The Solid State

Structure Types of A_NB_M Solids

The crystal structure of the elements

Crystal structure of elements in theperiodic table

1 H HEX																	2 He HCP
3 Li BCC	4 Be HCP											5 B RHO	6 C HEX	7 N HEX	8 O SC	9 F SC	10 Ne FCC
11 Na BCC	12 Mg HCP											13 Al FCC	14 Si DC	15 P ORTH	16 S ORTH	17 Cl ORTH	18 Ar FCC
19 K BCC	20 Ca FCC	21 Sc HCP	22 Ti HCP	23 V BCC	24 Cr BCC	25 Mn BCC	26 Fe BCC	27 Co HCP	28 Ni FCC	29 Cu FCC	30 Zn HCP	31 Ga ORTH	32 Ge DC	33 As RHO	34 Se HEX	35 Br ORTH	36 Kr FCC
37 Rb BCC	38 Sr FCC	39 Y HCP	40 Zr HCP	41 Nb BCC	42 Mo BCC	43 Tc HCP	44 Ru HCP	45 Rh FCC	46 Pd FCC	47 Ag FCC	48 Cd HCP	49 In TETR	50 Sn TETR	51 Sb RHO	52 Te HEX	53 I ORTH	54 Xe FCC
55 Cs BCC	56 Ba BCC	57* La DHCP	72 Hf HCP	73 Ta BCC/TETR	74 W BCC	75 Re HCP	76 Os HCP	77 Ir FCC	78 Pt FCC	79 Au FCC	80 Hg RHO	81 Tl HCP	82 Pb FCC	83 Bi RHO	84 Po SC/RHO	85 At [FCC]	86 Rn FCC
87 Fr [BCC]	88 Ra BCC	89** Ac FCC	104 Rf [HCP]	105 Db [BCC]	106 Sg [BCC]	107 Bh [HCP]	108 Hs [HCP]	109 Mt [FCC]	110 Ds [BCC]	111 Rg [BCC]	112 Cn [BCC]	113 Nh [HCP]	114 Fl [HCP]	115 Mc	116 Lv	117 Ts	118 Og [FCC]

*	58 Ce DHCP/FCC	59 Pr DHCP	60 Nd DHCP	61 Pm DHCP	62 Sm RHO	63 Eu BCC	64 Gd HCP	65 Tb HCP	66 Dy HCP	67 Ho HCP	68 Er HCP	69 Tm HCP	70 Yb FCC	71 Lu HCP
**	90 Th FCC	91 Pa TETR	92 U ORTH	93 Np ORTH	94 Pu MON	95 Am DHCP	96 Cm DHCP	97 Bk DHCP	98 Cf DHCP	99 Es FCC	100 Fm [FCC]	101 Md [FCC]	102 No [FCC]	103 Lr [HCP]

BCC: body centered cubic

FCC: face centered cubic (cubic close packed)

HCP: hexagonal close packed

DHCP: double hexagonal close packed

ORTH: orthorhombic

TETR: tetragonal

RHO: rhombohedral

HEX: hexagonal

SC: simple cubic

DC: diamond cubic

MON: monoclinic

Unknown or uncertain

	nonmetal structures	closest-packings of spheres†	body-centered cubic	other metal structures
nonmetals*				
ambient pressure	55	4‡	–	–
high pressure	4	8	7	31
metals				
up to 400 K	2	51	15	11
high temperature	–	7	23	6
high pressure	–	31	8	39
total	61	101	53	87

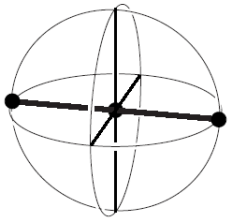
* including Si, Ge, As, Sb, Te. All temperature ranges

