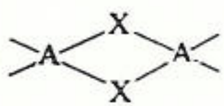
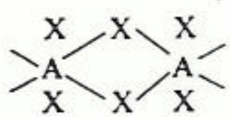
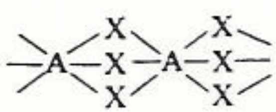
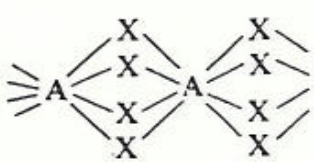
Infinite linear and layered structures

Infinite linear molecules and ions

Type of chain	*Formula*	*Molecules*	*Ions*
(i) –A–	A	S (plastic), Se, Te	$[B_3O_4(OH)_3]_n^{2n-}$
(ii) –A–X–	AX	AuI, AuCN, HgO, $In(C_5H_5)$, $(\phi SeO_2)H$	$(HCO_3)_n^{n-}$, $(HSO_4)_n^{n-}$
–A–X– X	AX_2	SeO_2, $Pb(C_5H_5)_2$	$(BO_2)_n^{n-}$, $[Cu(CN)_2]_n^{n-}$, $(AsO_2)_n^{n-}$
–A–X– X_2	AX_3	SO_3, CrO_3, AuF_3, $PNCl_2$, $SiOCl_2$	$(SiO_3)_n^{2n-}$ etc., $(Cu^{I}Cl_3)_n^{2n-}$, $(Cu^{II}Cl_3)_n^{n-}$
–A–X– X_4	AX_5	(*trans*): BiF_5, UF_5 (*cis*): CrF_5 etc., $MoOF_4$	$(AlF_5)_n^{2n-}$, $(PbF_5)_n^{n-}$ (in $SrPbF_6$)
(iii) 	AX_2	(planar): $PdCl_2$, $CuCl_2$ (tetrahedral): $BeCl_2$, SiS_2	
	AX_4	NbI_4, $TcCl_4$	$(HgCl_4)_n^{2n-}$
	AX_5	$PaCl_5$	
Similarly	AX_6		$(ZrF_6)_n^{2n-}$ in K_2ZrF_6
	AX_7		$(PaF_7)_n^{2n-}$ in K_2PaF_7
(iv) 	AX_3	ZrI_3 etc.	$(NiCl_3)_n^{n-}$ in $CsNiCl_3$
(v) 	AX_4	$U(ac)_4$	
Hybrid chains		See text	
Multiple chains		Sb_2O_3, $NbOCl_3$	$(Si_4O_{11})_n^{6n-}$, $(CdCl_3)_n^{n-}$, $(Cu^{I}_2Cl_3)_n^{n-}$

Crown S

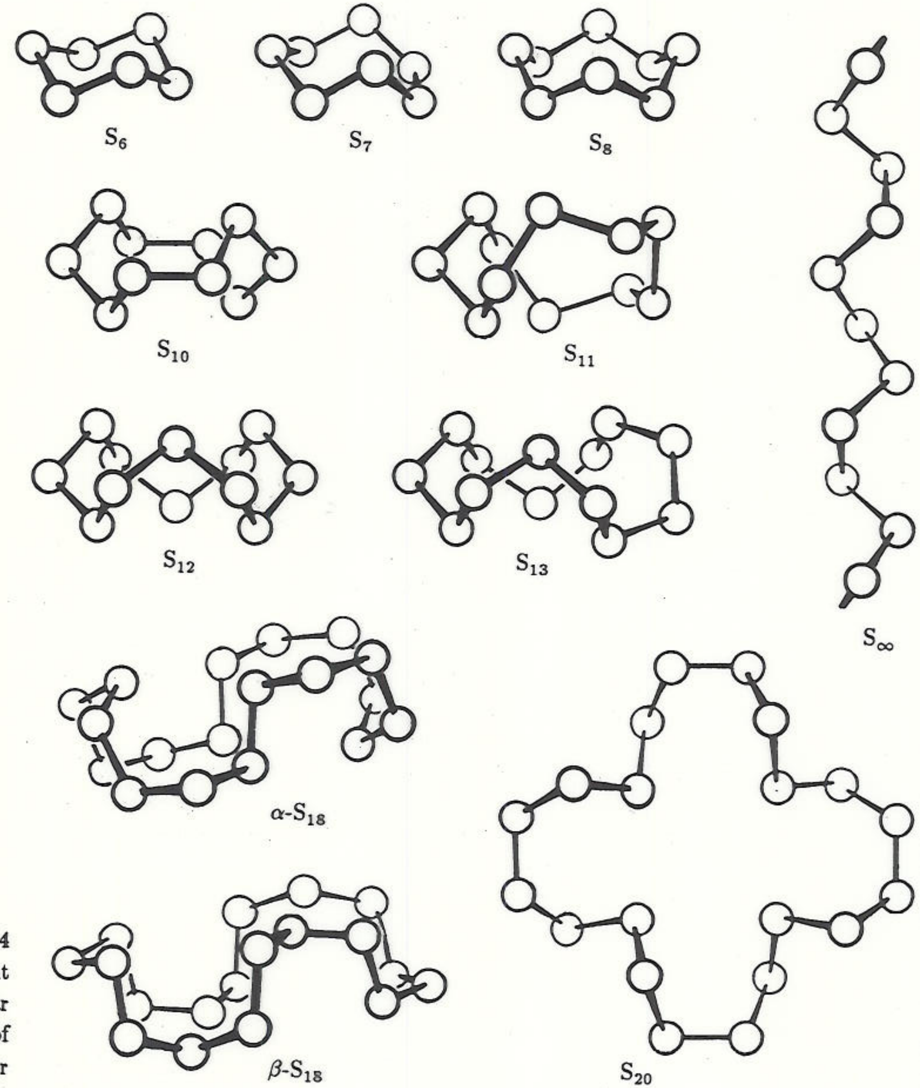
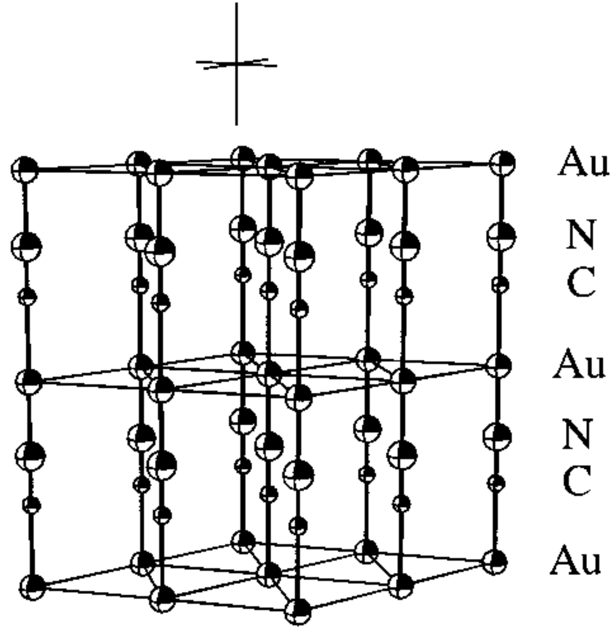
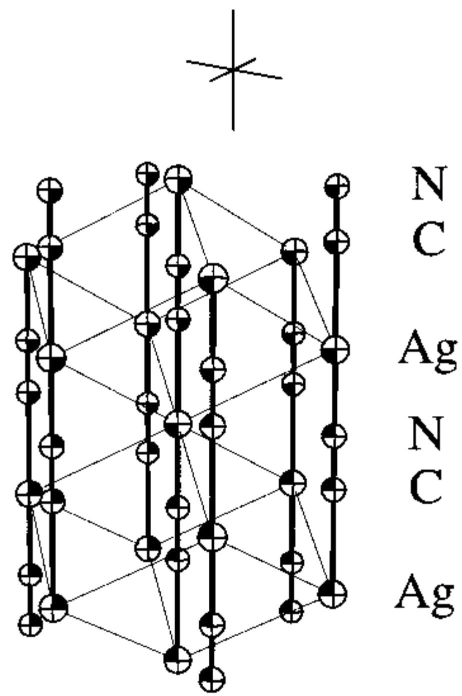


Fig. 44 Different molecular structures of sulfur

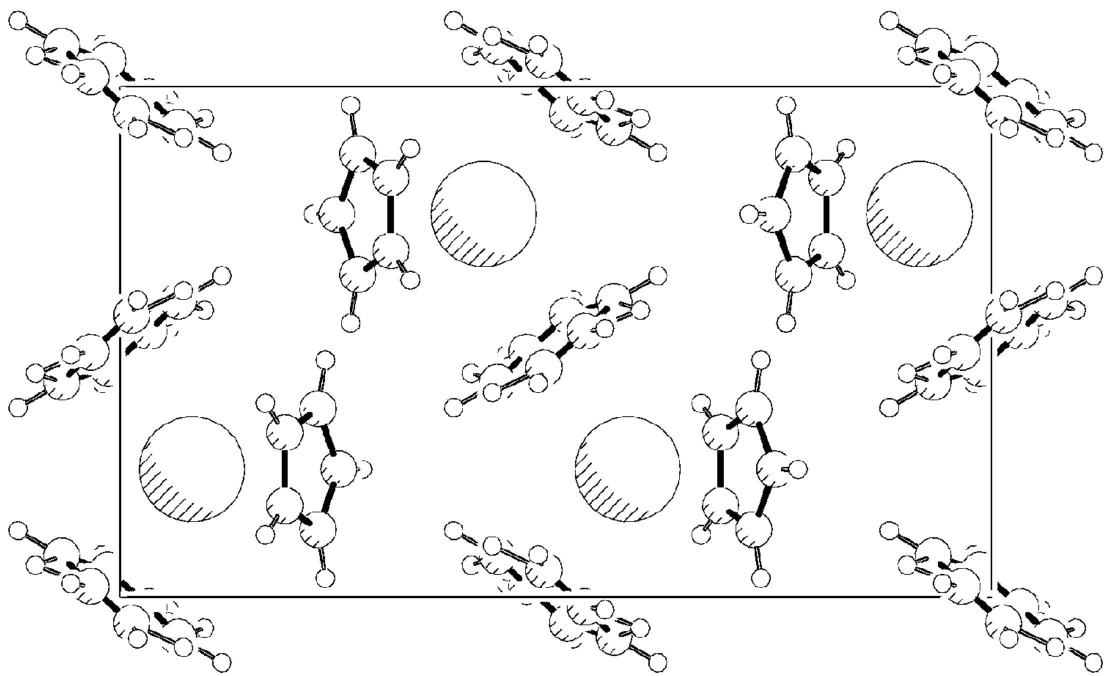
AuCN
chains



AgCN
chains



$Pb(\eta^5\text{-}C_5H_5)_2$ zig-zag chains



$BeCl_2$ solid

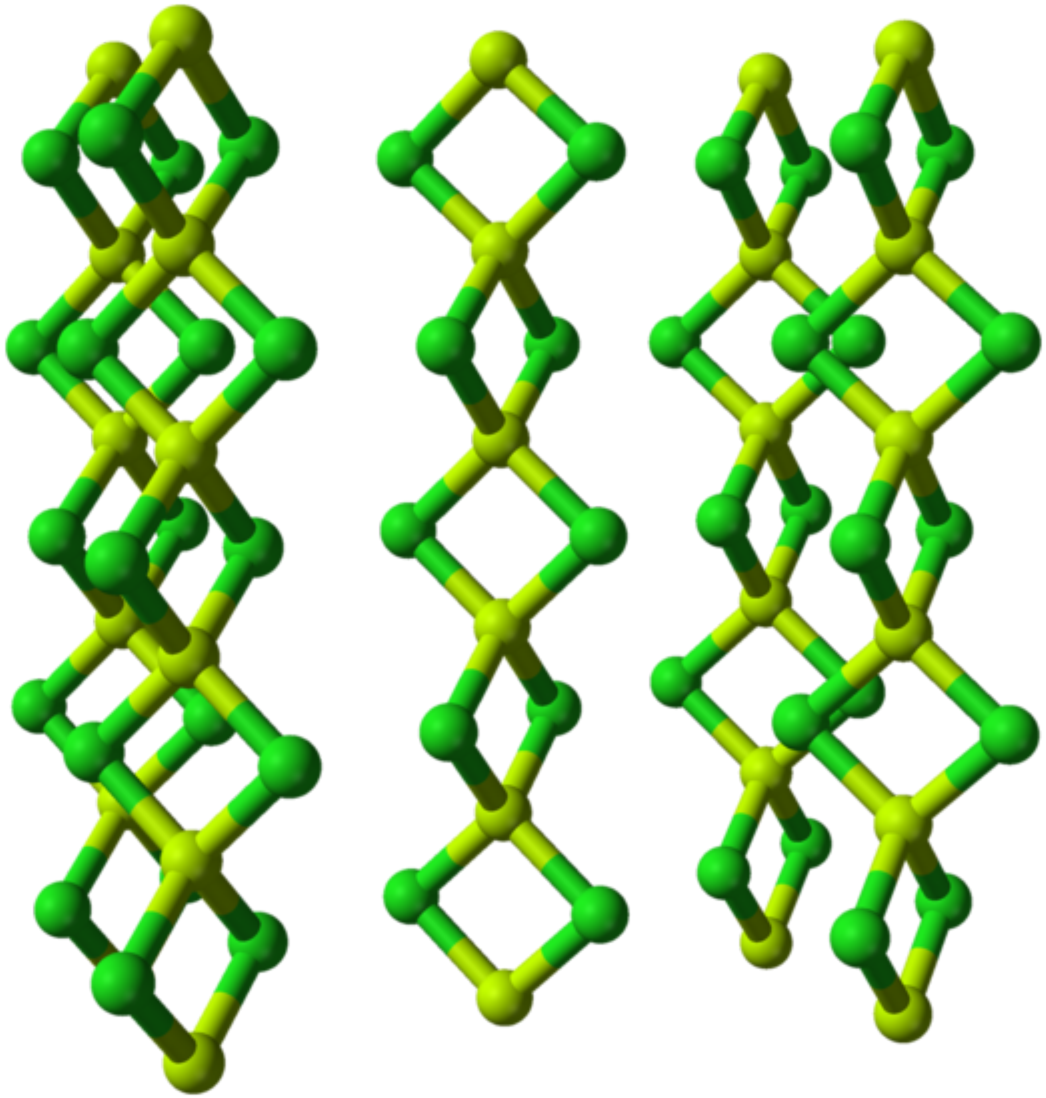
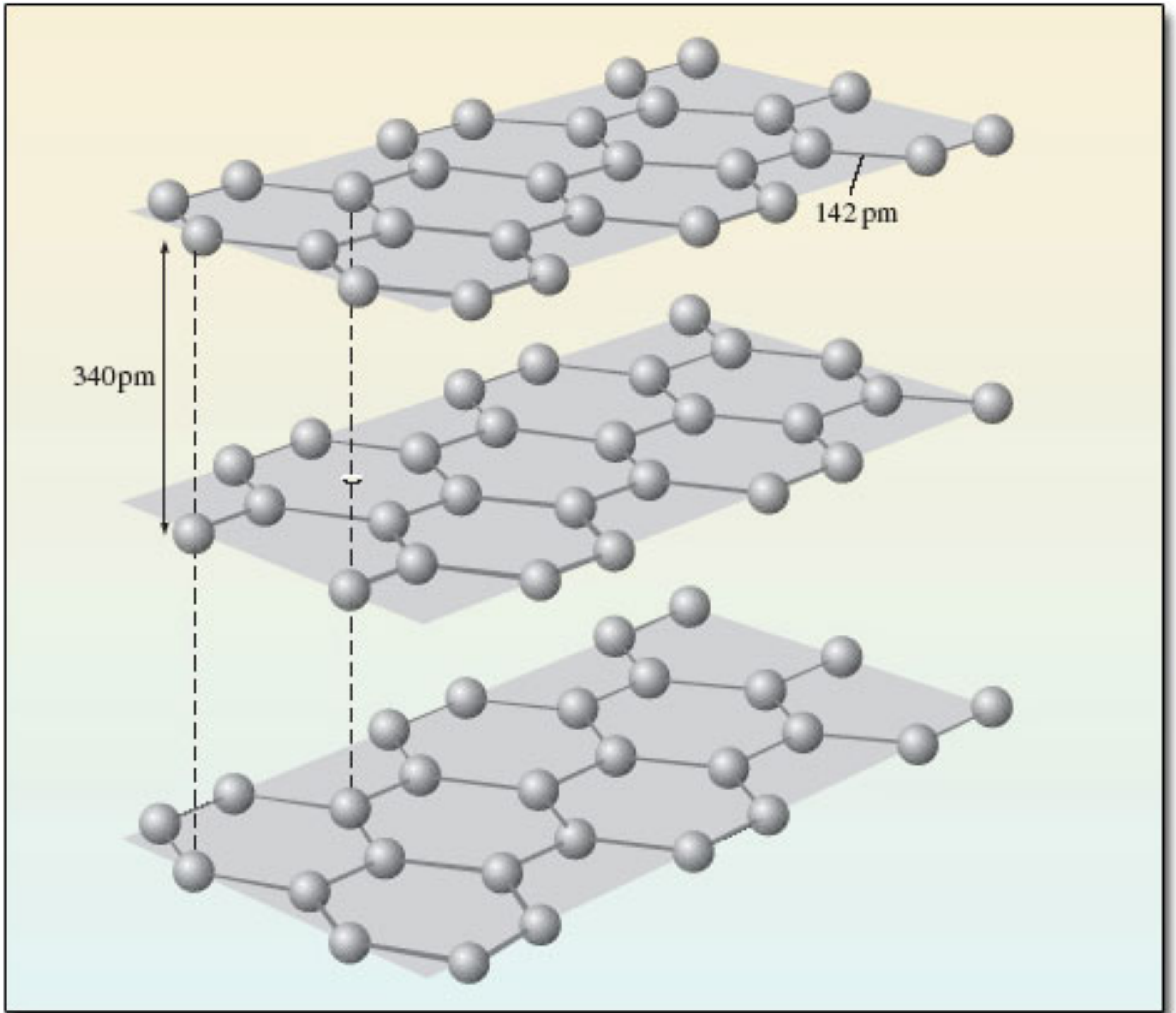


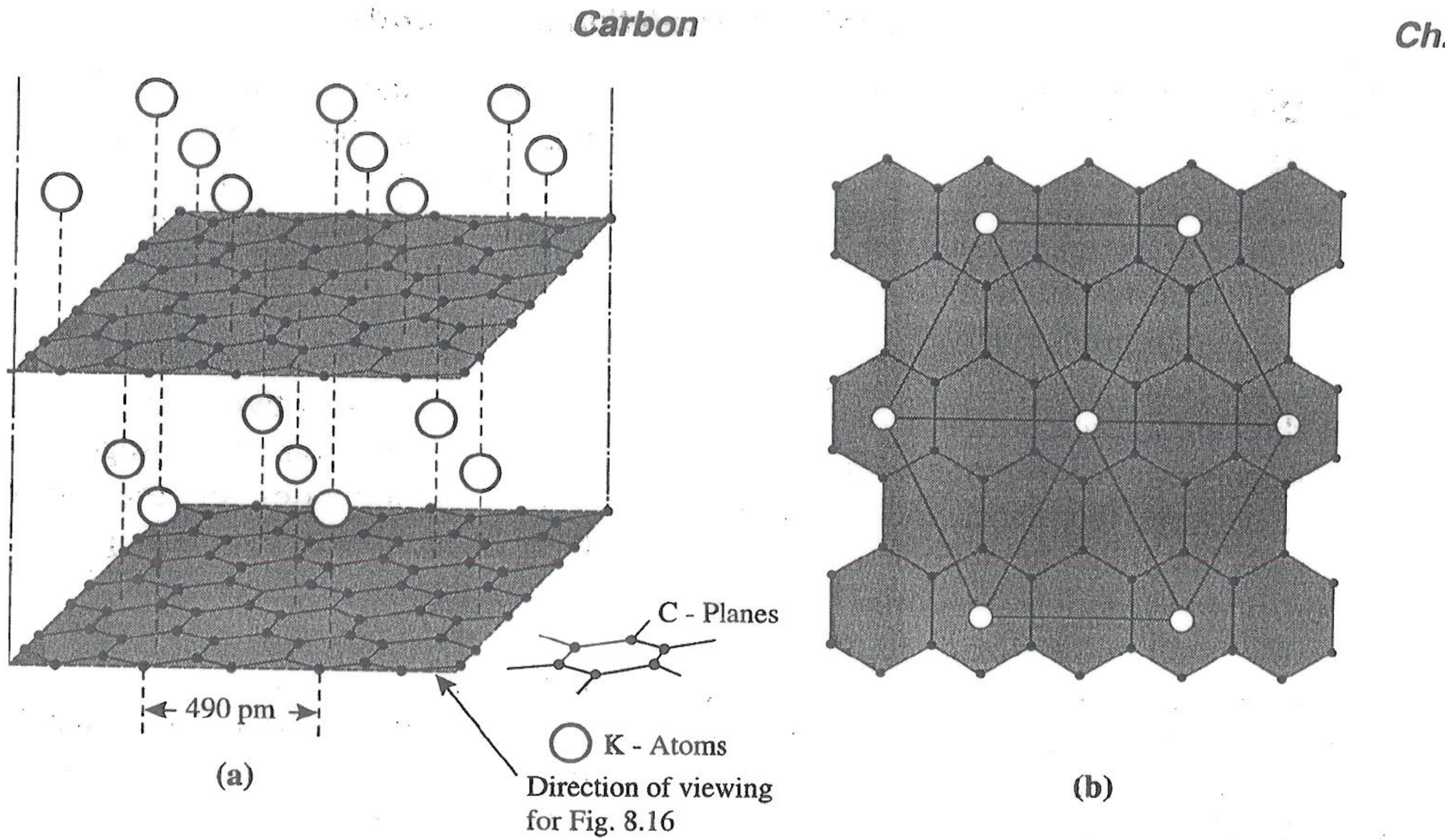
TABLE 3.11

Layers based on the simple hexagon net

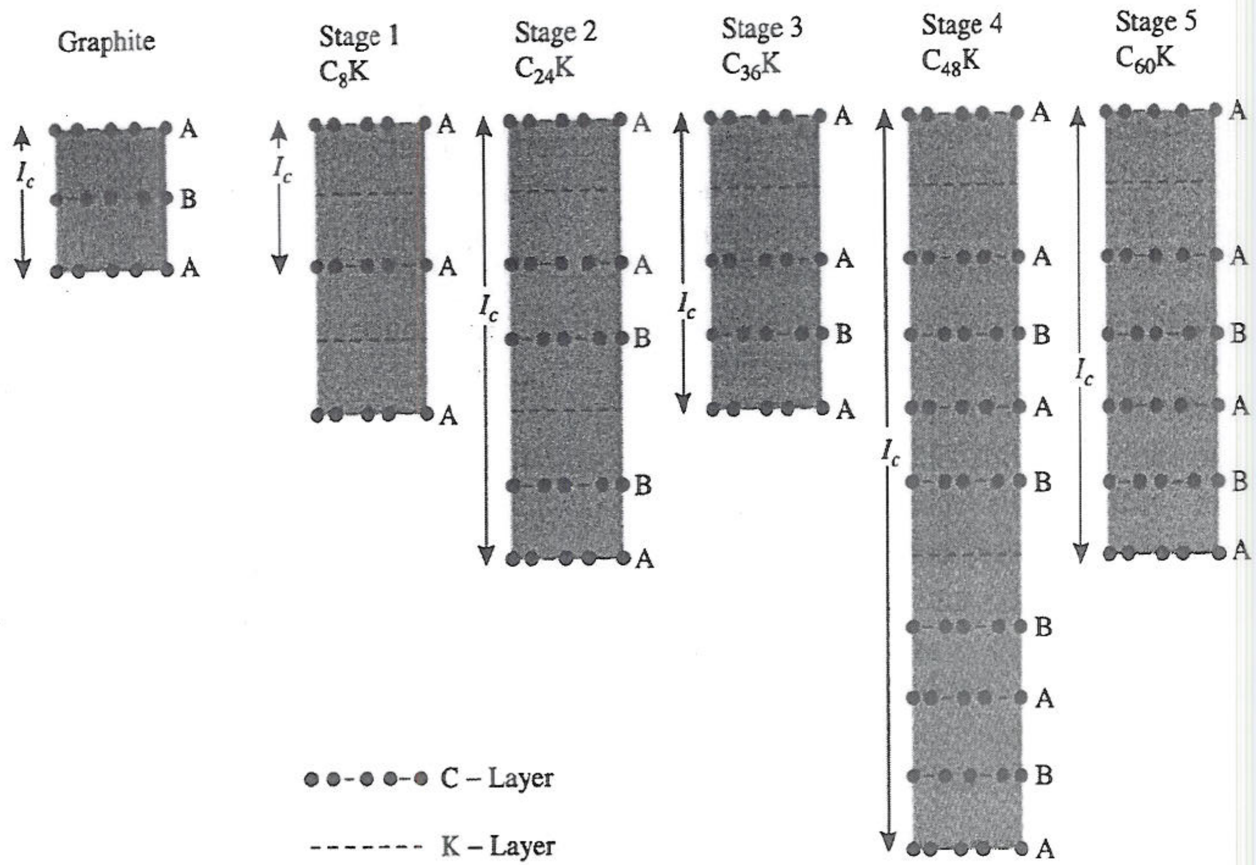
Layer type	*Examples*
A	C (graphite), As, Sb, Bi, P (black) $CaSi_2$, AlB_2 $B(OH)_3$
AB	BN, GeS, SnS $(H_3O)^+Cl^-$, $(H_3O)^+NO_3^-$, $(H_3O)^+ClO_4^-$ $Ag[S_3(CH_2)_3]ClO_4 . H_2O$, $Ag[S_3(CH_2)_3]NO_3 . H_2O$ $Ag[C(CN)_3]$ (two interwoven layers)
A_2X_3	As_2O_3, As_2S_3 $Na[H_3(SeO_3)_2]$, $(Te_2O_3)SO_4$
A_2X_5	P_2O_5 $Li_2(Si_2O_5)$, $Rb(Be_2F_5)$, $Pb_2(Ga_2S_5)$
AX_3	YCl_3, BiI_3, $Al(OH)_3$
AX_4	ThI_4


142 pm
340pm

Intercalation of inorganic cations between graphite layers



Stages of intercalation



ure 8.16 Layer-plane sequence along the c-axis for graphite in various stage 1–5 of alkali-metal gı intercalation compounds. Comparison with Fig. 8.15 shows that the horizontal planes are viewed diagonally across the figure. I_c is the interlayer repeat distance along the c-axis.

α-BN (hexagonal layered)

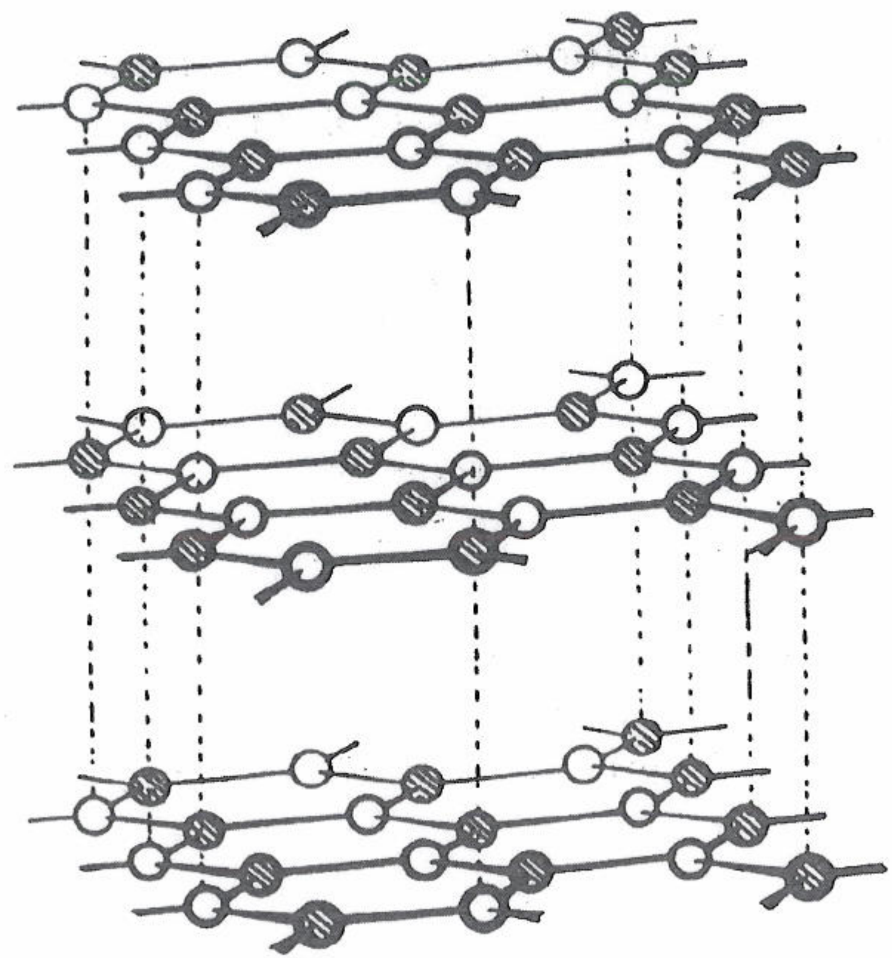
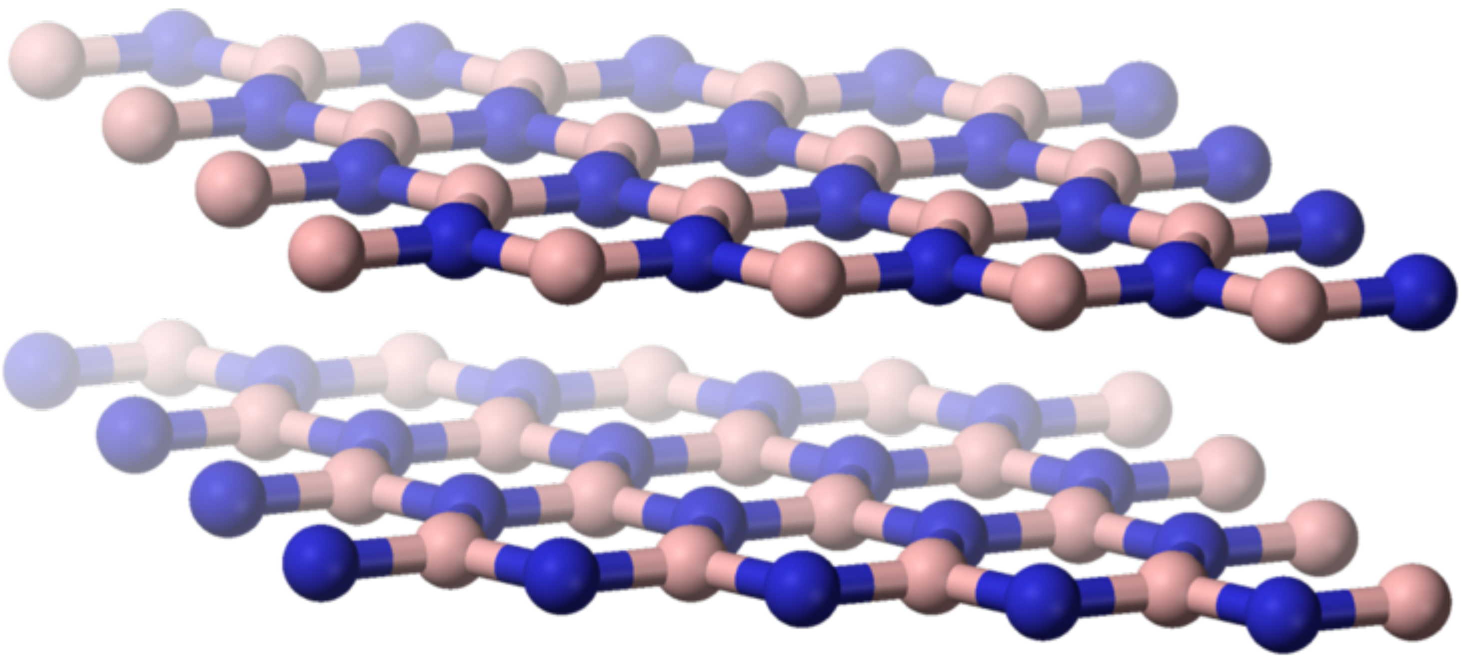
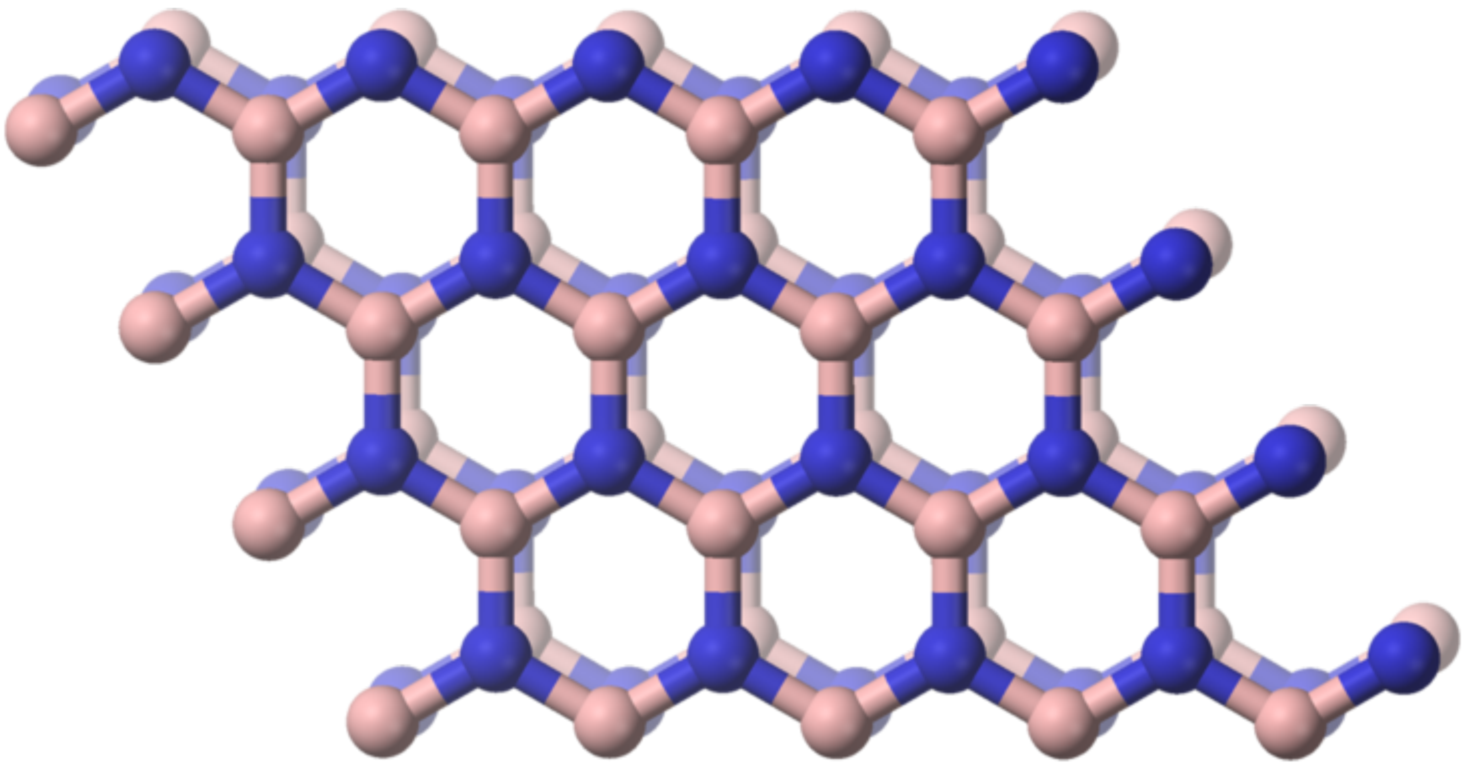


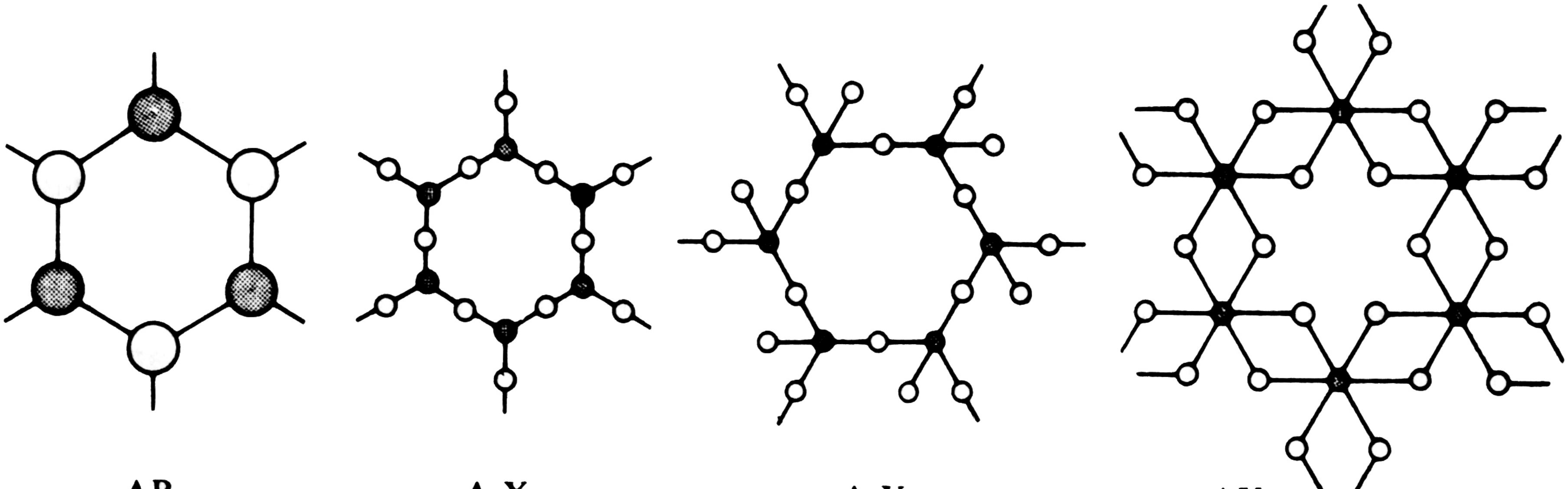
FIG. 24.9. The crystal structure of boron nitride, BN.

