Structure types

Table 1.4 *Some close packed structures*

Anion arrangement	Interstitial sites T_+	T_-	O	Examples
ccp	—	—	1	NaCl, rock salt
	1	—	—	ZnS, blende or sphalerite
	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{2}$	$MgAl_2O_4$, spinel
	—	—	$\frac{1}{2}$	$CdCl_2$
	—	—	$\frac{1}{3}$	$CrCl_3$
	1	1	—	K_2O, antifluorite
hcp	—	—	1	NiAs
	1	—	—	ZnS, wurtzite
	—	—	$\frac{1}{2}$	CdI_2
	—	—	$\frac{1}{2}$	TiO_2, rutile*
	—	—	$\frac{2}{3}$	Al_2O_3, corundum
	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{2}$	Mg_2SiO_4, olivine
ccp 'BaO_3' layers	—	—	$\frac{1}{4}$	$BaTiO_3$, perovskite

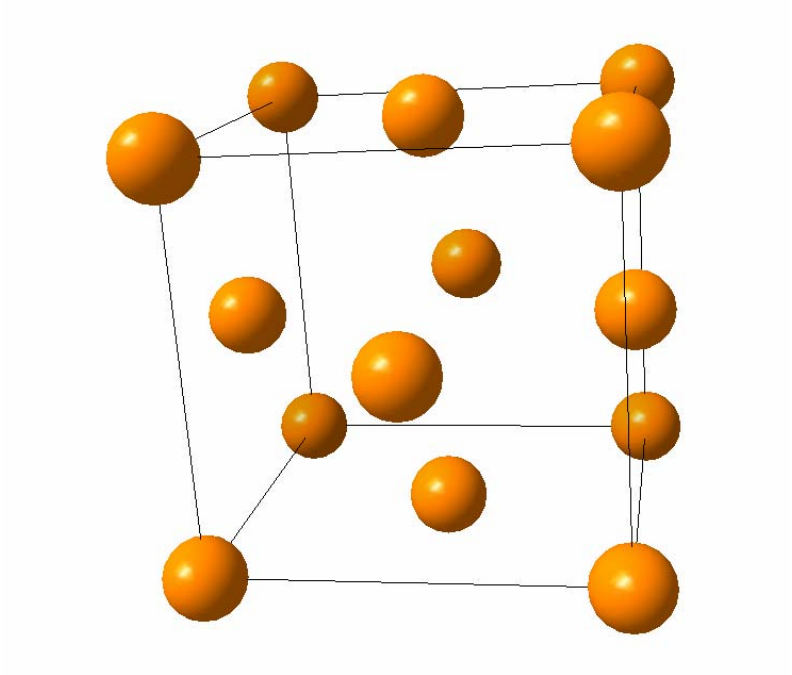
* The *hcp* oxide layers in rutile are not planar but are buckled; the oxide ion arrangement may alternatively be described as *tetragonal packed* (*tp*).

Cu
NaCl
ZnS (bl.)
$MgAl_2O_4$
$CdCl_2$ / Cs_2O
$CrCl_3$
K_2O / CaF_2
C (diamond)
$SrTiO_3$
ReO_3
CsCl
Fe (bcc)

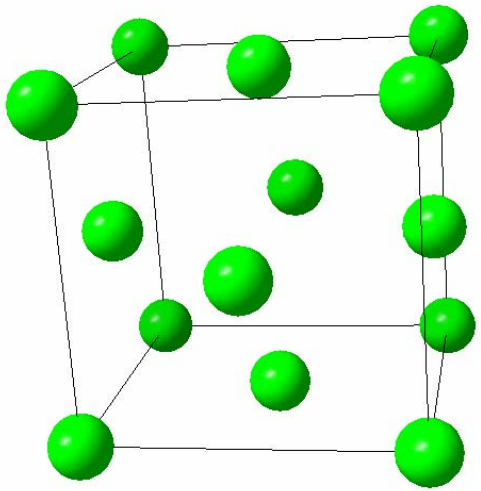
Mg
NiAs
ZnS (wu.)
CdI_2
C (graphite)
TiO_2
Al_2O_3

