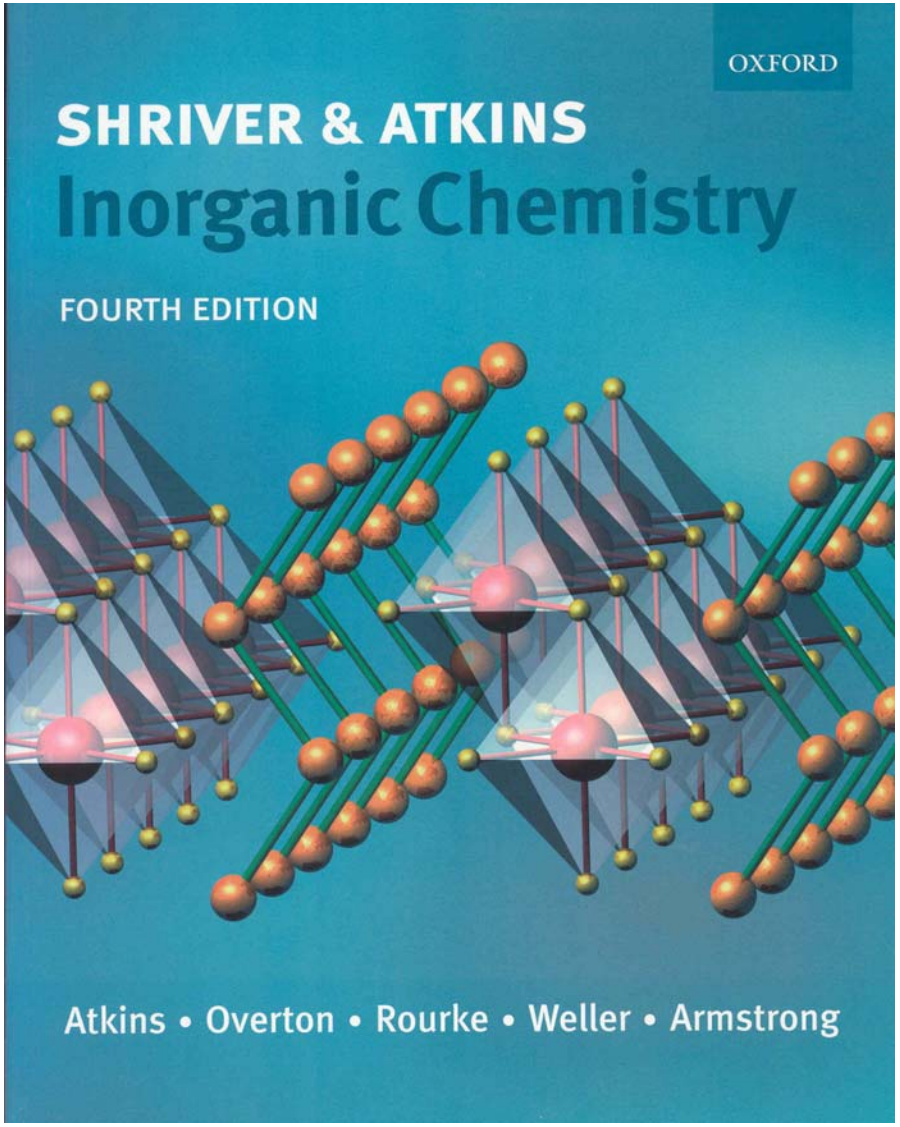
Lecture: Solid State Chemistry
WP I/II
H.J. Deiseroth, B. Engelen, SS 2011

Content

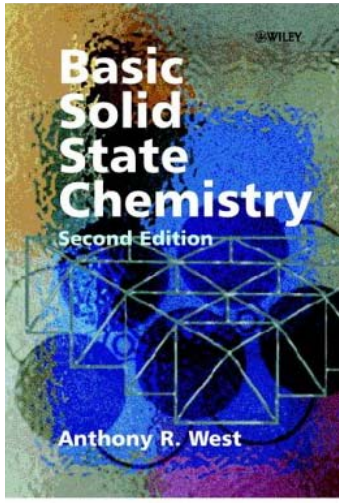
Resources

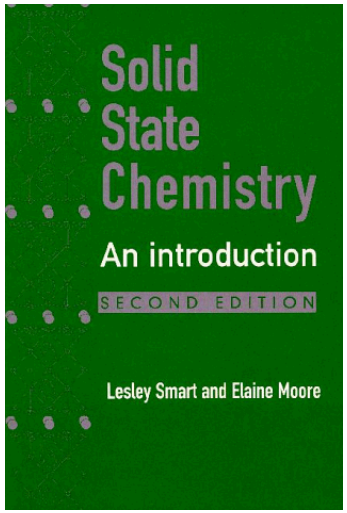

OXFORD
SHRIVER & ATKINS
Inorganic Chemistry
FOURTH EDITION
Atkins • Overton • Rourke • Weller • Armstrong

Resources

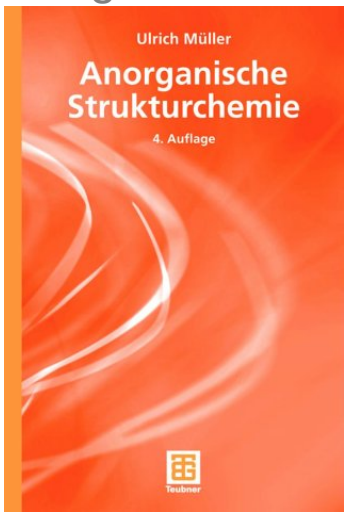
Textbooks: **Shriver, Atkins, *Inorganic Chemistry* (3rd ed, 1999)**
W.H. Freeman and Company (Chapter 2, 18 ...)

recommendation

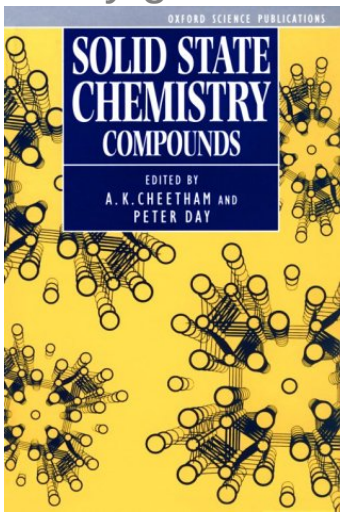


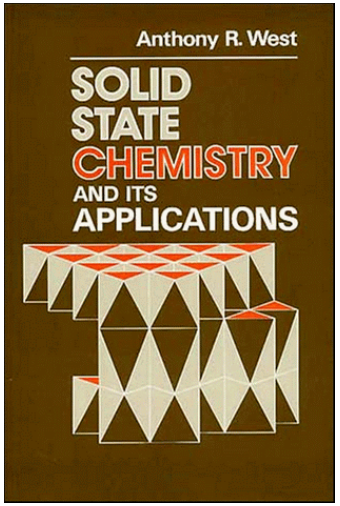


german



very good, but not basic level



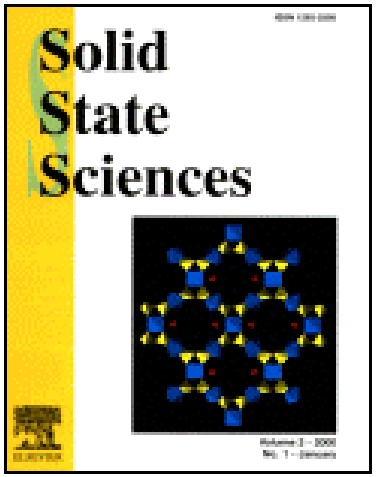


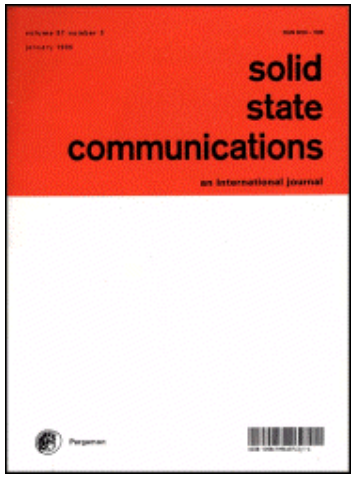
Internet resources

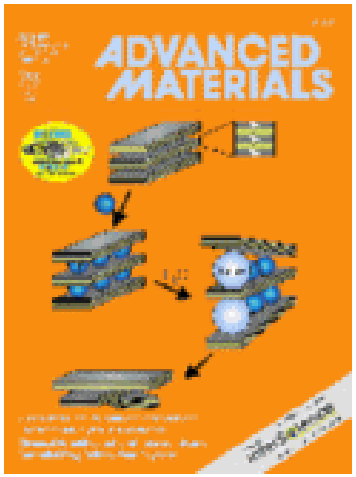
- **http://ruby.chemie.uni-freiburg.de/Vorlesung/ (german)**
- **http://www.chemistry.ohio-state.edu/~woodward/ch754... (pdf-downloads)**
- **IUCR-teaching resources (International Union for Crystallography, advanced level)**

Resources

Journals

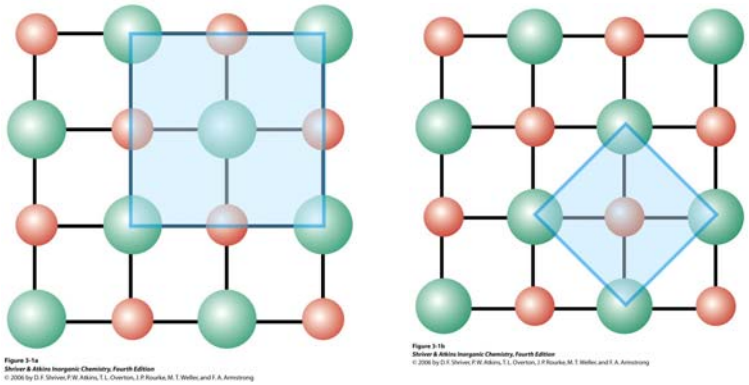






Chapter 1:
Introduction, Basic Structural Chemistry
(Repetition)

1.1 Unit cell, crystal systems, lattice constants, relative coordinates



Different possibilities for the choice of the unit cell

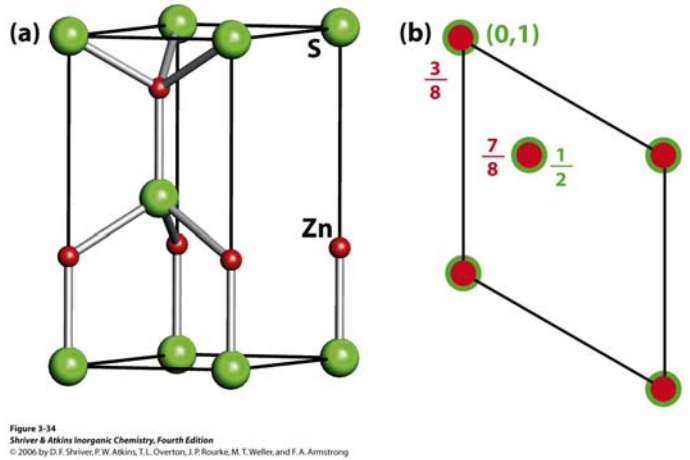


Figure 3-34
Shriver & Atkins Inorganic Chemistry, Fourth Edition
© 2006 by D.F. Shriver, P.W. Atkins, T.L. Overton, J.P. Rourke, M.T. Weller, and F.A. Armstrong

relative coordinates for atomic positions:
(contravariant atomic vector components)
$0 < x,,y,,z < 1$

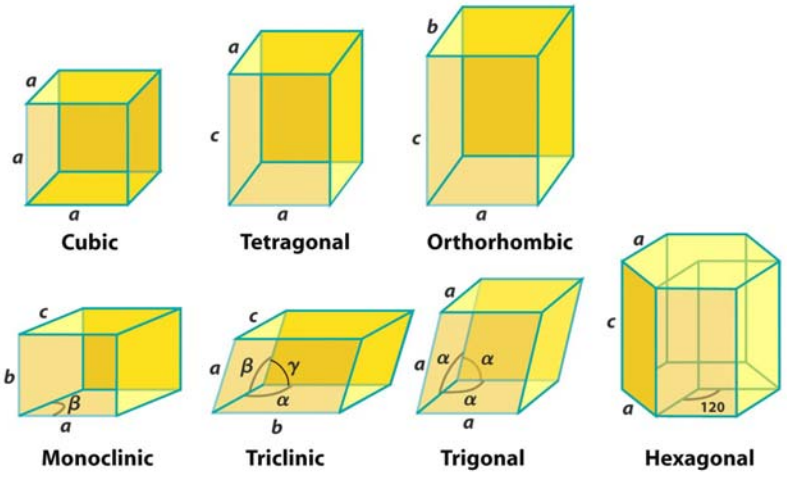


Figure 3-2
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Different crystal systems depending on unit cell symmetry