α-BN



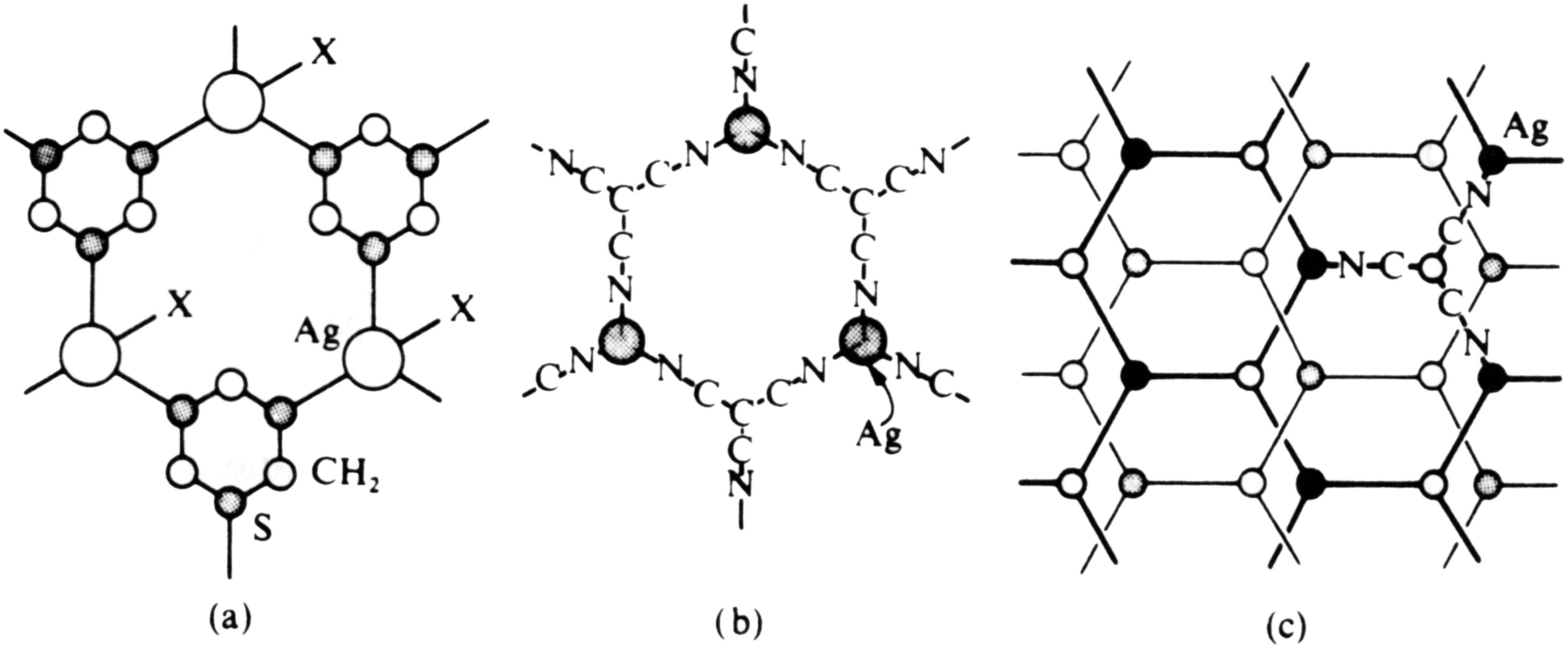
α-BN





AB A_2X_3 A_2X_5 AX_3

The structures of binary compounds based on the plane 6-gon net.



Layers in the structures of (a) $Ag[S_3(CH_2)_3]NO_3{\cdot}H_2O$; (b) $Ag[C(CN)_3]$; (c) two interwoven layers of type (b).

Black P

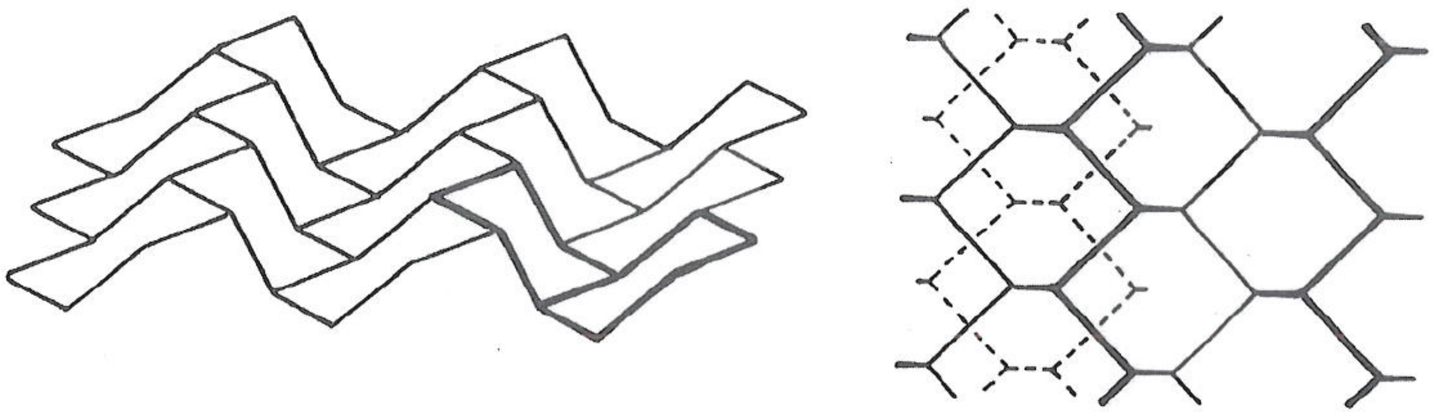
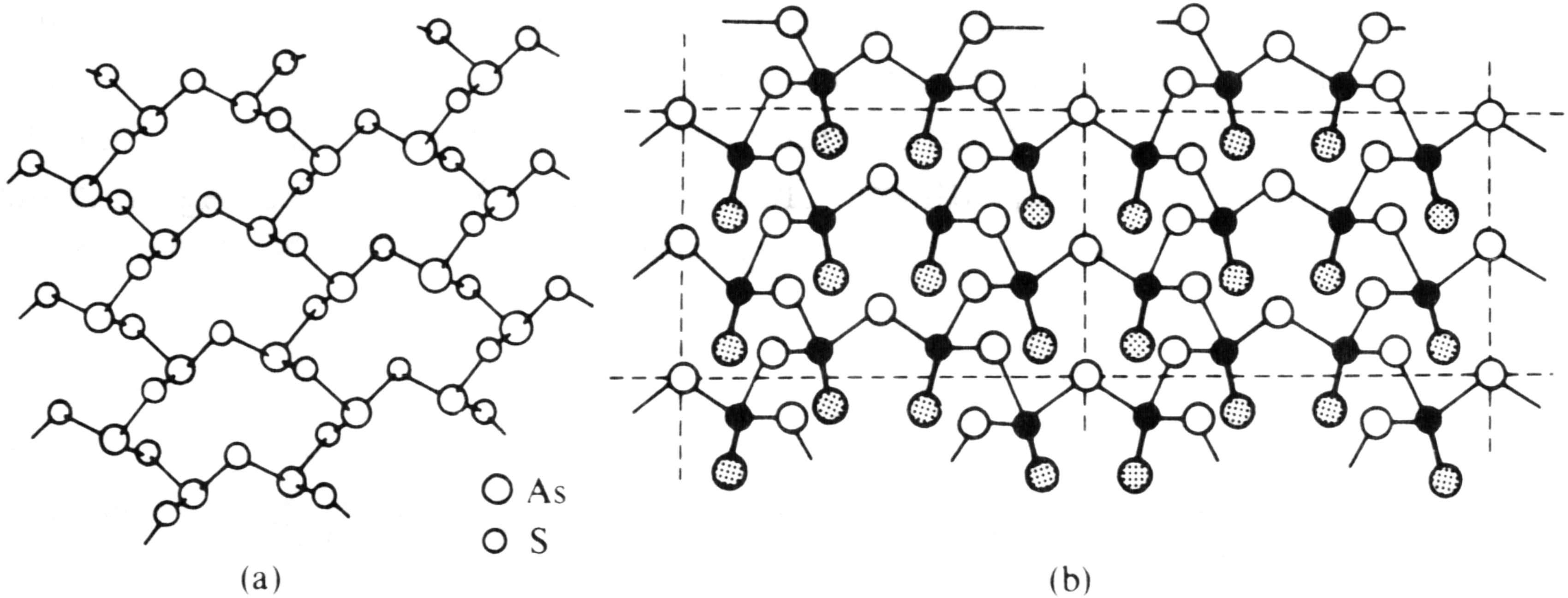
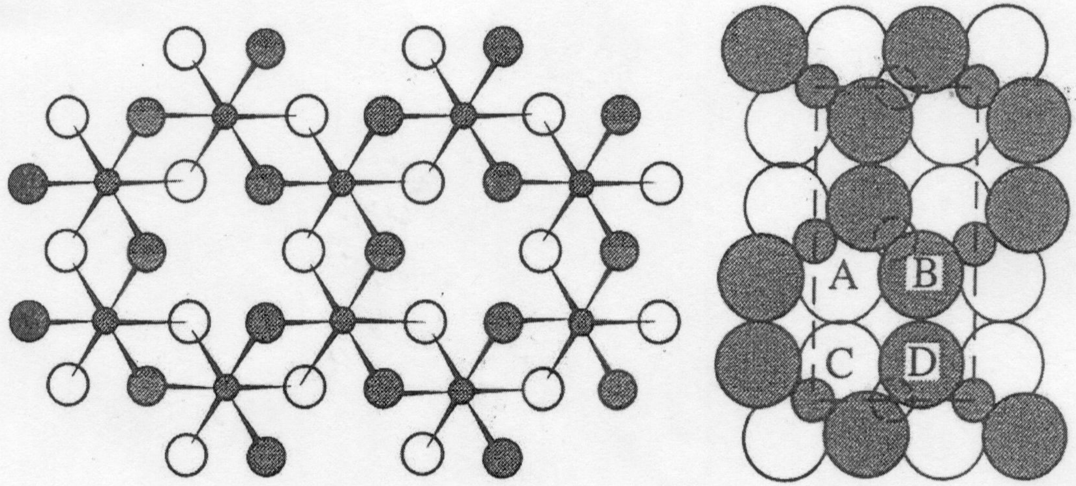


Fig. 48
The structure of black phosphorus.
Left: section of one layer; two rings with chair conformation and relative arrangement as in *cis*-decaline are emphasized. Right: top view of a layer showing the zigzag lines; the position of the next layer is indicated

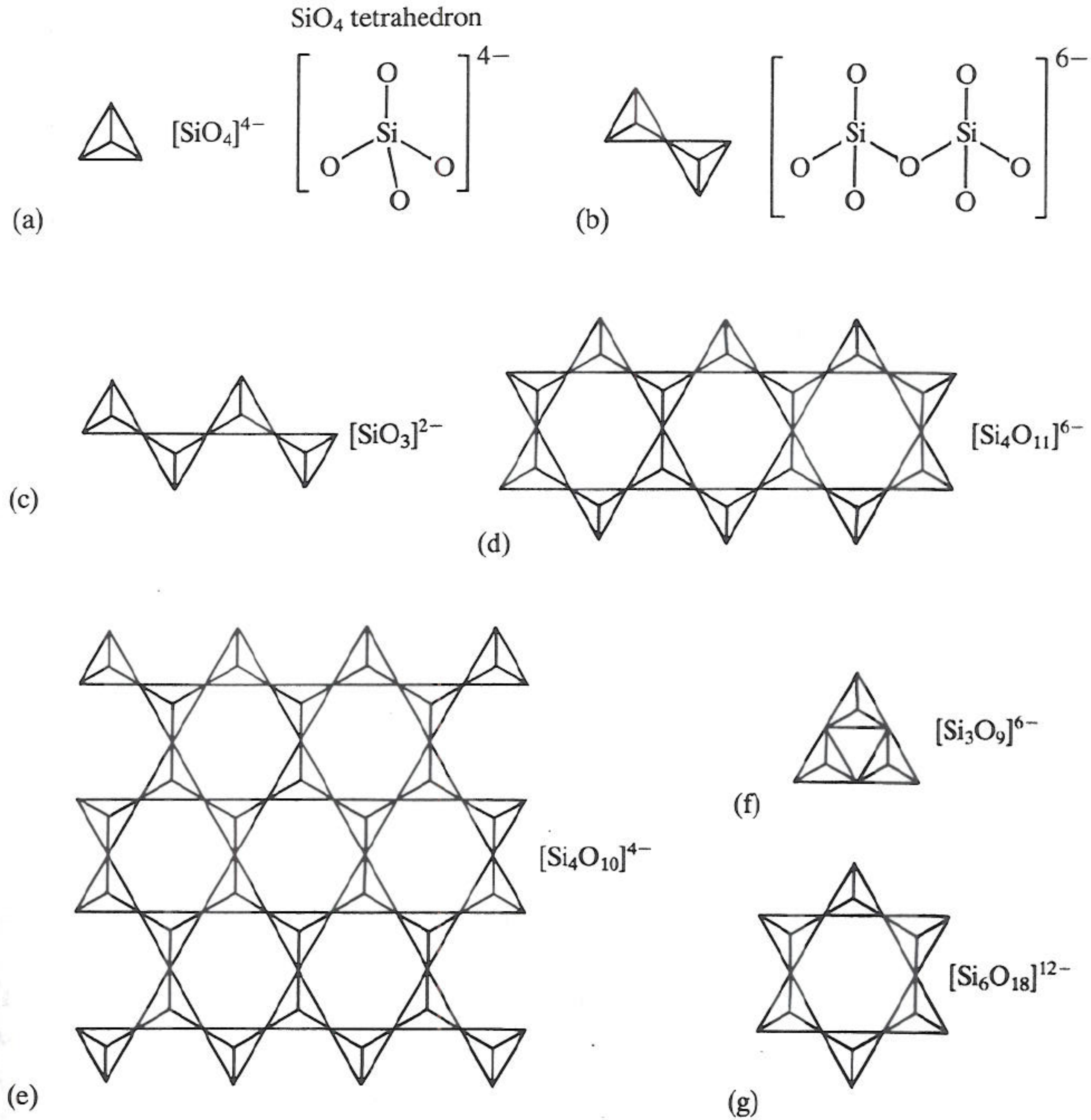


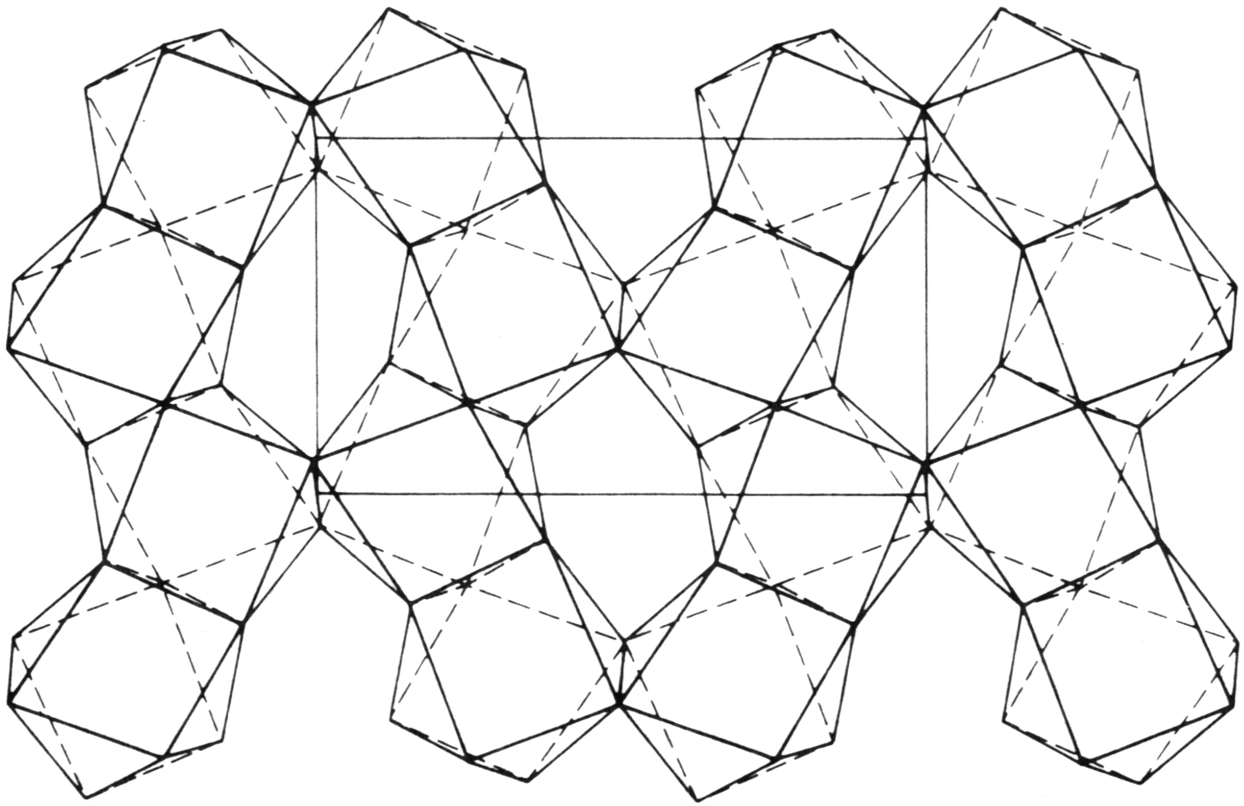
Layers in (a) As_2O_3 (orpiment); (b) P_2O_5.



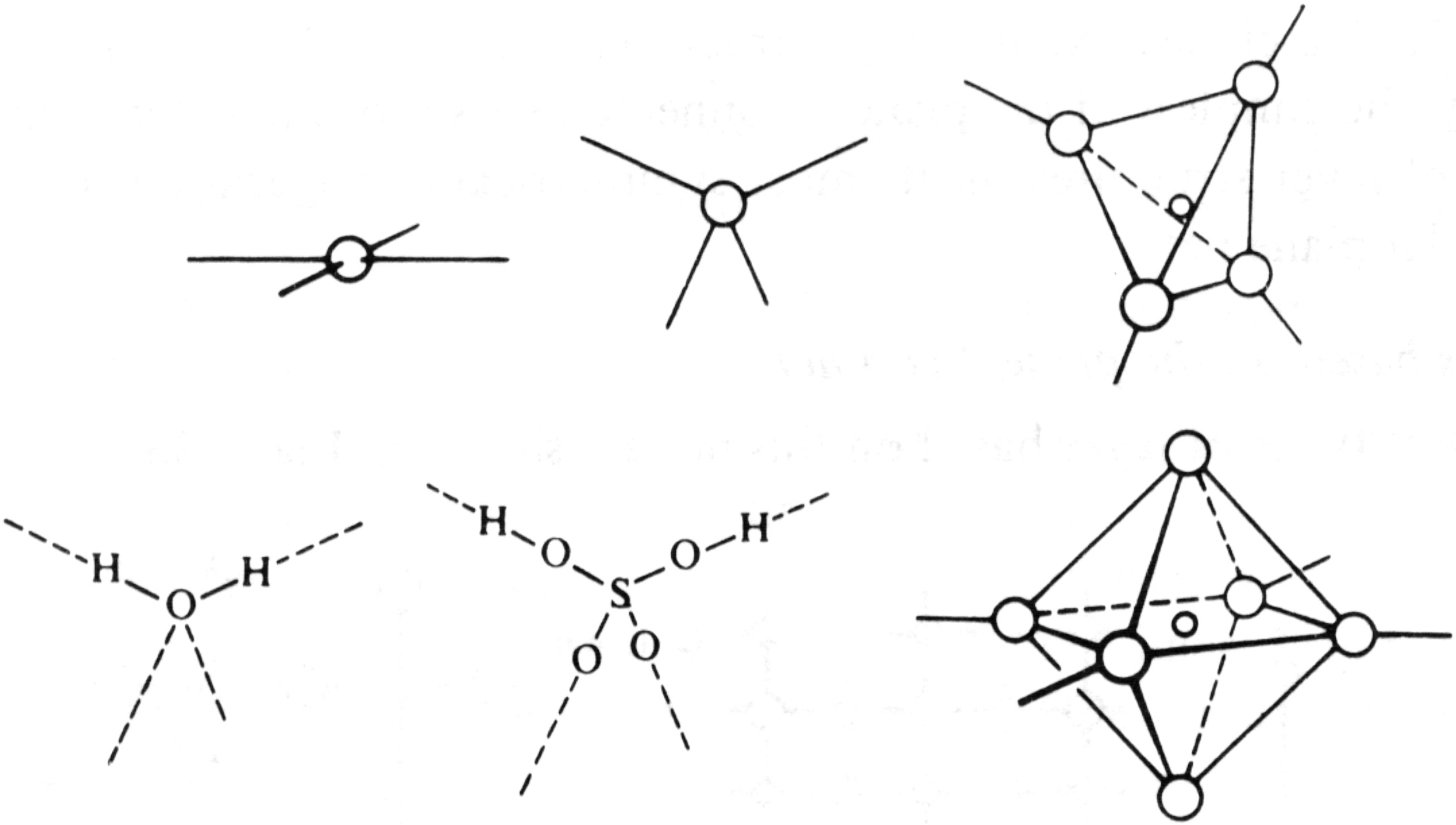
(a) (b)

Figure 7.12 (a) Part of a layer of $Al(OH)_3$ (idealized); the heavy and light open circles represent OH groups above and below the plane of the Al atoms. In α-$Al(OH)_3$ the layers are stacked to give approximately hcp. (b) Structure of γ-$Al(OH)_3$ viewed in a direction parallel to the layers; the OH groups labelled C and D are stacked directly beneath A and B. The six OH groups A, B, C, D and B′, D′ (behind B and D), form a distorted H-bonded trigonal prism.


SiO4 tetrahedron
[SiO4]4−
4−
O
Si
O
O
O
(a)
6−
O
O
Si
Si
O
O
O
O
O
(b)
[SiO3]2−
(c)
[Si4O11]6−
(d)
[Si4O10]4−
(e)
[Si3O9]6−
(f)
[Si6O18]12−
(g)



Layer in crystalline ThI_4.



Structural units forming 4-connected nets.

Structures based on 4-connected nets.

Plane 4-gon net

A *layers*

$SO_2(OH)_2$, $SeO_2(OH)_2$, $[B_3O_5(OH)]Ca$, $[B_6O_9(OH)_2]Sr \cdot 3\,H_2O$

AX *layers* (4 : 4)

PbO, LiOH, $Pd(S_2)$

AX_2 *layers* (4 : 2)

HgI_2 (red), γ-$ZnCl_2$, $(ZnO_2)Sr$, $Zn(S_2COEt)_2$, $Cu(CN)(N_2H_4)$

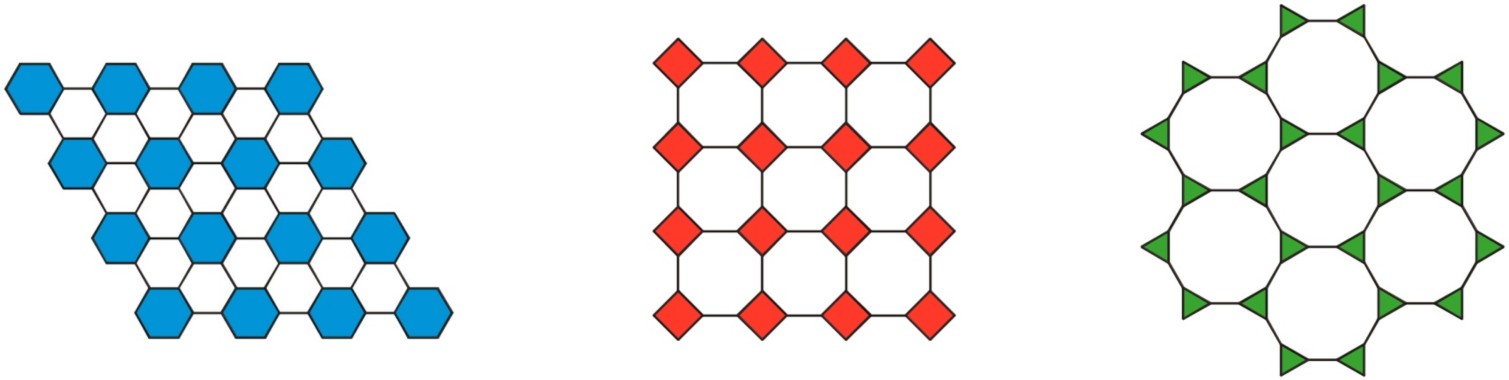
AX_2 *layers with additional ligands attached to* A

AX_2Y: $[Ni(CN)_2 \cdot NH_3]C_6H_6$

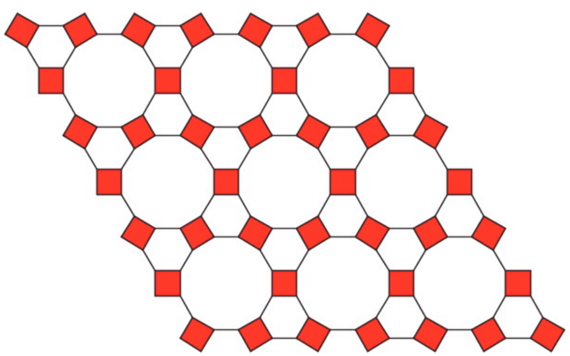
AX_2Y_2: $SnF_2(CH_3)_2$, $UO_2(OH)_2$

AX_4: SnF_4, $(NiF_4)K_2$, $(AlF_4)Tl$

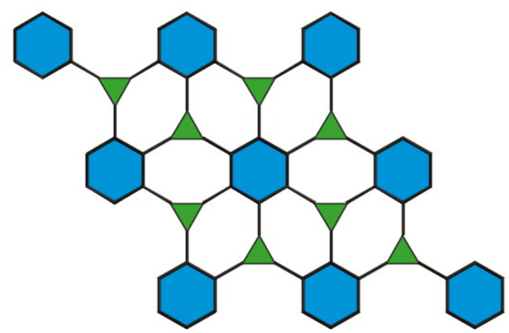
All possible ways of linking polygons with one kind of link to form 2-periodic structures



augmented regular nets



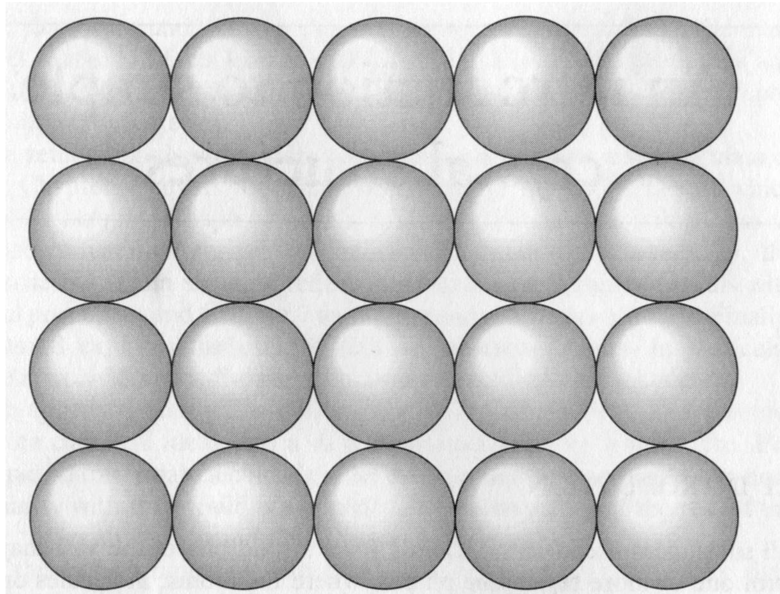
augmented quasiregular



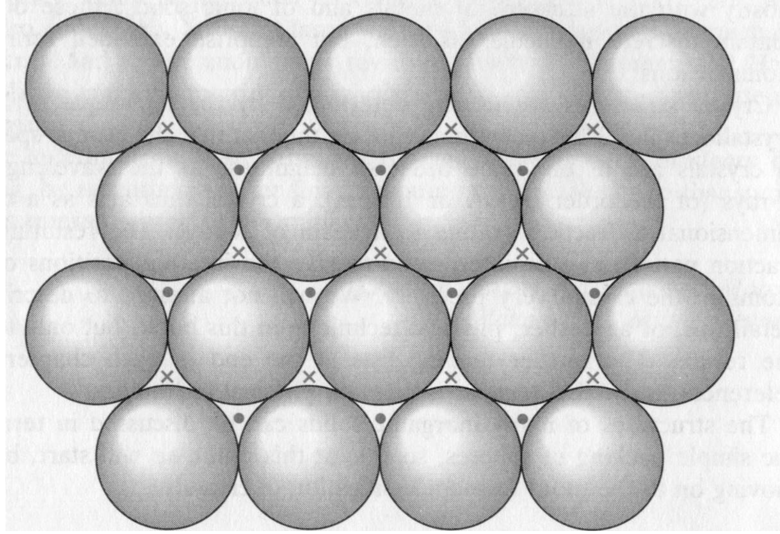
augmented dual of quasiregular

Infinite three dimensional networks

Packing of spheres



CLOSE Packing of spheres



Tetrahedral and octahedral holes

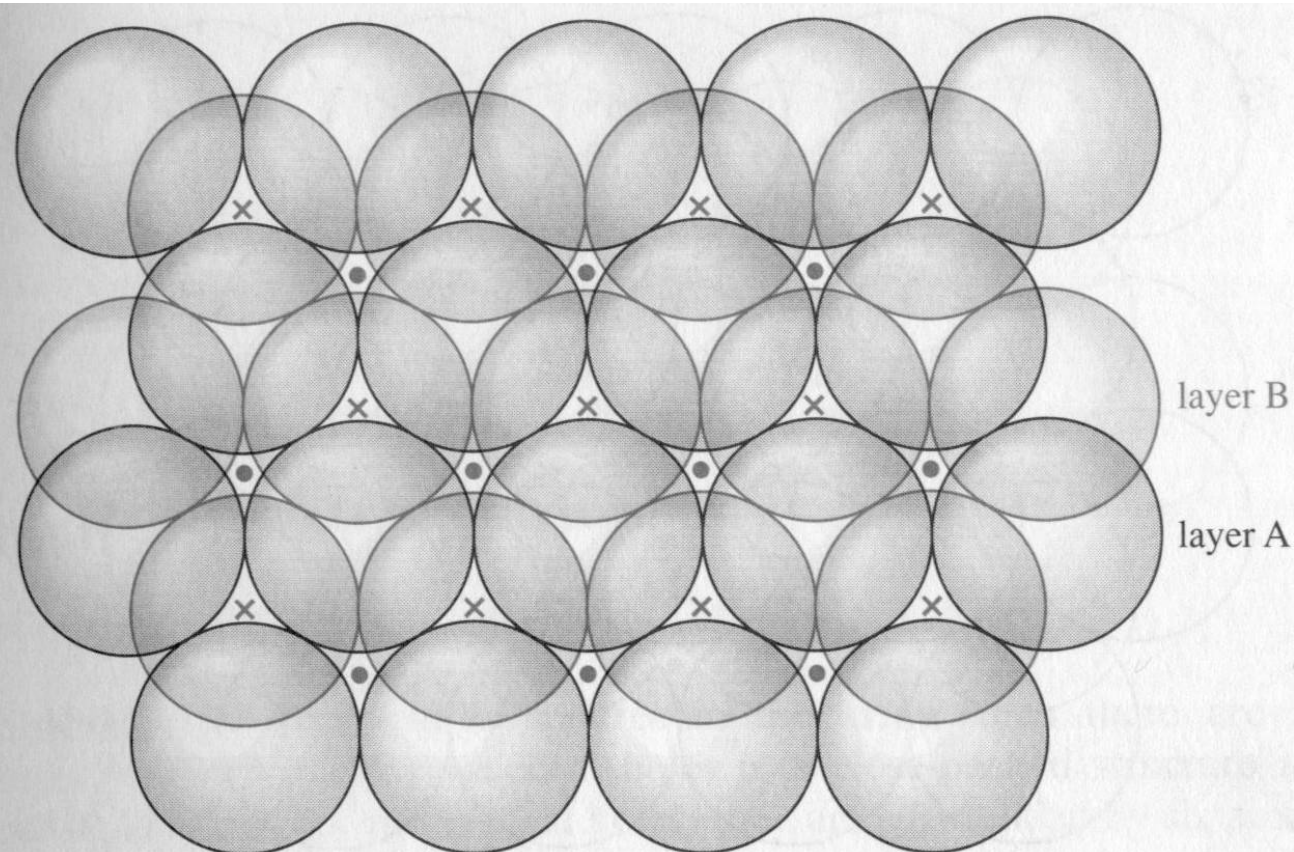


Figure 1.2 Two layers of close-packed spheres.

