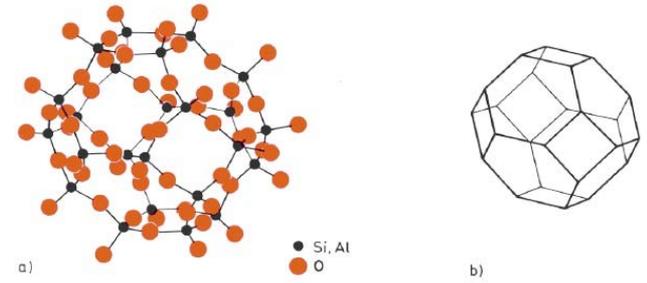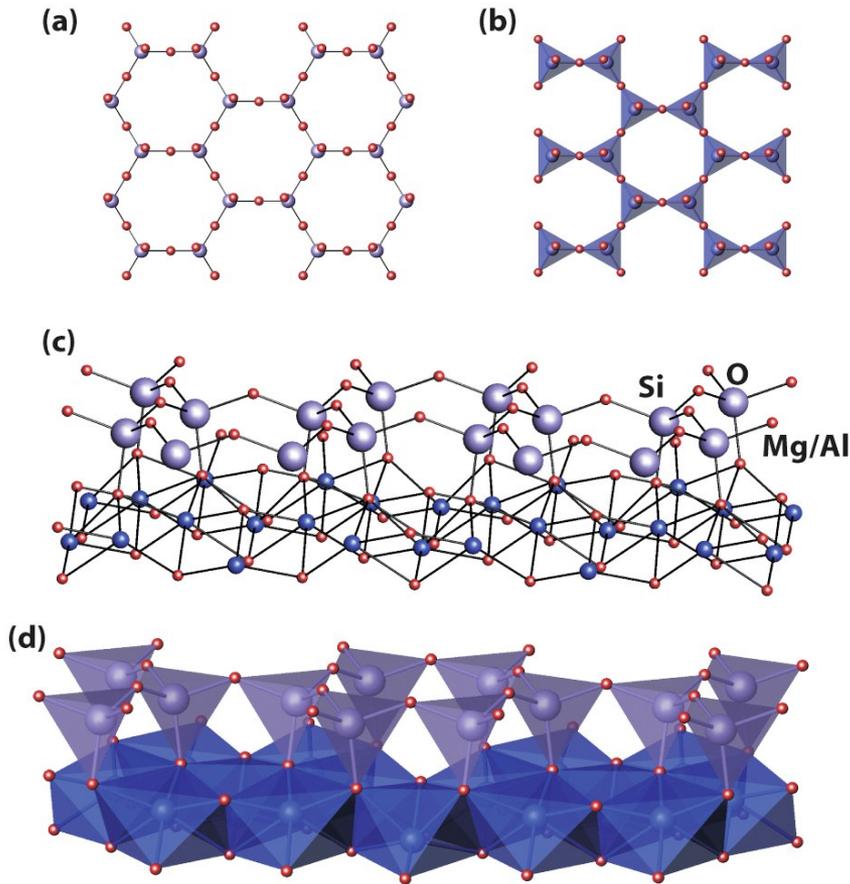
Struktur	Hohlräume	Durchmesser des Käfigs in pm	Durchmesser der Kanäle in pm
Sodalith	β-Käfig	660	220
Zeolith A	α-Käfig	1140	420
Faujasit	Super-Käfig	1270	720
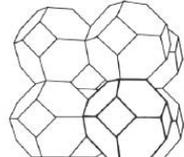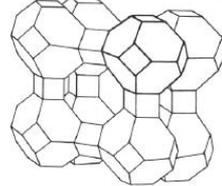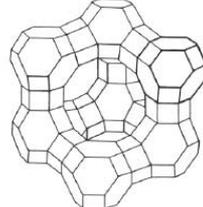
© 2007 Walter de Gruyter, Riedel/Janiak: Anorganische Chemie.