Table 3.1 The seven crystal systems

System	Relations between lattice parameters	Unit cell defined by	Essential symmetries
Triclinic	$a \neq b \neq c \quad \alpha \neq \beta \neq \gamma \neq 90°$	$a\ b\ c\ \alpha\beta\gamma$	None
Monoclinic	$a \neq b \neq c \quad \alpha \neq \gamma \neq 90° \quad \beta = 90°$	$a\ b\ c\ \beta$	One twofold rotation axis and/or a mirror plane
Orthorhombic	$a \neq b \neq c \quad \alpha = \beta = \gamma = 90°$	$a\ b\ c$	Three perpendicular twofold axes and/or mirror planes
Rhombohedral	$a = b = c \quad \alpha = \beta = \gamma \neq 90°$		One threefold rotation axis
Tetragonal	$a = b \neq c \quad \alpha = \beta = \gamma = 90°$	$a\ c$	One fourfold rotation axis
Hexagonal	$a = b \neq c \quad \gamma = 120°$	$a\ c$	One sixfold rotation axis
Cubic	$a = b = c \quad \alpha = \beta = \gamma = 90°$	a	Four threefold rotation axes tetrahedrally arranged

Table 3-1
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Unit cell and relative positional atomic parameters give a complete description of the crystal structure

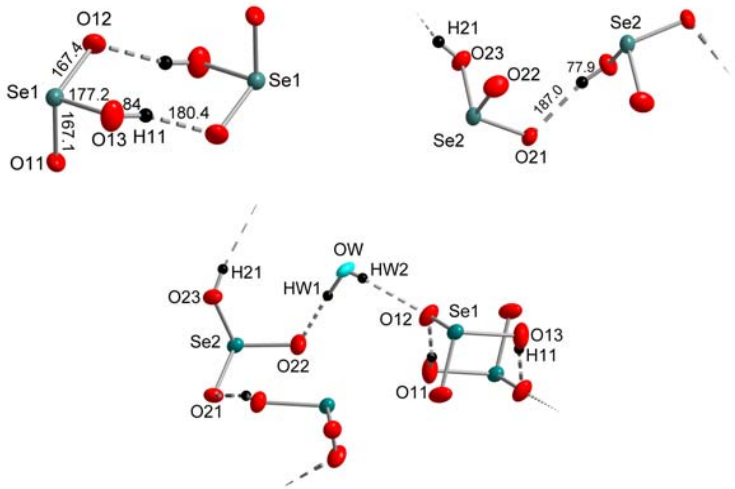
Name	Figure		Name	Figure
Formula	$Cs_2Co(HSeO_3)_4 \cdot 2H_2O$		Diffractometer	IPDS (Stoe)
Temperature	293(2) K		Range for data collection	$3.1° \leq \Theta \leq 30.4°$
Formula weight	872.60 g/mol		*hkl* ranges	$-10 \leq h \leq 10$
Crystal system	**Monoclinic**			$-17 \leq k \leq 18$
Space group	$\boldsymbol{P\,2_1/c}$			$-10 \leq l \leq 9$
Unit cell dimensions	$\boldsymbol{a}$ **= 757.70(20) pm**		Absorption coefficient	$\mu = 15.067\ mm^{-1}$
	$\boldsymbol{b}$ **= 1438.80(30) pm**		No. of measured reflections	9177
	$\boldsymbol{c}$ **= 729.40(10) pm**		No. of unique reflections	2190
	$\boldsymbol{\beta}$ **= 100.660(30) °**		No. of reflections ($I_0 \geq 2\sigma\ (I)$)	1925
Volume	$781.45(45) \times 10^6\ pm^3$		Extinction coefficient	$\varepsilon = 0.0064$
Formula units per unit cell	$Z = 2$		$\Delta\rho_{min}$ / $\Delta\rho_{max}$ / $e/pm^3 \times 10^{-6}$	-2.128 / 1.424
Density (calculated)	$3.71\ g/cm^3$		R_1 / wR_2 ($I_0 \geq 2\sigma\ (I)$)	0.034 / 0.081
Structure solution	SHELXS – 97		R_1 / wR_2 (all data)	0.039 / 0.083
Structure refinement	SHELXL – 97		Goodness-of-fit on F^2	1.045
Refinement method	Full matrix LSQ on F^2			

Crystallographic and structural refinement data of $Cs_2Co(HSeO_3)_4 \cdot 2H_2O$

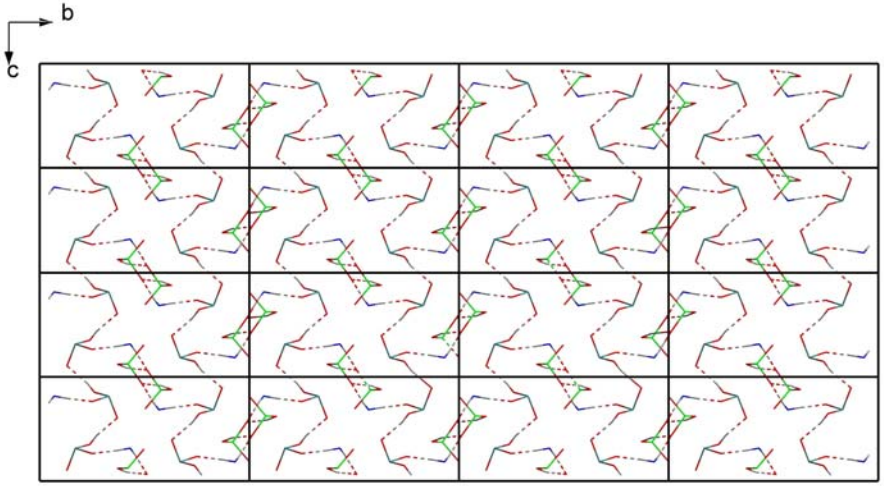
Unit cell and relative positional atomic parameters give a complete description of the crystal structure

Atom	**WP**	**x**	**y**	**z**	**U_{eq}/pm^2**
Cs	*4e*	0.50028(3)	0.84864(2)	0.09093(4)	0.02950(11)
Co	*2a*	0.0000	1.0000	0.0000	0.01615(16)
Se1	*4e*	0.74422(5)	0.57877(3)	0.12509(5)	0.01947(12)
O11	*4e*	0.7585(4)	0.5043(3)	0.3029(4)	0.0278(7)
O12	*4e*	0.6986(4)	0.5119(3)	-0.0656(4)	0.0291(7)
O13	*4e*	0.5291(4)	0.6280(3)	0.1211(5)	0.0346(8)
H11	*4e*	0.460(9)	0.583(5)	0.085(9)	0.041
Se2	*4e*	0.04243(5)	0.67039(3)	-0.18486(5)	0.01892(12)
O21	*4e*	-0.0624(4)	0.6300(2)	-0.3942(4)	0.0229(6)
O22	*4e*	0.1834(4)	0.7494(3)	-0.2357(5)	0.0317(7)
O23	*4e*	-0.1440(4)	0.7389(2)	-0.1484(4)	0.0247(6)
H21	*4e*	-0.120(8)	0.772(5)	-0.062(9)	0.038
OW	*4e*	-0.1395(5)	1.0685(3)	0.1848(5)	0.0270(7)
HW1	*4e*	-0.147(8)	1.131(5)	0.032	0.032
HW2	*4e*	-0.159(9)	1.045(5)	0.247(9)	0.032

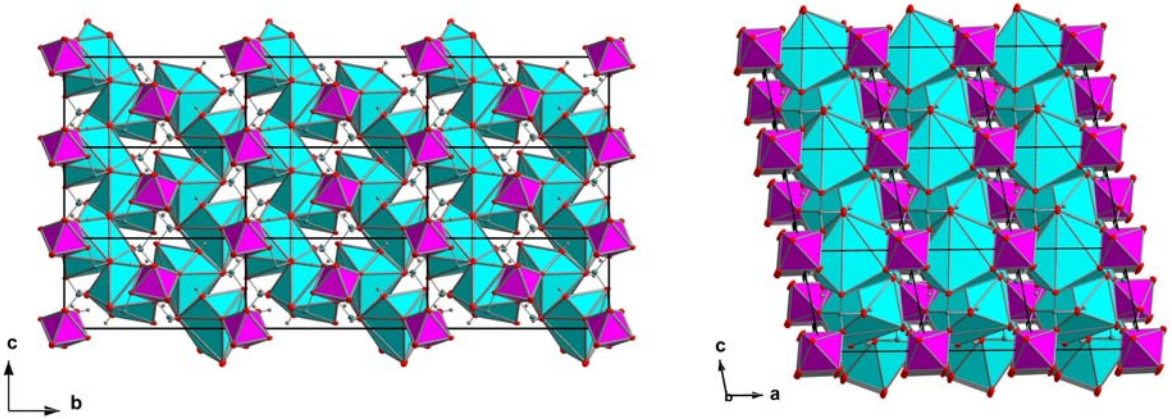
Positional and isotropic temperature parameters of $Cs_2Co(HSeO_3)_4 \cdot 2H2O$



Hydrogen bonds in $Cs_2Co(HSeO_3)_4 \cdot 2H_2O$

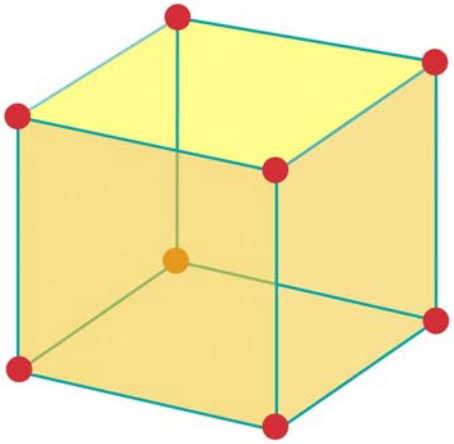


Hydrogen bond system of $Cs_2Co(HSeO_3)_4 \cdot 2H_2O$



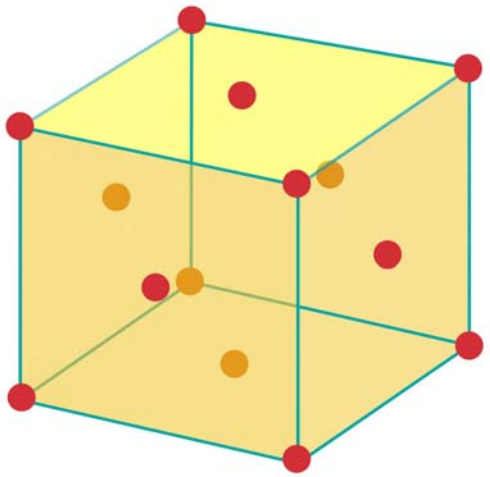
Crystal structure of $Cs_2Co(HSeO_3)_4 \cdot 2H_2O$

1.2 Primitive and centered unit cells, Bravais lattices,



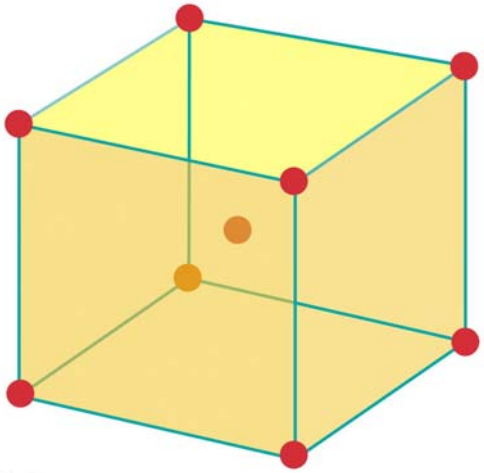
(P)

Figure 3-3
Shriver & Atkins Inorganic Chemistry, Fourth Edition



(F)