MoS_2
AlB_2

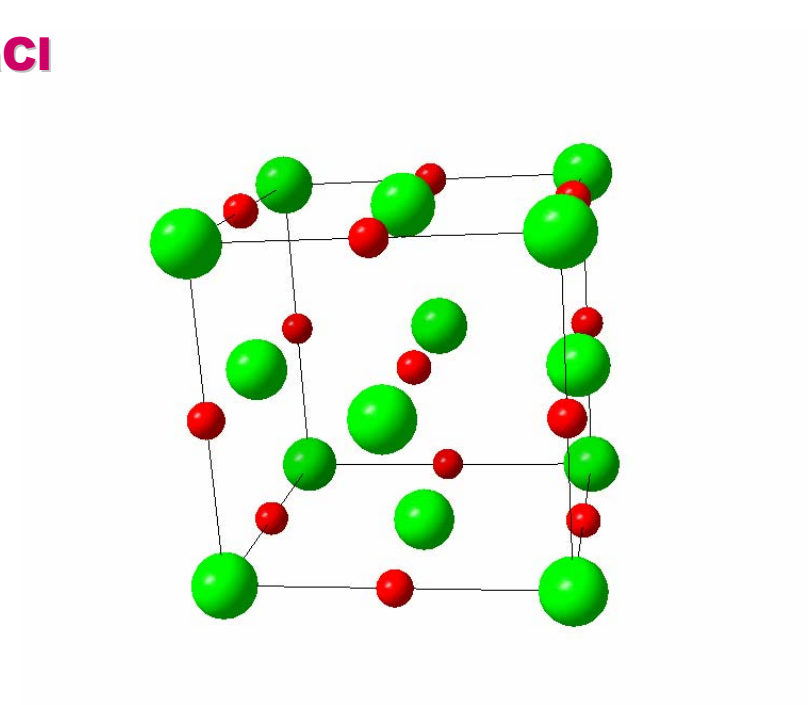
Cu



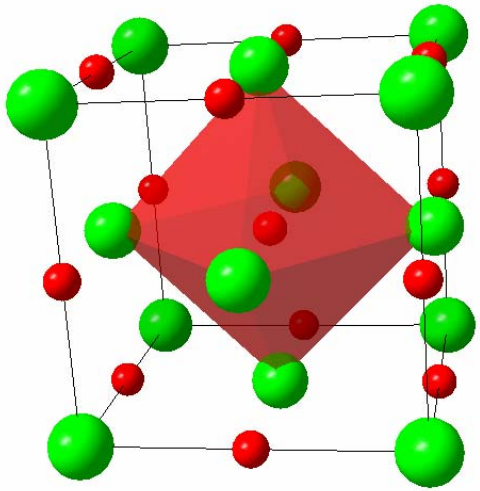
NaCl



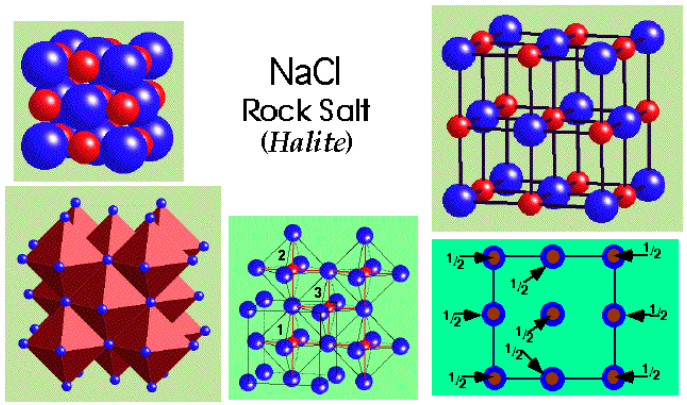
NaCl



NaCl

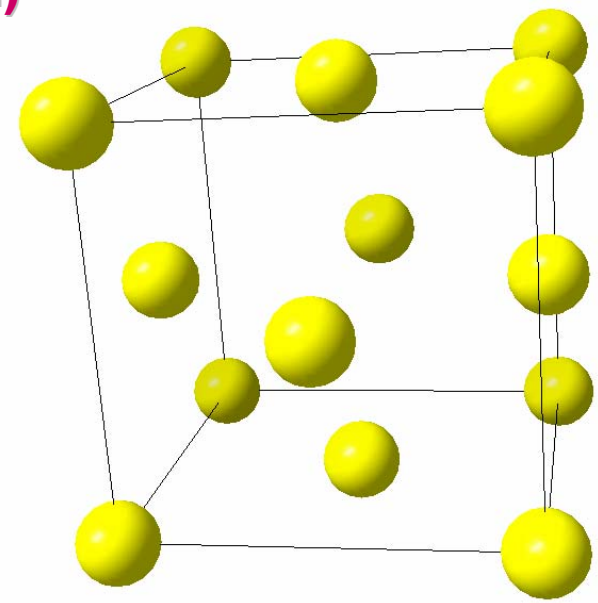


NaCl

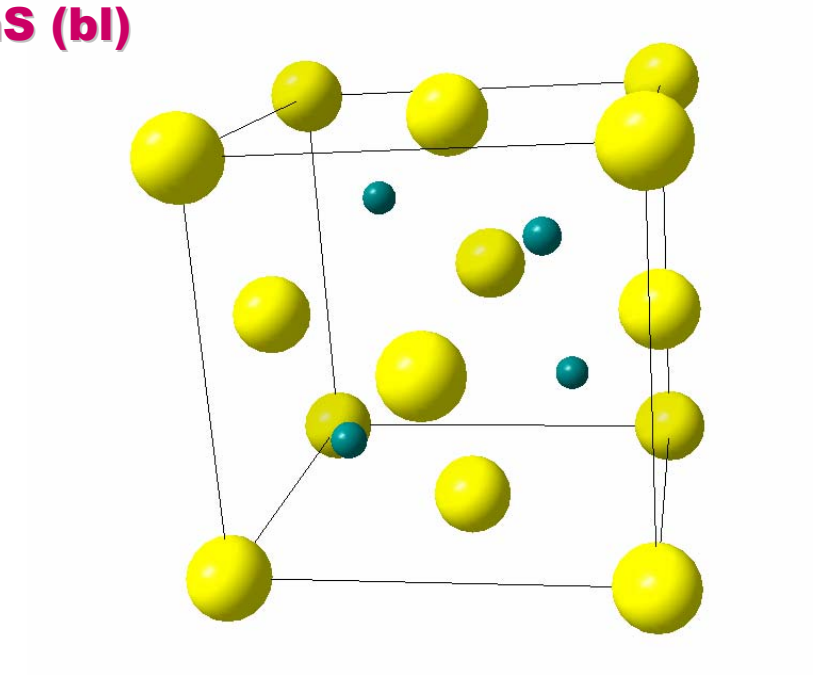


CCP Cl- with Na+ in all Octahedral holes
Lattice: fcc
Motif: Cl at (0,0,0); Na at (1/2,0,0)
4NaCl in unit cell
Coordination: 6:6 (octahedral)
Cation and anion sites are topologically identical

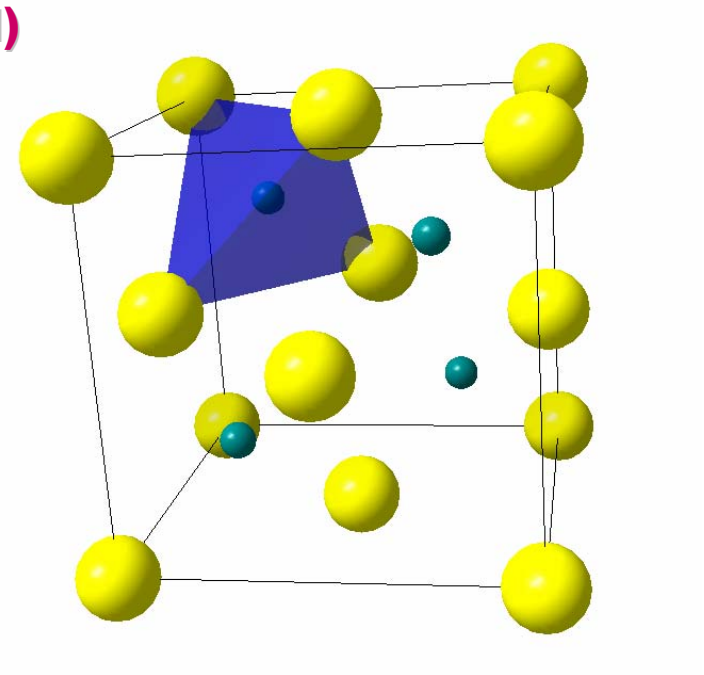
ZnS (bl)



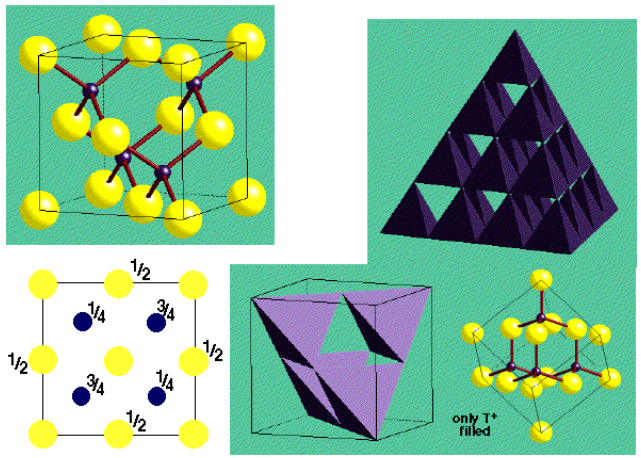
ZnS (bl)



ZnS (bl)



ZnS (bl)



CCP S^{2-} with Zn^{2+} in half Tetrahedral holes (only T+ {or T-} filled)
Lattice: fcc
4ZnS in unit cell
Motif: S at (0,0,0); Zn at (1/4,1/4,1/4)
Coordination: 4:4 (tetrahedral)
Cation and anion sites are topologically identical

ZnS

Structural polymorphs:

Zink blende **Stable at normal P,T**
Wurstitt **Stable at T > 1020 °C at P = 1 atm**

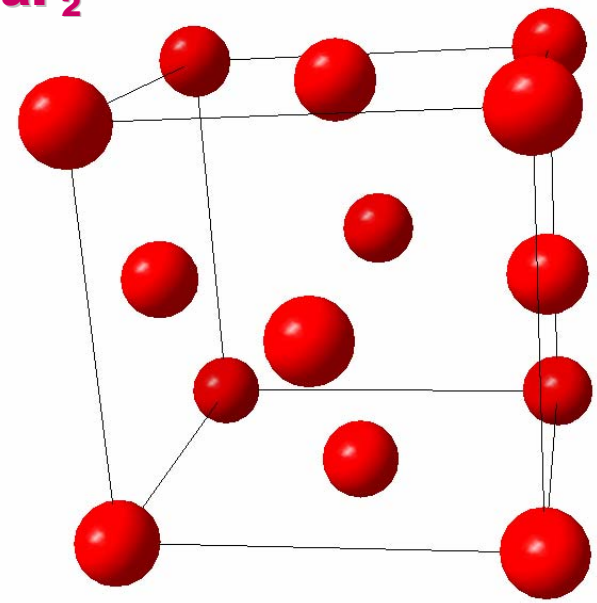
Metastable at RT, but transforms by crushing

Thermodinamics
Kinetics

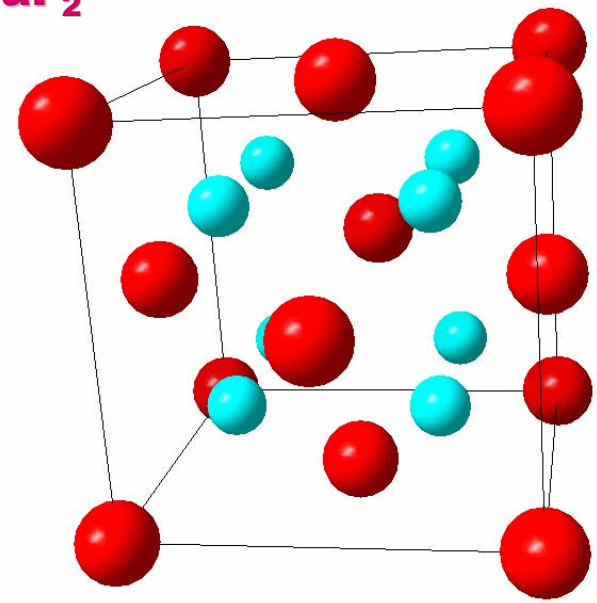
Zink blende
ccp
½ tetraedra holes filled