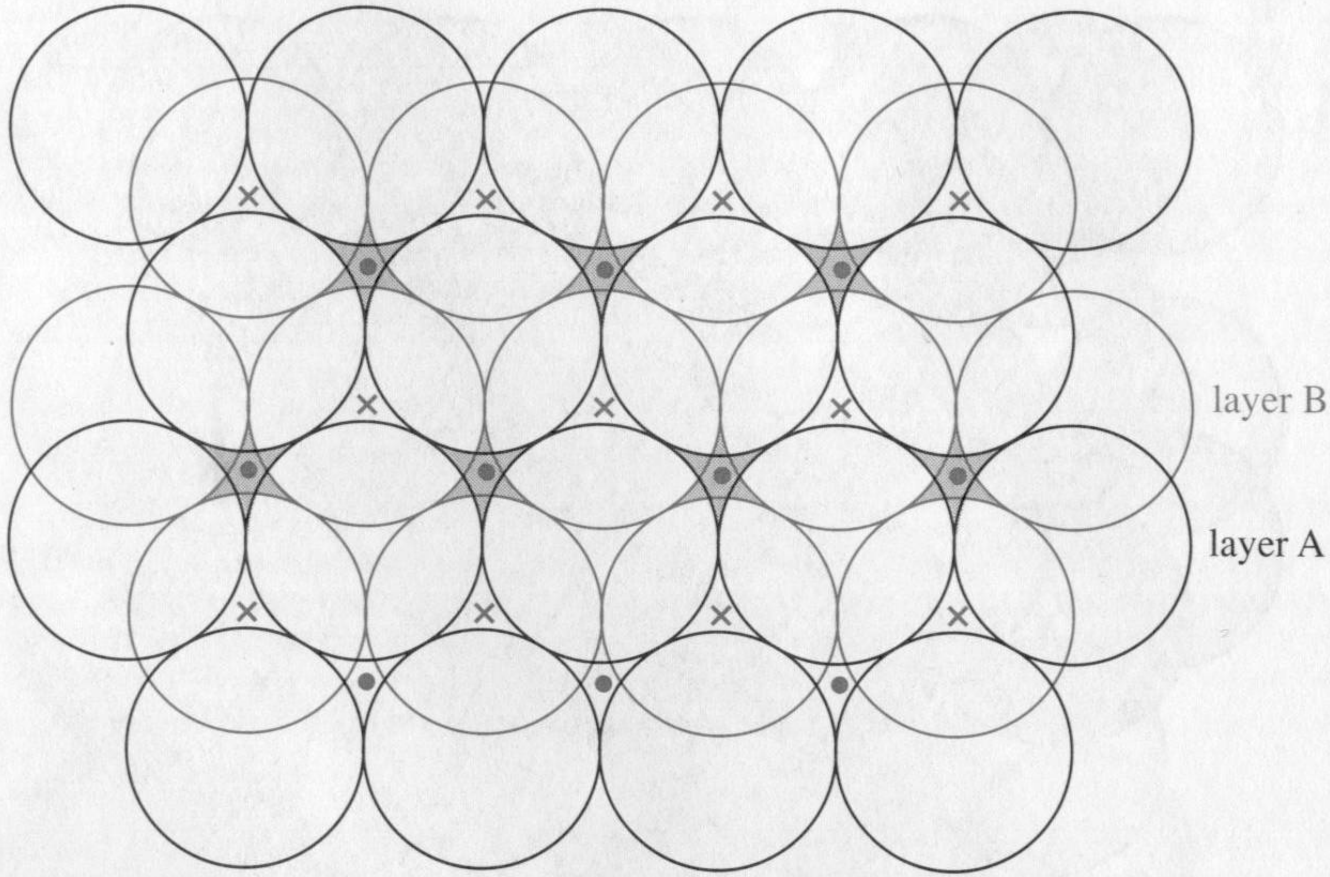


Figure 1.3 Two layers of close-packed spheres with the enclosed octahedral holes picked out in colour.

One octahedral hole per sphere. Twice as many tetrahedral holes per sphere

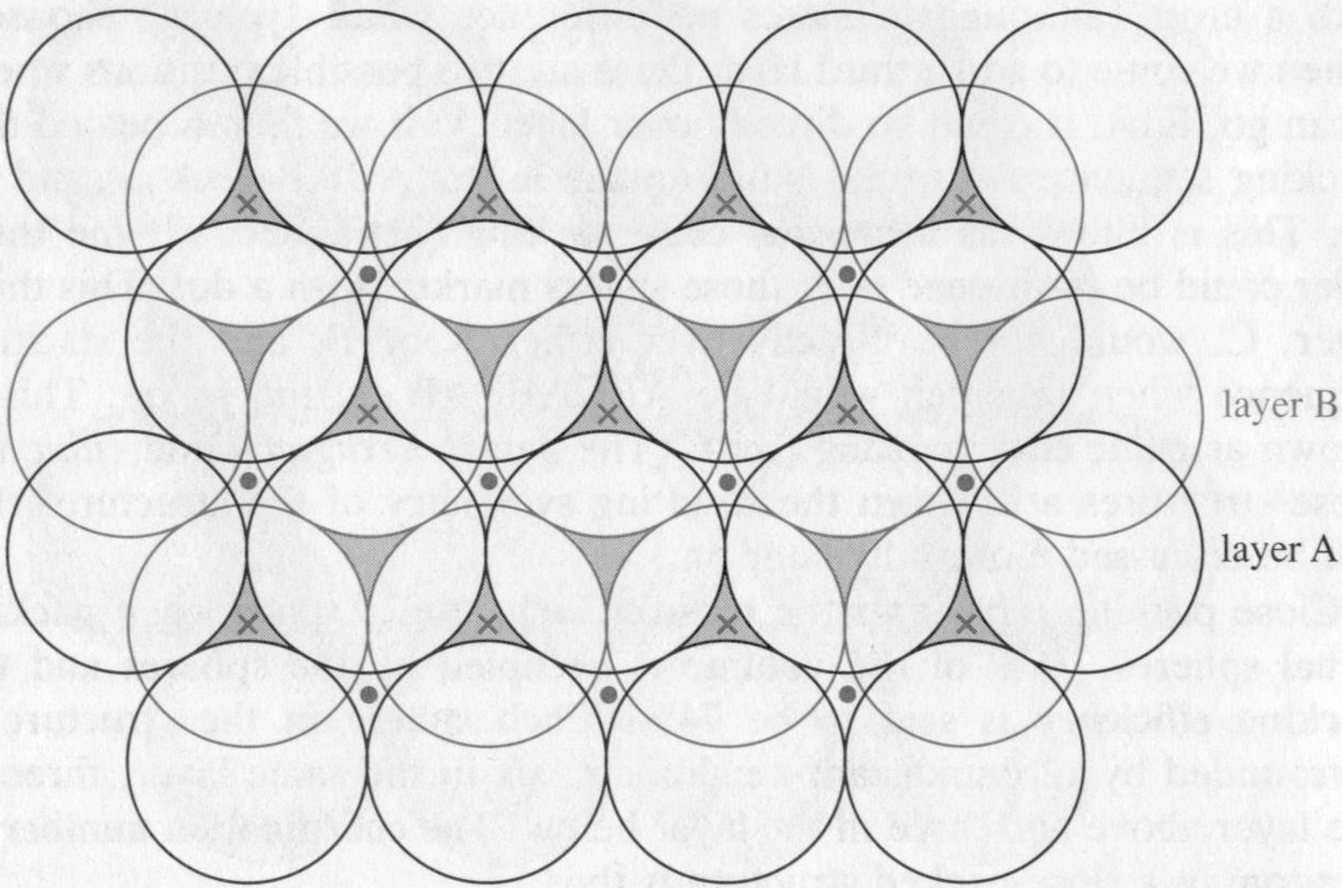
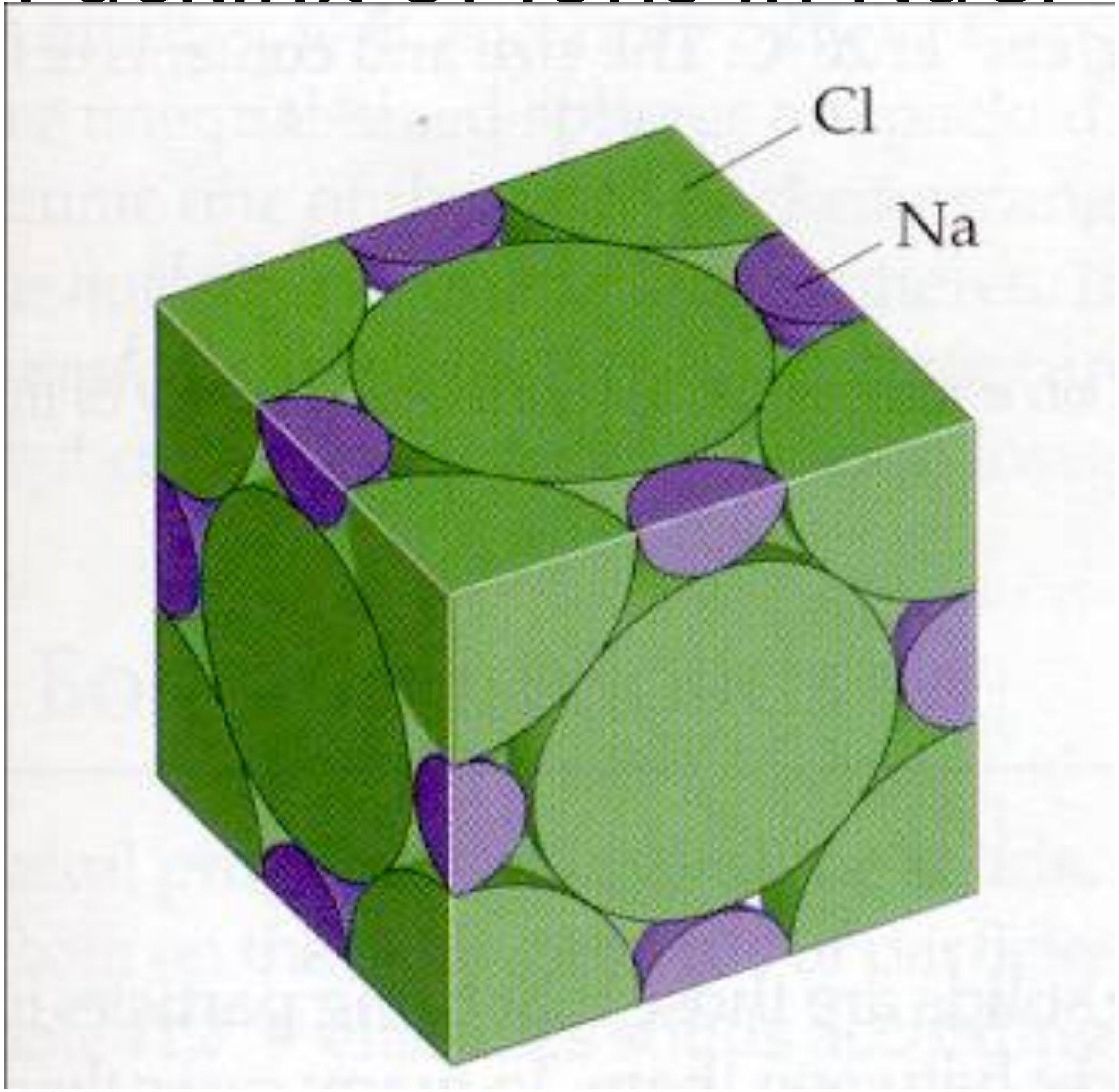


Figure 1.4 Two layers of close-packed spheres with the tetrahedral holes picked out in colour.

Packing of ions in NaCl



Packing of metals

Table 5.1. Packing in Metals

Type of Packing	Packing Efficiency[a]	Coordination Number
Simple cubic (sc)♦	52%	6
Body-centered cubic (bcc)♦	68%	8
Hexagonal close-packed (hcp)♦	74%	12
Cubic close-packed (ccp)♦[b]	74%	12

[a]Measurement of the volumes of the cubic unit cells and the volumes of the spheres used to build the structures, for example with the SSMK, will allow an experimental determination of the packing efficiency that is in reasonably good agreement with these values.

[b]Identical to face-centered cubic (fcc).

Structures of metals

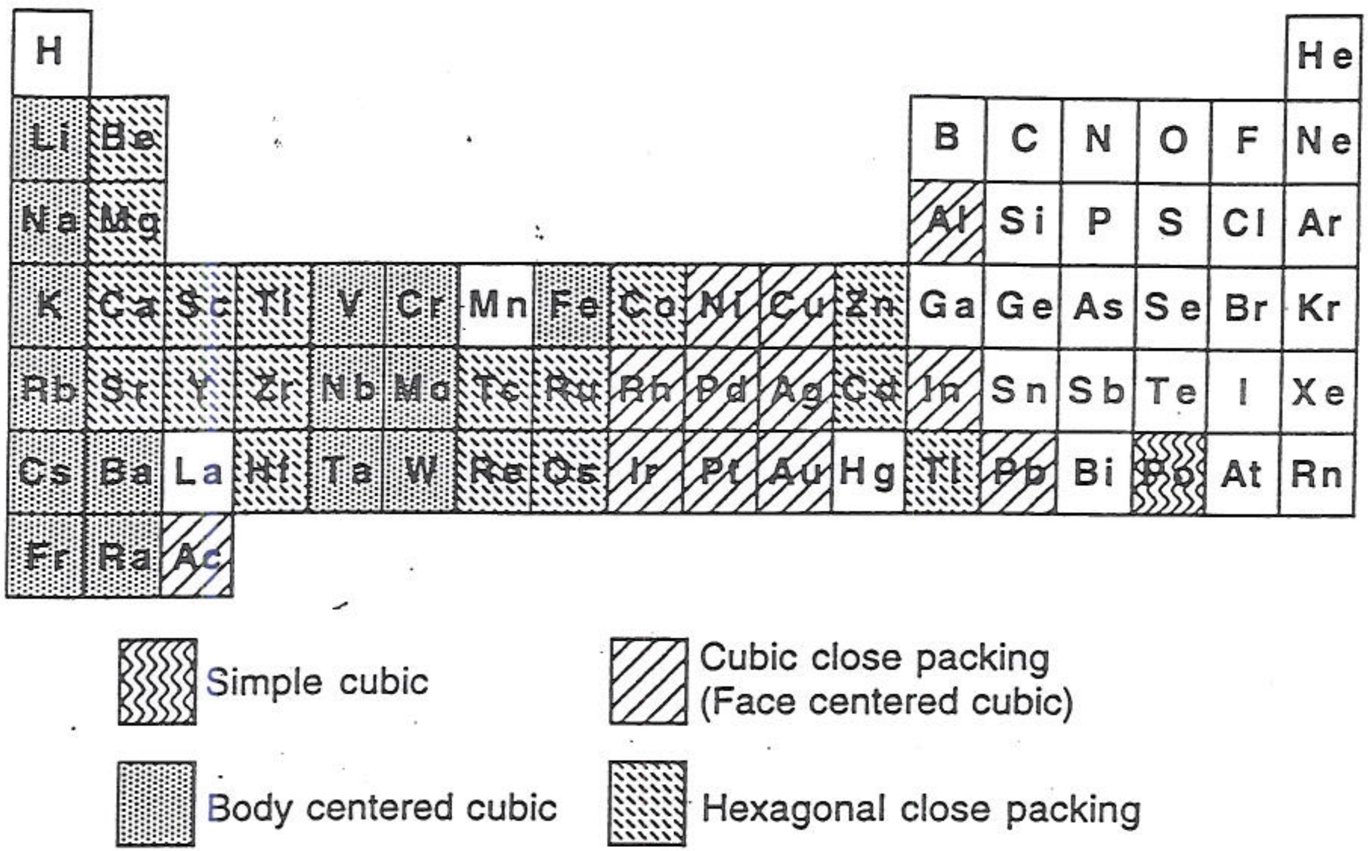


Figure 3.11. Periodic table showing the metallic elements that have one of the four indicated packing arrangements. (Data from reference 1.)

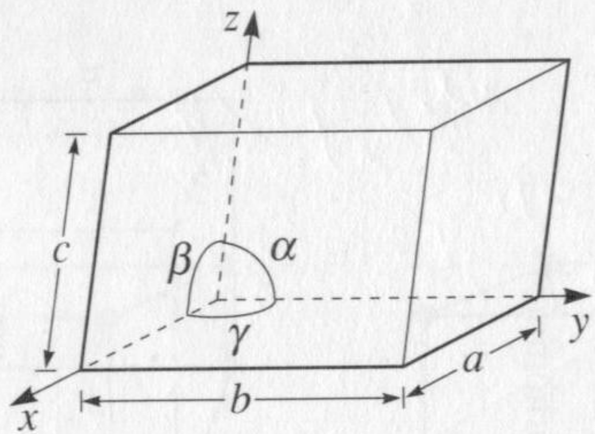
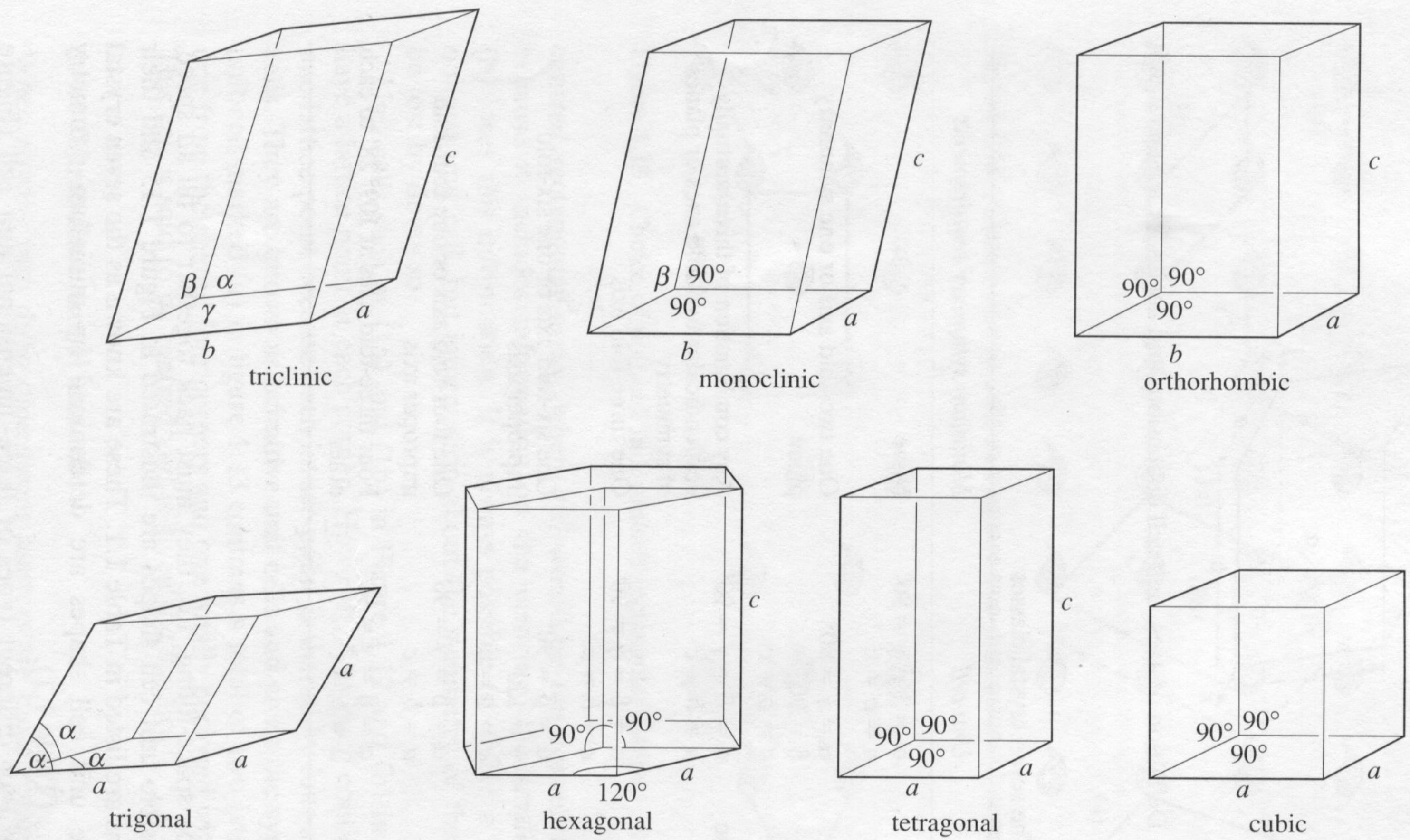


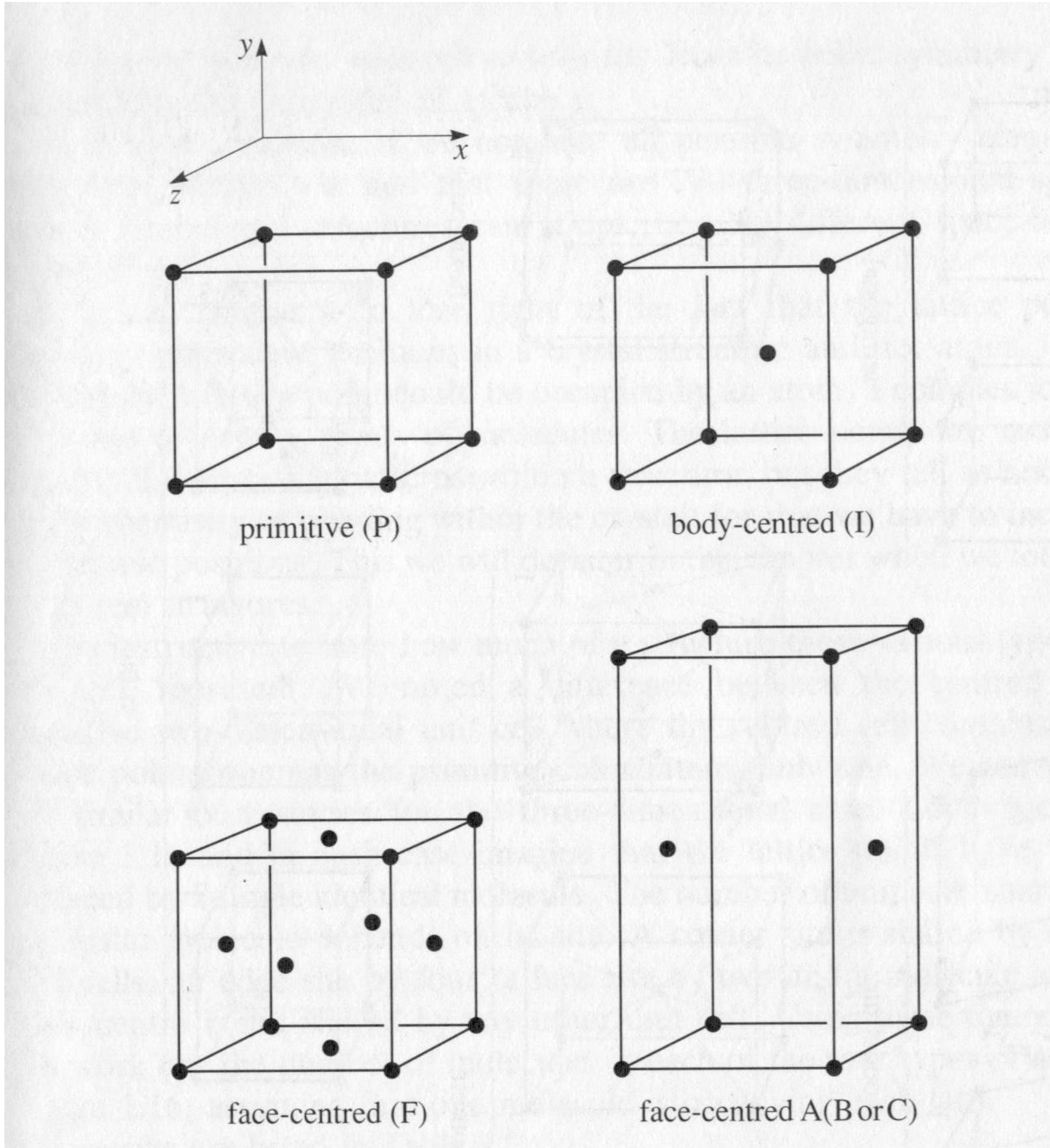
Figure 1.14 Definition of axes, unit cell dimensions and angles for a general unit cell.

Table 1.1 The seven crystal classes

System	*Unit cell*	*Minimum symmetry requirements*
Triclinic	$\alpha \neq \beta \neq \gamma \neq 90°$ $a \neq b \neq c$	None
Monoclinic	$\alpha = \gamma = 90°$ $\beta \neq 90°$ $a \neq b \neq c$	One two-fold axis or one symmetry plane
Orthorhombic	$\alpha = \beta = \gamma = 90°$ $a \neq b \neq c$	Any combination of three mutually perpendicular two-fold axes or planes of symmetry
Trigonal	$\alpha = \beta = \gamma \neq 90°$ $a = b = c$	One three-fold axis
Hexagonal	$\alpha = \beta = 90°$ $\gamma = 120°$ $a = b = c$	One six-fold axis or one six-fold improper axis
Tetragonal	$\alpha = \beta = \gamma = 90°$ $a = b \neq c$	One four-fold axis or one four-fold improper axis
Cubic	$\alpha = \beta = \gamma = 90°$ $a = b = c$	Four three-fold axes at 109° 28′ to each other


β
α
γ
c
a
b
triclinic
β
90°
90°
c
a
b
monoclinic
90°
90°
90°
c
a
b
orthorhombic
α
α
α
a
a
a
trigonal
90°
90°
c
a
a
120°
hexagonal
90°
90°
90°
c
a
a
tetragonal
90°
90°
90°
a
a
a
cubic

There are four different types of three-dimensional unit cell



The 14 Bravais lattices

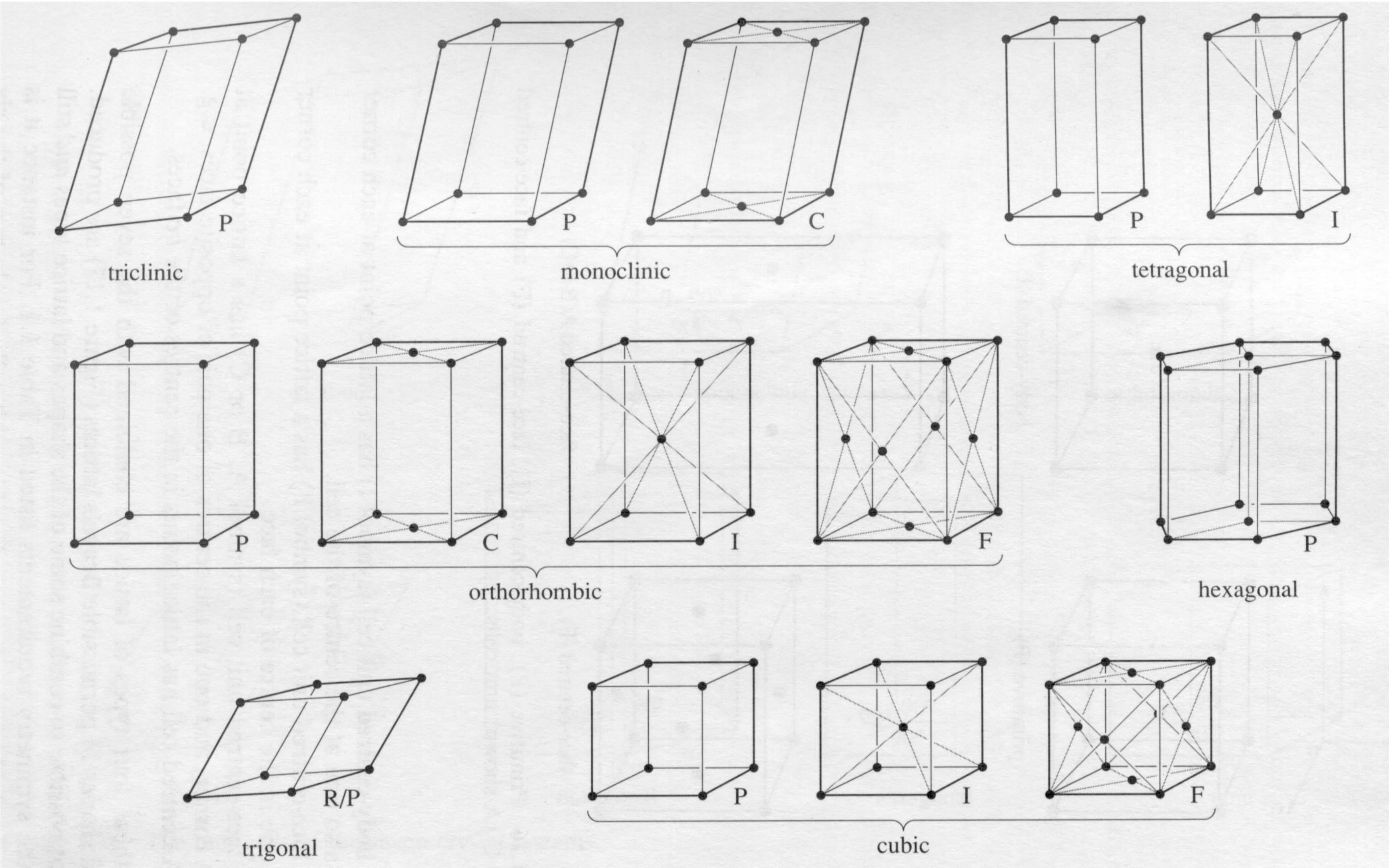
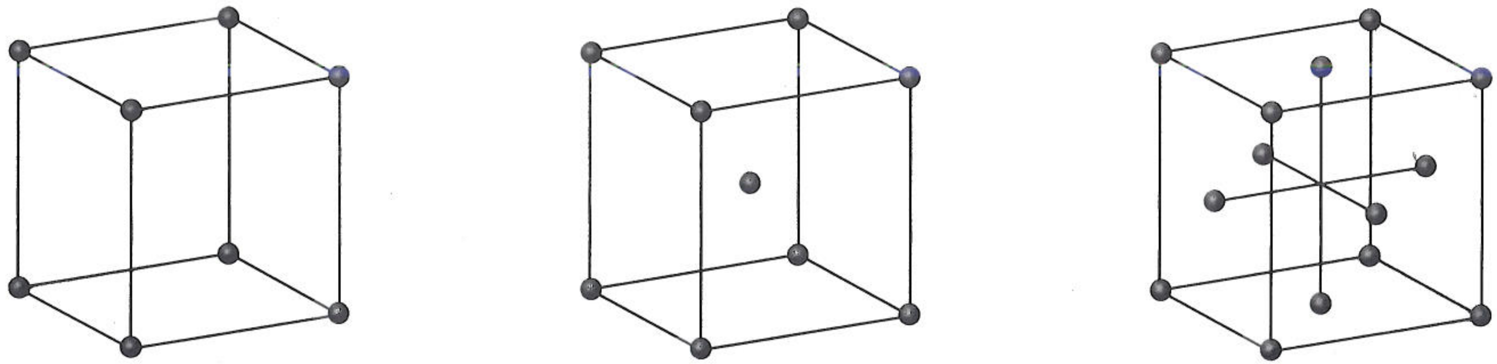
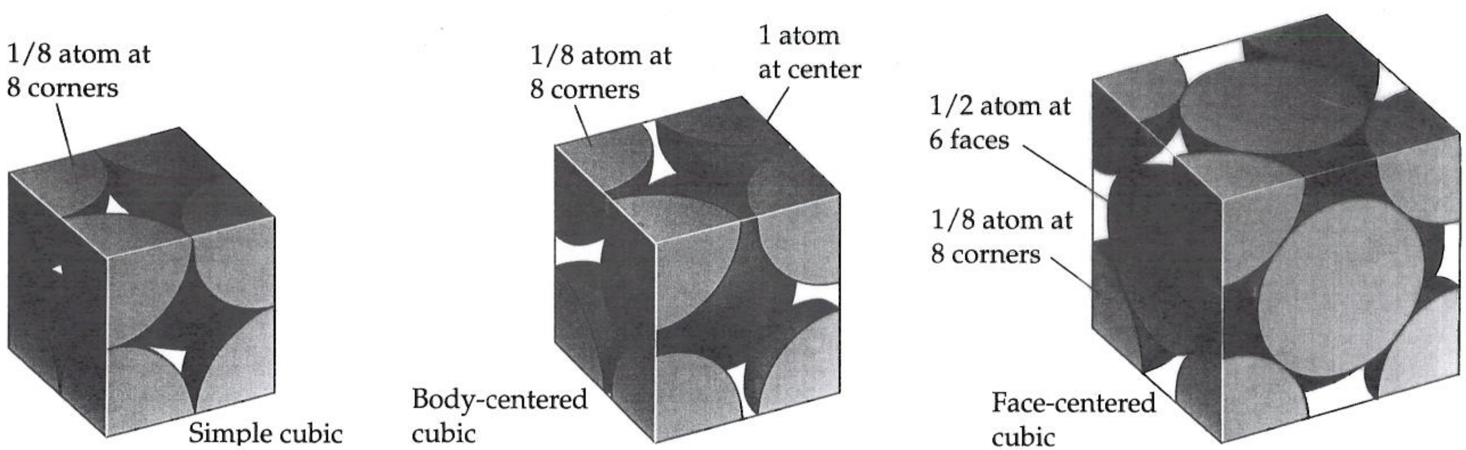