Figure 3-5
Shriver & Atkins Inorganic Chemistry, Fourth Edition



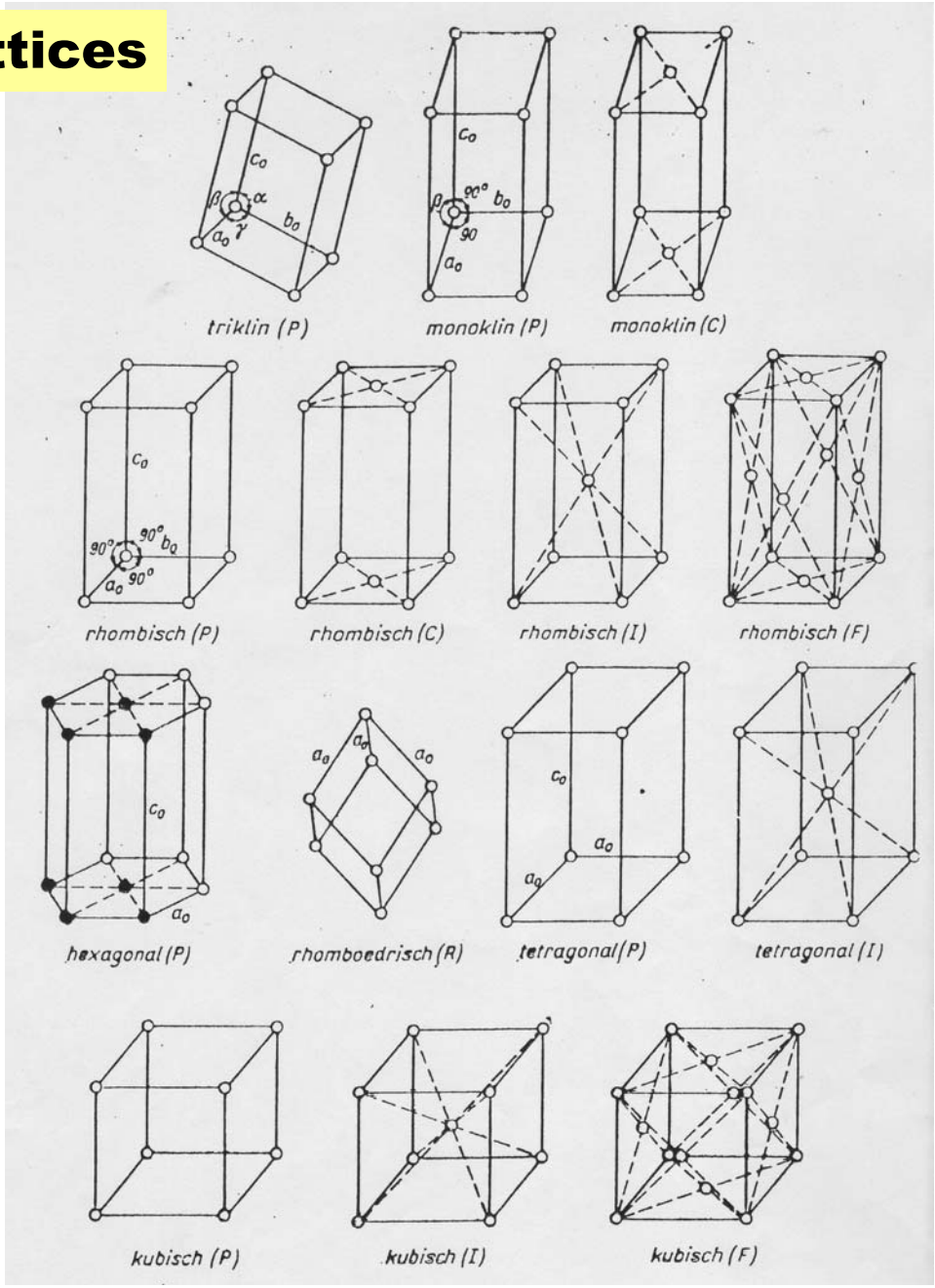
(I)

Figure 3-4
Shriver & Atkins Inorganic Chemistry, Fourth Edition

F-, I-, A-, B-, C-Centering in general means that a corresponding shift vector is applied to all atoms or molecules in the unit cell:

e.g. A → vector [0½½]

Bravais lattices



1.3 Most important sphere packings and space filling

hcp

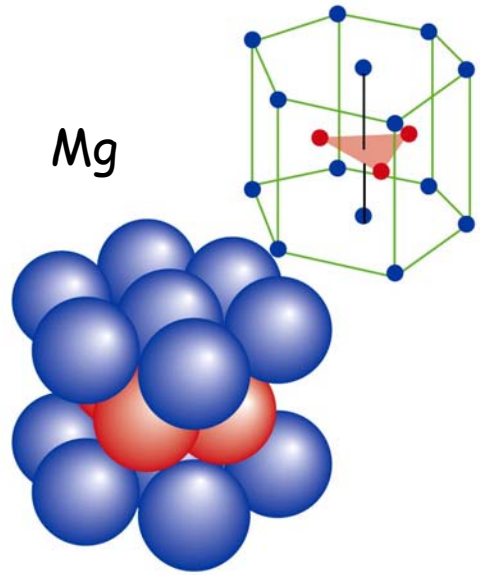


Figure 3-11
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74%

ccp, fcc

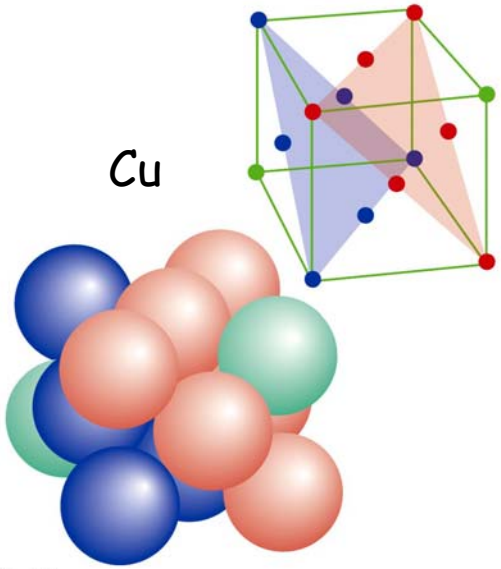

Figure 3-12
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74%

bcc

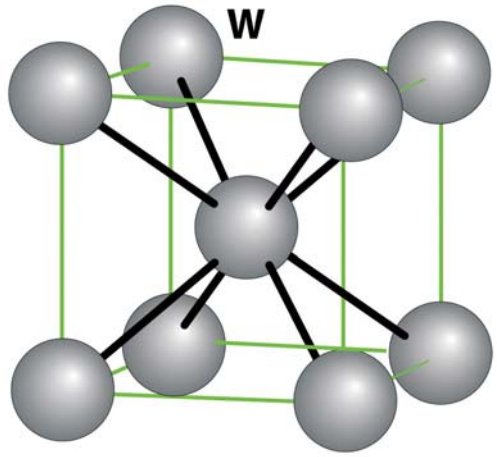

Figure 3-6a
Shriver & Atkins Inorganic Chemistry, Fourth Edition

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1.4 Elemental metals and the distribution of sphere packings in the periodic system

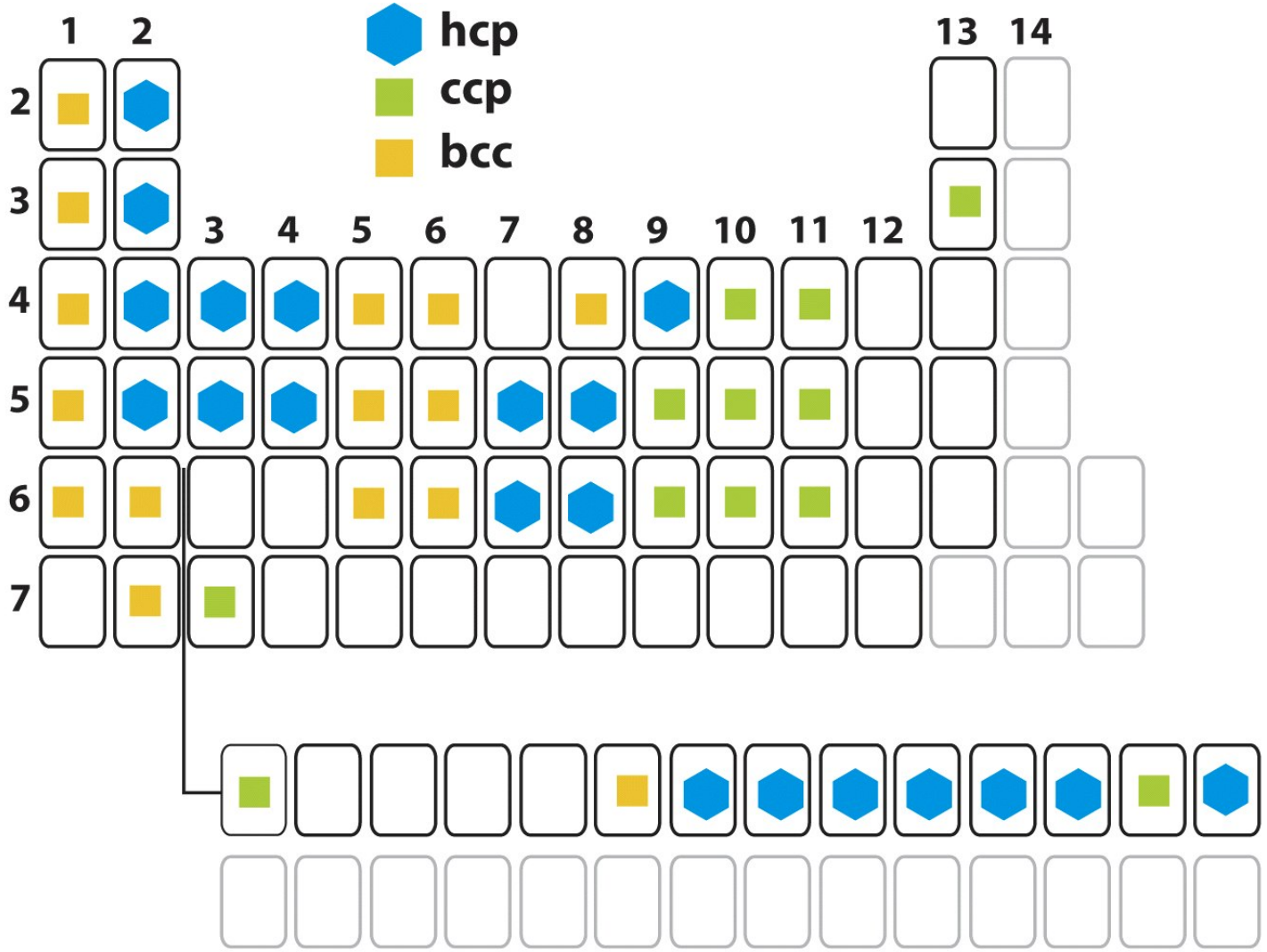

Figure 3-19
Shriver & Atkins Inorganic Chemistry, Fourth Edition

1.4 Elemental metals and the distribution of sphere packings among their structures

Table 3.2 The crystal structures adopted by metals under normal conditions

Crystal structure	Element
Hexagonal close-packed (hcp)	Be, Cd, Co, Mg, Ti, Zn
Cubic close-packed (ccp)	Ag, Al, Au, Ca, Ca, Cu, Ni, Pb, Pt
Body-centred cubic (bcc)	Ba, Cr, Fe, W, alkali metals
Primitive cubic (cubic-P)	Po

Table 3-2
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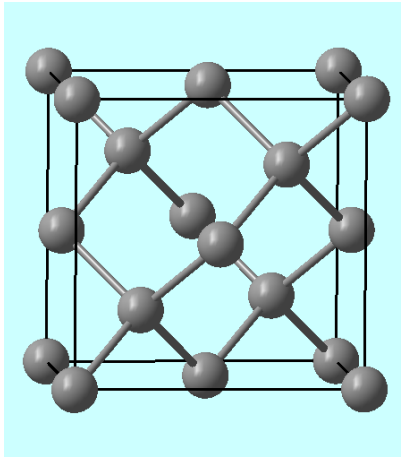
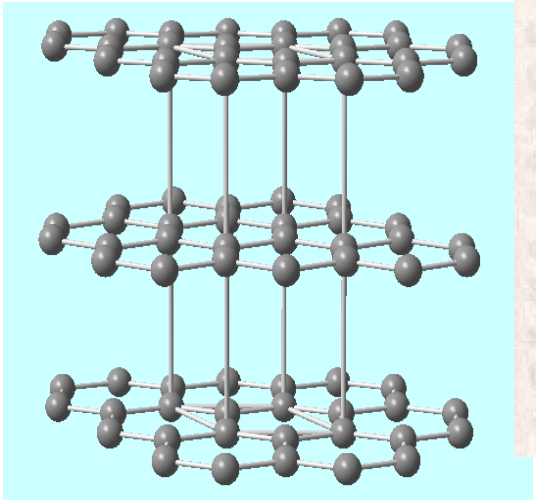
1.5 Elemental structures which **do not** fit to the model of close packed spheres