Wurstitt
hcp
½ tetraedra holes filled

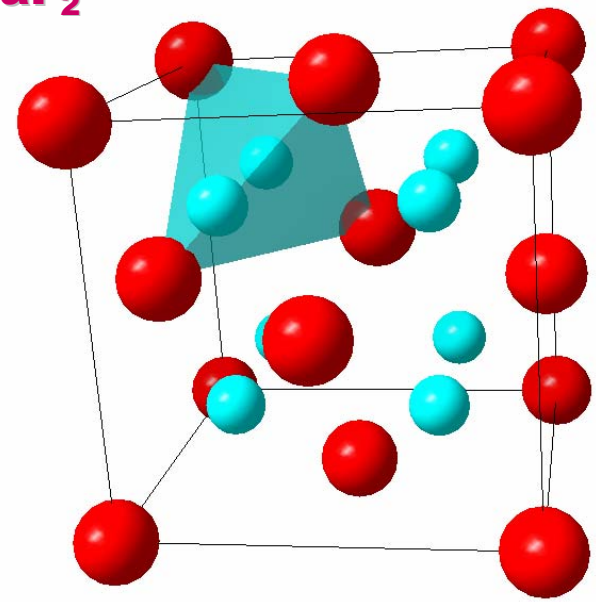
K_2O / CaF_2



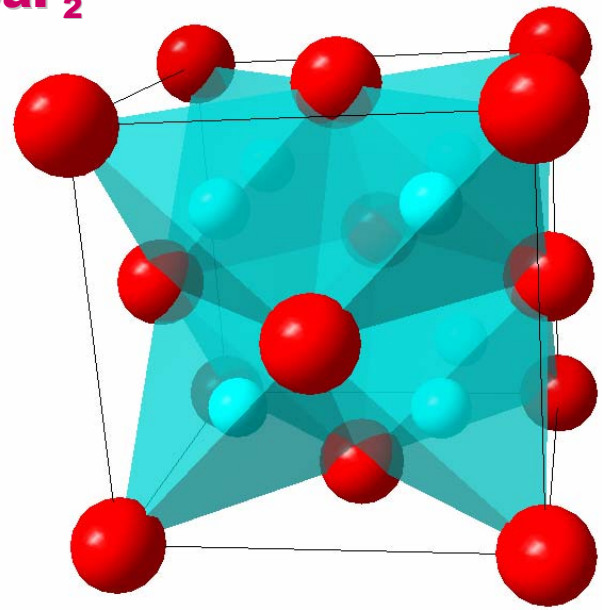
K_2O / CaF_2



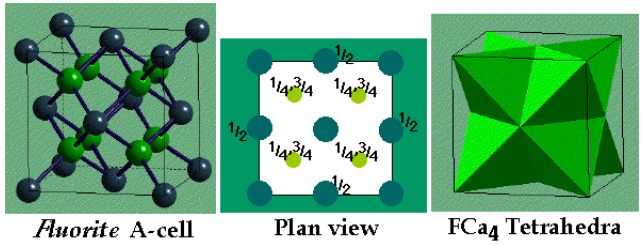
K_2O / CaF_2



K_2O / CaF_2



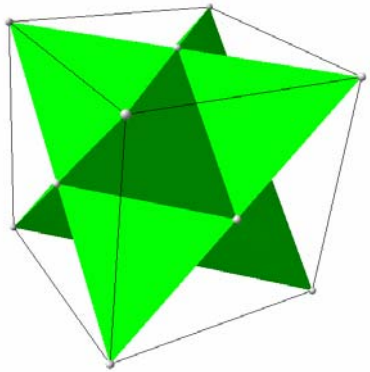
CaF_2



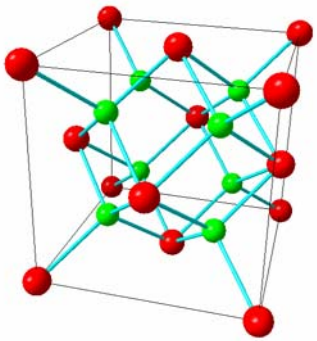
CCP Ca2+ with F- in all Tetrahedral holes
Lattice: fcc
Motif: Ca2+ at (0,0,0); 2F- at (1/4,1/4,1/4) & (3/4,3/4,3/4)
4CaF2 in unit cell
Coordination: Ca2+ 8 (cubic) : F- 4 (tetrahedral)
In the related Anti-Fluorite structure Cation and Anion positions are reversed

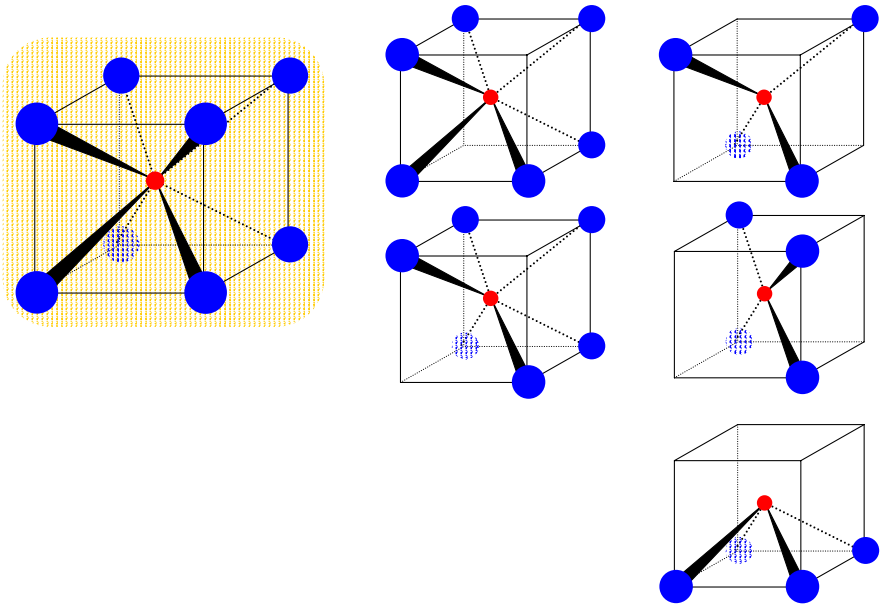
K_2O / CaF_2

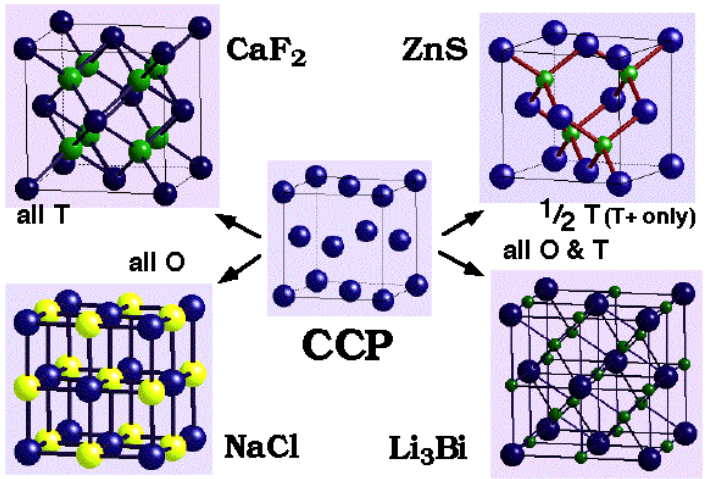
CaF_2
FCa_4 - tetraheda



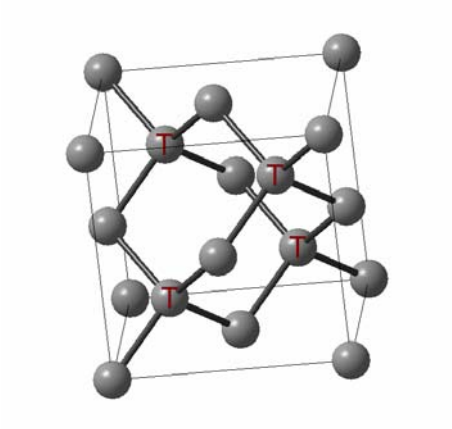
Na_2O
NaO_4 - tetraheda







C (diamond)



The diamond lattice is composed of two interpenetrating fcc lattices, one displaced 1/4 of a lattice constant in each direction from the other. Each site is tetrahedrally coordinated with four other sites in the other sublattice. When the two sublattices are of different atoms, then the diamond lattice becomes the zincblende or sphalerite lattice. Examples of materials with the diamond crystal structure are diamond, silicon and germanium.