70

6.1 Special structures and materials: Silicates
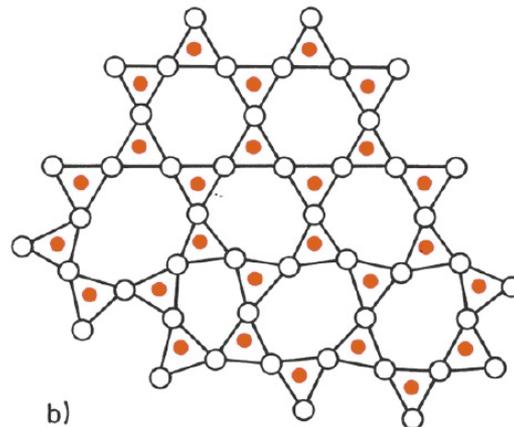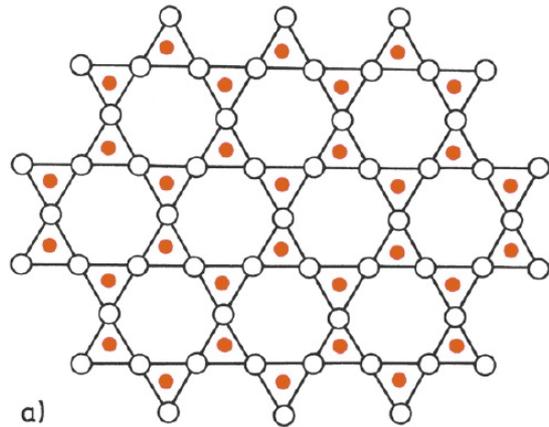
a) crystallline silicate

b) quartz glass (SiO_2)

c) silicate with network modifier
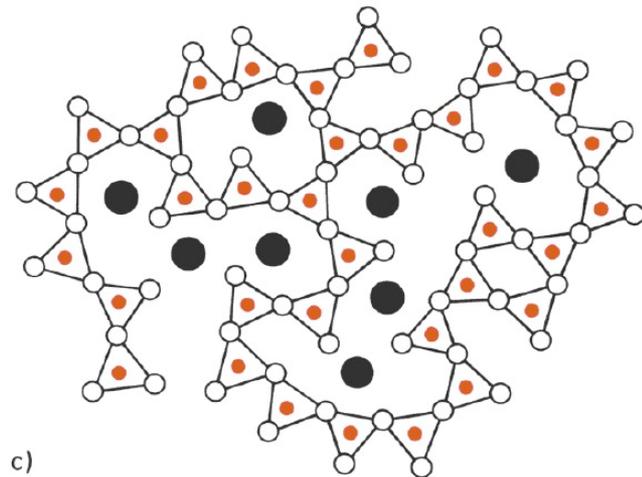
not shown:
glass ceramic: partially crystallized glass; crystalline parts < 50 nm;