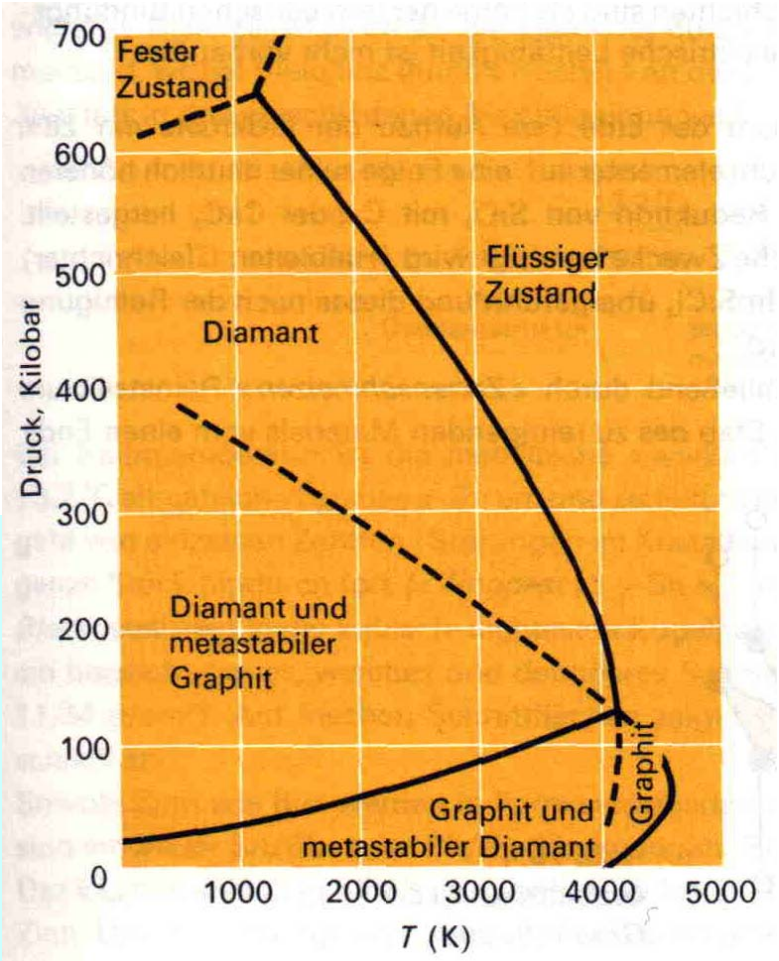
Diamond (C, Si, Ge)



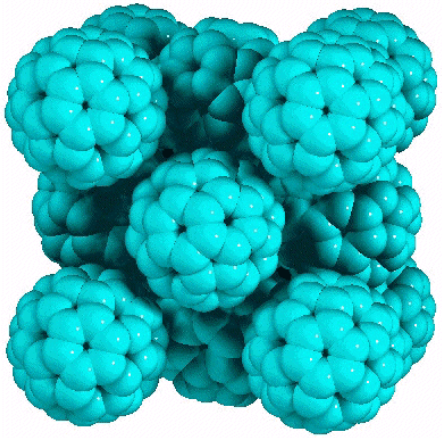
Graphite

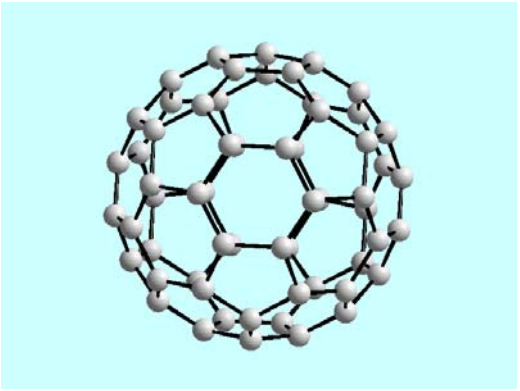


The carbon phase diagram



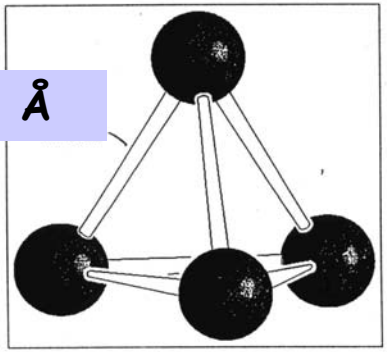
Fullerene (C_{60})



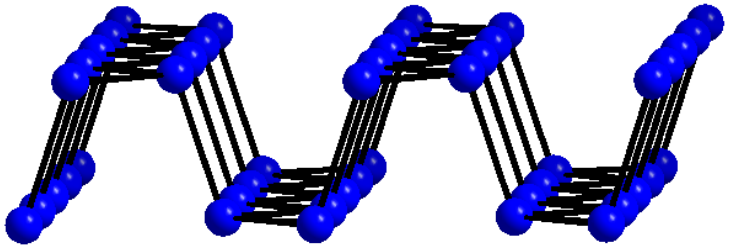


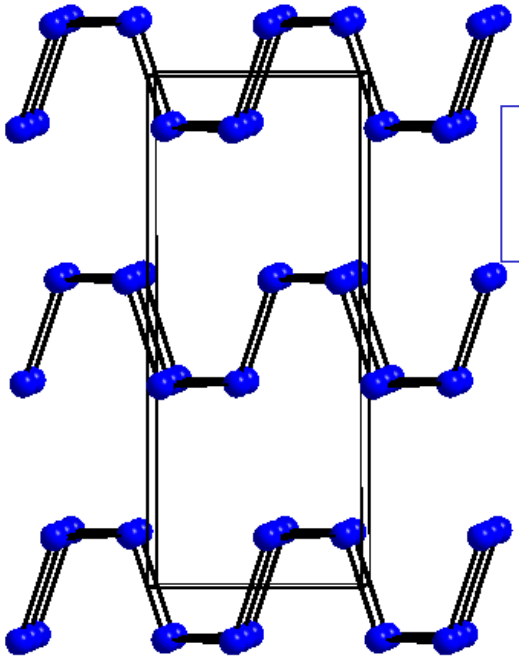
1.5 Elemental structures which **do not** fit to the model of close packed spheres

P_4 (white): instable



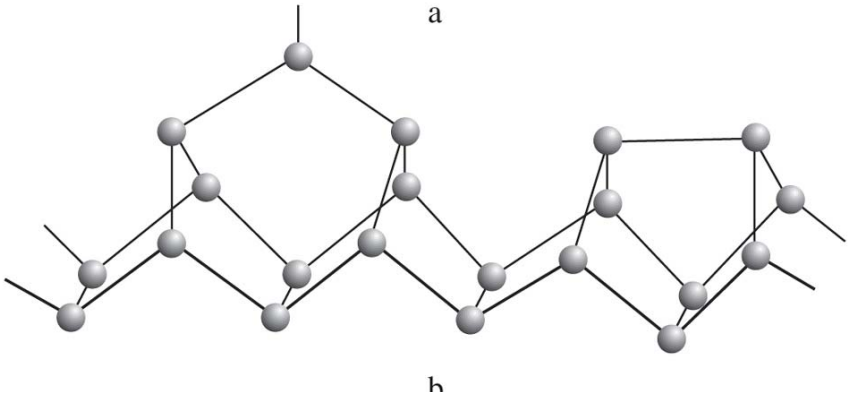
P (black): stable





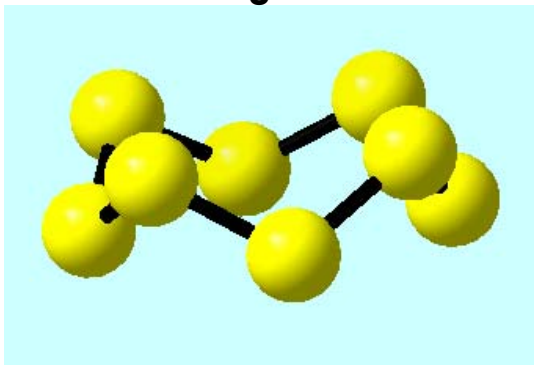
van der Waals-bonding

P (purple, red): instable

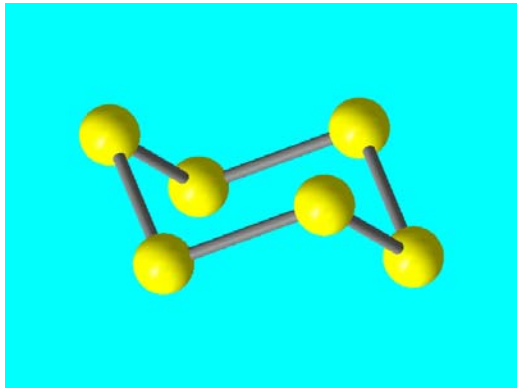


1.5 Elemental structures which **do not** fit to the model of close packed spheres

α-S: „S_8-crowns"

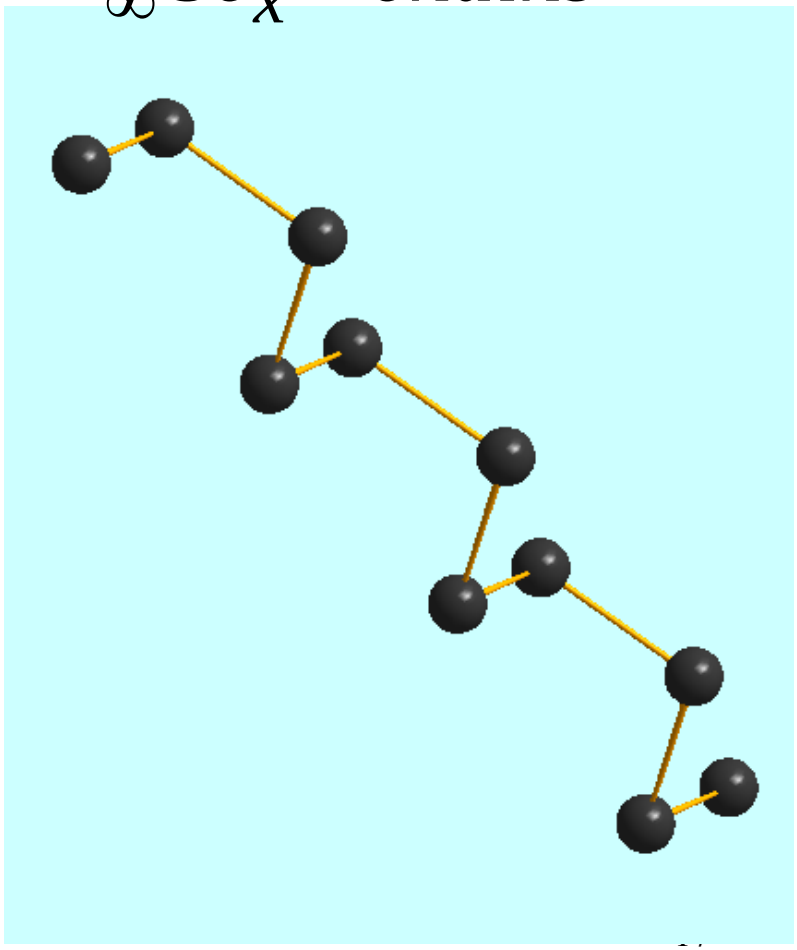


S_6 and others

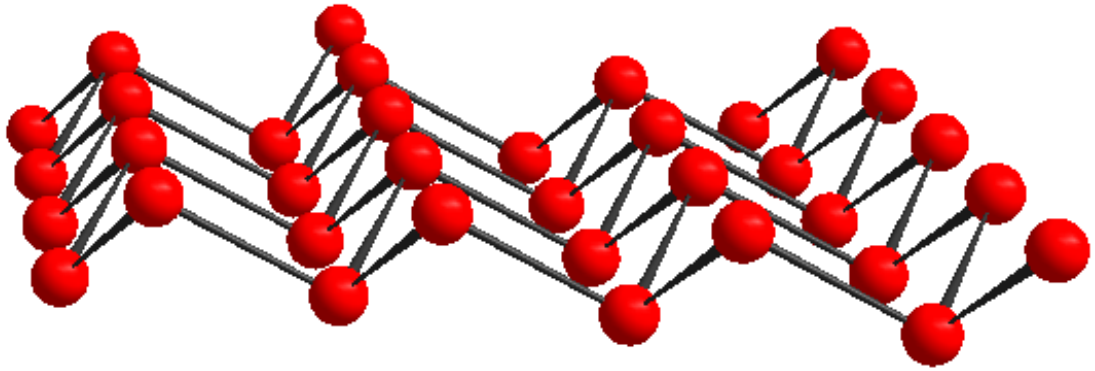


α-Se:

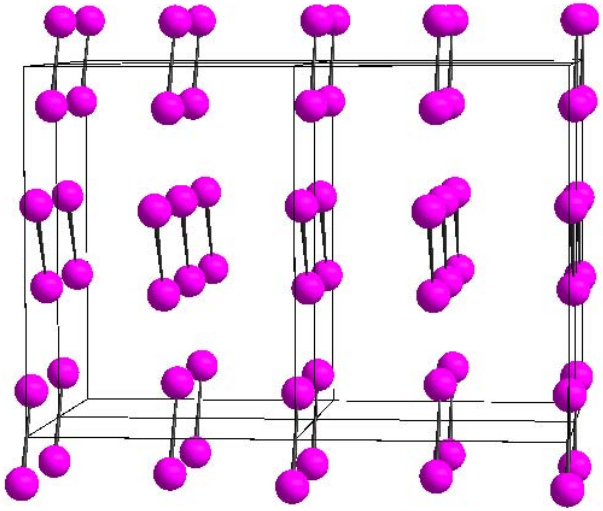
$$^{2}_{\infty}Se_x - chains$$



1.5 Elemental structures which **do not** fit to the model of close packed spheres



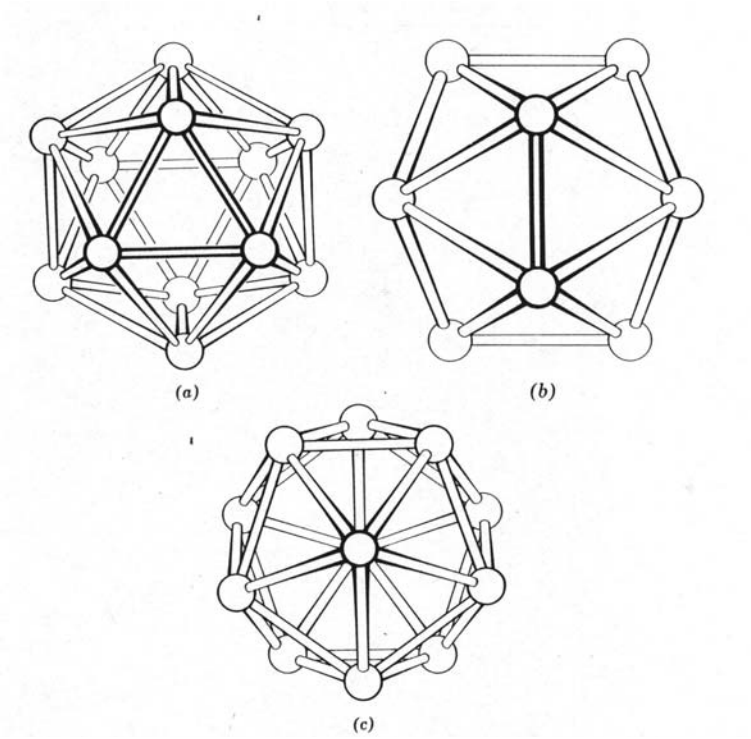
As (grey), Sb



Iodine

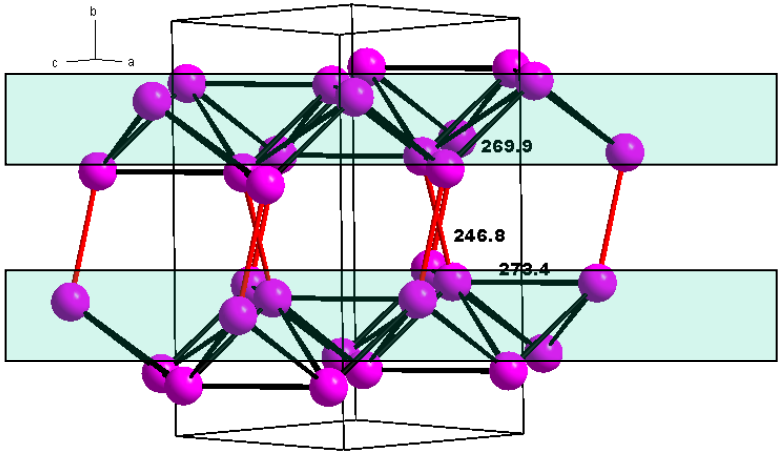
1.5 Elemental structures which **do not** fit to the model of close packed spheres

α-Boron



B_{12} - Icosahedron

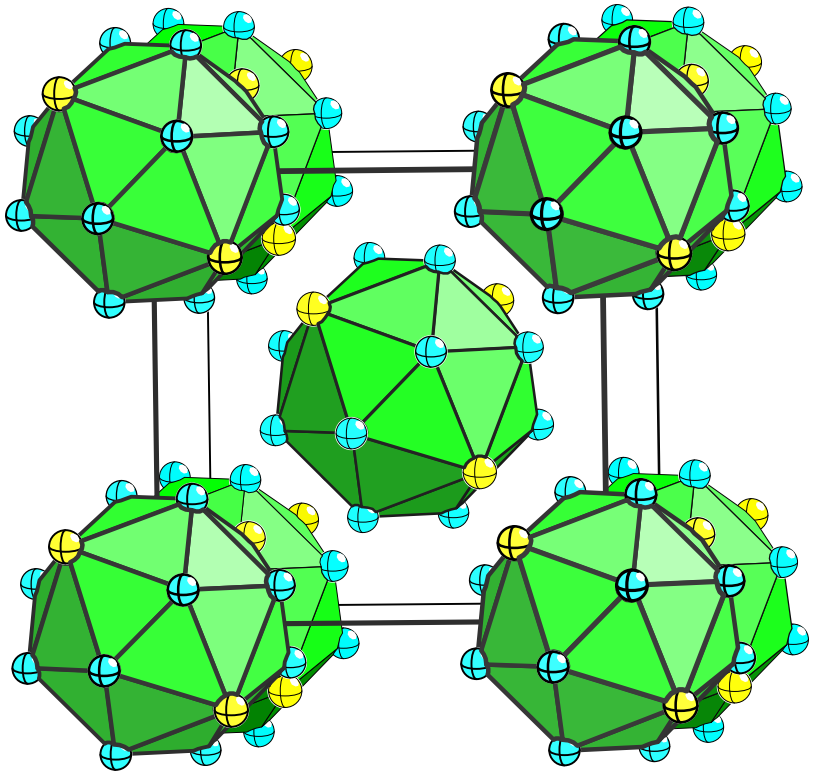
α-Gallium: puckered layers,



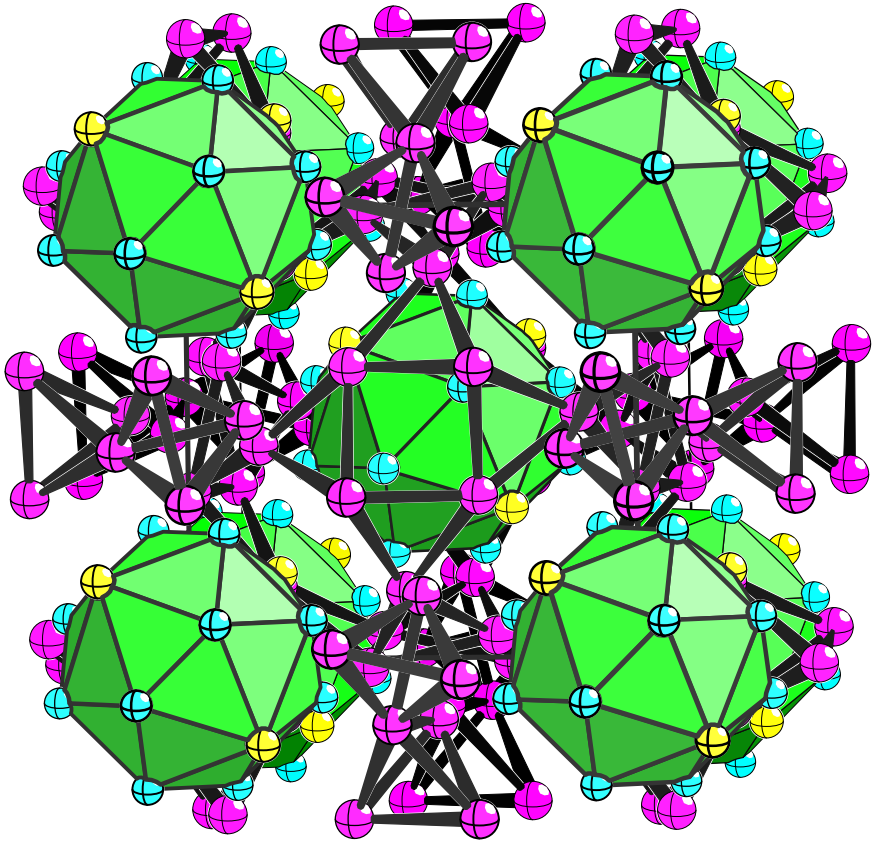
Short d(Ga-Ga) = 248 pm between layers: Ga_2-molecules ?

m.p. = 30 °C

1.6 Specific element structures: α-manganese

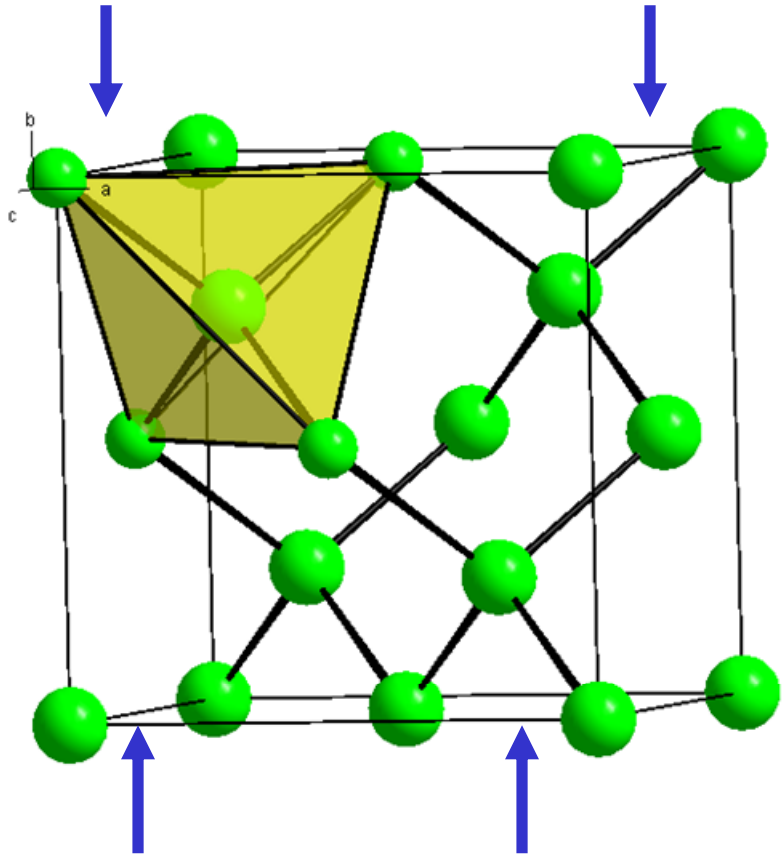


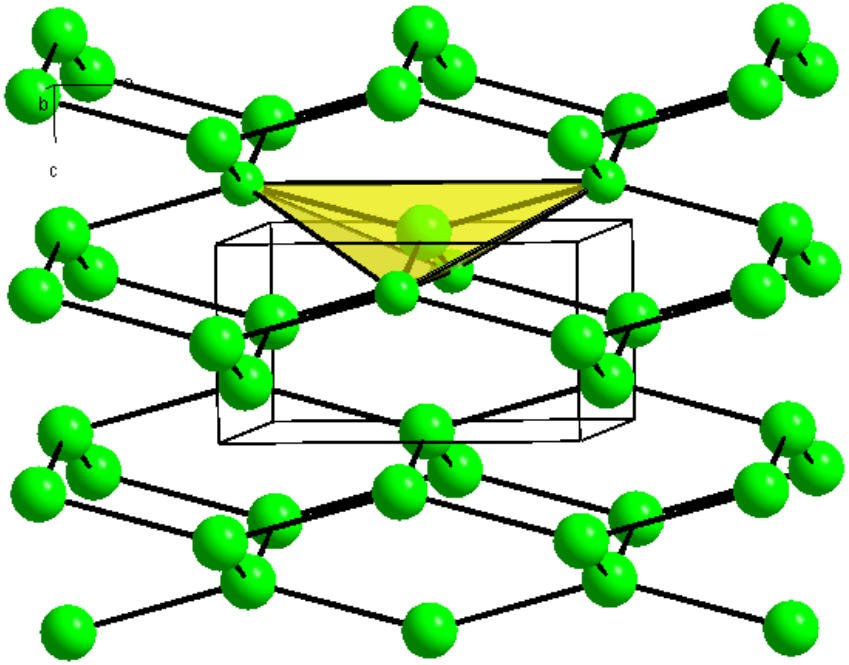
Mn1: CN = 16(Mn2, Mn4)