Fig. 11.31 Three Types of Unit Cells
Fig. 11.33 Space-Filling View of Cubic Unit Cells

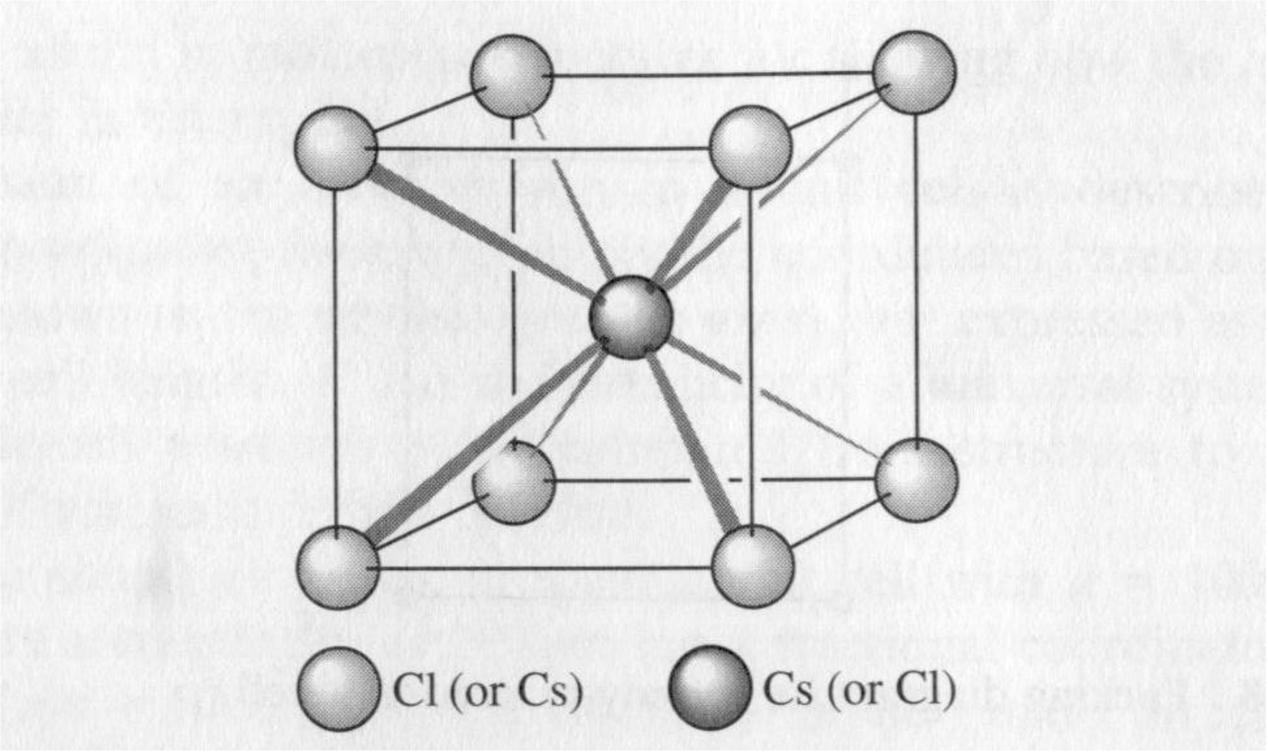


Primitive cubic | Body-centered cubic | Face-centered cubic



CHEMISTRY: The Central Science 7/e
by Brown/LeMay/Bursten

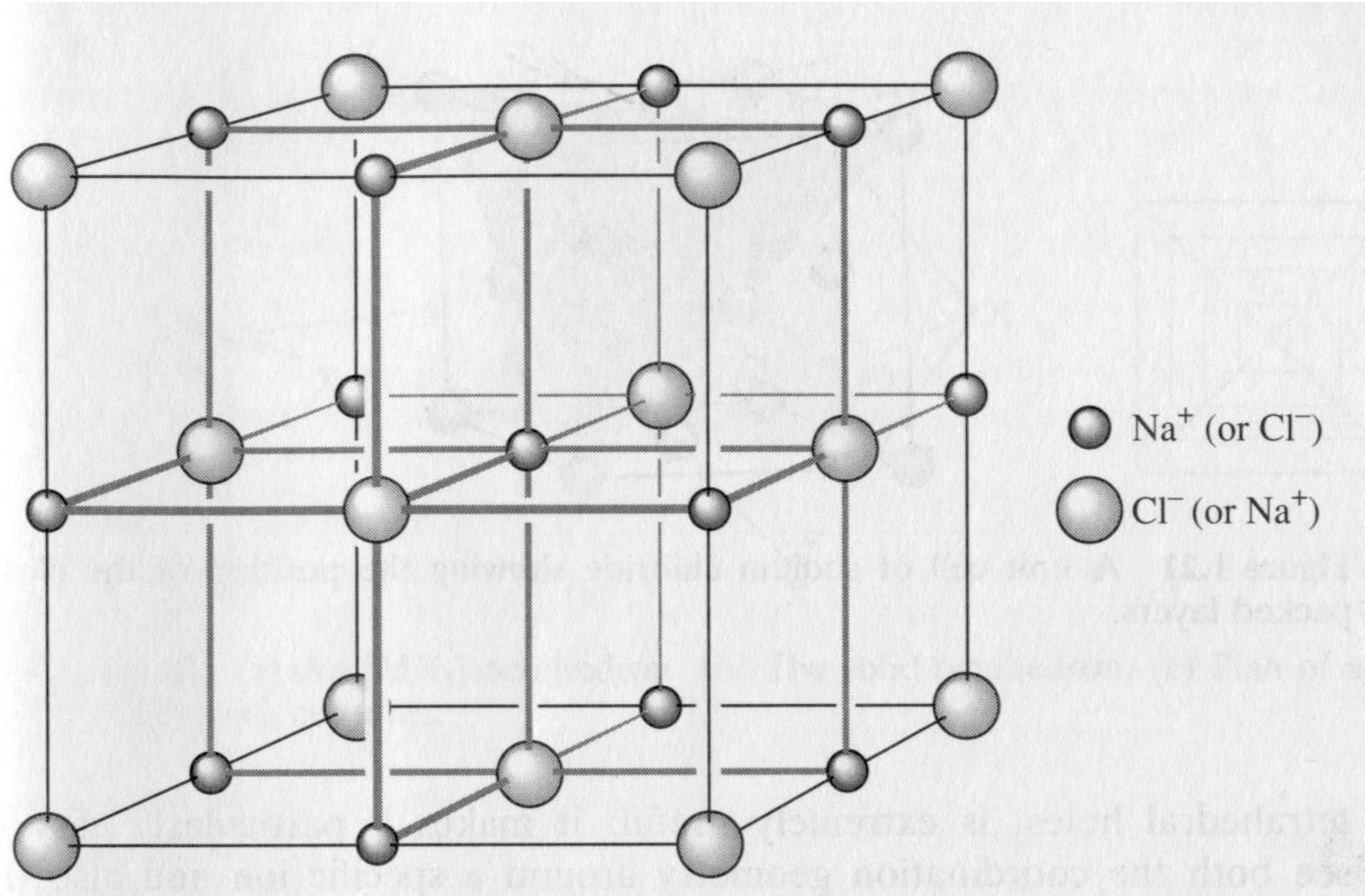
Crystal structure of CsCl (unit cell shown)



Two interpenetrating primitive cubic arrays
(note: it is not a body centered cubic because the environment of the atom at the center (Cs) is not the same as that on the corners (Cl).

Examples: CsBr, CsI, TlCl, TlI, NH4Cl and metal structures of the first group

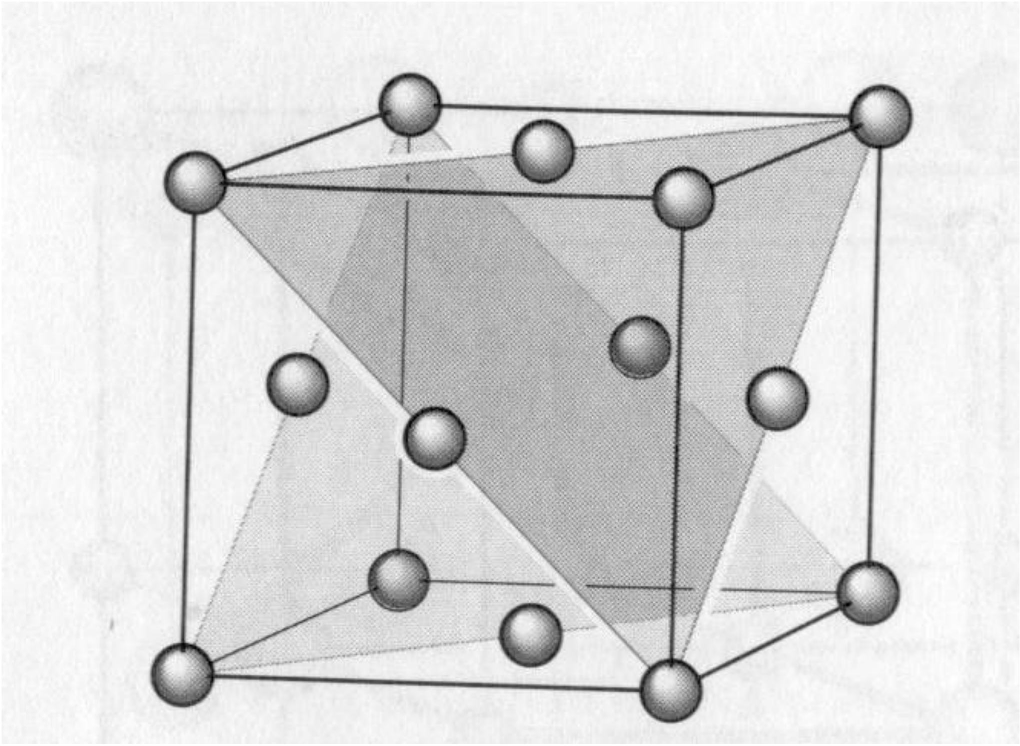
Crystal structure of NaCl (rock salt)



Two interpenetrating face centered cubic arrays: one of Na^+ and the other of Cl^-. Each Na^+ is surrounded by 6 equivalent Cl^- and vice versa. Coordination is 6 for each.

Examples: Most alkali halides (MX) and AgF, AgCl, AgBr. All the alkali hydrides, MH. Monoxides, MO of Mag, Ca, Sr, Ba and their monosulfides, MS.

Close-packed layers of NaCl



Edge-sharing octahedra of Na^+ (or Cl^-)

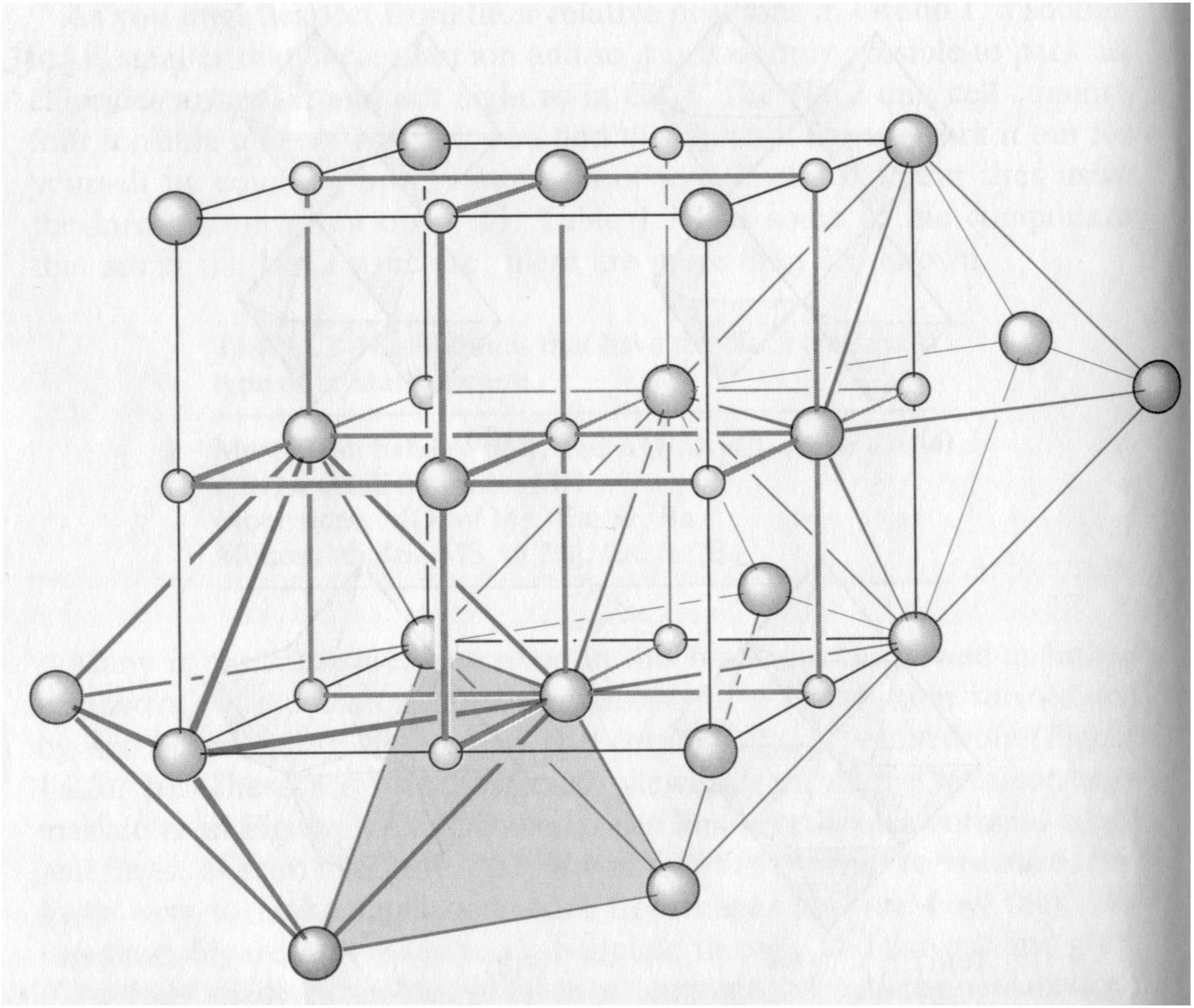
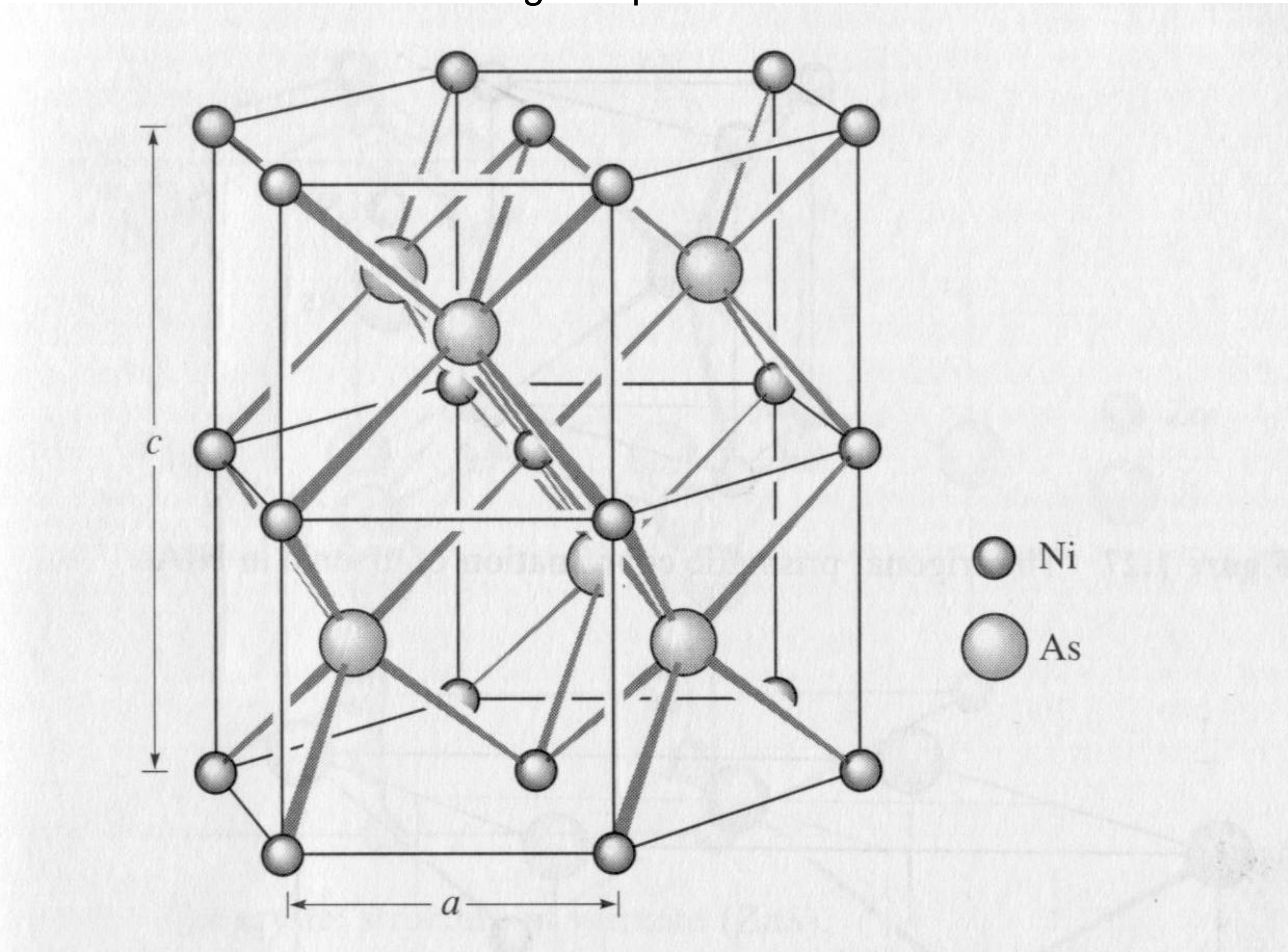


Table 1.4 Structures related to close-packed arrangements of anions

Formula	*Cation: anion coordination*	*Type and number of holes occupied*	*Examples*	
			Cubic close packing	*Hexagonal close packing*
MX	6:6	All octahedral	Sodium chloride: NaCl, FeO, MnS, TiC	Nickel arsenide: NiAs, FeS, NiS
	4:4	Half tetrahedral; every alternate site occupied	Zinc blende: ZnS, CuCl, γ-AgI	Wurtzite: ZnS, β-AgI
MX_2	8:4	All tetrahedral;	Fluorite: CaF_2, ThO_2, ZrO_2, CeO_2	None
	6:3	Half octahedral; alternate layers have fully occupied sites	Cadmium chloride: $CdCl_2$	Cadmium iodide: CdI_2, TiS_2
MX_3	6:2	One-third octahedral; alternate pairs of layers have two-thirds of the octahedral sites occupied		Bismuth iodide: BiI_3, $FeCl_3$, $TiCl_3$, VCl_3
M_2X_3	6:4	Two-thirds octahedral		Corundum: Al_2O_3, Fe_2O_3. V_2O_3, Ti_2O_3, Cr_2O_3
ABO_3		Two-thirds octahedral		Ilmenite: $FeTiO_3$
AB_2O_4		One-eighth tetrahedral and one-half octahedral	Spinel: $MgAl_2O_4$ Inverse spinel: $MgFe_2O_4$	Olivine: Mg_2SiO_4

NiAs structure. Similar to NaCl but hexagonal close packings of As.
Ni is Octahedral and As is trigonal prismatic



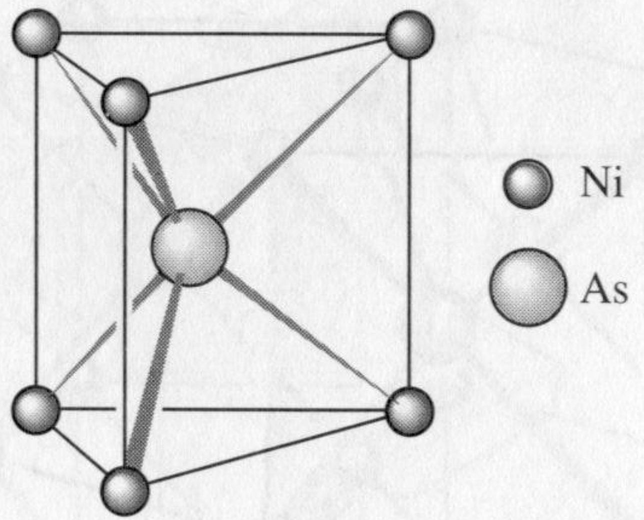
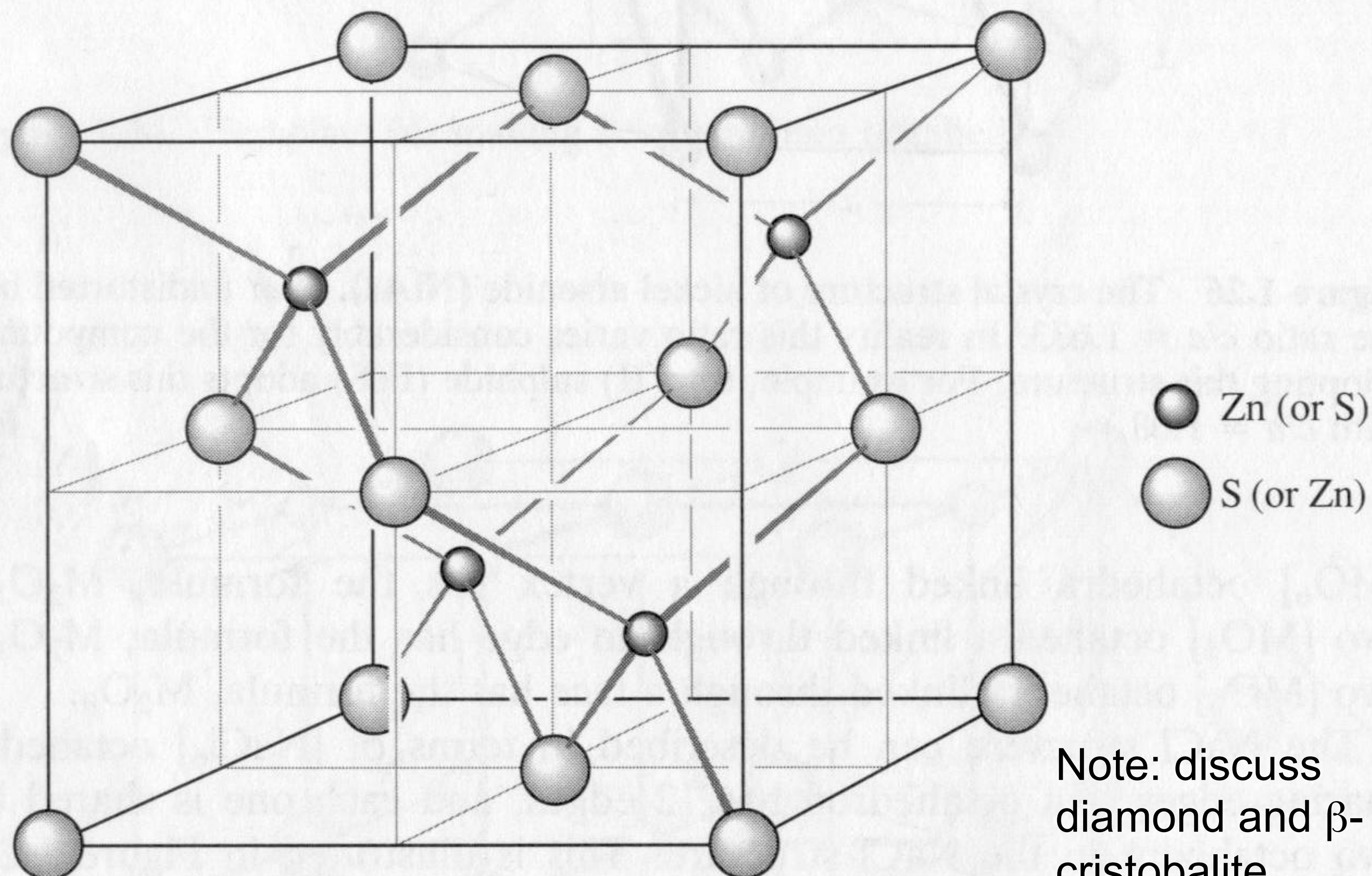


Figure 1.27 The trigonal prismatic coordination of arsenic in NiAs.

Crystal structures of ZnS (Zinc blend and Wurtzite; polymorphs)



Note: discuss diamond and β-cristobalite

Figure 1.28 The crystal structure of zinc blende (ZnS).

ccp of S with Zn in half of tetrahedral holes (i.e. every other tetrahedral hole)

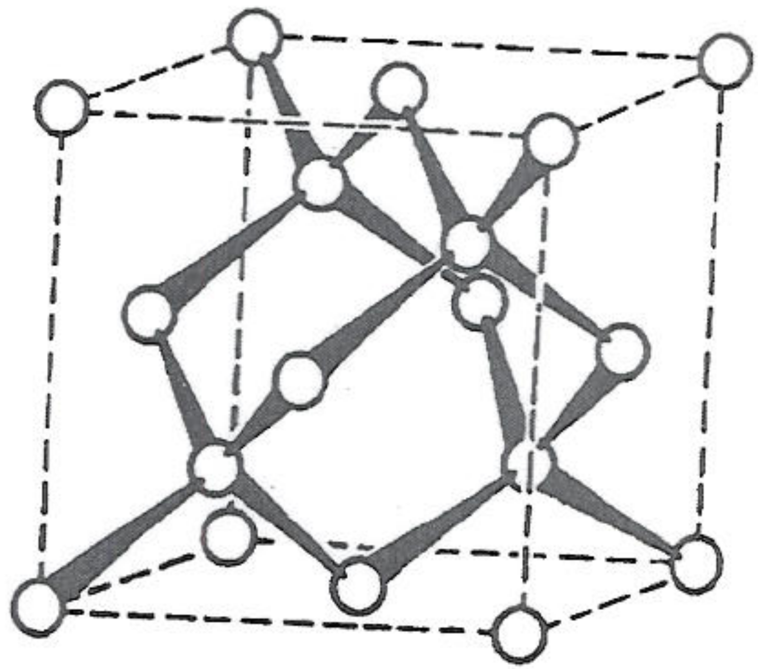
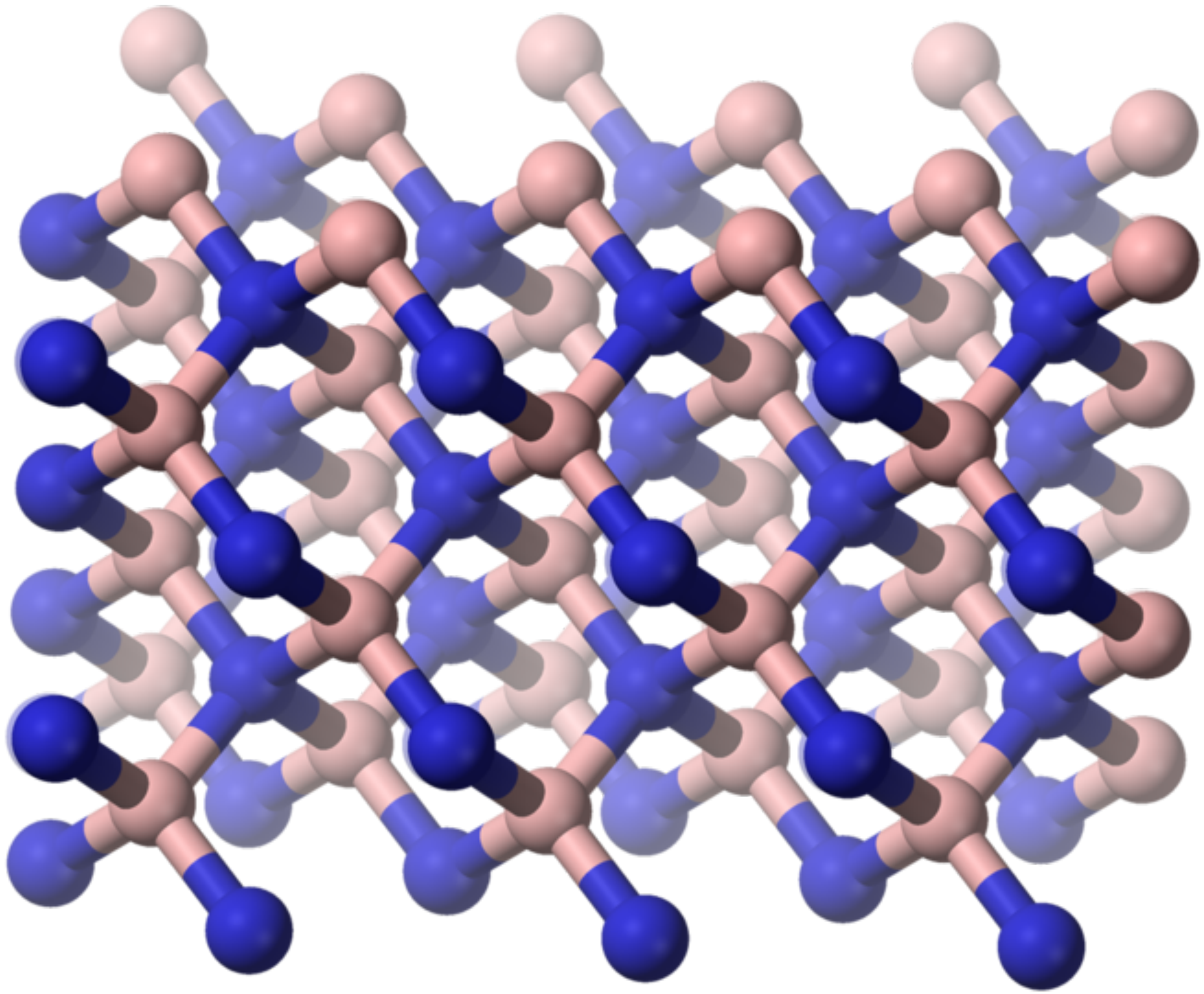


Figure 8.3 Structure of diamond showing the tetrahedral coordination of C; the dashed lines indicate the cubic unit cell containing 8 C atoms.