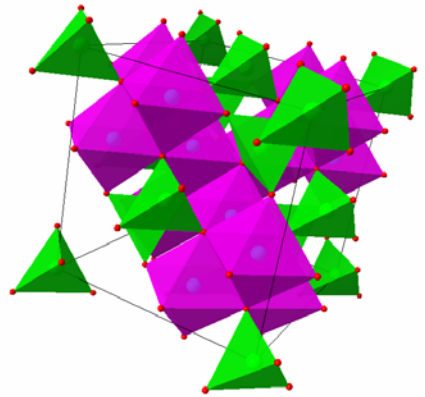
Spinel, $MgAl_2O_4$

1/8 T+
1/8 T-
1/2 O

T O

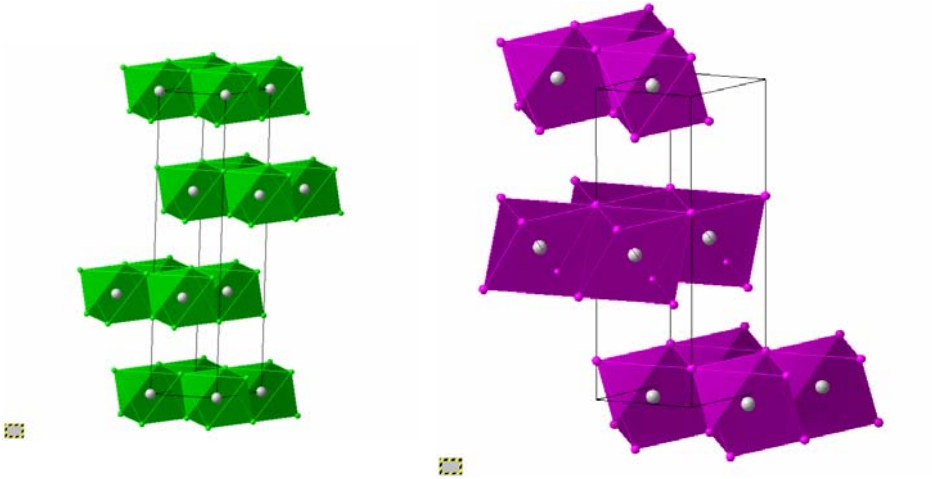
Normal spinel $M^{2+}(M^{3+})_2O_4$

Inverse spinel $M^{3+}(M^{2+}M^{3+})O_4$

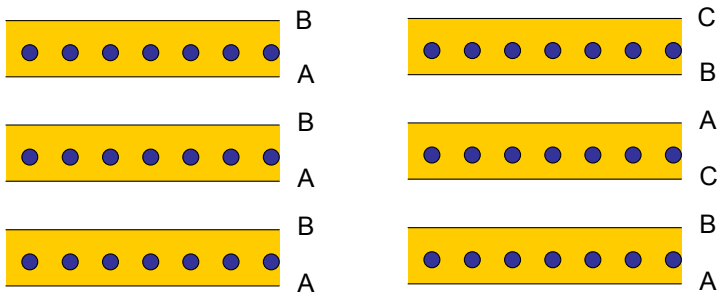


$CdCl_2$

$CdCl_2$ CdI_2



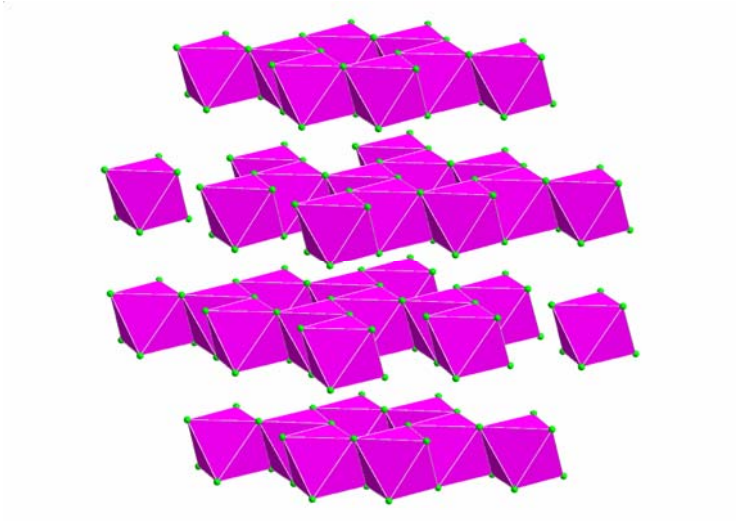
$CdCl_2$ / CdI_2 type structures



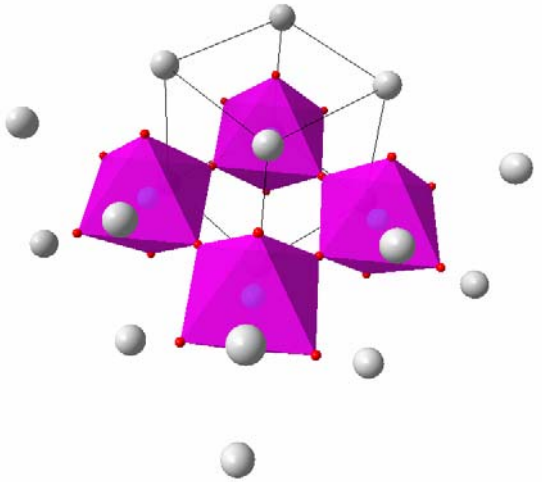
Within the layers: CdX_6-octahedra
Between the layers: only van der Waals interactions

Polytypes:
in 2-dimensions -> same structure with strong bonds
different repetition in the 3rd direction, can have week bonds