Interpenetrating network of Mn3

1.6 Specific element structures: tin





α-Sn ⟷ **β-Sn**

13 °C

d = 5,75 gcm^{-3}	d = 7,3 g cm^{-3}
CN = 4 (281 pm)	CN = 4+2 (302, 318 pm)
cubic (diamond)	tetragonal (compressed diamond)

1.7 Octahedral and tetrahedral holes in ccp (fcc) and hcp sphere packings

optimal radius ratio for different coordination numbers

oct (CN 6): spheres / holes = 1:1

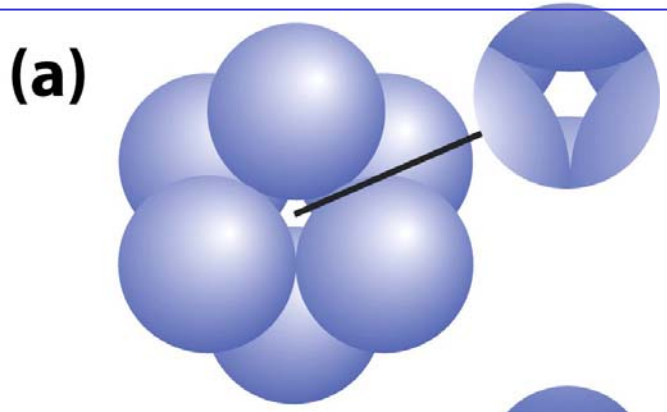


Figure 3-15
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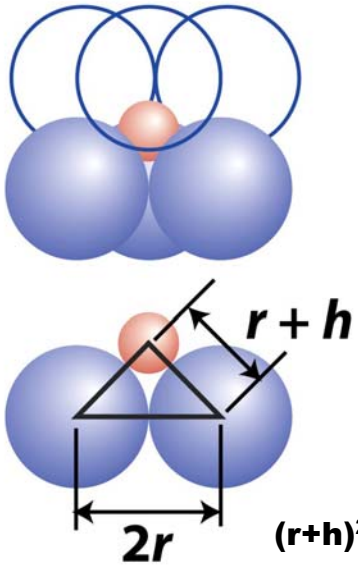

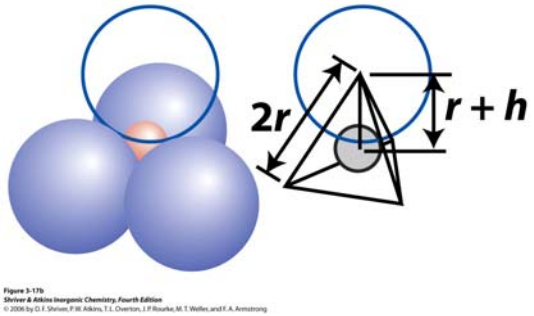

Figure 3-17a
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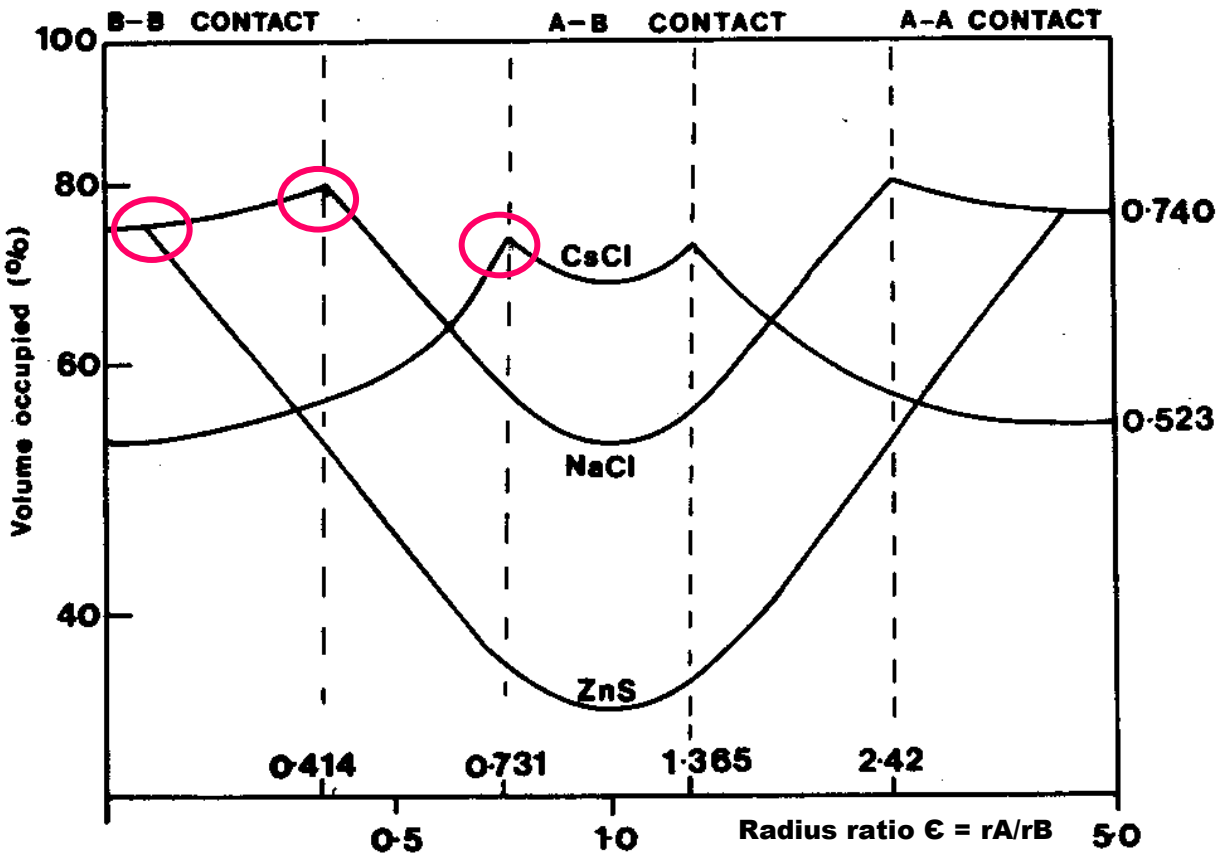
$(r+h)^2 + (r+h)^2 = (2r)^2$, $h = (2^{1/2}-1)r = 0.41r$

CN	geometry	r^+/r^- (r^+ = h, r^- = r)
3	triangle	0.15
4	tetrahedron	0.22
6	octahedron	0.41
8	cube	0.73

tetr (CN 4): spheres / holes = 1:2

1.7 Octahedral and tetrahedral holes in ccp (fcc) and hcp sphere packings (space filling curves → Parthé, 1961)



1.8 Basic structures of binary solids derived from sphere packings by a systematic filling of tetrahedral and octahedral holes

Table 3.5 The relation of structure to the filling of holes

Close-packing type	Hole filling	Structure type (exemplar)
Cubic (ccp)	All octahedral	Rock salt (NaCl)
	All tetrahedral	Fluorite (CaF_2)
	Half tetrahedral	Sphalerite (ZnS)
Hexagonal (hcp)	All octahedral	Nickel arsenide (NiAs); with some distortion from perfect hcp
	Half octahedral	Rutile (TiO_2); with some distortion from perfect hcp
	All tetrahedral	No structure exists: tetrahedral holes share faces
	Half tetrahedral	Wurtzite (ZnS)

Table 3-5
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1.8 Basic structures of binary solids derived from sphere packings by a systematic filling of tetrahedral and octahedral holes

crystal system: cubic

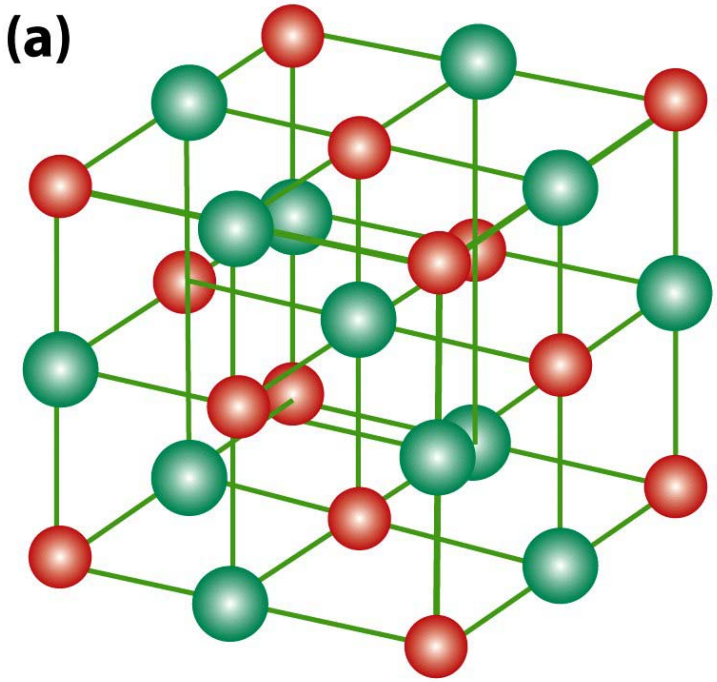

Figure 3-28
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crystal system: tetragonal (!)

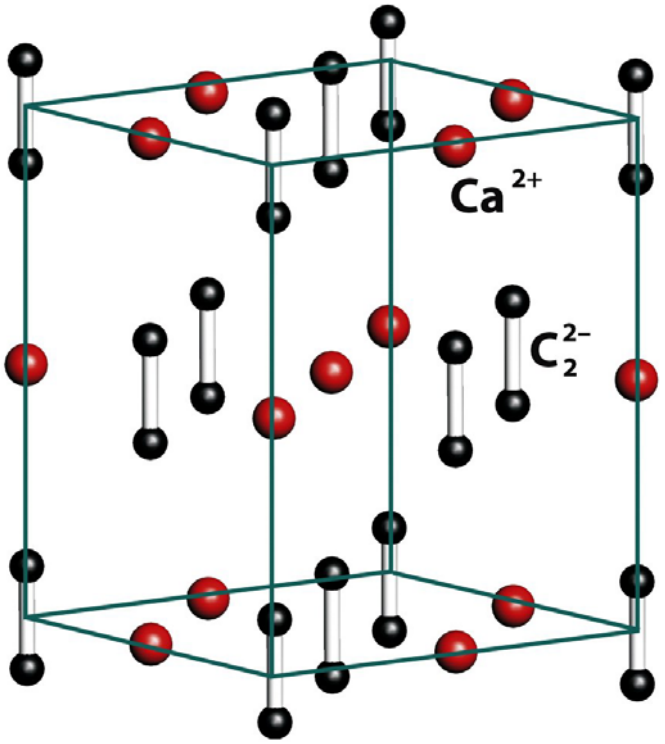

Figure 3-29
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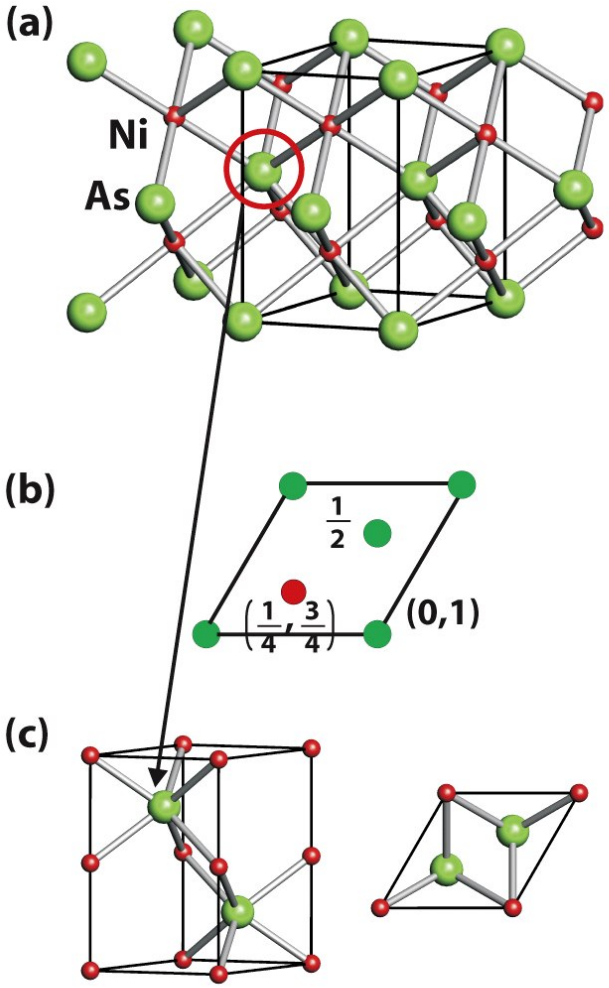
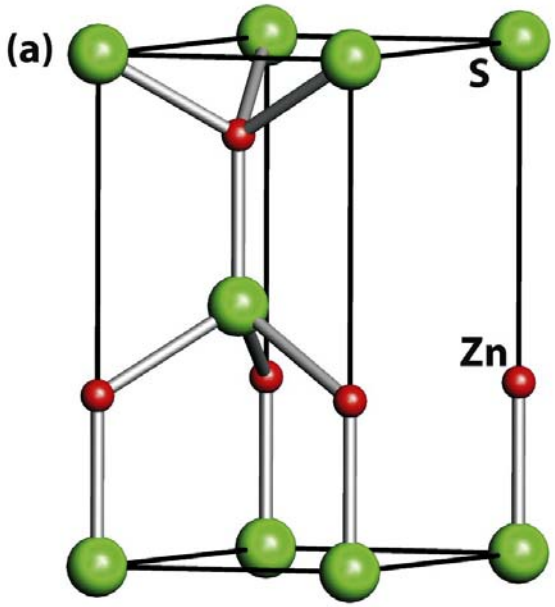
1.8 Basic structures of binary solids derived from sphere packings by a systematic filling of tetrahedral and octahedral holes