extreme hardness and temperature resistance

O O
• Si
● Na, K, Ca

6.2 Special structures and materials: zeolithes
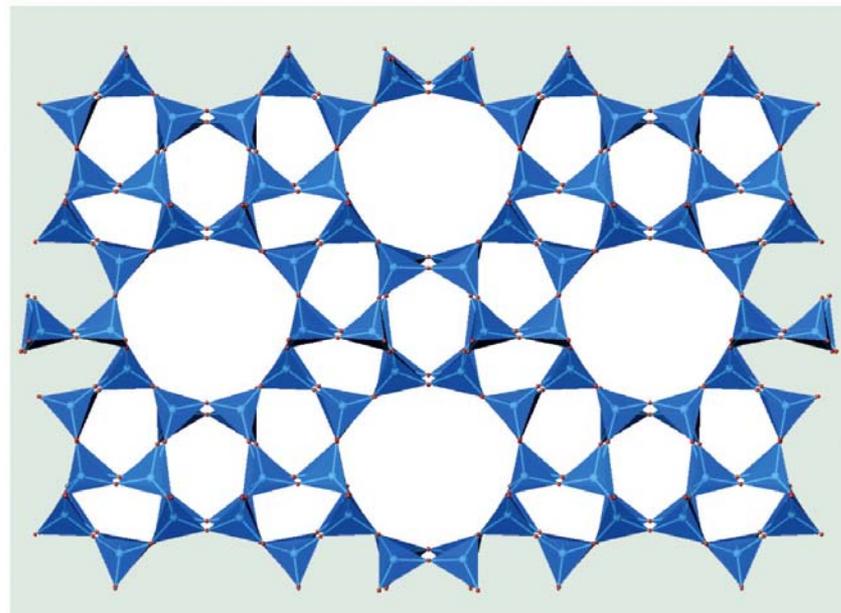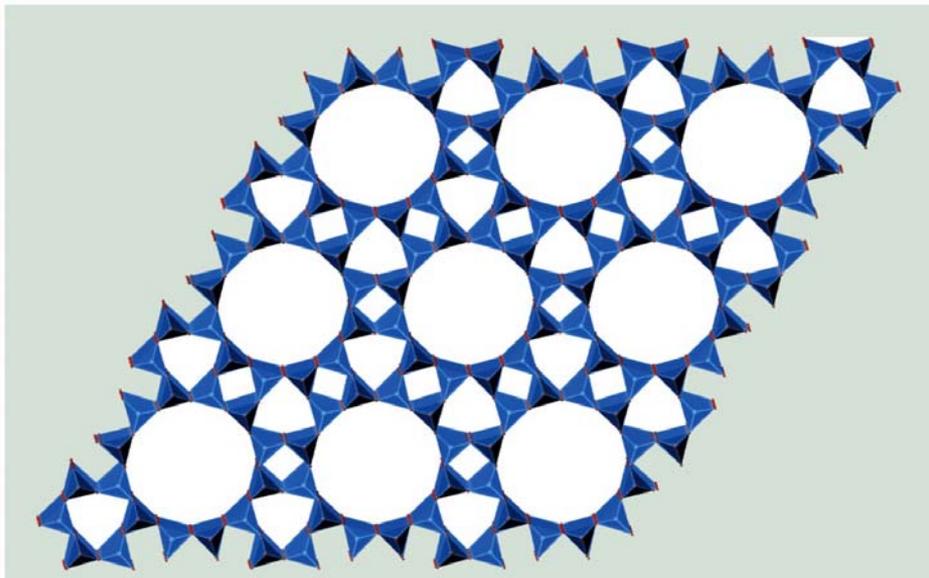
Table 13.6 Some uses of zeolites

Function	Application
Ion exchange	Water softeners in detergents
Absorption of molecules	Selective gas separation Gas chromatography
Solid acid	Cracking high molar mass hydrocarbons for fuel and petrochemical intermediates
	Shape-selective alkylation and isomerization of aromatics for petroleum and polymer intermediates

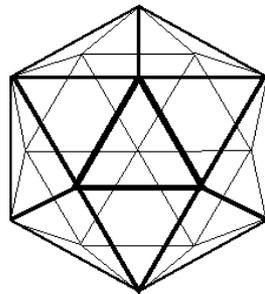# 6.3 Special structures and materials: Intermetallic compounds

Intermetallic compounds are alloys with structures different from either component (e.g. Laves phases, Zintl phases, Hume-Rothery phases (brass))

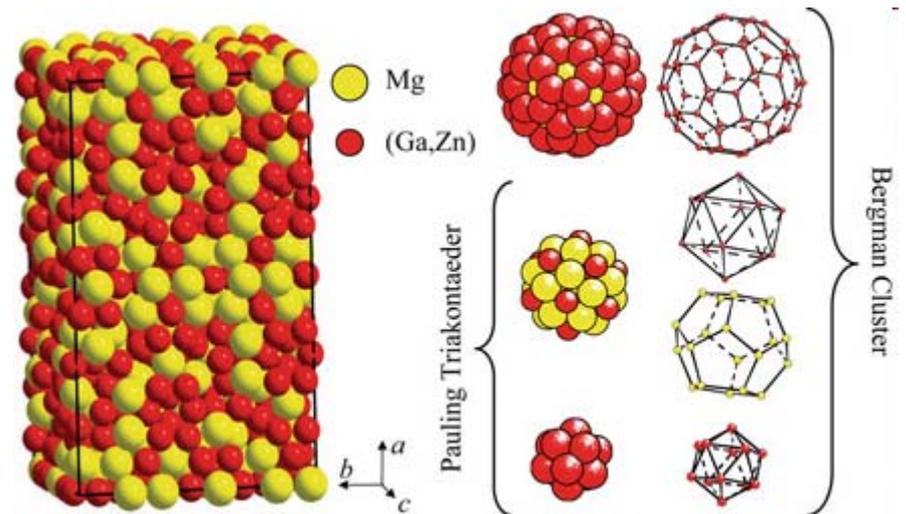In alloys coordination numbers of 12, 14, 16, 20 and higher are very common !
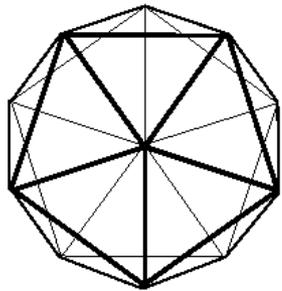
CN 12