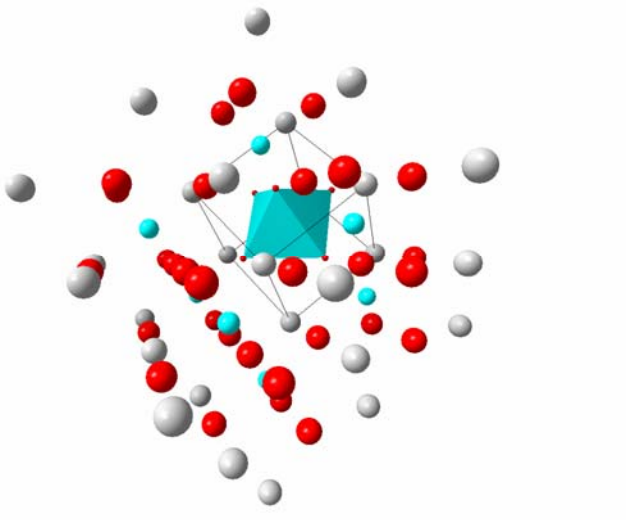
$CrCl_3$



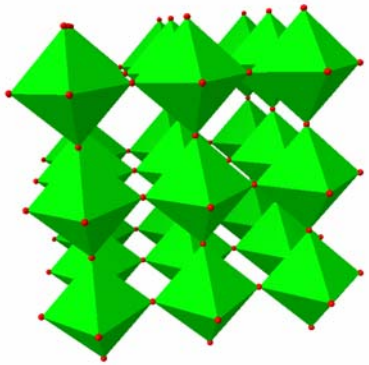
Perovskite



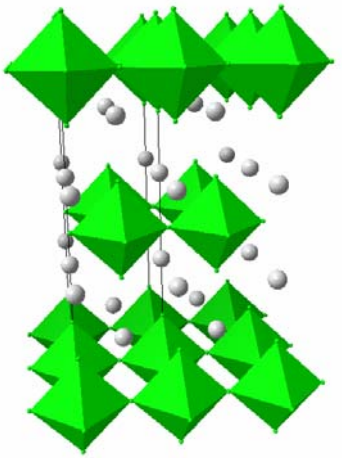
Perovskite



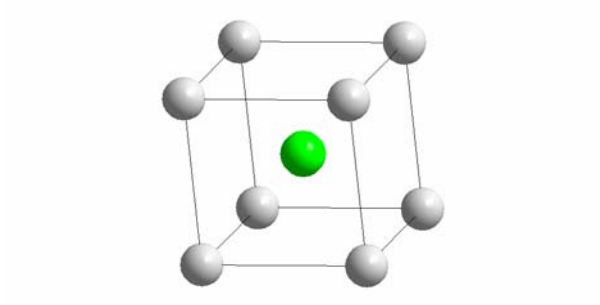
ReO_3

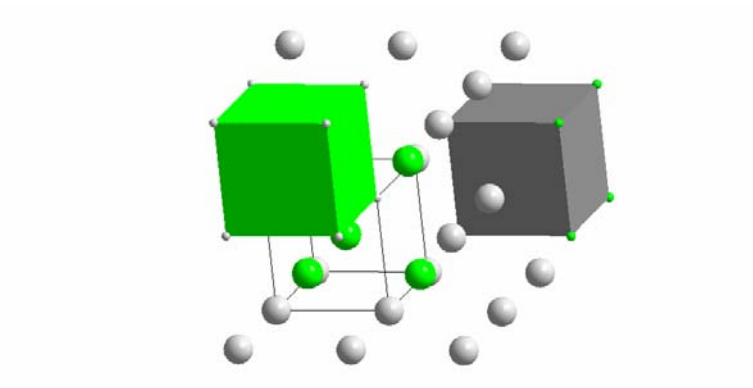


K_2NiF_4

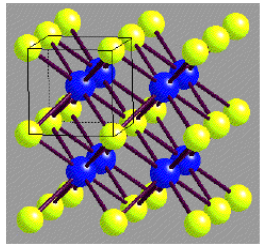


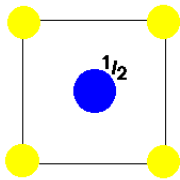
CsCl

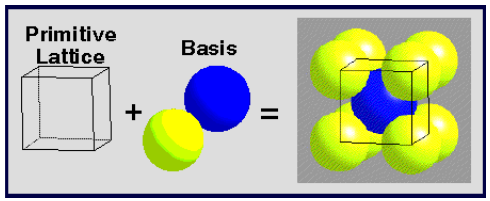




CsCl *Cesium Chloride*

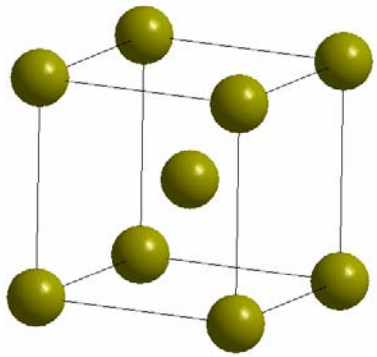




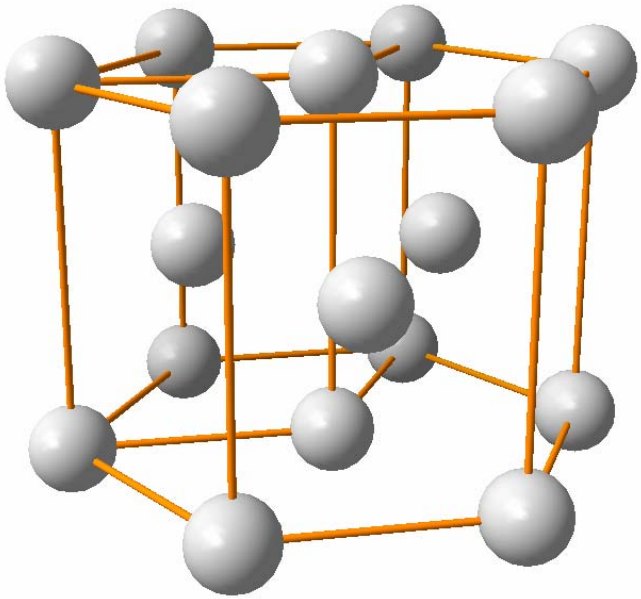


- *Lattice*: Cubic - P (N.B.**Primitive**!)
- *Motif*: Cl at (0,0,0); Cs at ($^1/_2$,$^1/_2$,$^1/_2$)
- **1**CsCl in unit cell
- *Coordination*: 8:8 (cubic)
- Adoption by chlorides, bromides and iodides of larger cations, *e.g.* Cs^+, Tl^+, NH_4^+