β-BN (zinc blend, cubic structure)



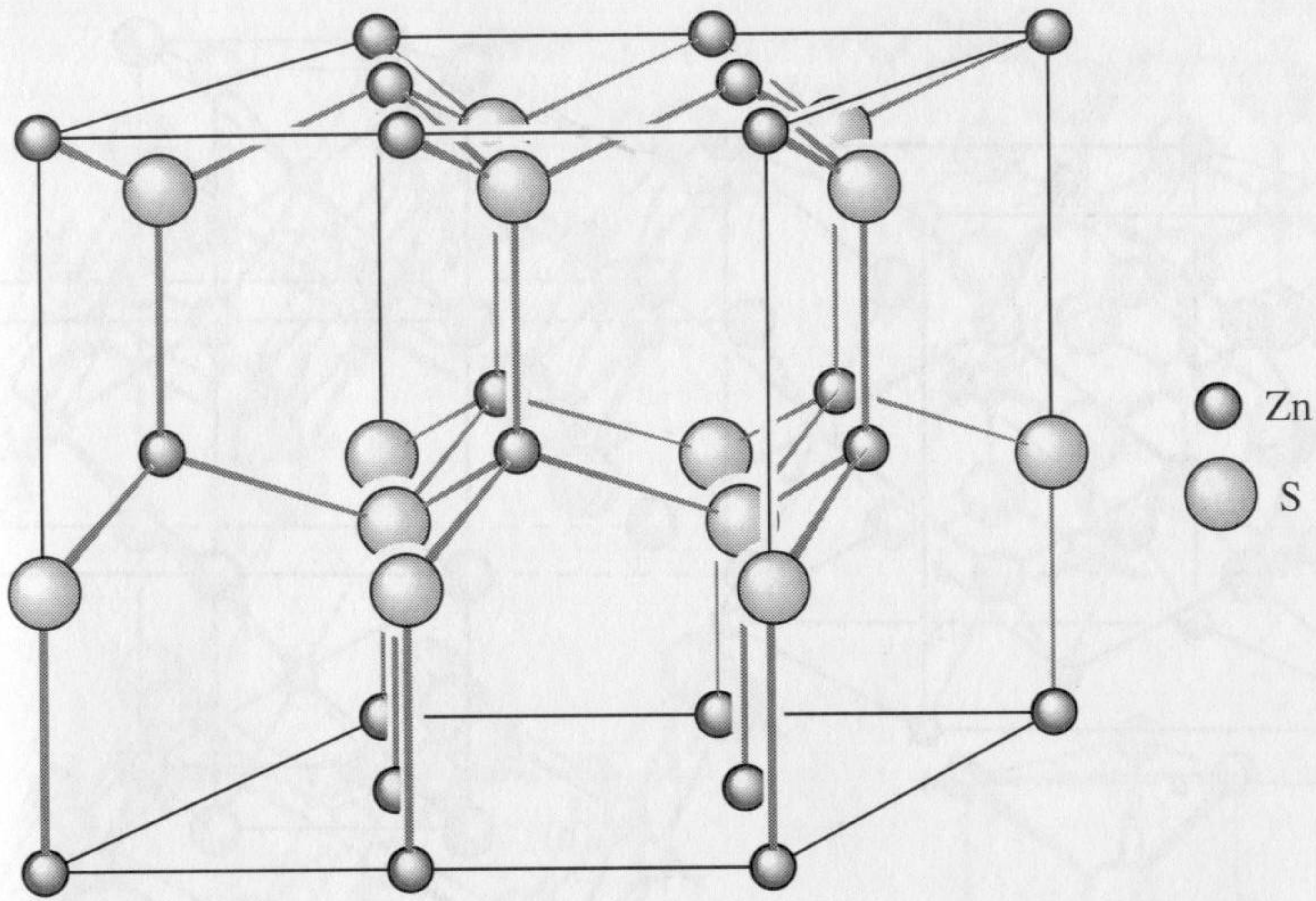
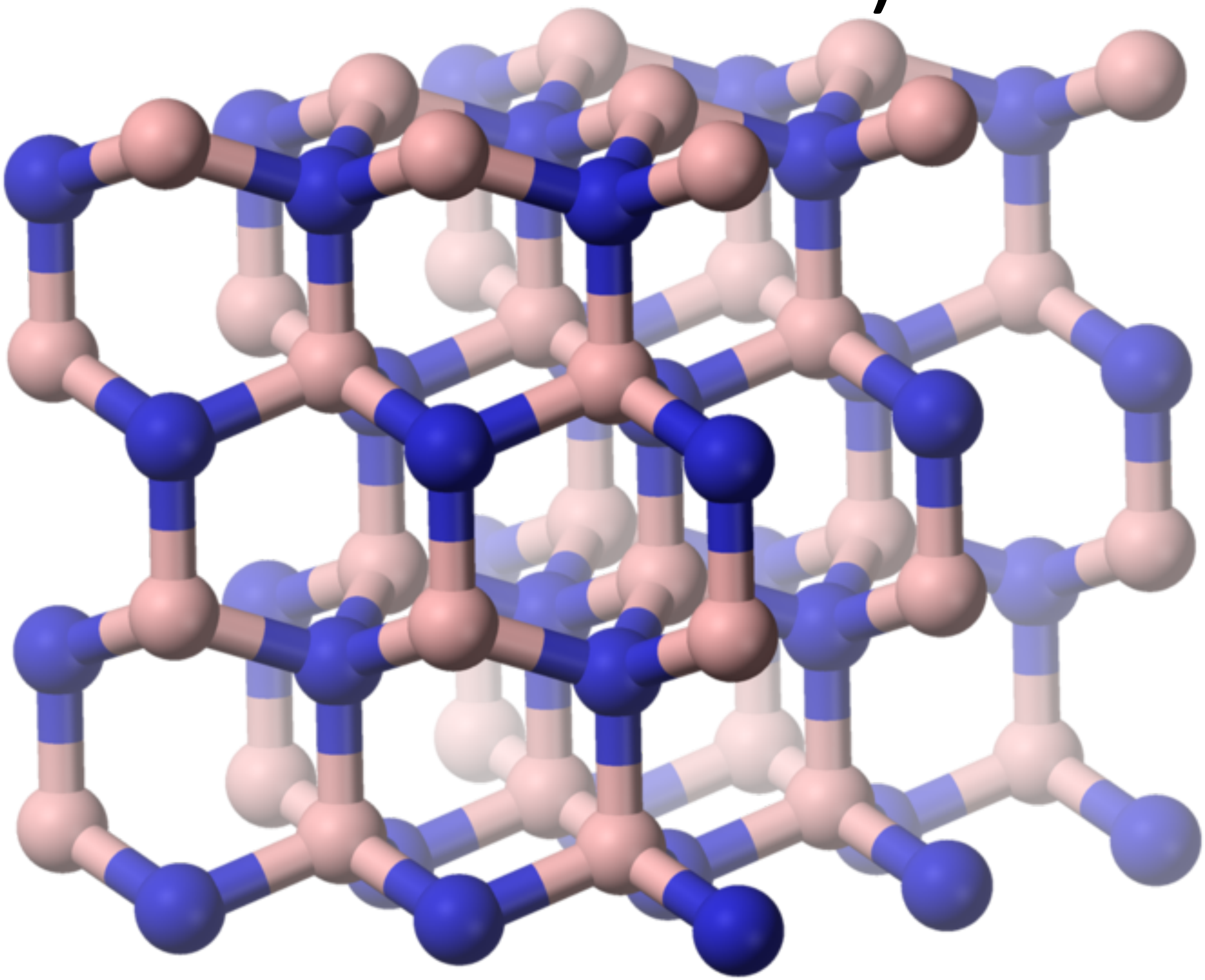


Figure 1.29 The crystal structure of wurtzite (ZnS).

hcp of S with Zn in half of tetrahedral holes (i.e. every other tetrahedral hole

BN (wurtzite, hexagonal 3-D structure)



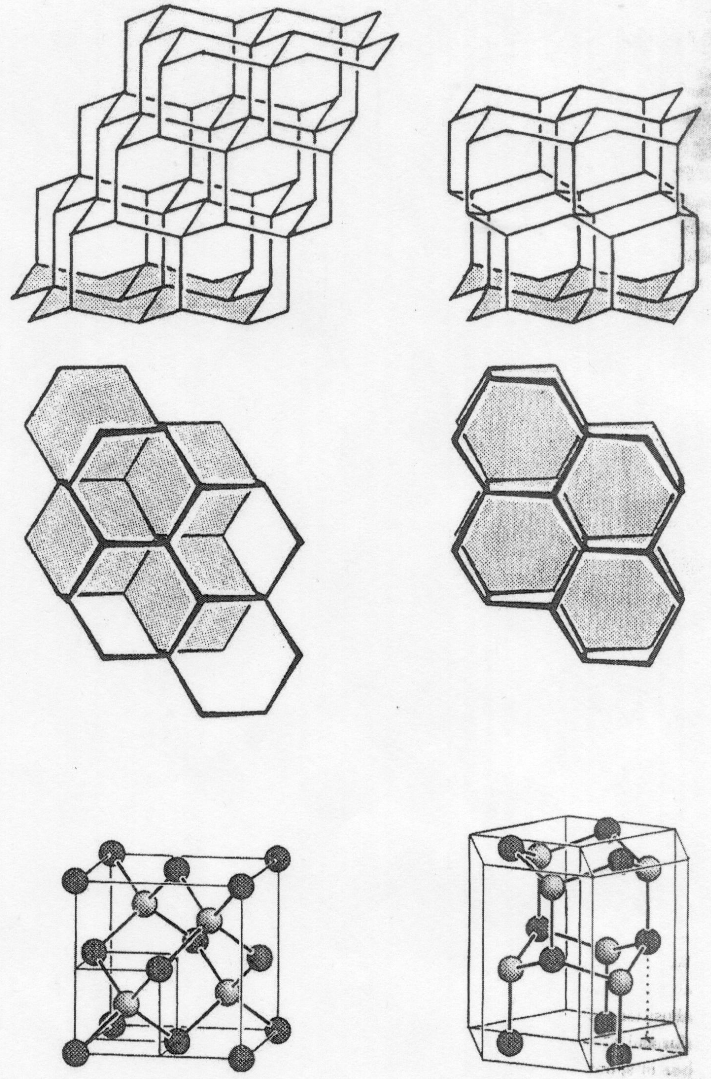


Fig. 55 Structure of cubic (left) and hexagonal (right) diamond. Top row: connected layers as in α-As. Central row: the same layers in projection perpendicular to the layers. Bottom: unit cells; when the light and dark atoms are different, this corresponds to the structures of sphalerite (zinc blende) and wurtzite, respectively

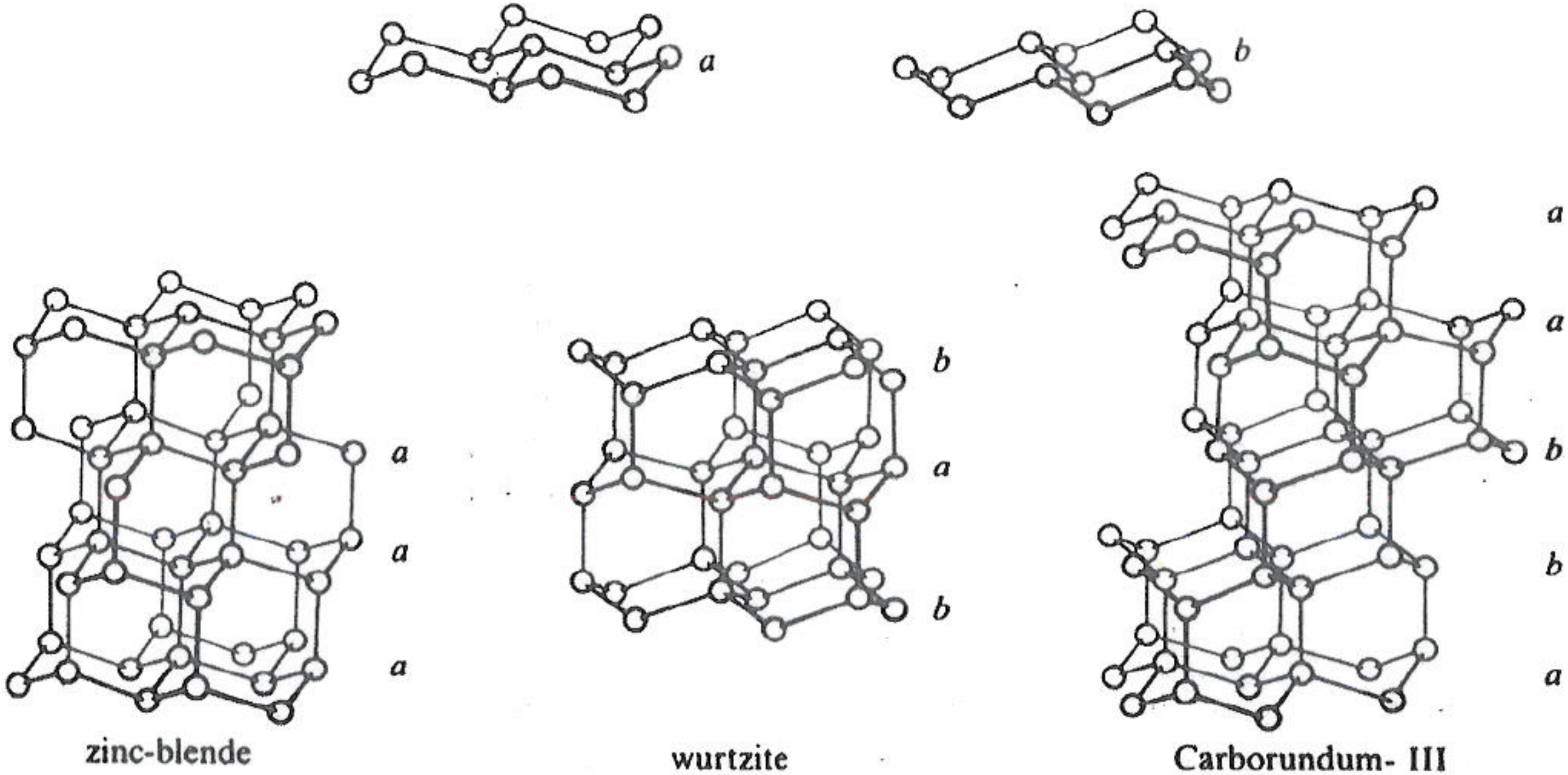


FIG. 23.1. The geometrical relationship between the structures of zinc-blende, wurtzite, and carborundum III.

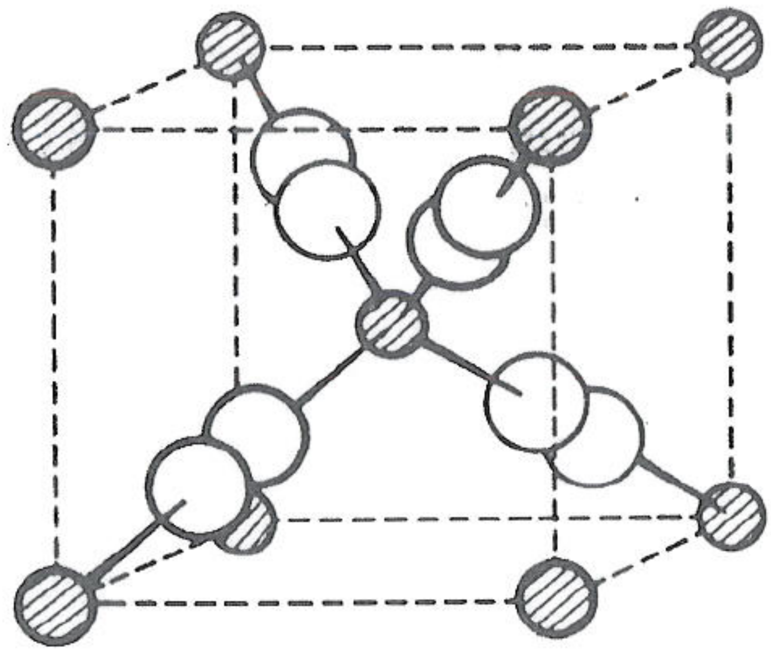
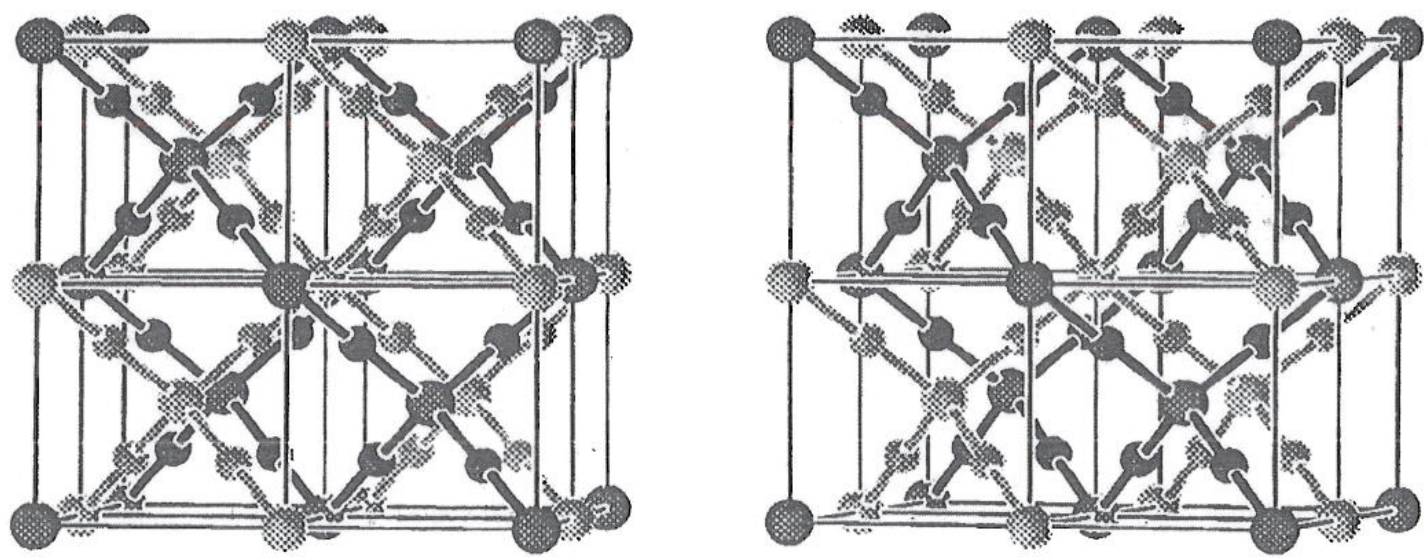


FIG. 22.4. Structure proposed for $Cd(CN)_2$ and the isostructural $Zn(CN)_2$.

Doubly interpenetrated diamond frameworks of Cu_2O

Fig. 62
The structure of Cu_2O (cuprite). Eight unit cells are shown; they correspond to one unit cell of cristobalite. The gray network has no direct bonds to the black network (stereo image)



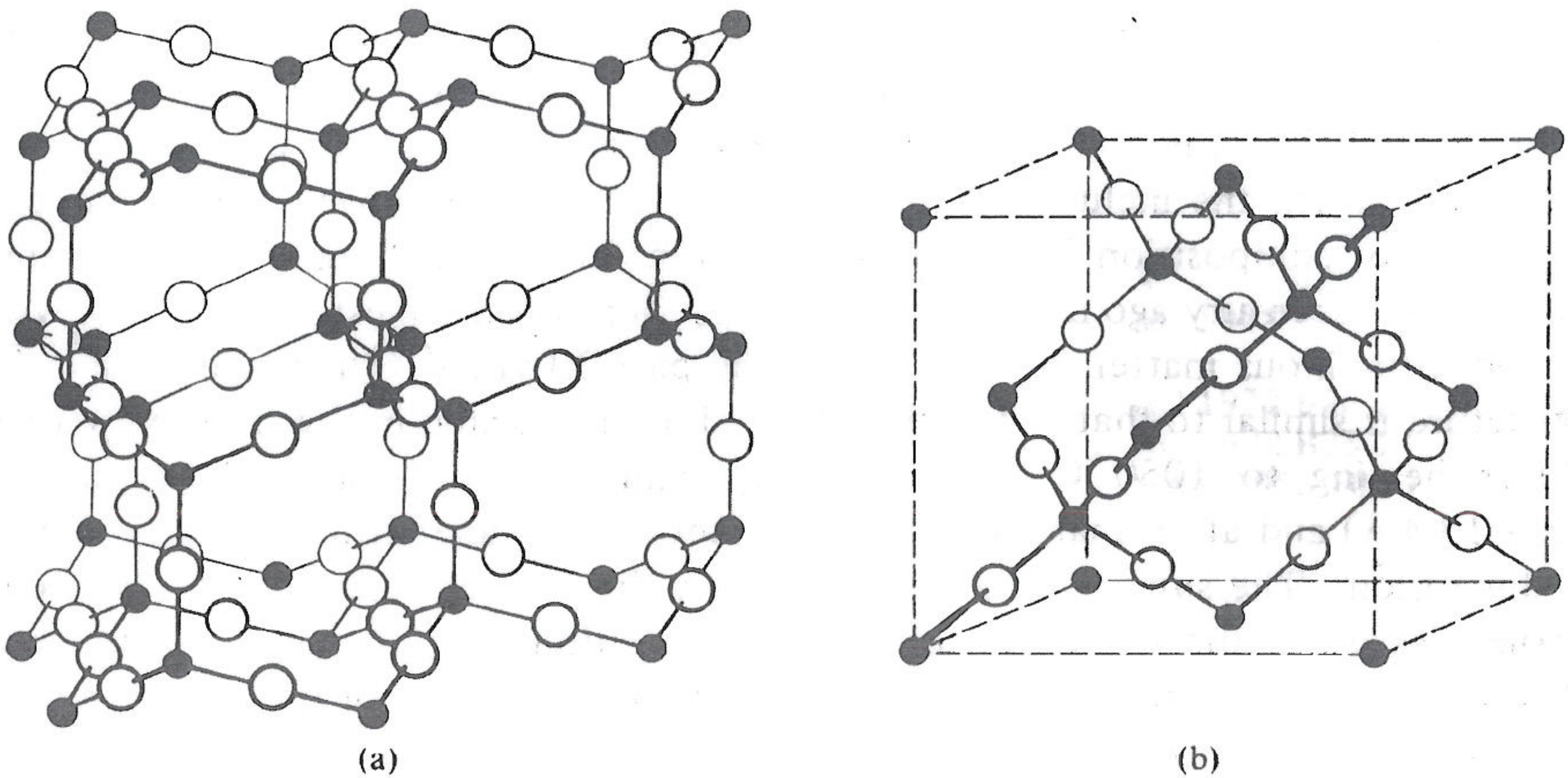
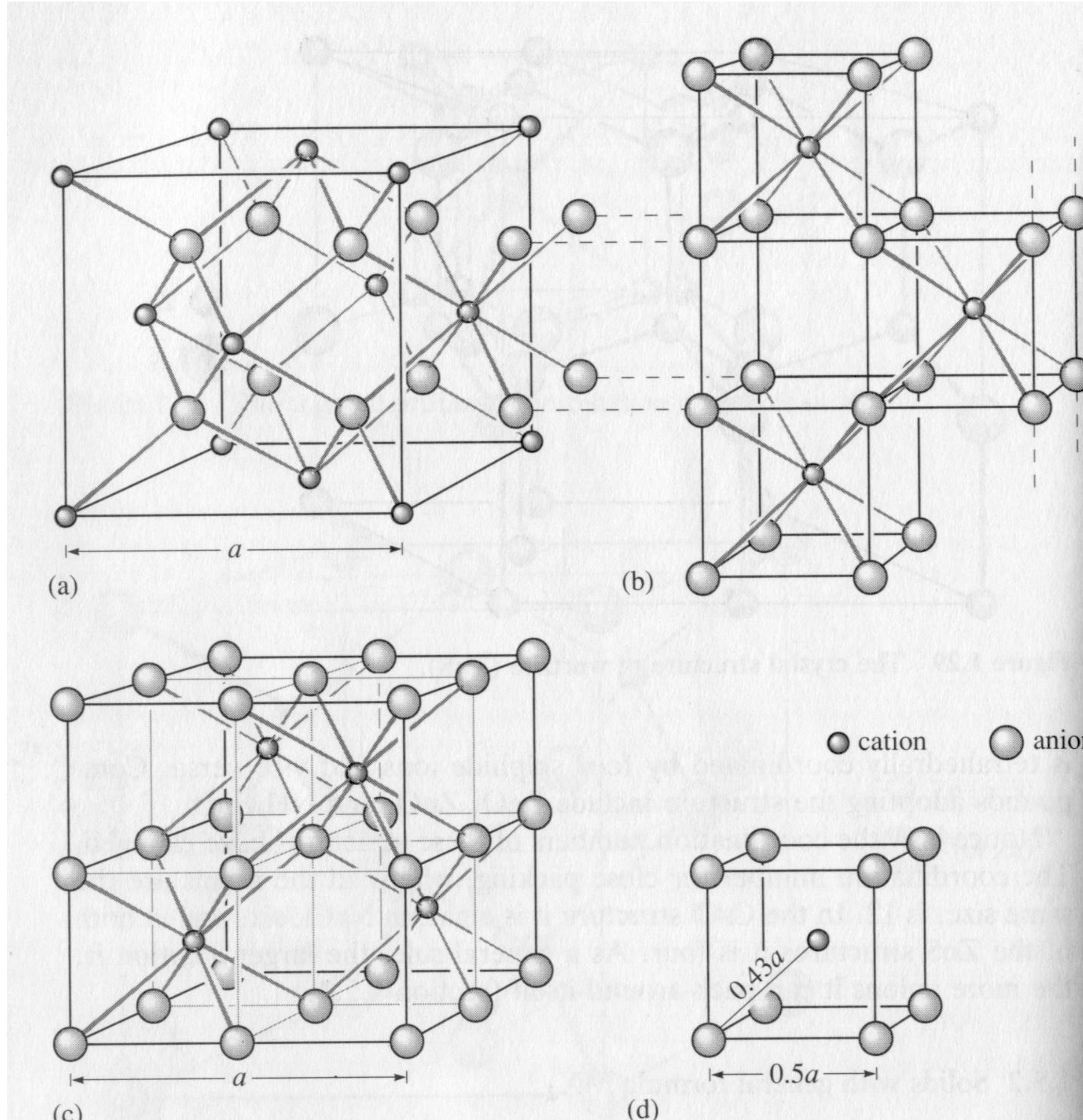


FIG. 23.8. The idealized structures of (a) β-tridymite, and (b) β-cristobalite (see text). Small black circles represent Si atoms.

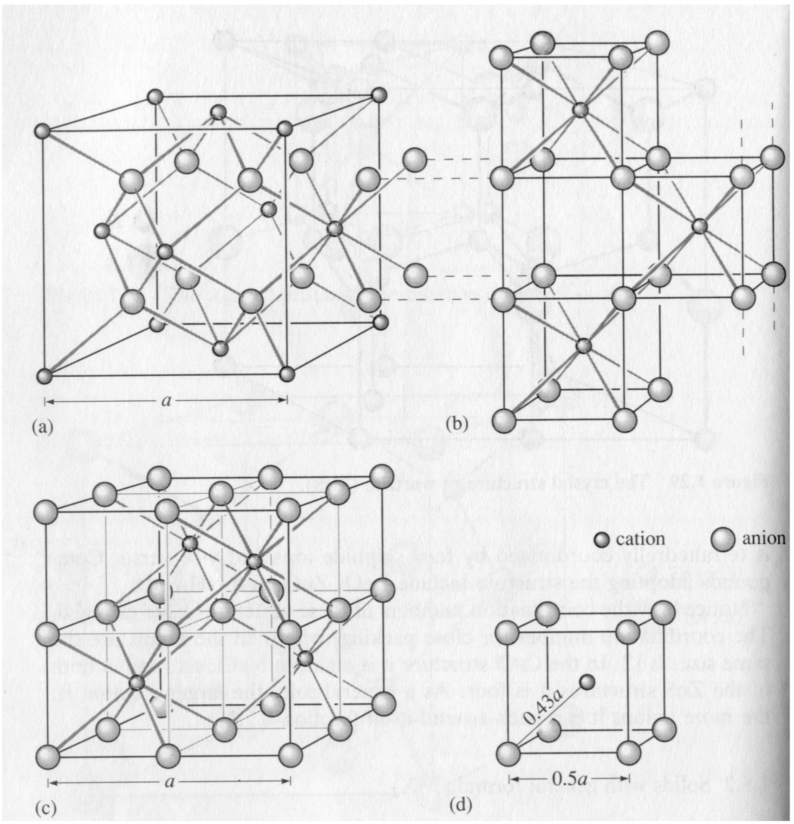
Fluorite and Antifluorite structures

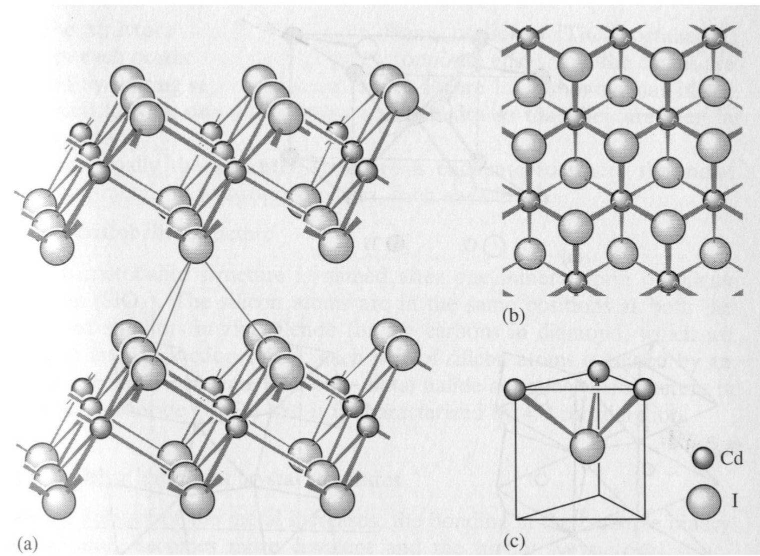
a. ccp array of Ca^{2+}
b. Redrawn as primitive cubic array of F^-
c. Unit cell
d. Primitive anion cube

Antifluorite: Ca and F switch places



From CaF_2 to CdI_2



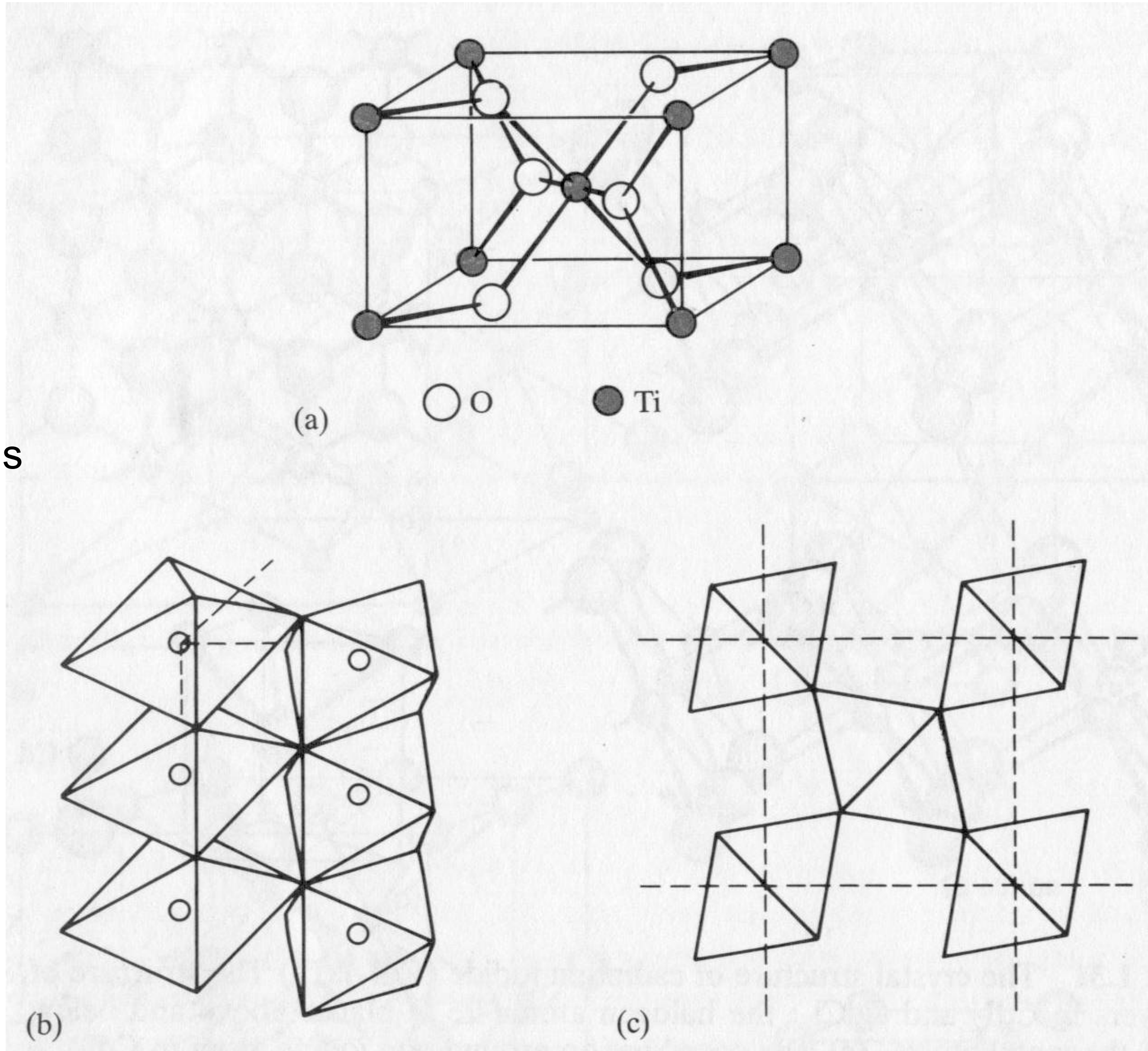


a. hexagonal close packing of I^- with half of octahedral holes filled in a manner such that alternate layers have fully occupied octahedral sites ($CdCl_2$ same but ccp)
b. Layer of CdX

Rutile (TiO_2) structure: Not based on close-packings

a. Tetragonal cell with Ti (6-coordination octahedral geometry and oxygen in trigonal planar geometry. Both geometries are imperfect because mathematically impossible to have a perfect geometry in this kind of cell.

b. TiO_2 structure best viewed as columns of octahedra TiO_6 in which octahedra are sharing opposite edges, then linked to other columns by sharing vertices as in (c)



ReO_3: Primitive cubic array of O but with ¼ of them missing
Best viewed as Octahedra sharing corners