nickelarsenide: NiAs



wurtzite: ZnS



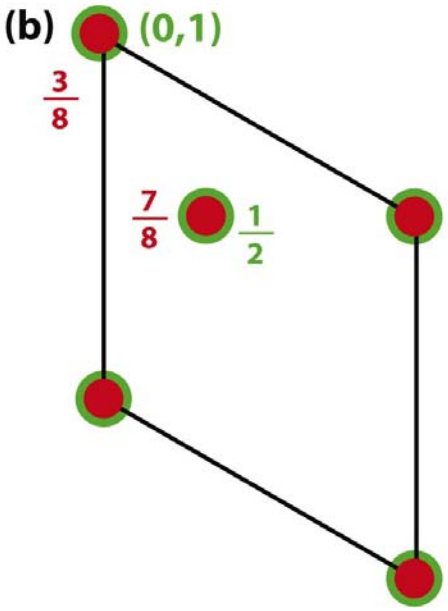


Figure 3-34
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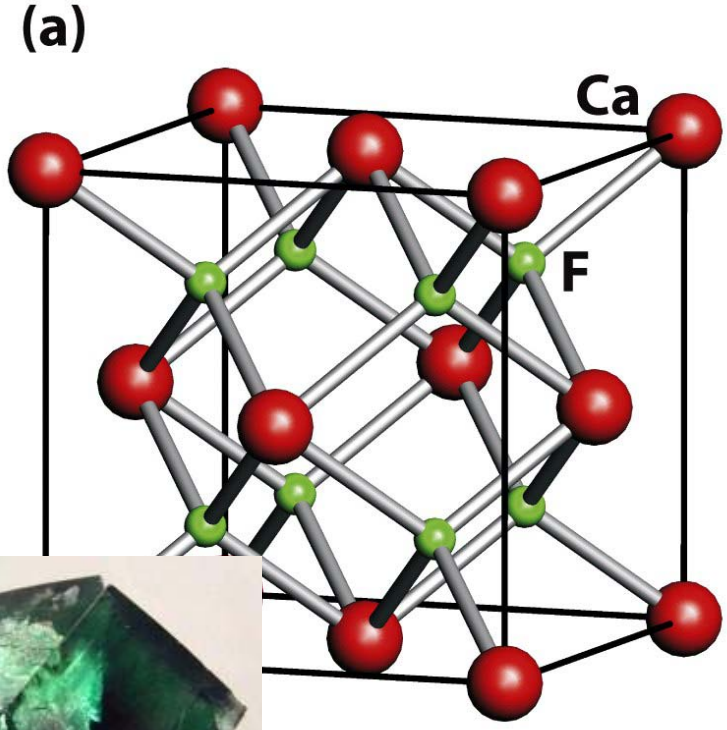
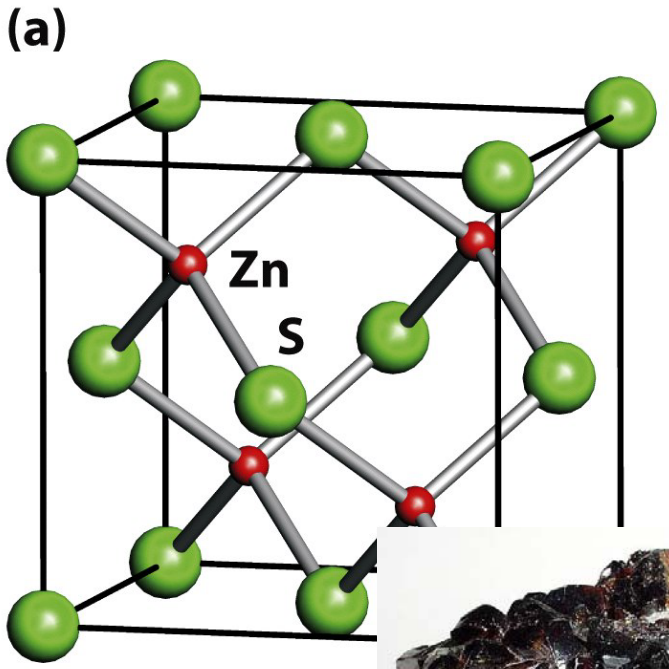
1.8 Basic structures of binary solids derived from sphere packings by a systematic filling of tetrahedral and octahedral holes

„fluorite": CaF_2

zinkblende, sphalerite: ZnS

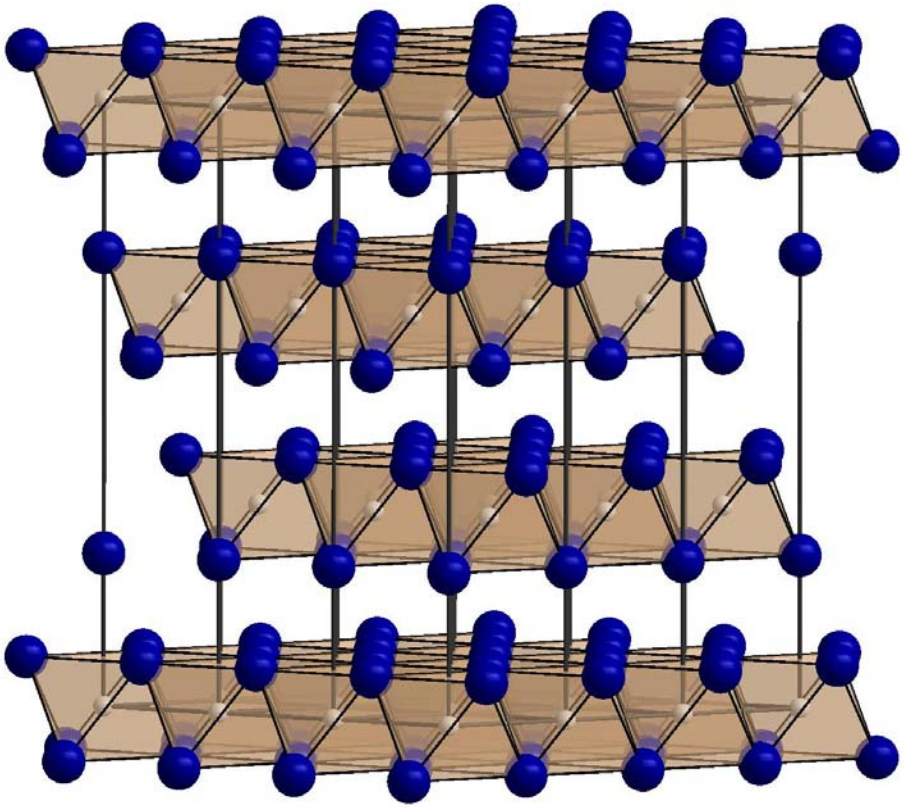




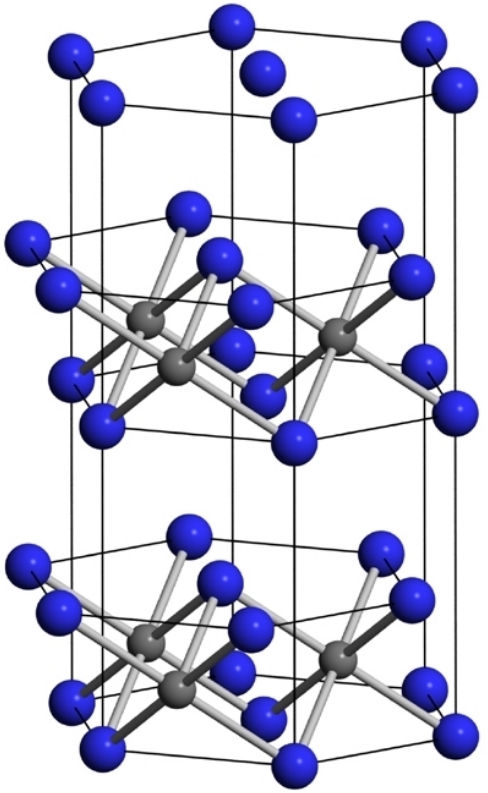
derive connectivity formulas !

1.8 Basic structures of binary solids derived from sphere packings by a systematic filling of tetrahedral and octahedral holes

Cadmiumchloride: $CdCl_2$ (based on ccp,fcc)



Cadmiumiodide: CdI_2 (based on hcp)



1.9 Important structures of binary solids without direct relations to close packings of spheres

cesiumchloride: CsCl

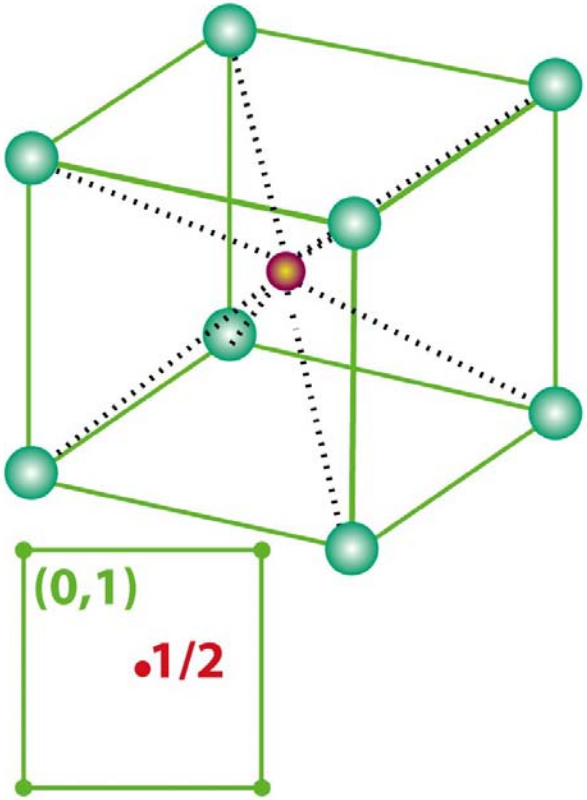


Figure 3-30
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ammoniumchloride: NH_4Cl (rotating NH_4)