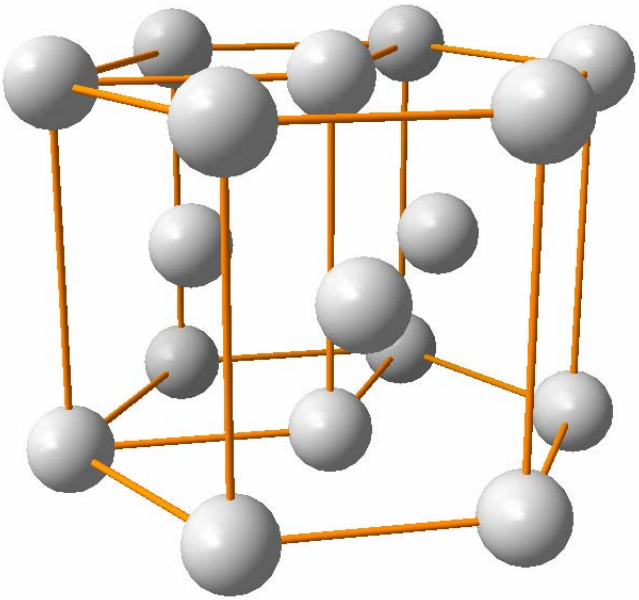
α-Fe



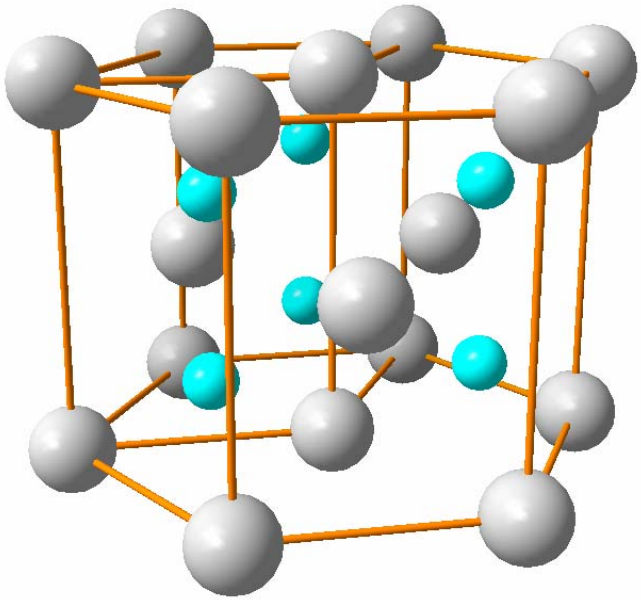
Mg



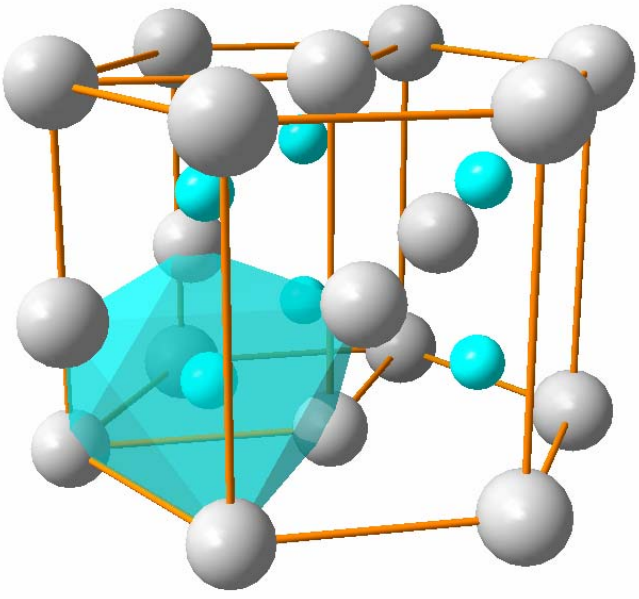
NiAs



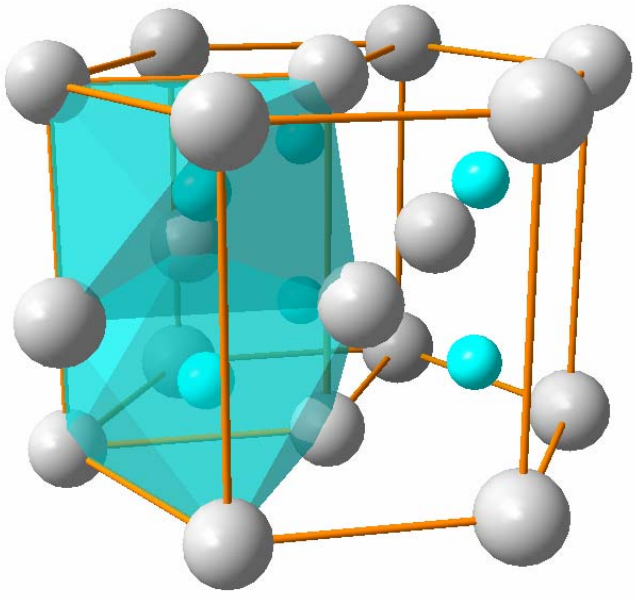
NiAs



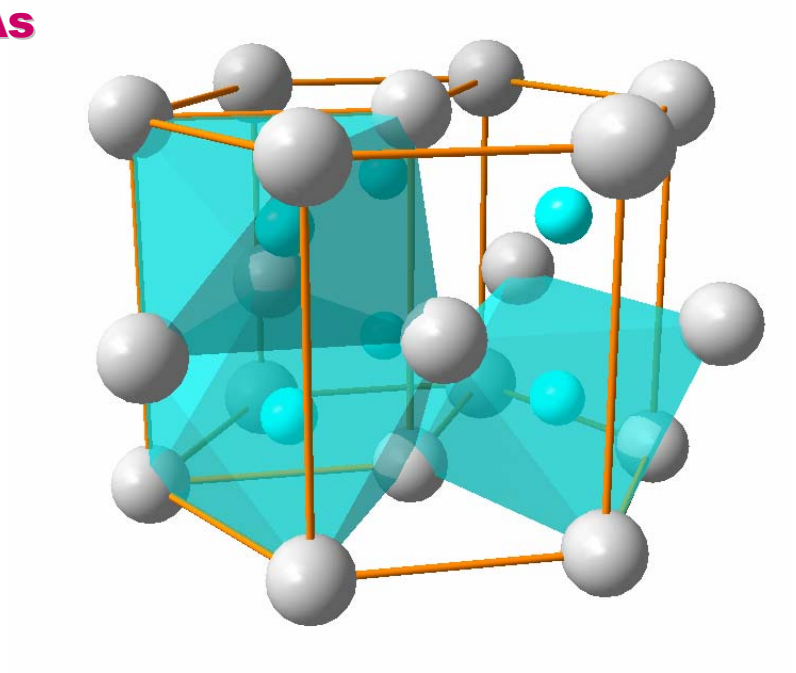
NiAs



NiAs

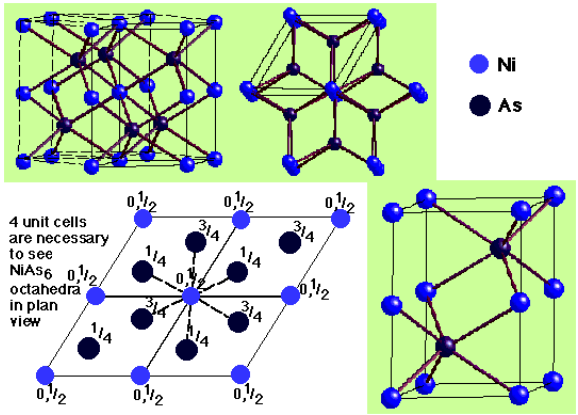


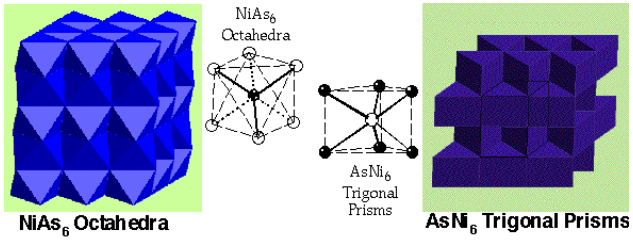
NiAs



NiAs *Nickel Arsenide*

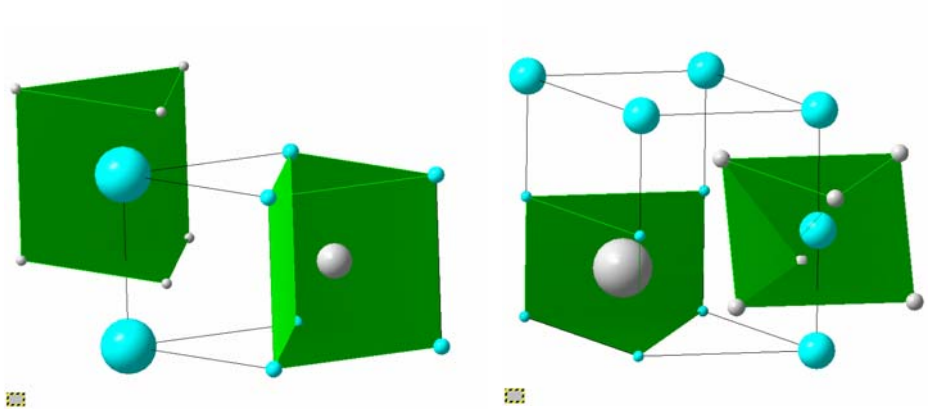
HCP As with Ni in all Octahedral holes
Lattice: Hexagonal - P
a = *b*, *c* Å Ã(8/3)*a*
Motif: 2Ni at (0,0,0) & (0,0,1/2)
2As at (2/3,1/3,1/4) &
(1/3,2/3,3/4)
2NiAs in unit cell
Coordination: Ni 6 (octahedral) :
As 6 (trigonal prismatic)



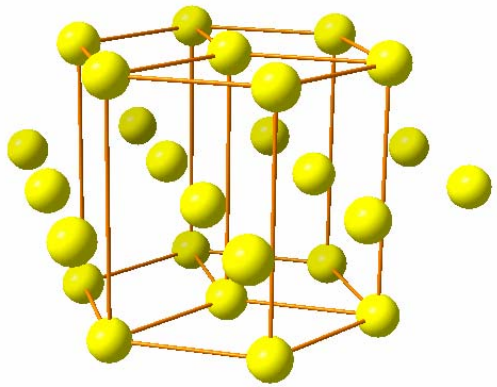


WC
WC_6, CW_6 trigonal prismatic

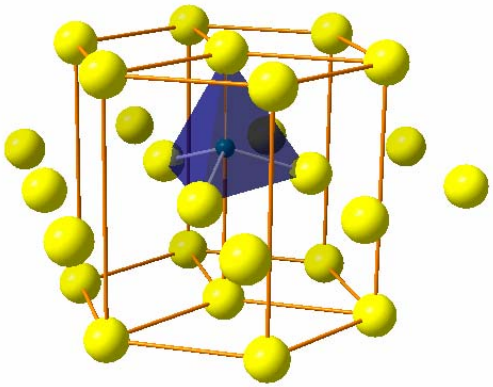
NiAs
$NiAs_6$ octahedra
$AsNi_6$ trigonal prismatic



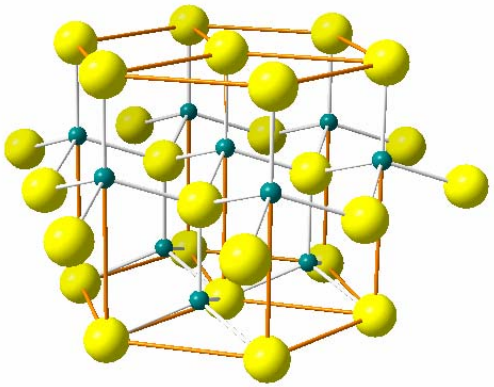
ZnS (wurtsite)



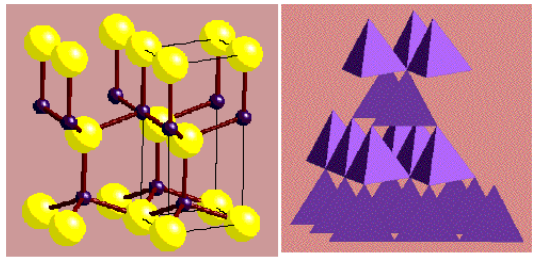
ZnS (wurtsite)