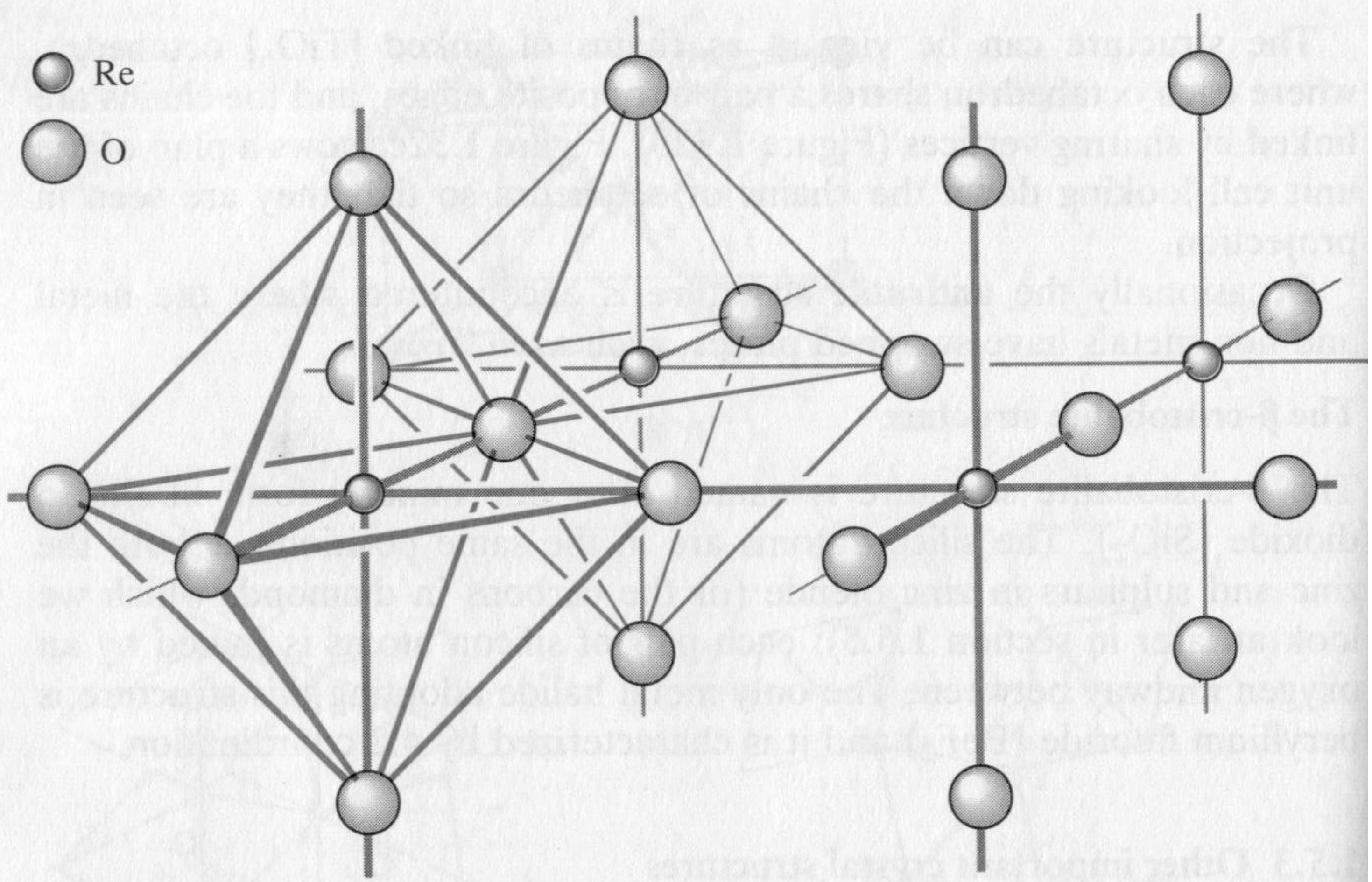
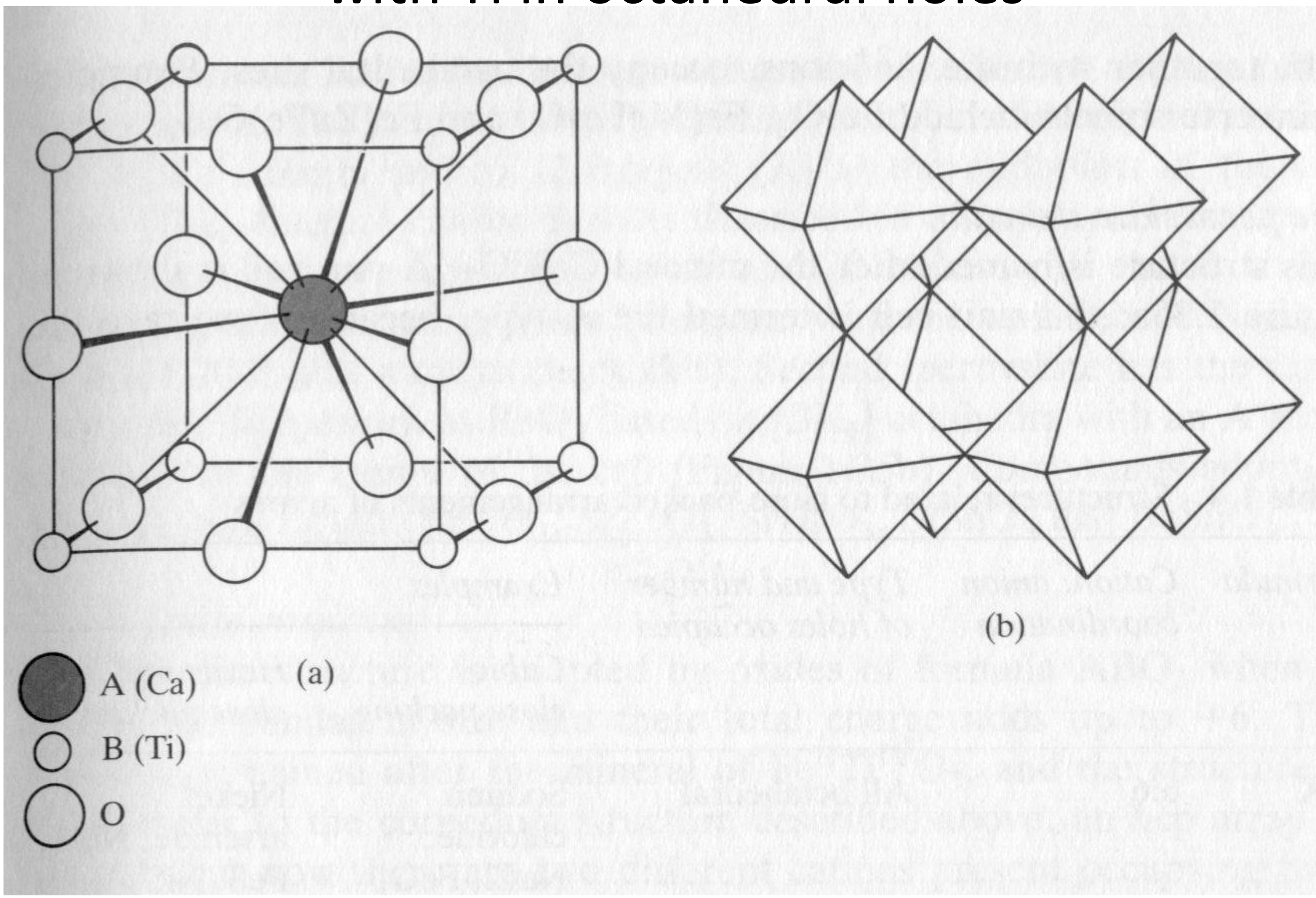


Figure 1.33 Part of the ReO_3 structure showing the linking of octahedra through the corners. Part of a single layer.

Pervoskite ABO_3 compounds ($CaTiO_3$) and ReO_3 (shown in (b). $CaTiO_3$ can be viewed as ccp array of Ca and O with Ti in octahedral holes



Spinel structure (cubic close packed array of O with A^{2+} ions occupy 1/8 tetrahedral holes and B^{3+} ions occupy ½ octahedral holes): $MgAl_2O_4$

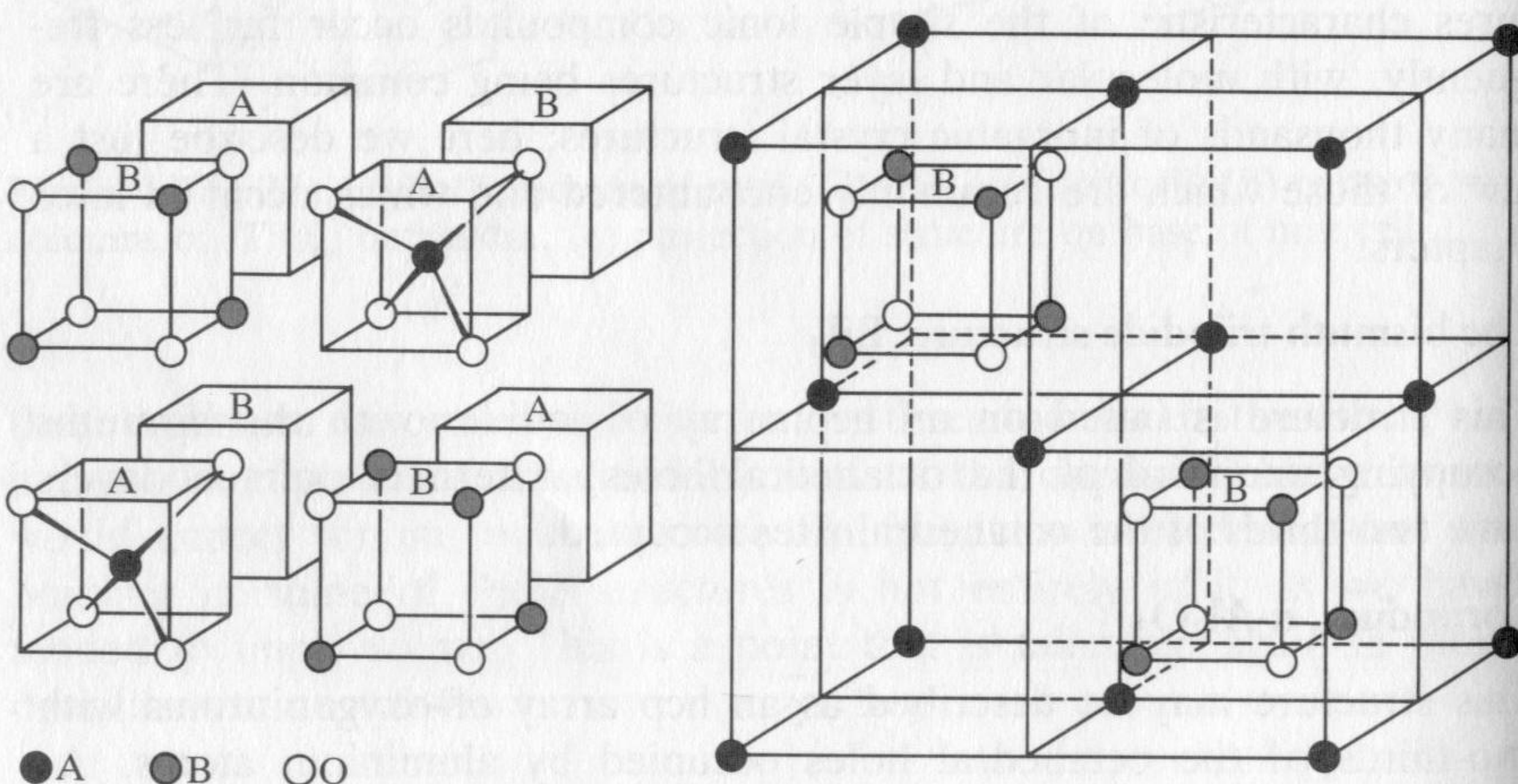
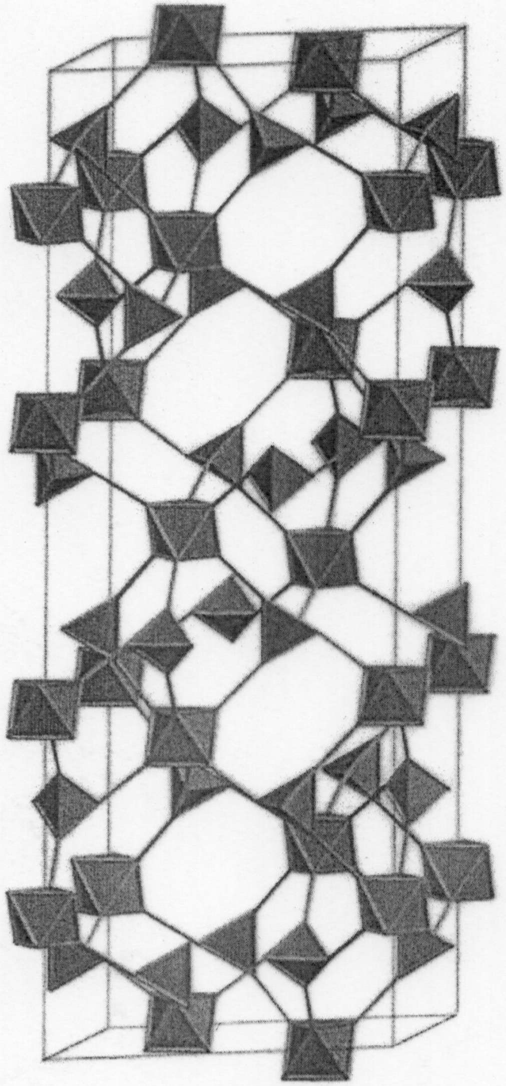


Figure 1.34 The spinel structure, AB_2O_4.



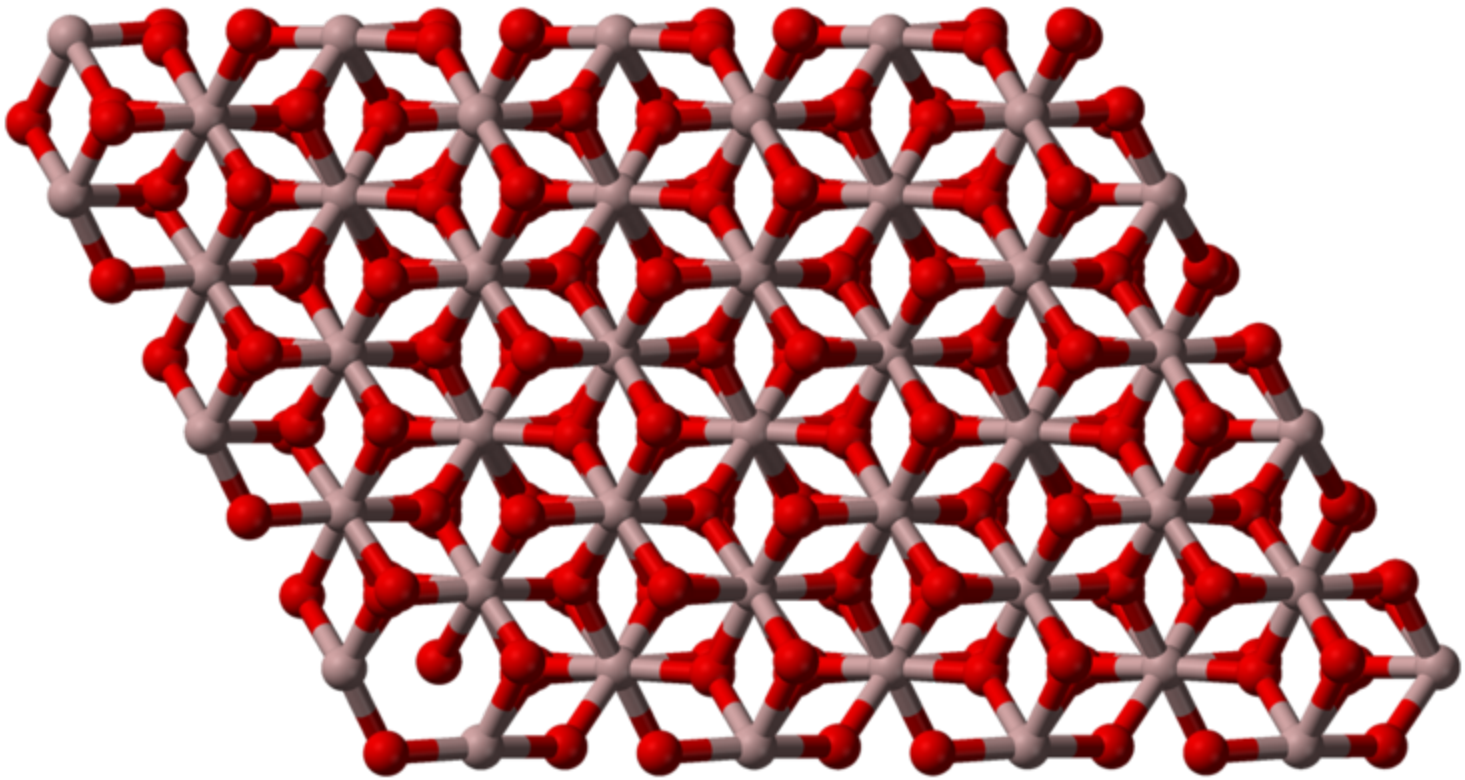
$Al_1O_{6/4}$

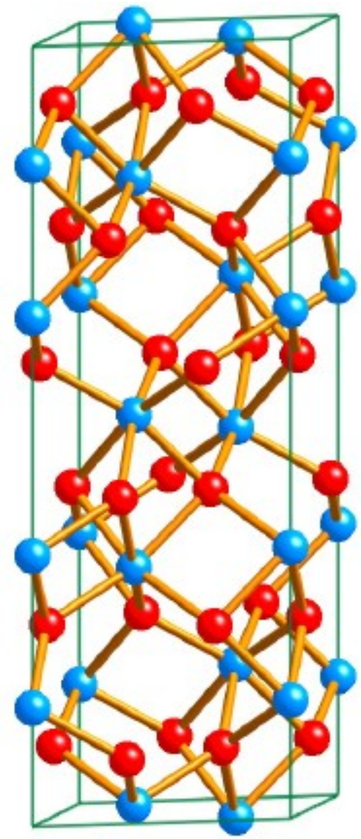
Al_2O_3

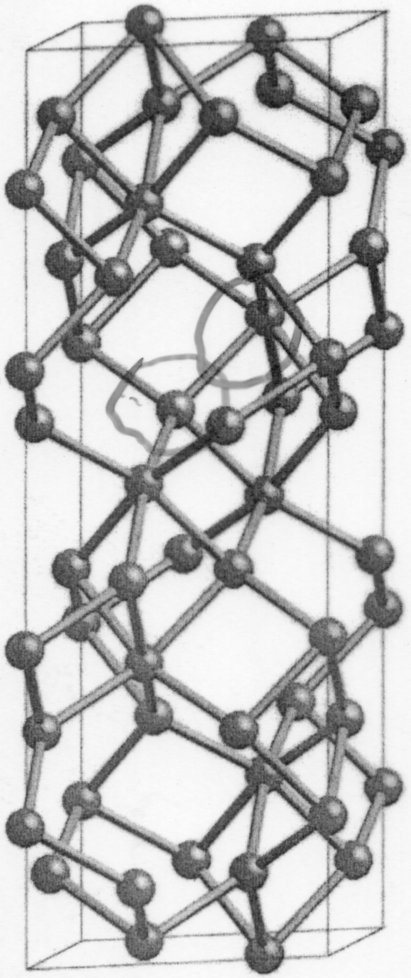
Corrundum

2/3 of octahedral holes occupied in an hcp arrays of O

$\alpha-Al_2O_3$ (Corundum)





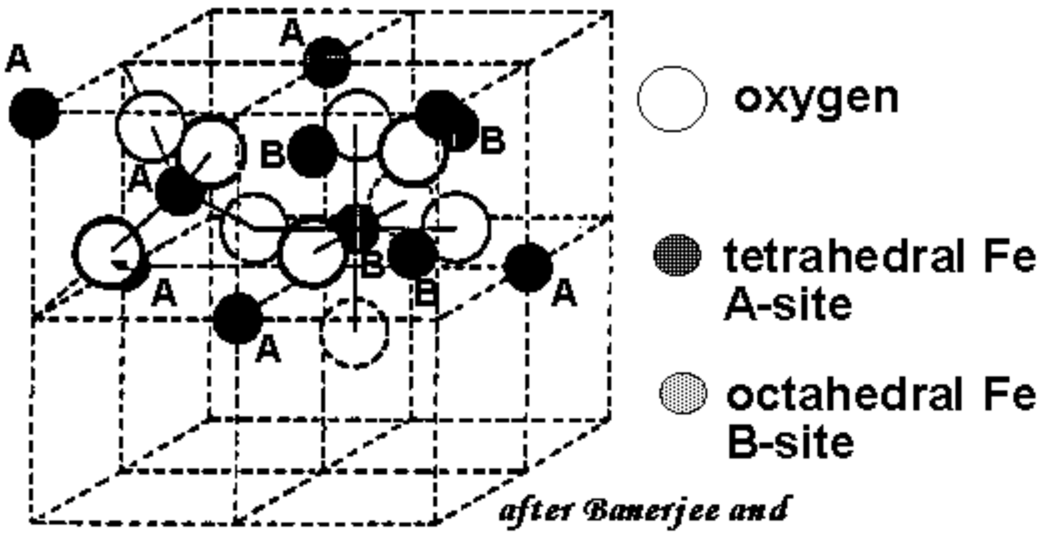


6-coordinate
Oh Al.
each Al is
linked to
other Al
through
a tetrahedral
O

$AlO_{1.5}$

Al_2O_3

each T_d oxygen
is linked 4 Oh Al.



after Banerjee and Moskowitz (1985)

Magnetite, Fe_3O_4 crystallizes with the spinel structure. The large oxygen ions are close packed in a cubic arrangement and the smaller Fe ions fill in the gaps. The gaps come in two flavors:

tetrahedral site: Fe ion is surrounded by four oxygens

octahedral site: Fe ion is surrounded by six oxygens

Note: The tetrahedral and octahedral sites form the two magnetic sublattices, A and B respectively. The spins on the A sublattice are antiparallel to those on the B sublattice. The two crystal sites are very different and result in complex forms of exchange interactions of the iron ions between and within the two types of sites.

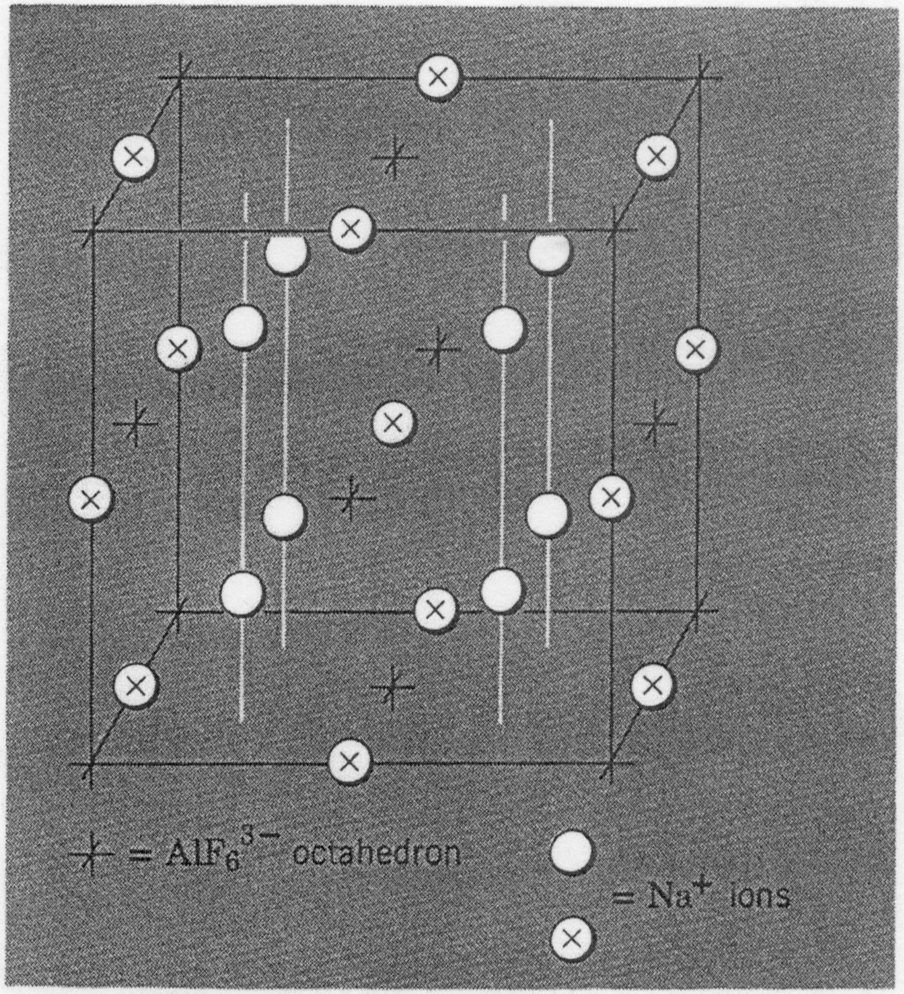
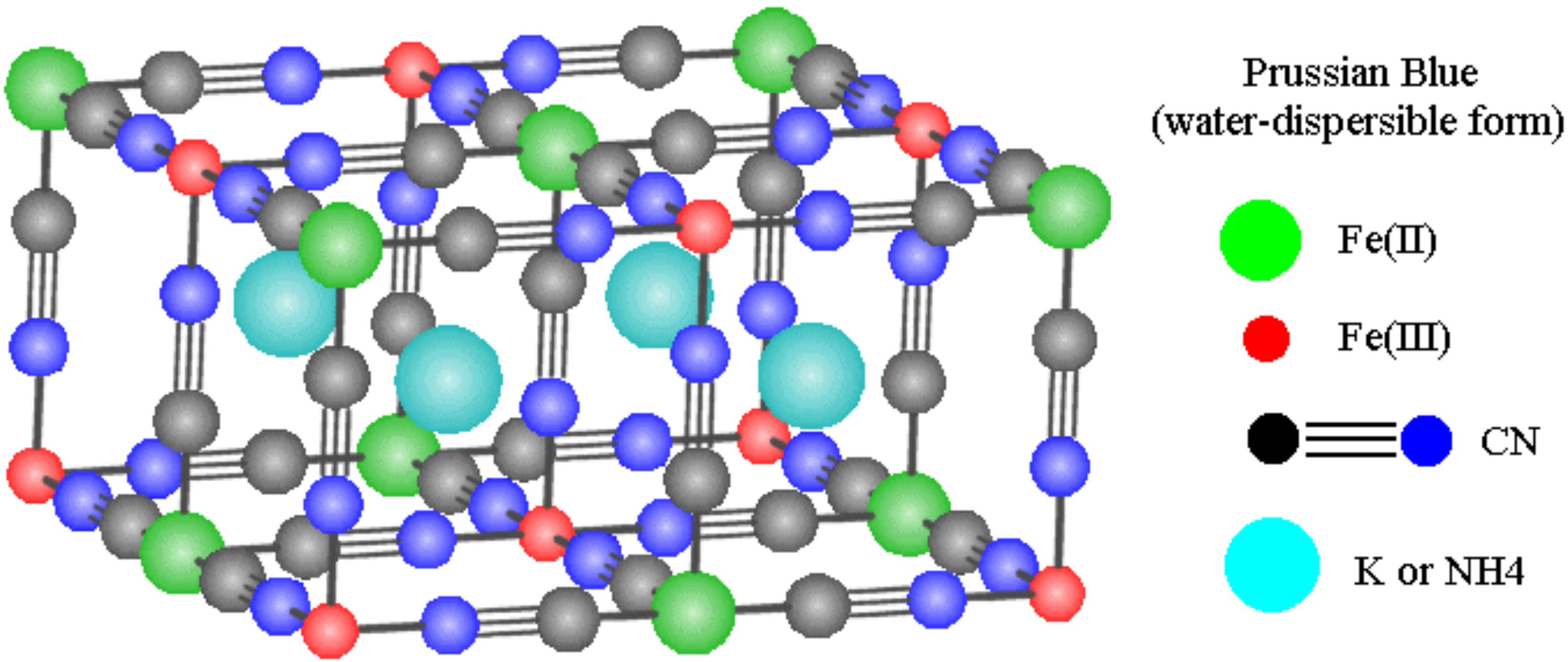
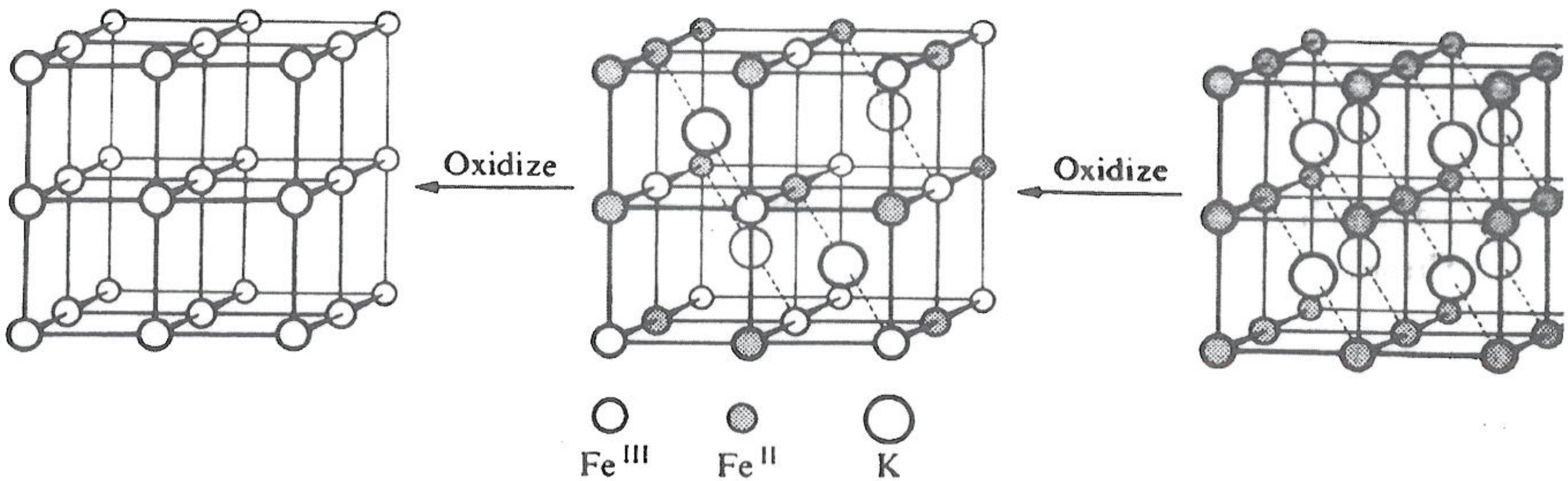


Figure 13-2 The cubic structure of cryolite (Na_3AlF_6).


Prussian Blue
(water-dispersible form)
Fe(II)
Fe(III)
CN
K or NH4



(a) Fe Fe $(CN)_6$ (b) K Fe Fe $(CN)_6$ (c) K_2 Fe Fe $(CN)_6$

FIG. 22.5. The relationship between (a) Berlin green; (b) soluble Prussian blue; and (c) potassiu
ferrous ferrocyanide.

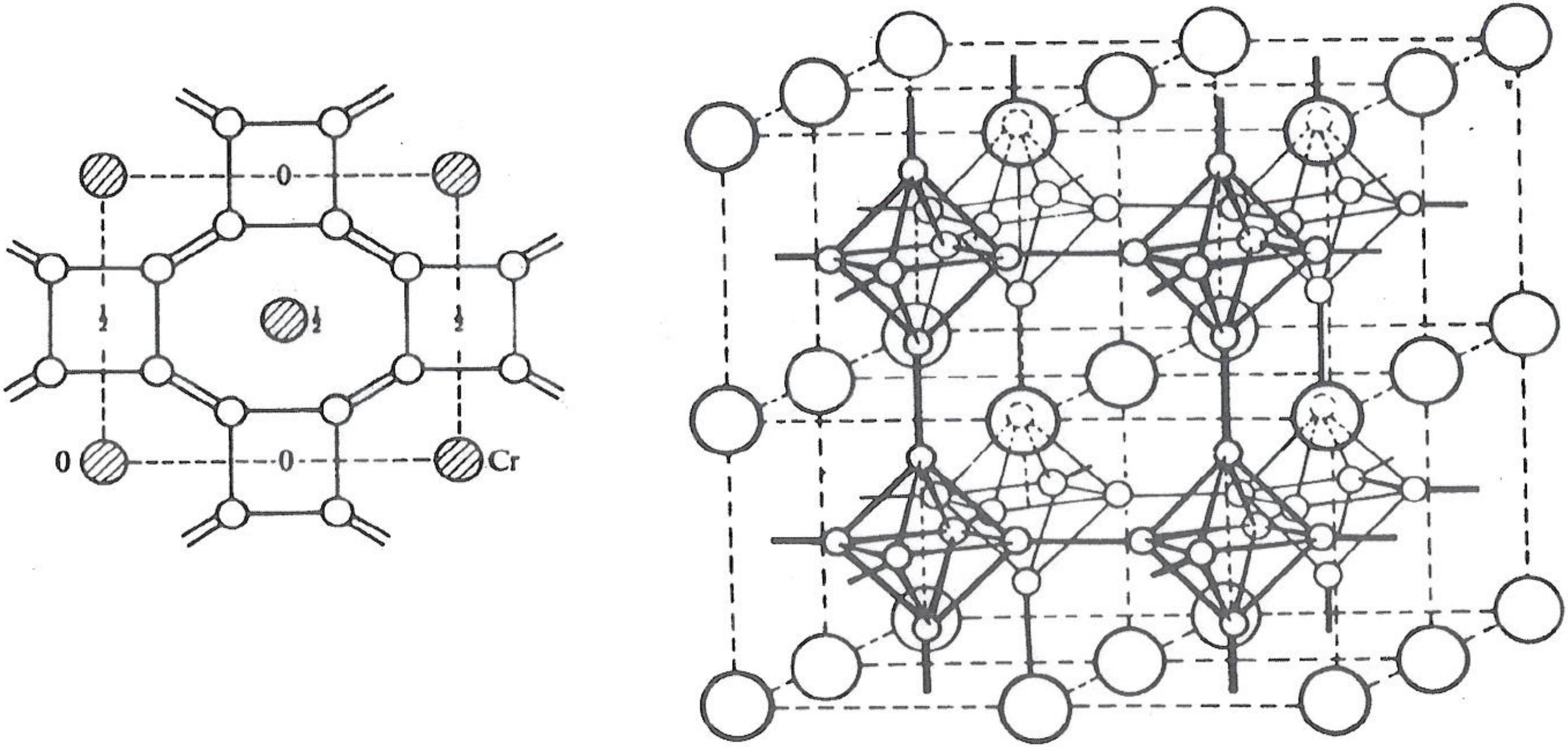
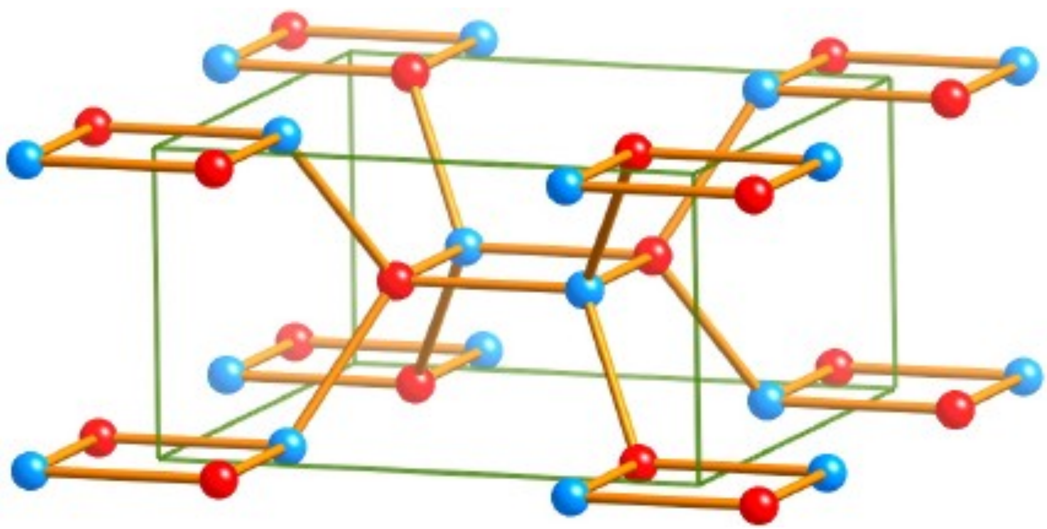
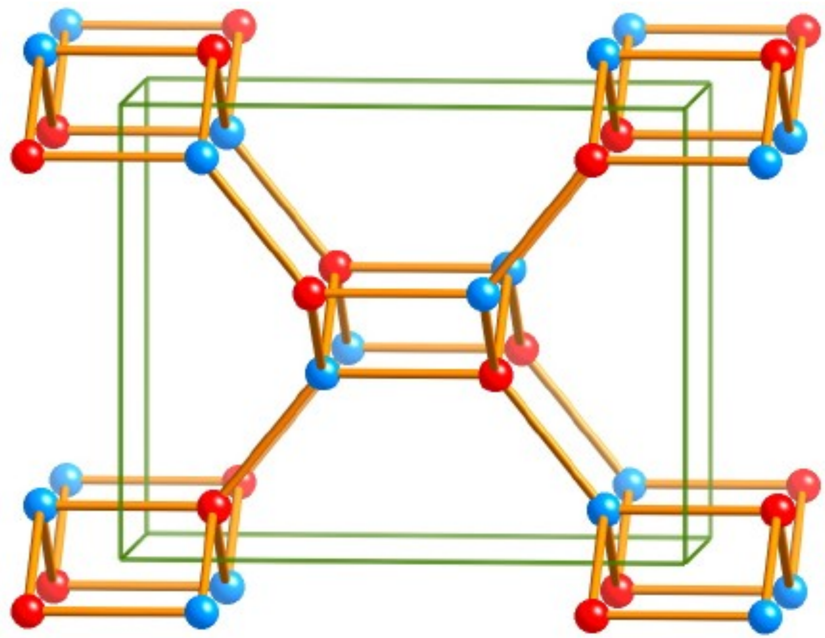


FIG. 24.6. The crystal structures of (a) CrB_4 and (b) CaB_6.