CN 16

Icosahedron   Friauf polyhedron

Bergman cluster: 104 atoms; three shells with icosahedral symmetry

6.4 Special structures and materials: Zintl phases

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^-, $Ca^{2+}Si^{2-}$ …

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

6.4 Special structures and materials: Zintl phases
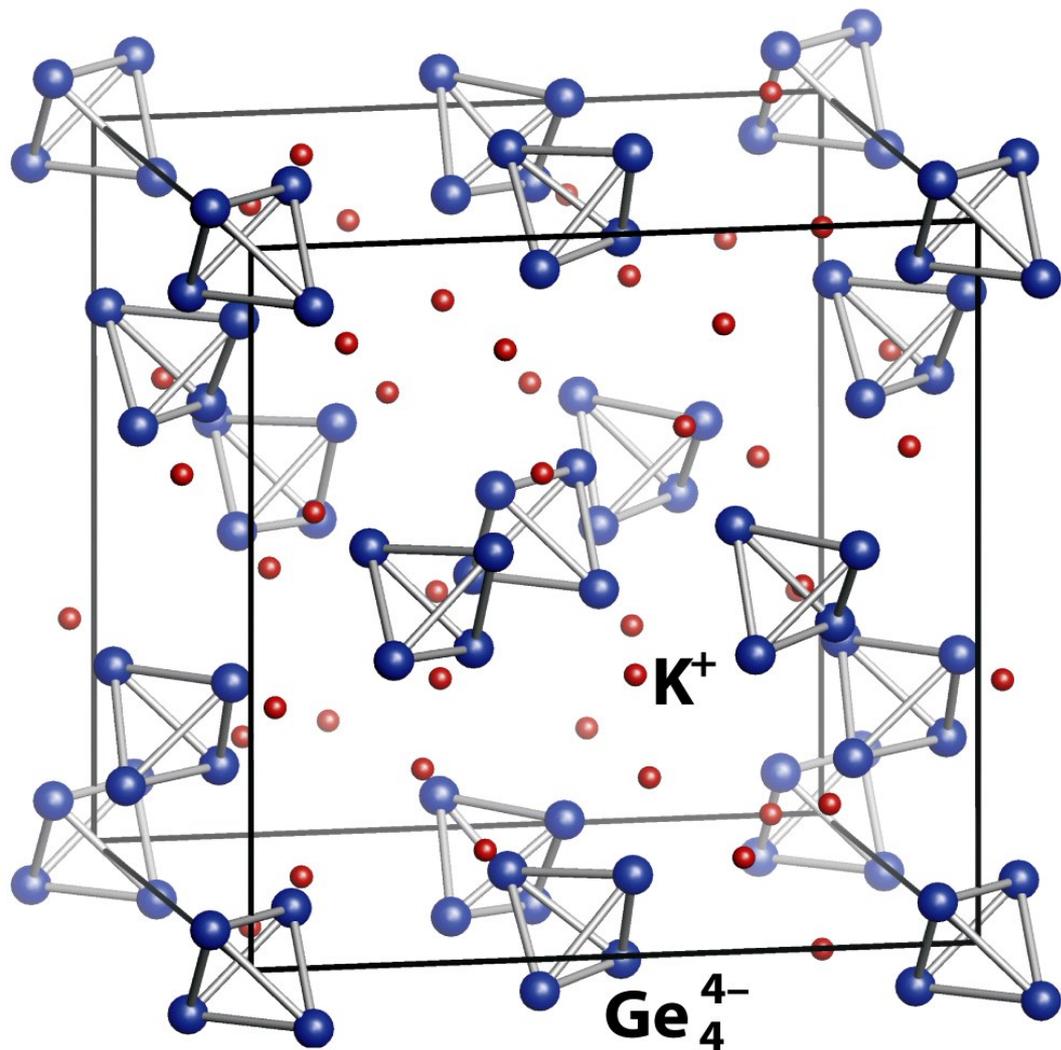
The crystal structure of the Zintl phase KGe

K^+

Ge_4^{4-}

7. Structure determination methods

For the structure determination methods see part
Inorganic Molecules