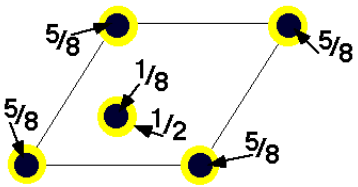


ZnS (wurtsite)



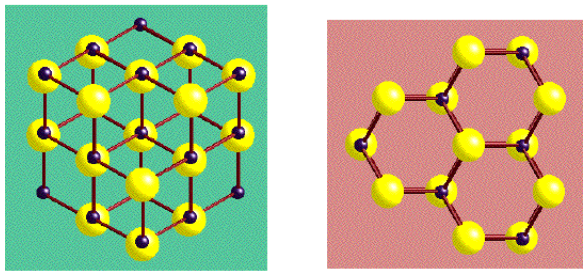
ZnS *Wurtzite*





HCP S2- with Zn2+ in half Tetrahedral holes (only T+ {or T-} filled)
Lattice: Hexagonal - P
a = *b*, *c* Å Ã(8/3)*a*
Motif: 2S at (0,0,0) & (2/3,1/3,1/2); 2Zn at (2/3,1/3,1/8) & (0,0,5/8)
2ZnS in unit cell
Coordination: 4:4 (tetrahedral)

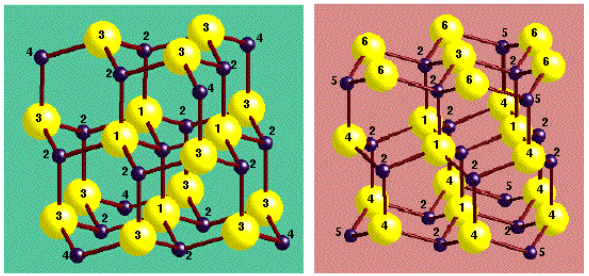
PLAN VIEWS



Zinc Blende — *CCP ABC repeat*

Wurtzite — *HCP AB repeat*

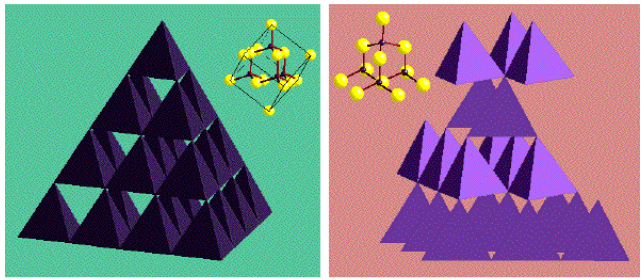
COORDINATION ENVIRONMENTS



Zinc Blende — Wurtzite

4 Nearest Neighbours (*Tetrahedral*)
12 Next-Nearest Neighbours
Cuboctahedral ← → *Anti-Cuboctahedral*
Very different Next, Next-Nearest Neighbour Coordinations & beyond

POLYHEDRAL REPRESENTATIONS

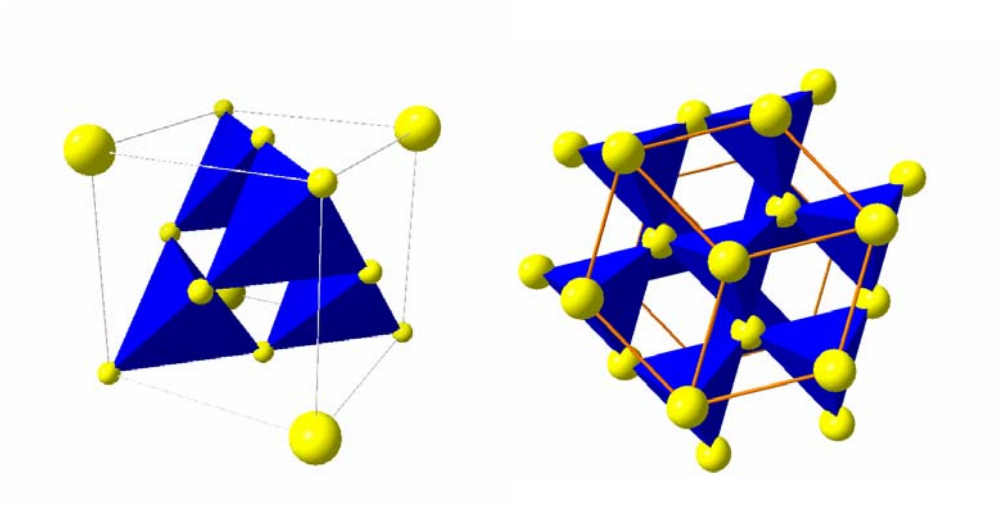


Zinc Blende Wurtzite

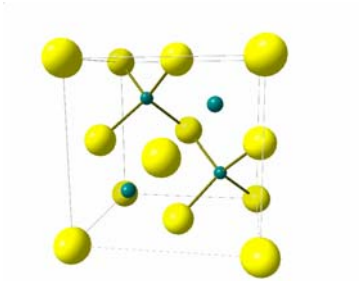
Vertex-linked tetrahedra only, but layers skewed in Wurtzite, & not in Blende

Sink blende
ZnS_4, SZn_4

Wurtsitt
ZnS_4, SZn_4

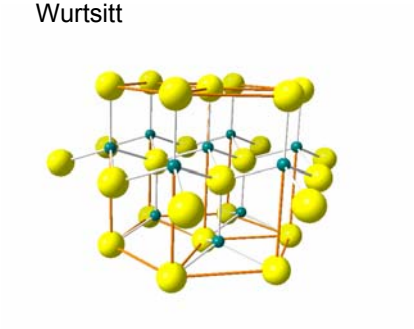


Zink-blende



ZnS_4 –tetrahedra
Diamond type structure if Zn = S
Non-centrosymmetric

Wurtsitt



ZnS_4 –tetrahedra of + type

ZnS – würtsitt

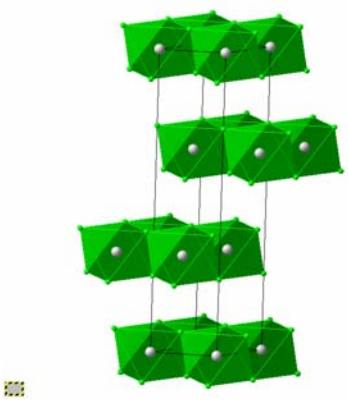
Z = 2 pr. hexagonal unit cell

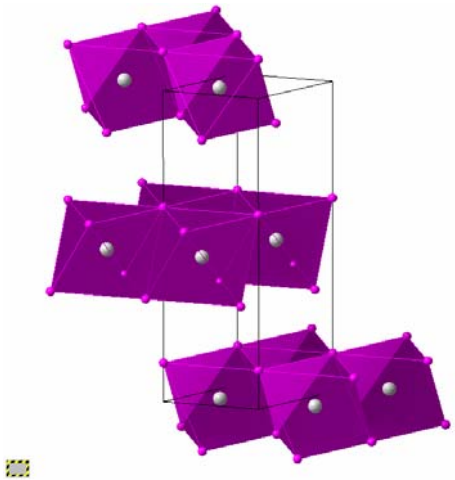
Other related structures:

MX	**ZnO**
$MM'X_2$	**$LiGaO_2$**
$M_2M'M''X_4$	**Li_2BeSiO_4**
	$LiPO_4$
	…

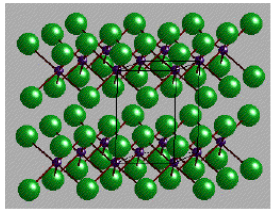
$CdCl_2$

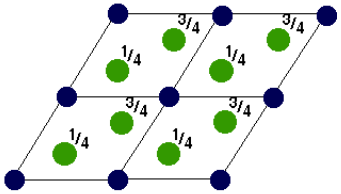
$CdCl_2$ CdI_2

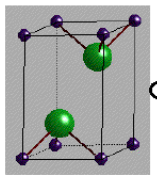




CdI2 *Cadmium Iodide*

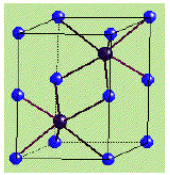


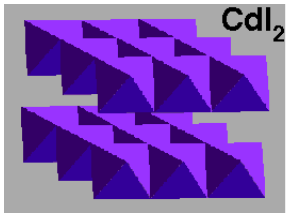


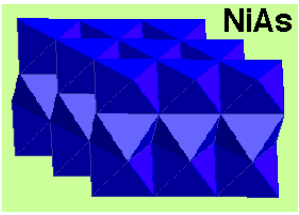


Comparison

CdI_2 *vs* NiAs

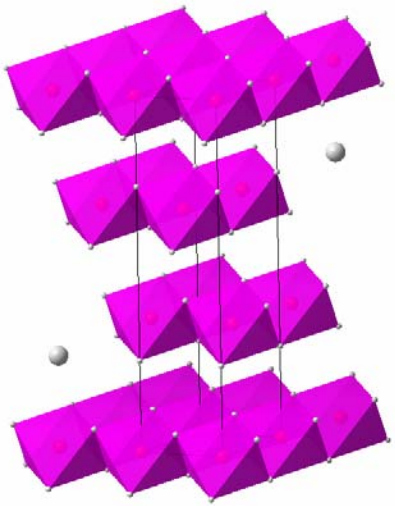




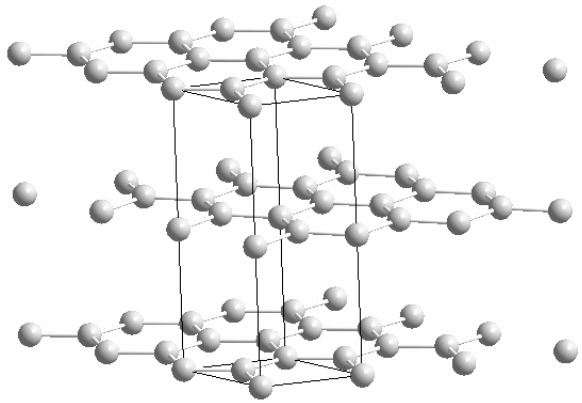


Lattice: Hexagonal - P
Motif: Cd at (0,0,0); 2I at (2/3,1/3,1/4) & (1/3,2/3,3/4)
1CdI2 in unit cell
Coordination: Cd - 6 (Octahedral) : I - 3 (base pyramid)

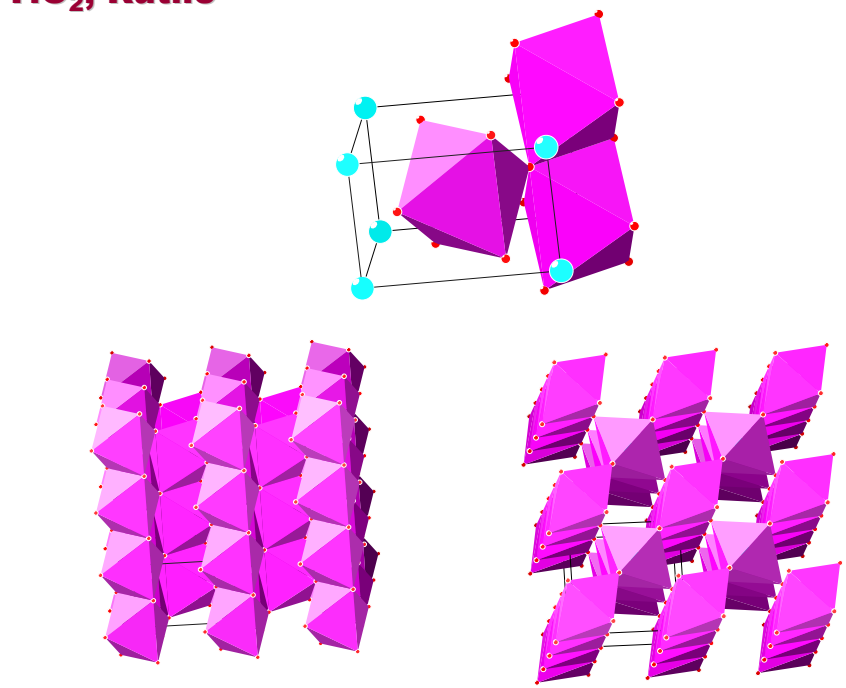
Cs_2O, anti $CdCl_2$



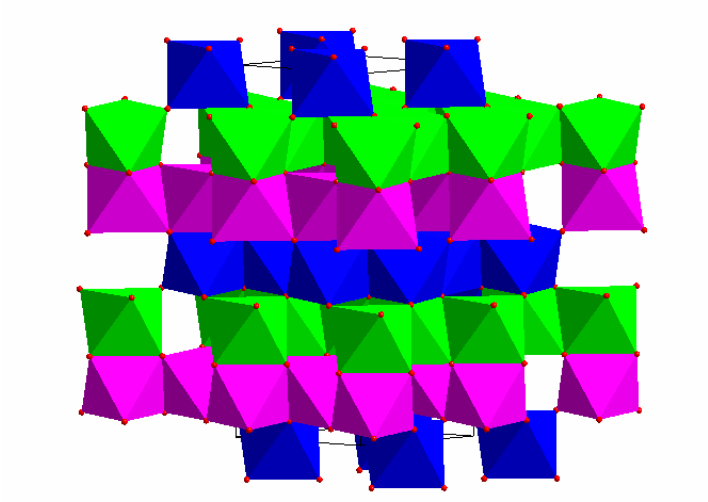
C (graphite)



TiO_2, Rutile

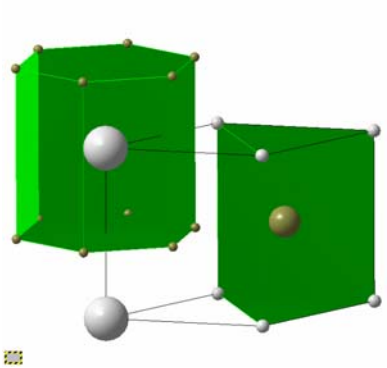


Al_2O_3, Corundum

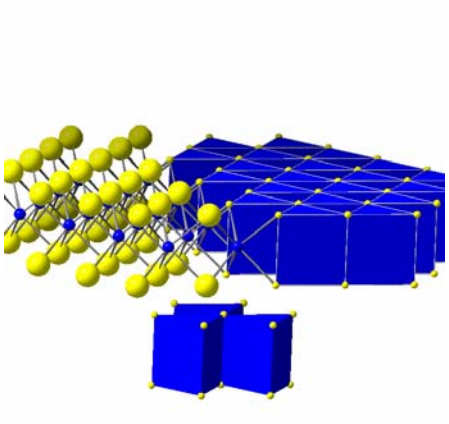


MoS_2

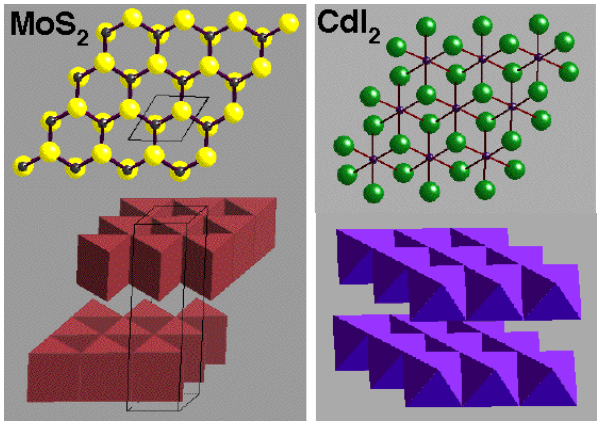
AlB_2
AlB_{12} hexagonal prismatic
BAl_6 trigonal prismatic



MoS_2
SMo_3 trigonal pyramid
MoS_6 trigonal prismatic

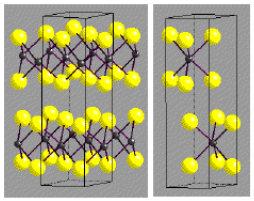


MoS2 *Molybdenite*

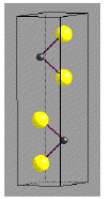


Note: Hexagonal layers of S atoms are **NOT** Close-packed in 3D
Lattice: Hexagonal - P
Motif: 2Mo at (2/3,1/3,3/4) & (1/3,2/3,1/4)
4I at (2/3,1/3,1/8), (2/3,1/3,3/8), (1/3,2/3,5/8) & (1/3,2/3,7/8)
2MoS2 in unit cell
Coordination: Mo 6 (**Trigonal Prismatic**) : S 3 (base pyramid)

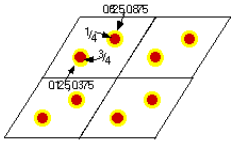
MoS2 *Molybdenite*



Clinographic Views



Unit Cell



Plan View