Other common tetrahedral structures

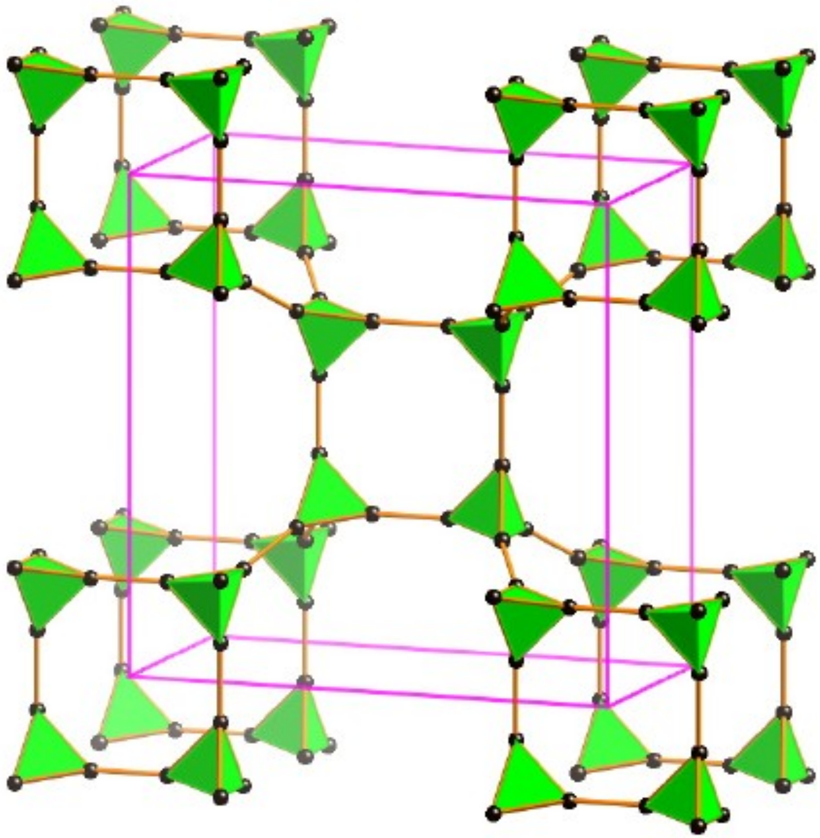


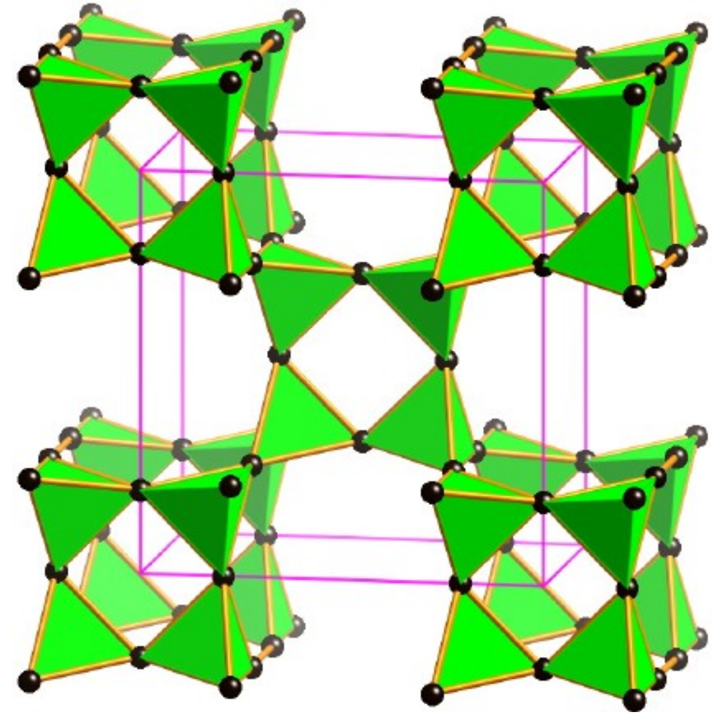
CrB_4



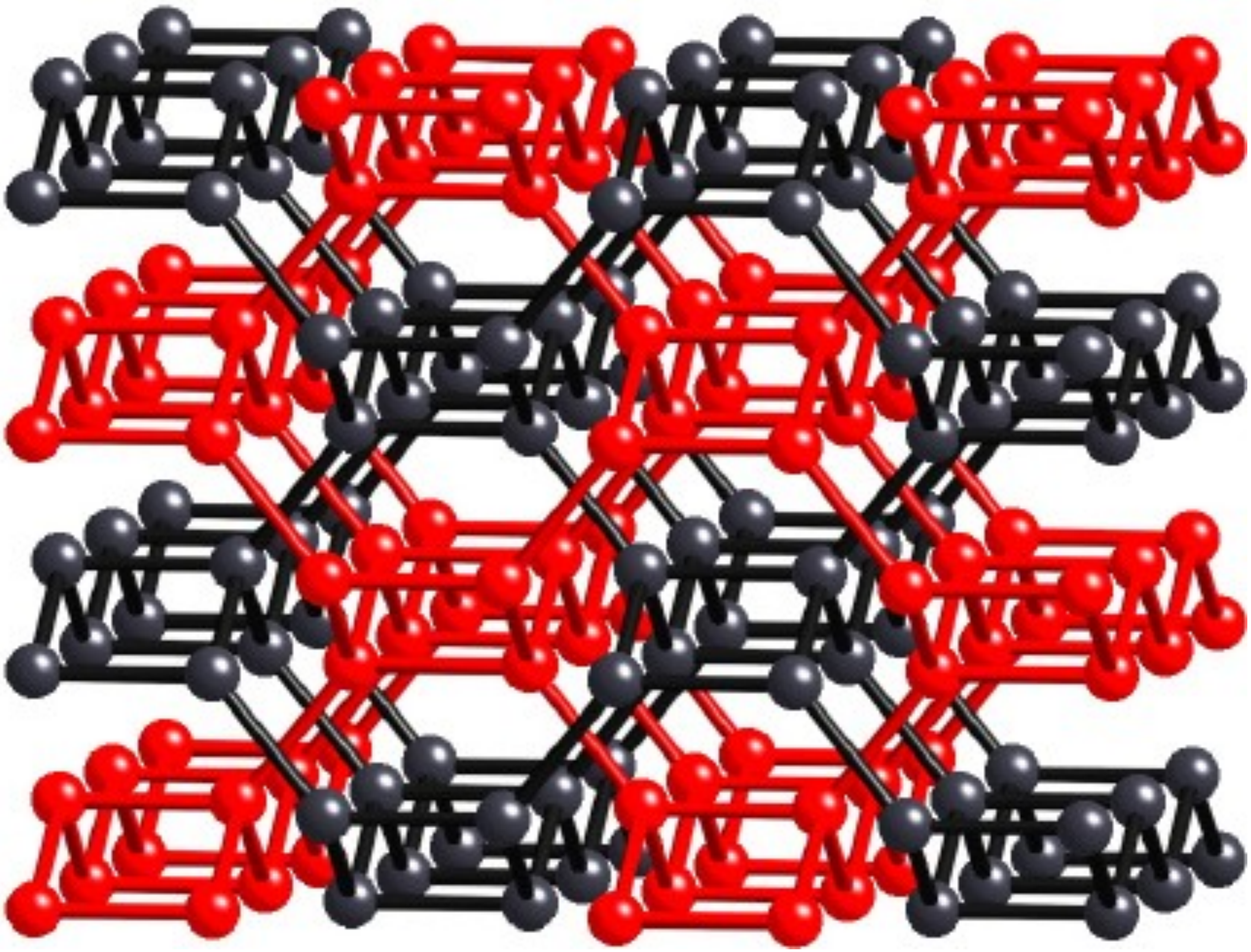
$SrAl_2$

Decorated CaB_4

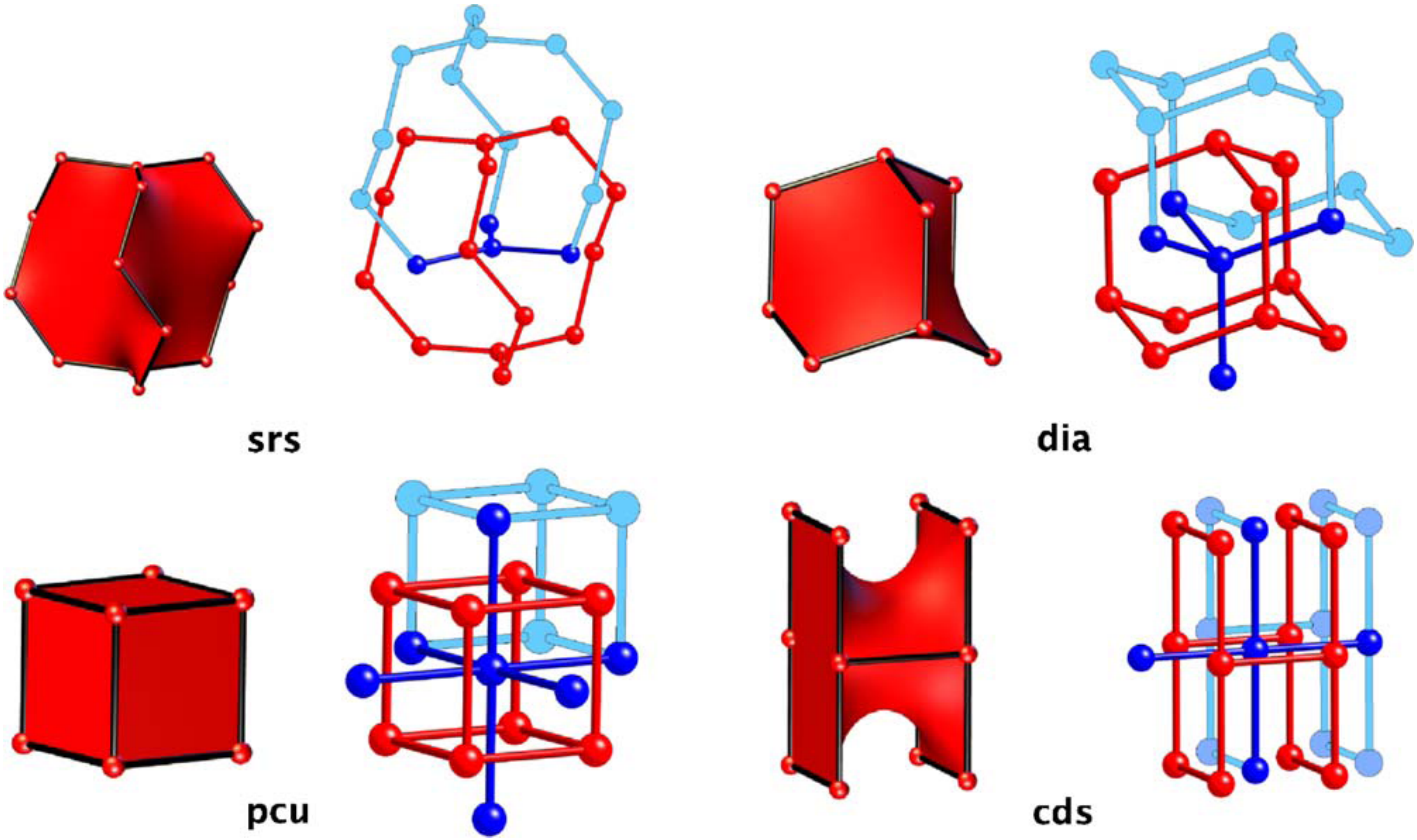




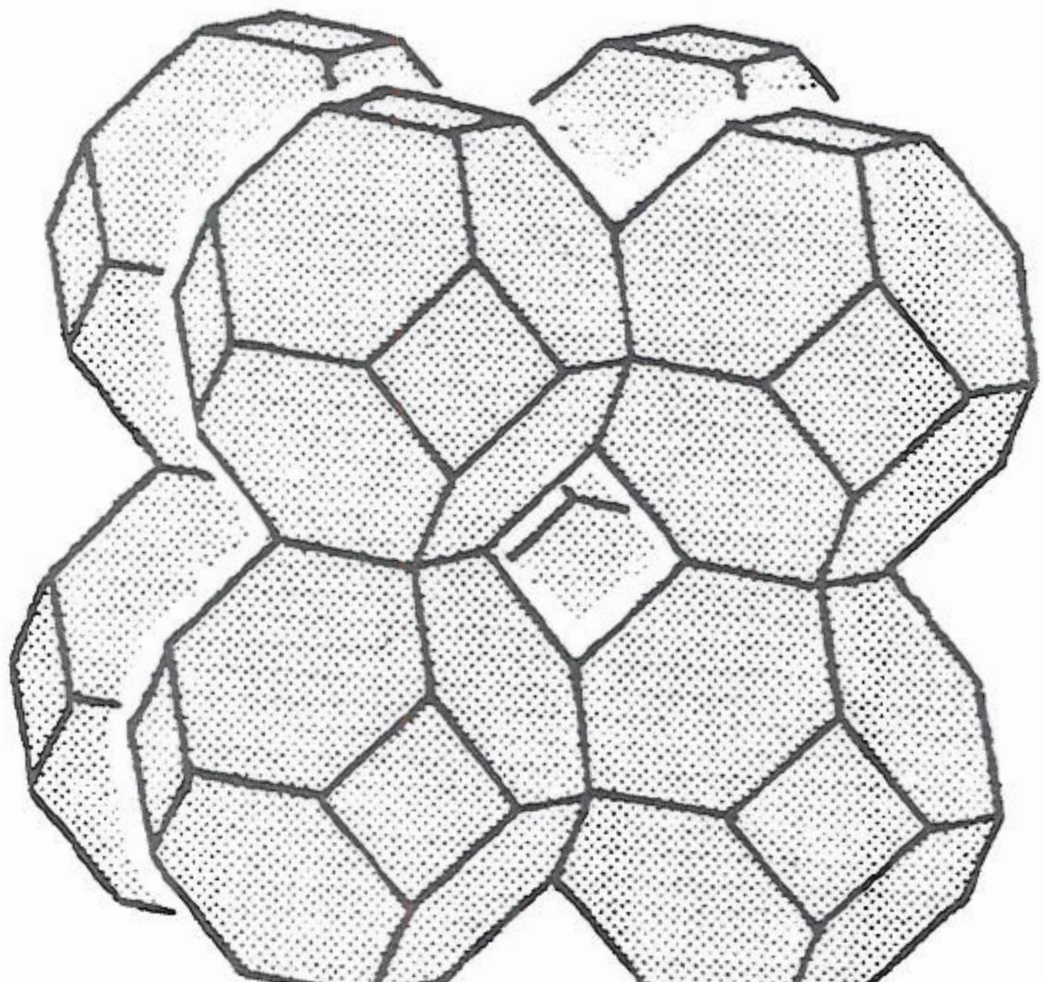
Interpenetrating $SrAl_2$



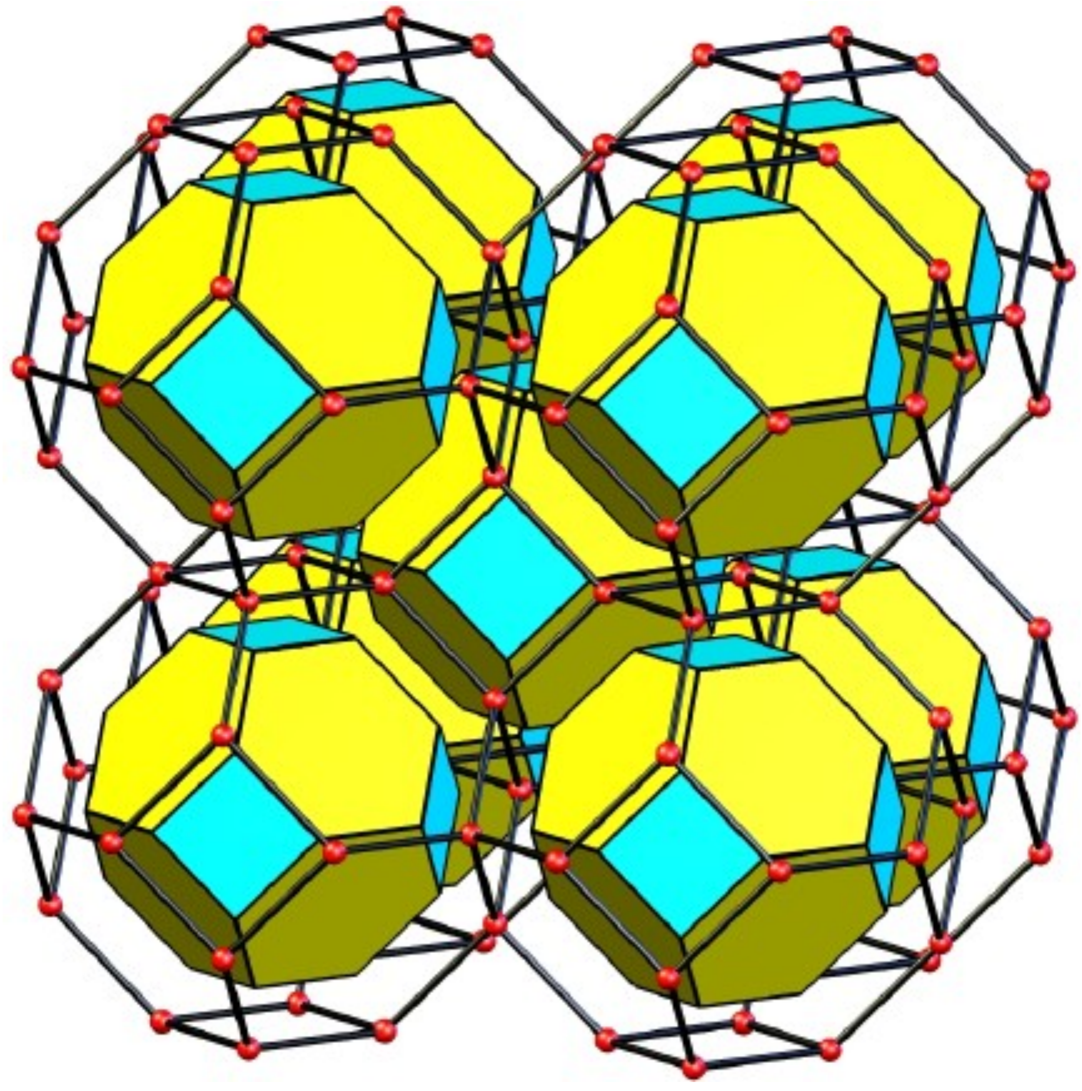
Common interpenetrations



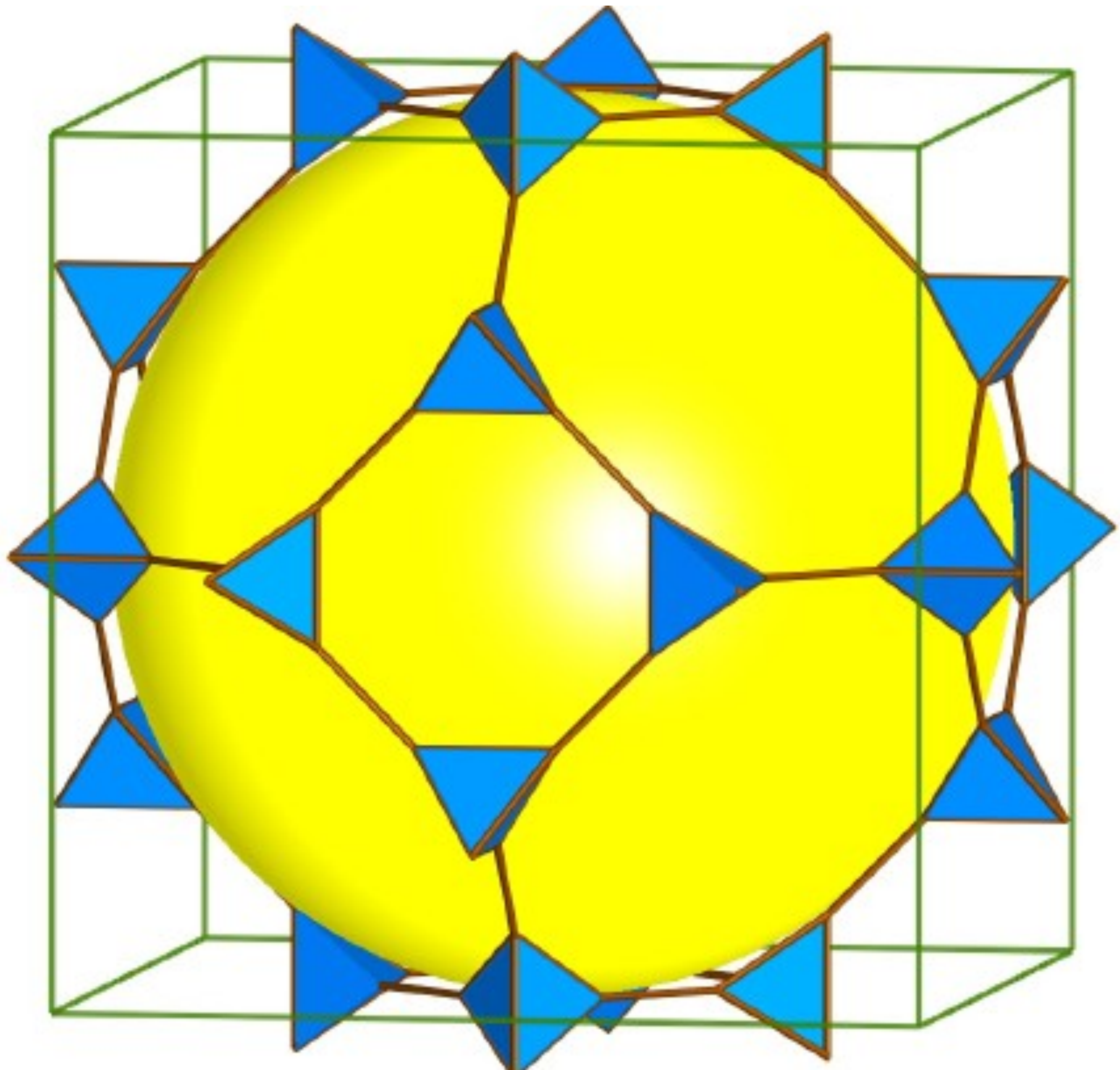
Sodalite

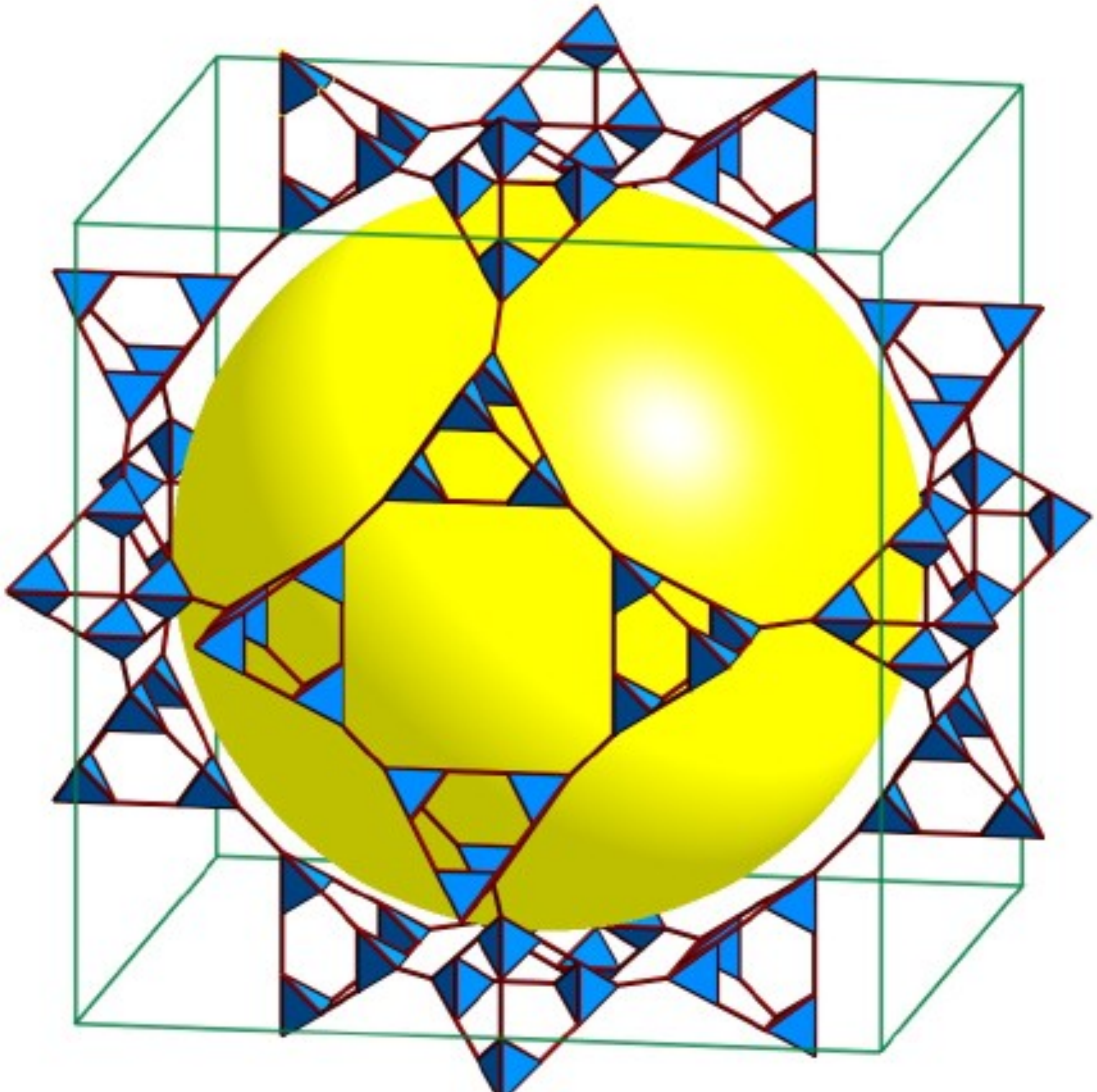


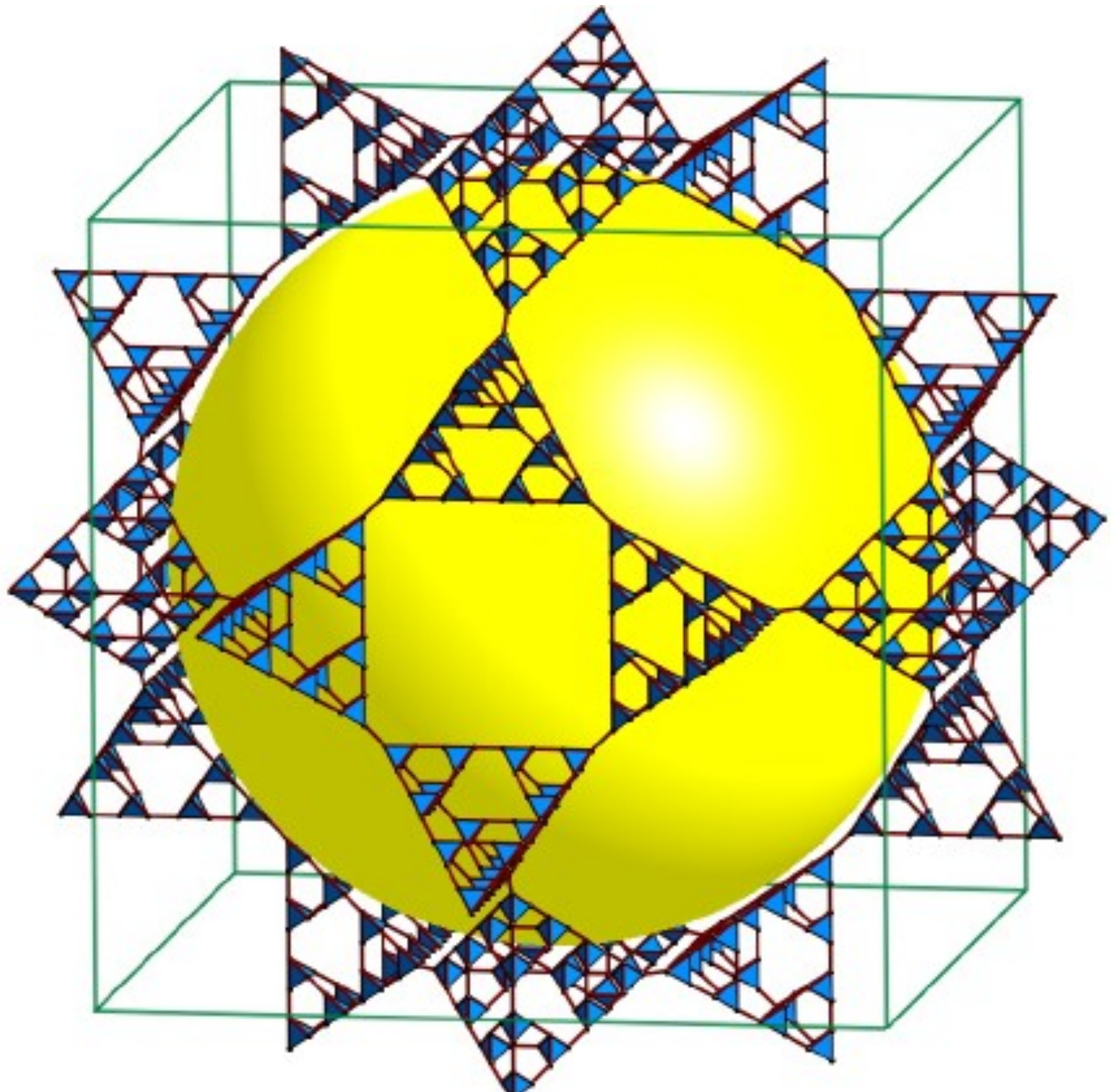
sodalite



Decorated sodalite







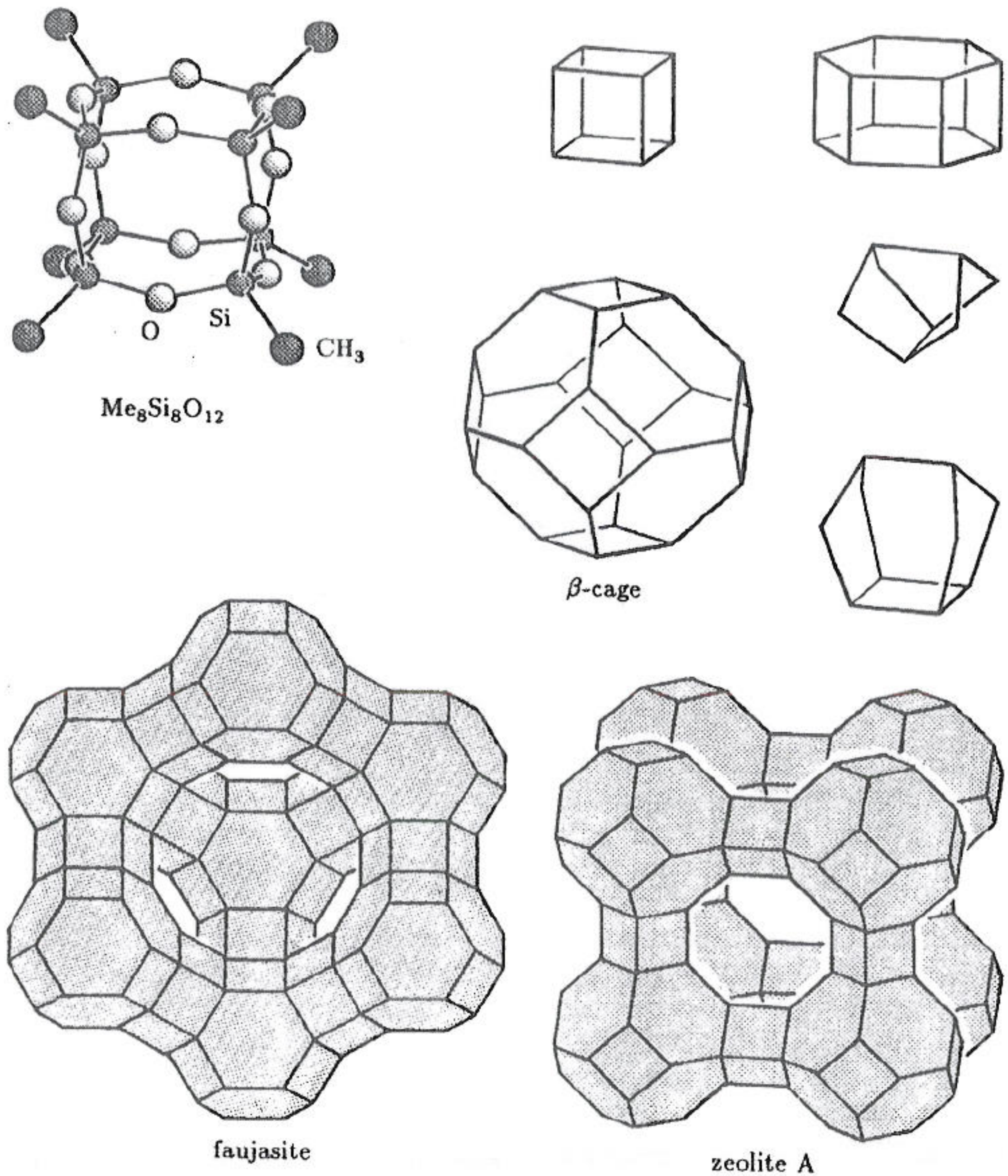
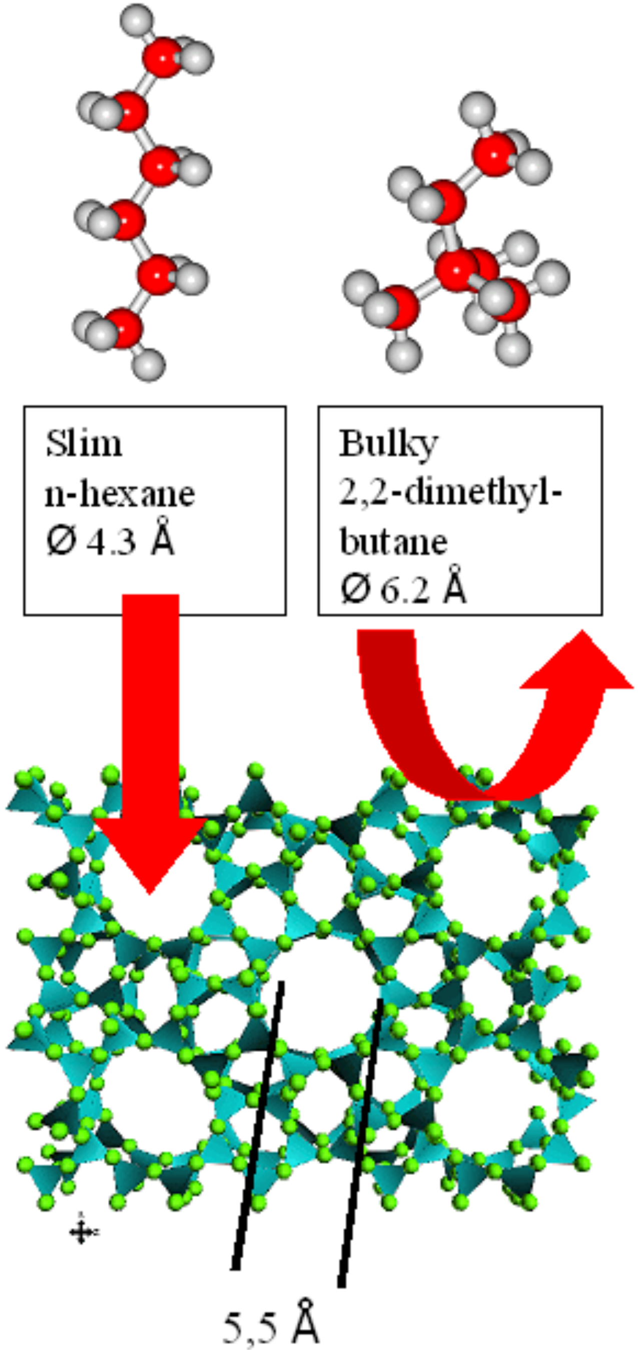