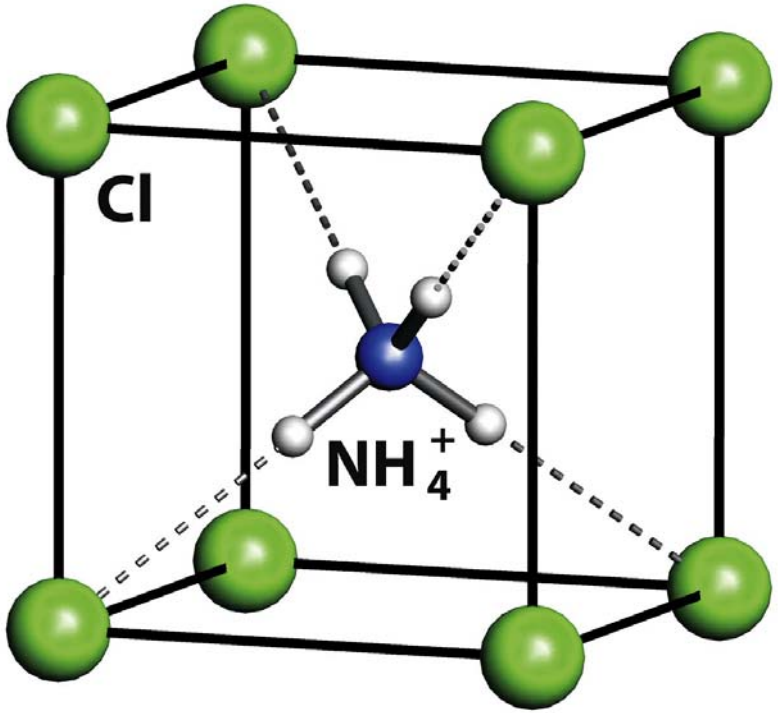

Figure 3-31
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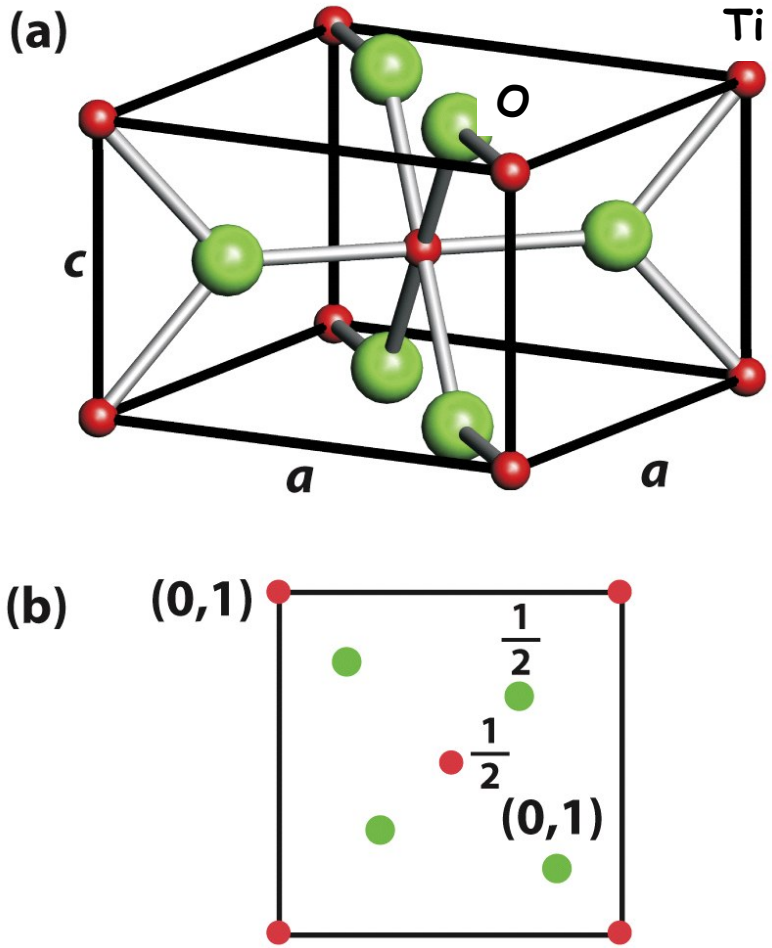
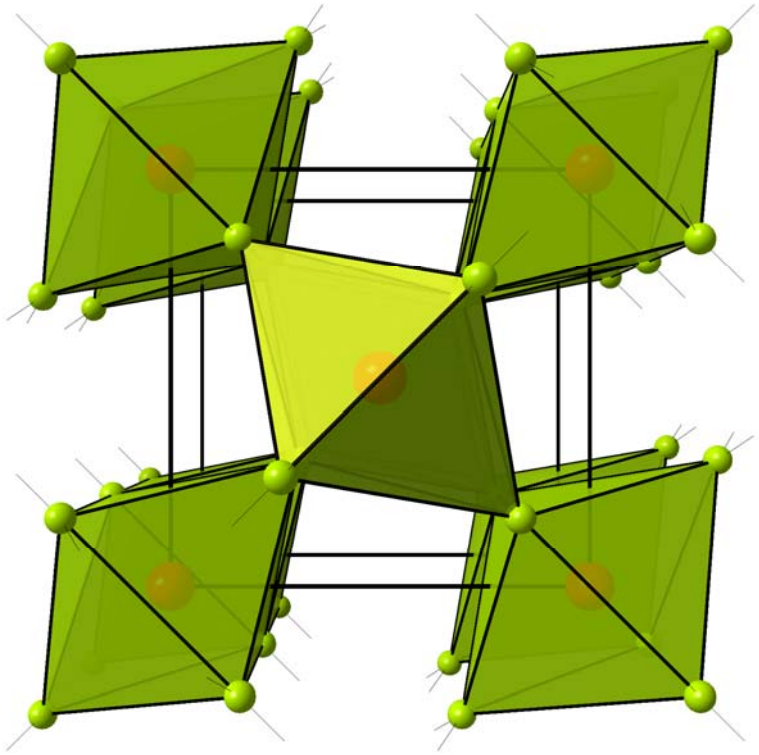
1.9 Important structures of binary solids without direct relations to close packings of spheres

rutile: TiO_2

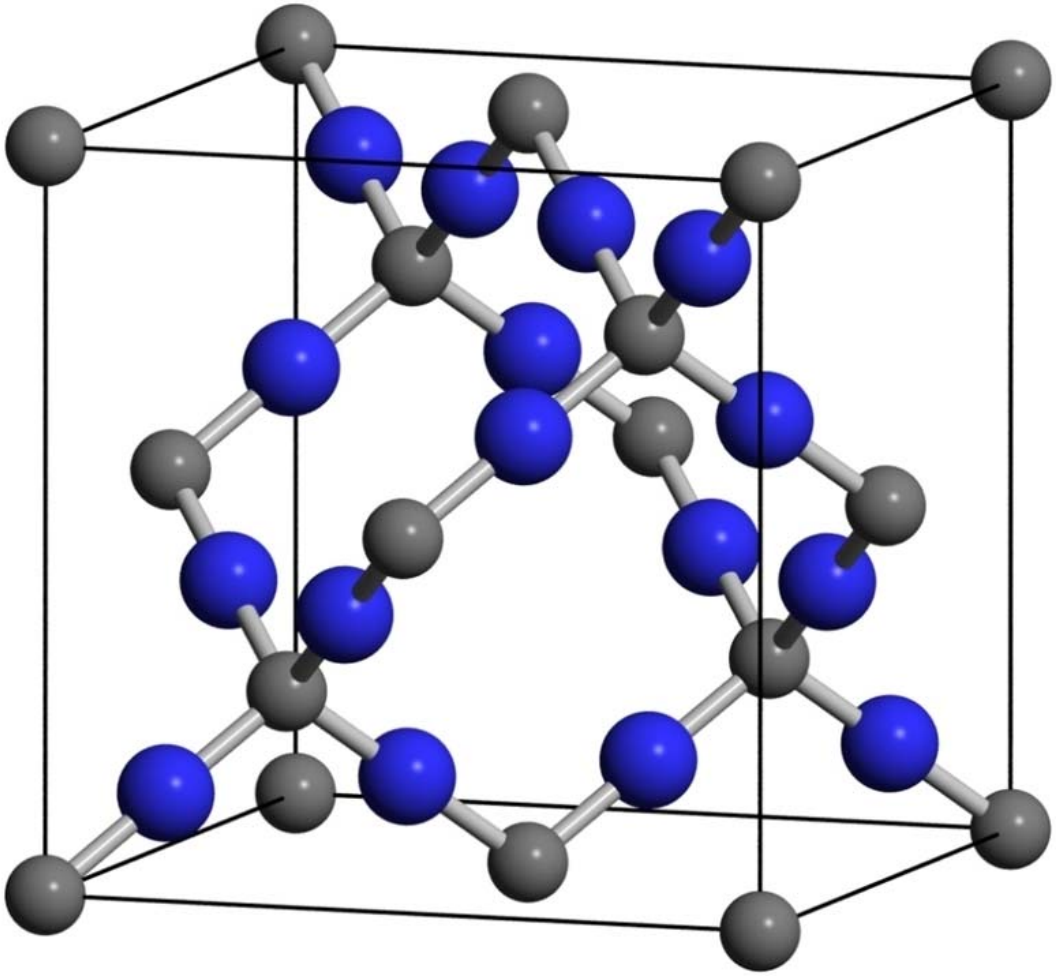
polyhedral representation





1.9 Important structures of binary solids without direct relations to close packings of spheres

cristobalite: SiO_2



other natural varieties of SiO_2 with different structures:

Quarz, Cristobalit, Tridymit, Stishovit

1.10 Basic structures of binary solids derived from sphere packings by a systematic filling of tetrahedral and/or octahedral holes

Table 3.4 The crystals structures of compounds

Crystal structure	Example*
Antifluorite	K_2O, K_2S, Li_2O, Na_2O, Na_2Se, Na_2S
Caesium chloride	**CsCl**, CaS, TlSb, CsCN, CuZn
Fluorite	**CaF_2**, UO_2, $BaCl_2$, HgF_2, PbO_2
Nickel arsenide	**NiAs**, NiS, FeS, PtSn, CoS
Perovskite	**$CaTiO_3$**, $SrTiO_3$, $PbZrO_3$, $LaFeO_3$, $LiSrH_3$, $KMnF_3$
Rock salt	**NaCl**, KBr, RbI, AgCl, AgBr, MgO, CaO, TiO, FeO, NiO, SnAs, UC, ScN
Rutile	**TiO_2**, MnO_2, SnO_2, WO_2, MgF_2, NiF_2
Sphalerite (zinc blende)	**ZnS**, CuCl, CdS, HgS, GaP, InAs
Spinel	**$MgAl_2O_4$**, $ZnFe_2O_4$, $ZnCr_2S_4$
Wurtzite	**ZnS**, ZnO, BeO, MnS, AgI, AlN, SiC, NH_4F

* The substance in bold type is the one that gives its name to the structure.

Table 3-4
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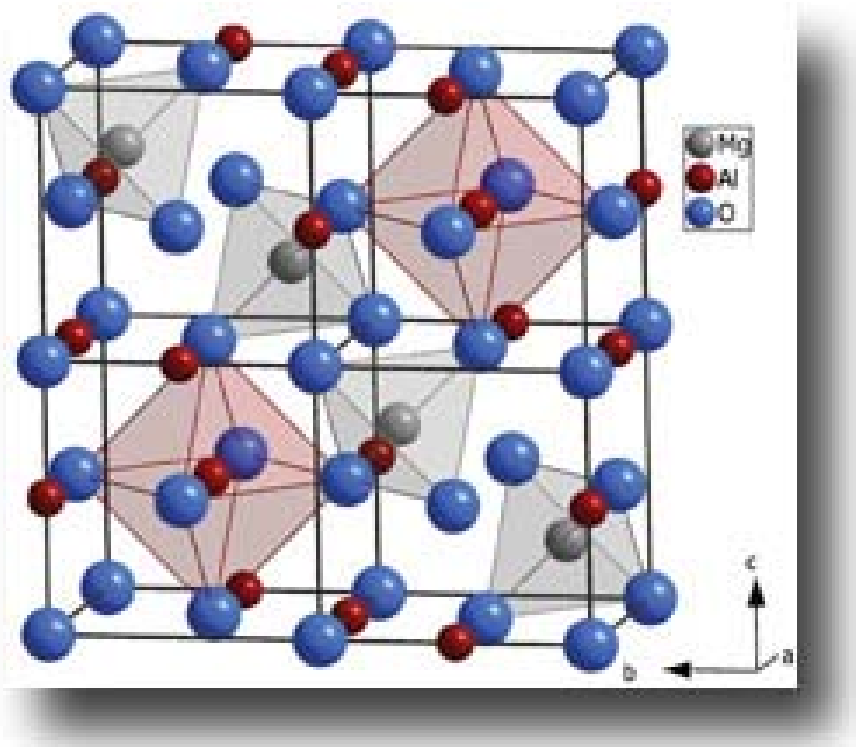
1.11 Important structures of ternary solids

spinell: $MgAl_2O_4$

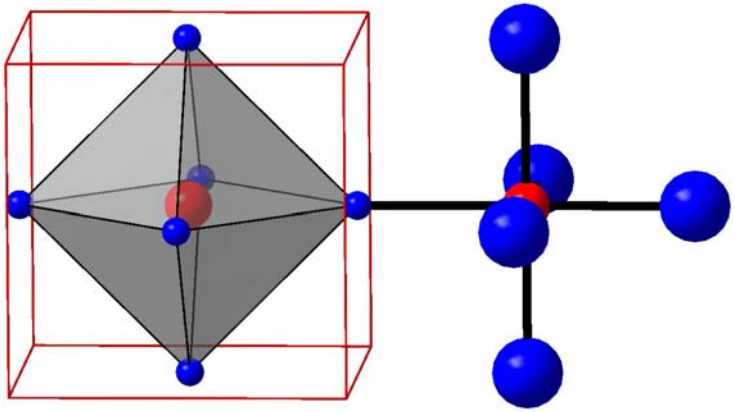


normal spinell: AB_2O_4, $\frac{1}{8}$ T-holes (A), $\frac{1}{2}$ O-holes (B)

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

1.11 Important structures of ternary solids: relation between ReO_3 and $CaTiO_3$ (perovskite)

ReO_3



$CaTiO_3$