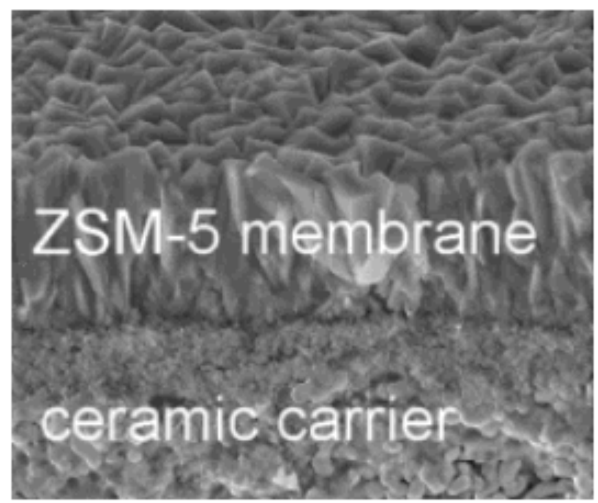
Fig. 110
Structure of $Me_8Si_8O_{12}$ and schematic representations of some Si–O polyhedra; linking of these polyhedra to the frameworks of two zeolites

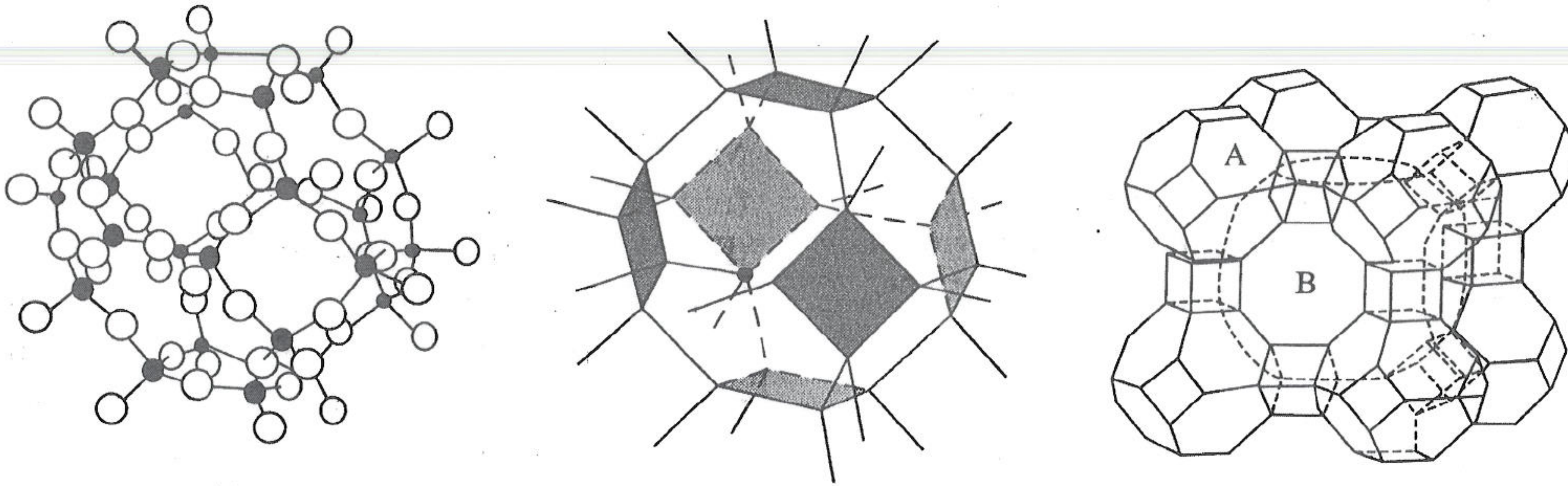
Natrolite zeolite

Minerals (boiling-stone, zeo-lite)

$Na_2Al_2Si_3O_{10} \cdot 2H_2O$


Slim
n-hexane
Ø 4.3 Å
Bulky
2,2-dimethyl-
butane
Ø 6.2 Å
5,5 Å

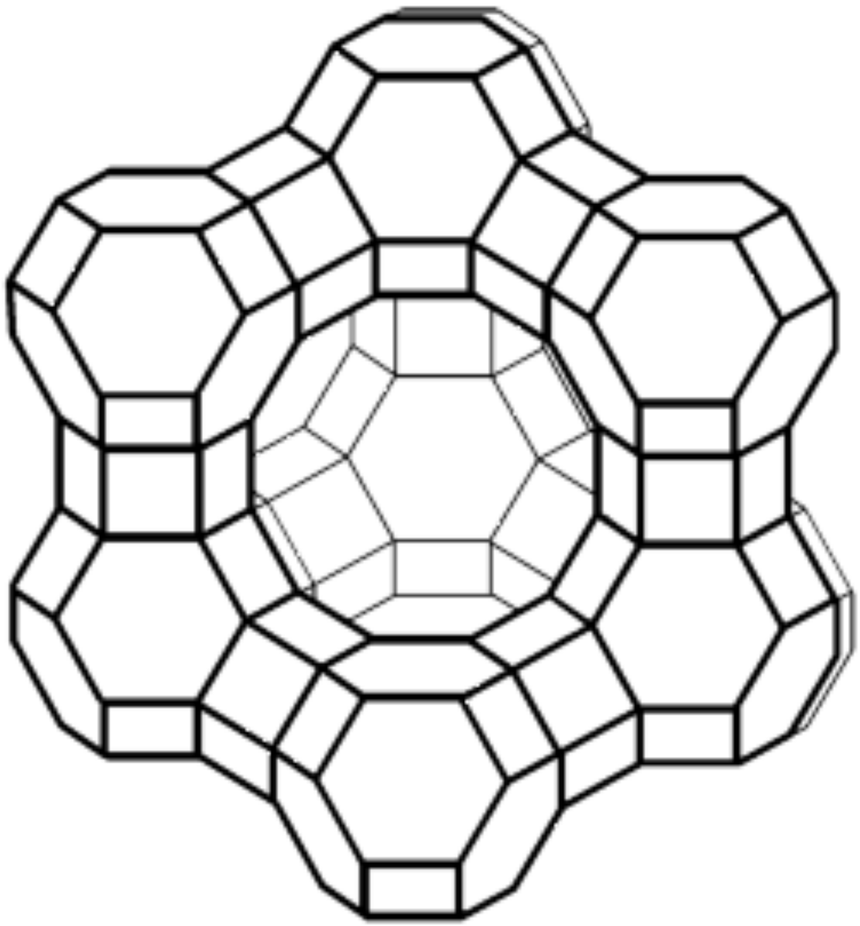

ZSM-5 membrane
ceramic carrier



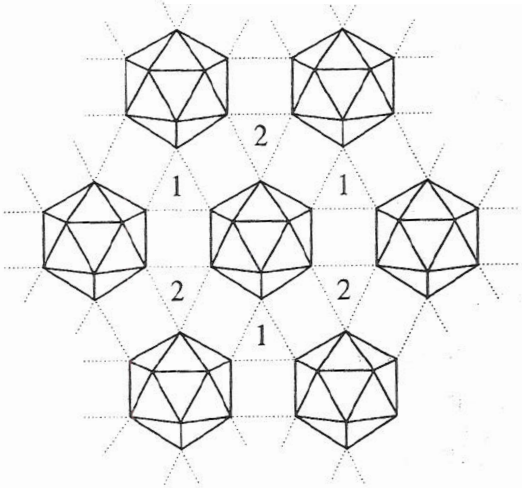
(a) (b) (c)

9.15 (a) 24 $\{SiO_4\}$ tetrahedra linked by corner sharing to form a framework surrounding a cubo-octahedral cavity; (b) conventional representation of the polyhedron in (a); and (c) spa arrangement of the polyhedra A which also generates larger cavities B.

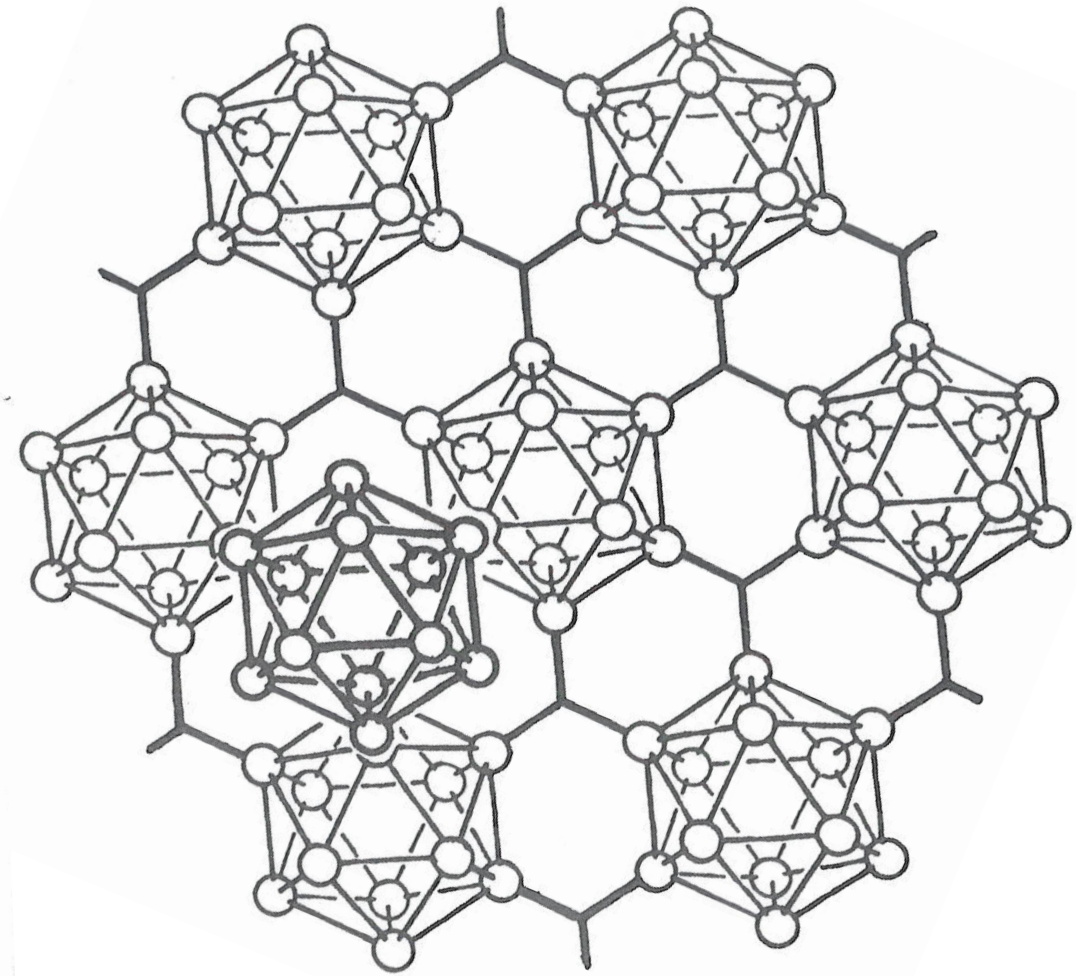
Faujasite



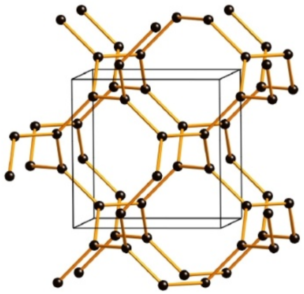
Elemental boron exists in more than one form (polymorphs). α-B



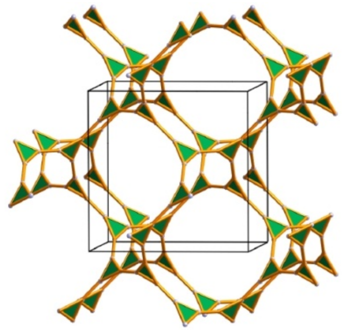
re 6.2 Basal plane of α-rhombohedral boron showing close-packed arrangement of B_{12} icosahedra. The B–B distances within each icosahedron vary regularly between 173–179 pm. Dotted lines show the 3-centre bonds between the 6 equatorial boron atoms in each icosahedron to 6 other icosahedra in the same sheet at 202.5 pm. The sheets are stacked so that each icosahedron is bonded by six 2-centre B–B bonds at 171 pm (directed rhombohedrally, 3 above and 3 below the icosahedron). B_{12} units in the layer above are centred over 1 and those in the layer below are centred under 2.



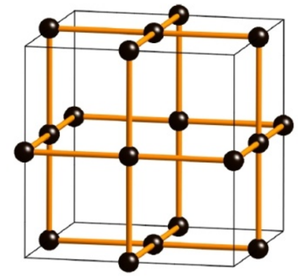
Default Structures (transitivity 1111)



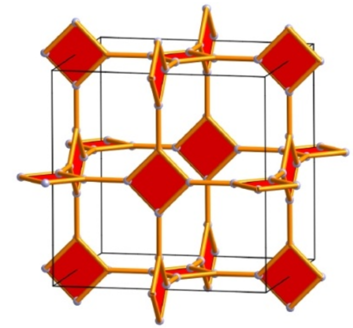
srs



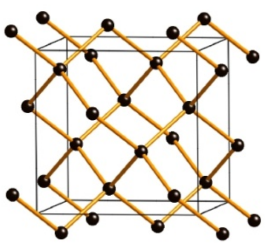
srs-a



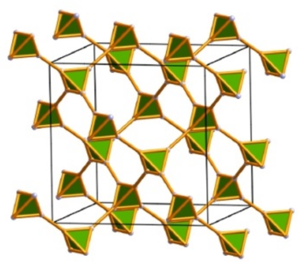
nbo



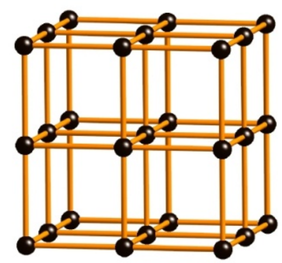
nbo-a



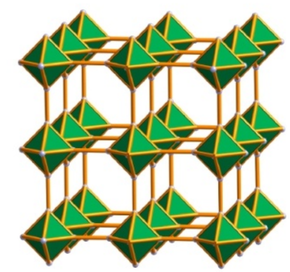
dia



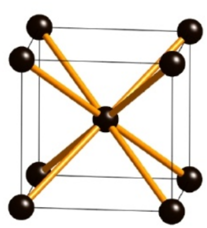
dia-a



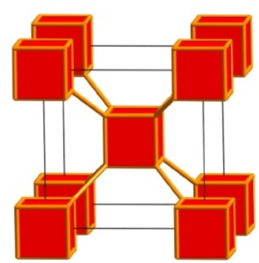
pcu



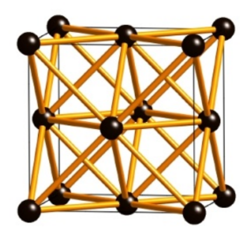
pcu-a



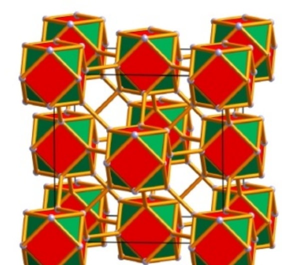
bcu



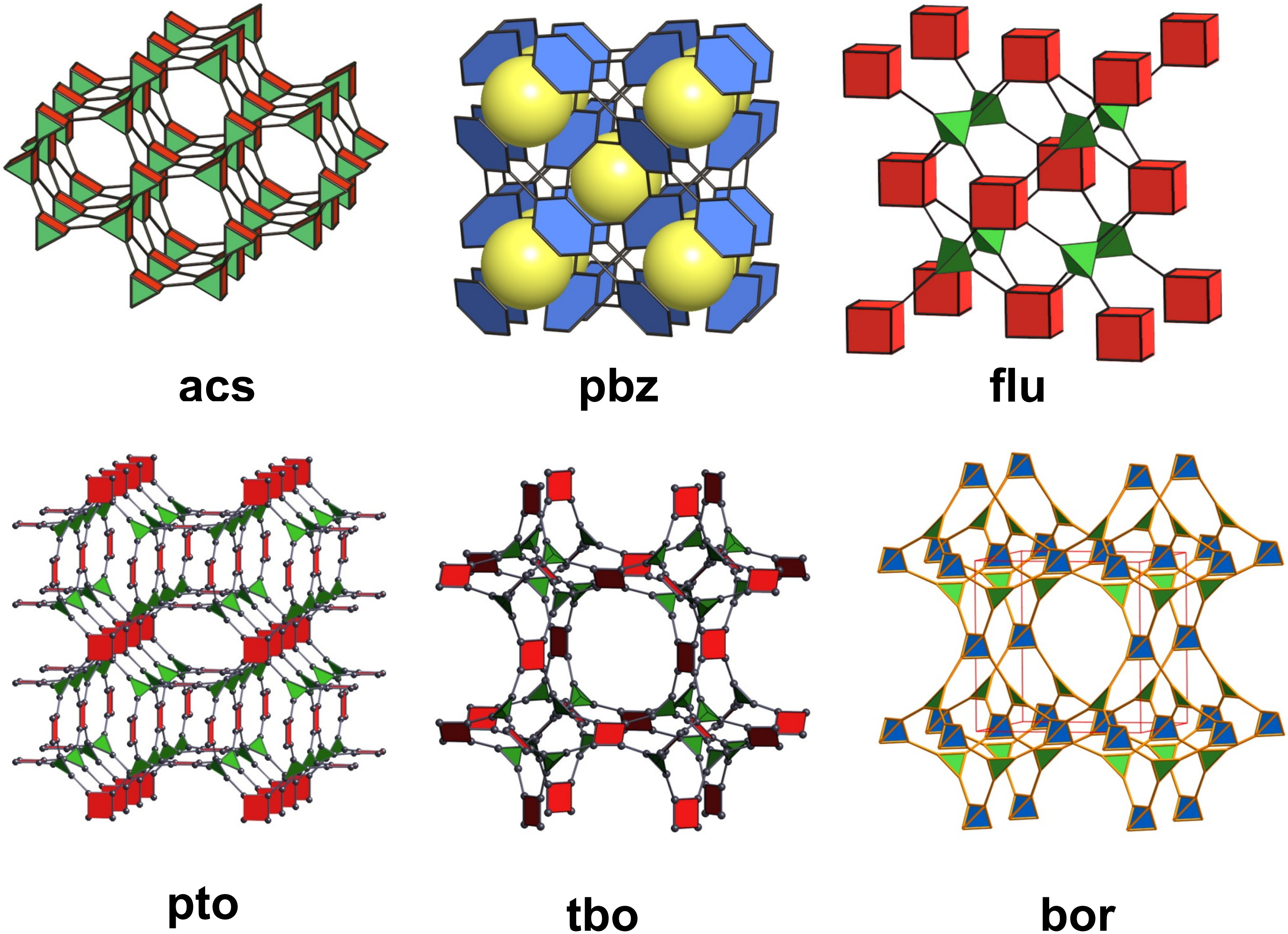
bcu-a = pcb

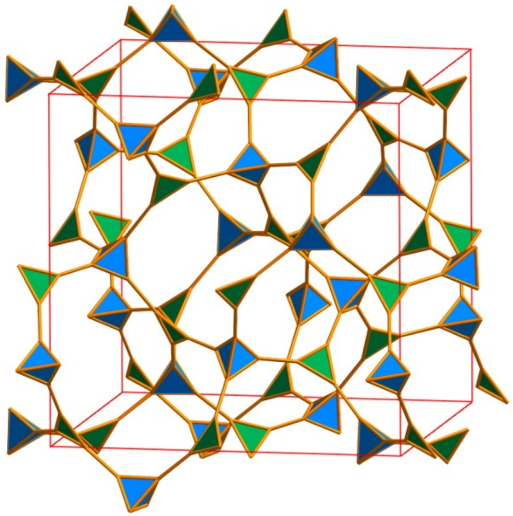


fcu

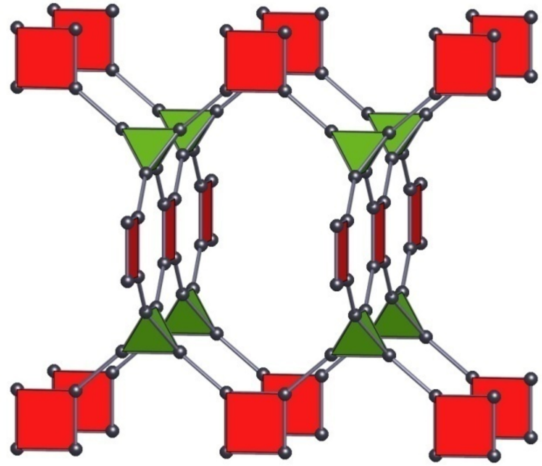


fcu-a = ubt

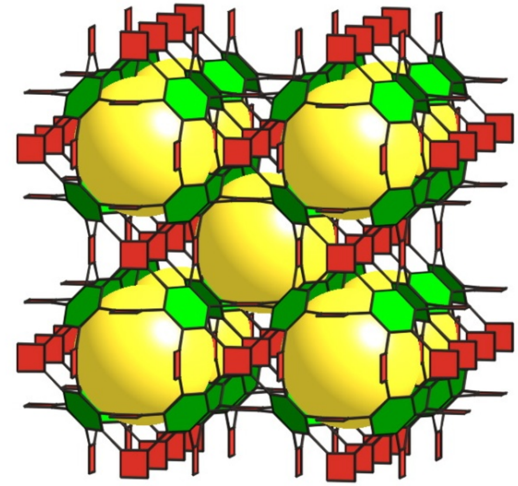

acs
pbz
flu
pto
tbo
bor



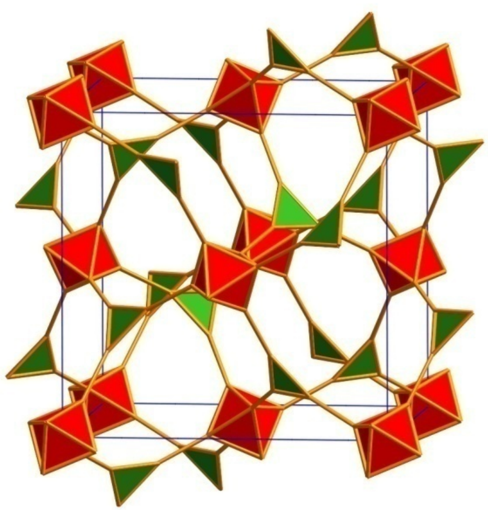
ctn



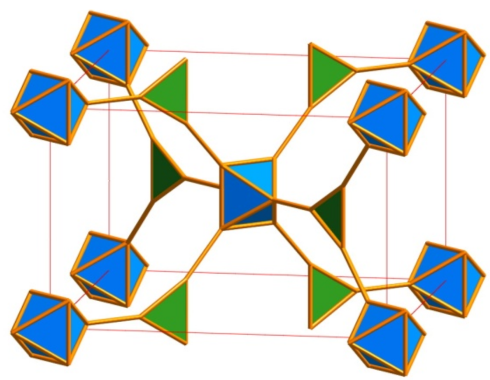
pts



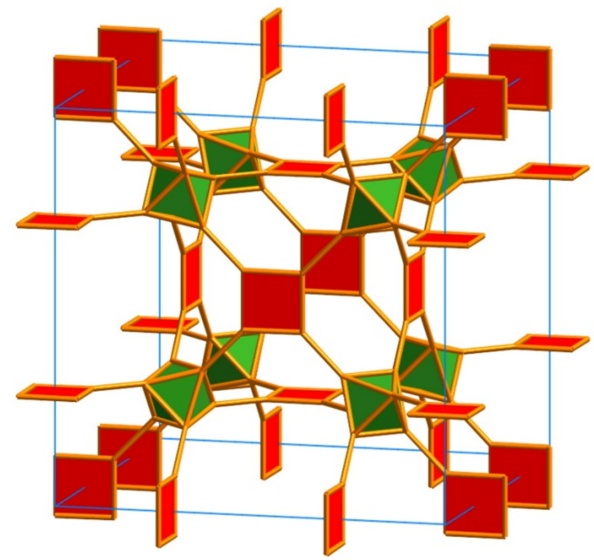
she



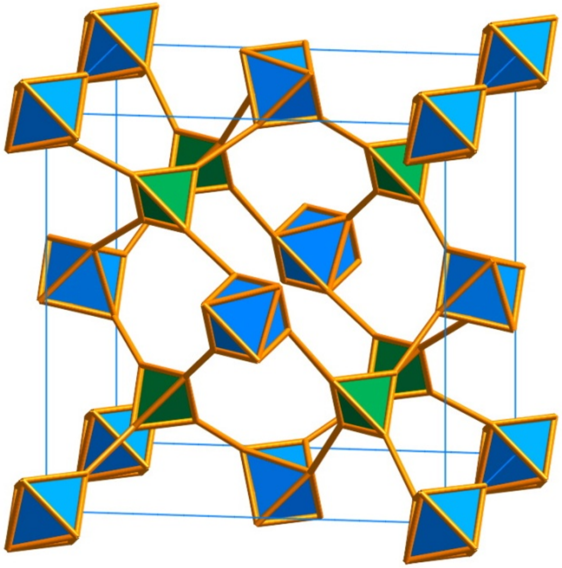
pyr



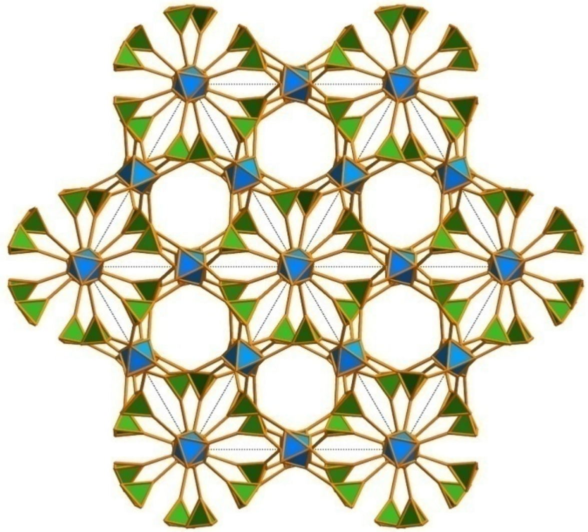
rtl



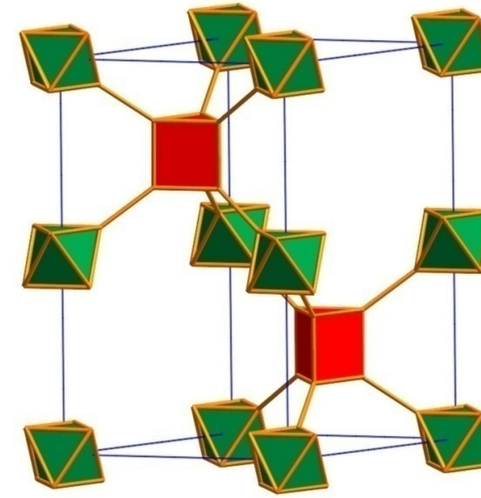
soc



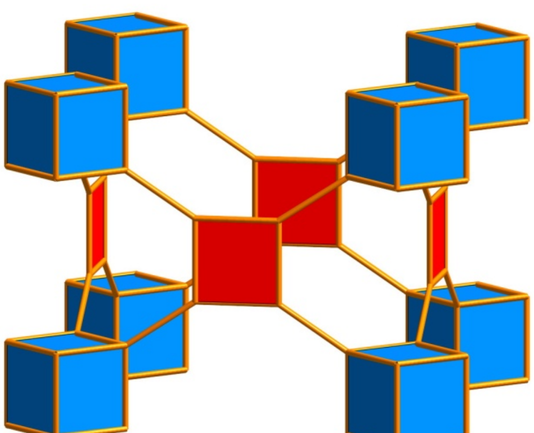
toc



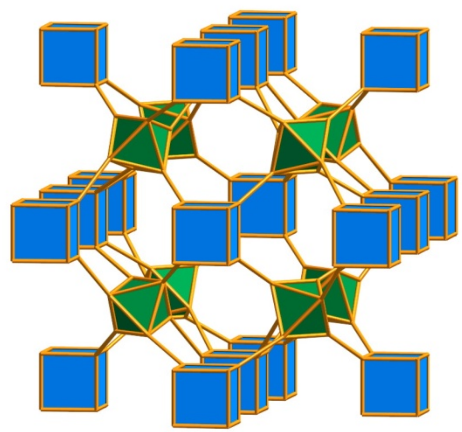
gar



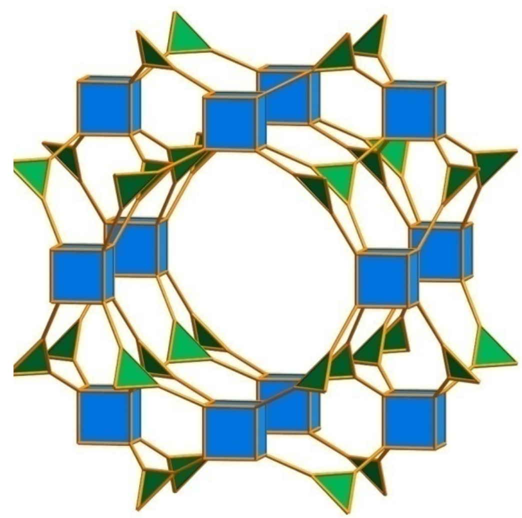
nia



scu



ocu



the