† including slightly distorted variants

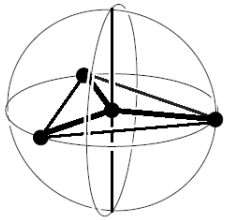
‡ noble gases

The crystal structure of molecules

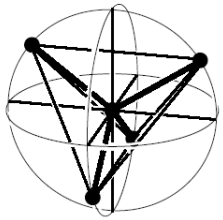
VSEPR and Bond-Valence theory



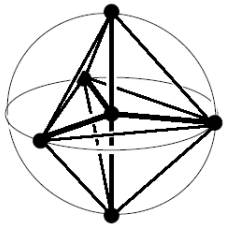
2
linear arrangement



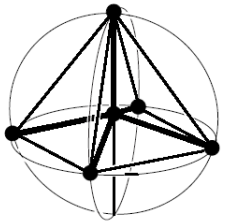
3
triangle



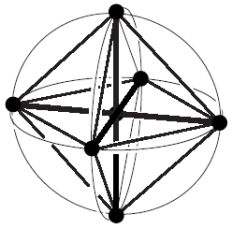
4
tetrahedron



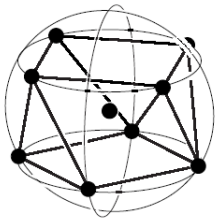
5 = 2+3
trigonal bipyramid



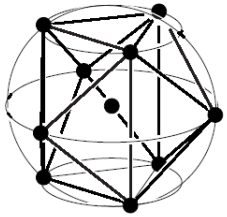
5 = 1+4
square pyramid



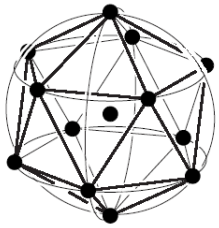
6
octahedron



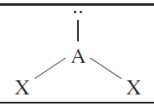
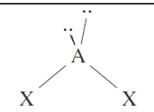
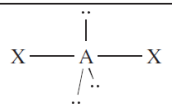
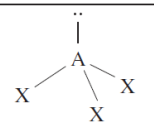
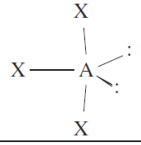
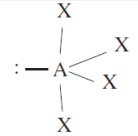
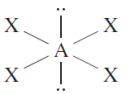
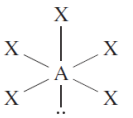
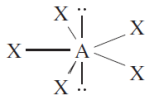
8
square
antiprism



9 = 6+3
triply capped
trigonal prism

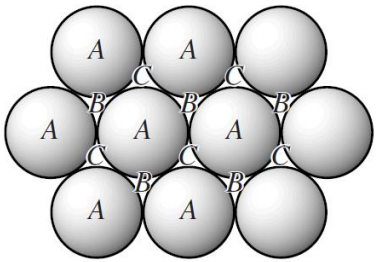


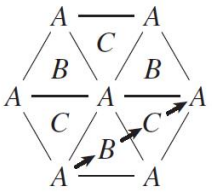
12
icosahedron

composition	structure	angle XAX	examples
AX_2E		$< 120^\circ$	$SnCl_2(g)$, $GeBr_2(g)$
AX_2E_2		$< 109,5^\circ$	H_2O, F_2O, Cl_2O, H_2S, H_2N^-
AX_2E_3		180°	XeF_2, I_3^-
AX_3E		$< 109,5^\circ$	NH_3, NF_3, PH_3, PCl_3, OH_3^+, SCl_3^+, $SnCl_3^-$
AX_3E_2		$< 90^\circ$	ClF_3
AX_4E		$< 90^\circ$ and $< 120^\circ$	SF_4
AX_4E_2		90°	XeF_4, BrF_4^-, ICl_4^-
AX_5E		$< 90^\circ$	$SbCl_5^{2-}$, SF_5^-, BrF_5
AX_5E_2		72°	XeF_5^-

The crystal structure of the metals

Hard-sphere model

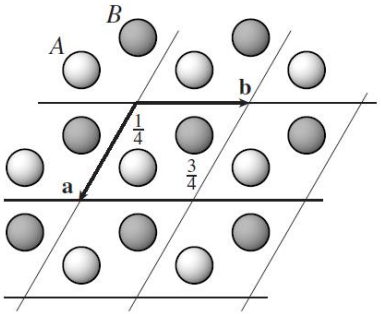


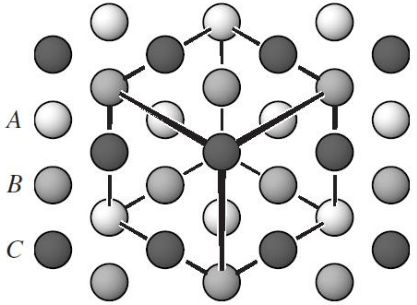


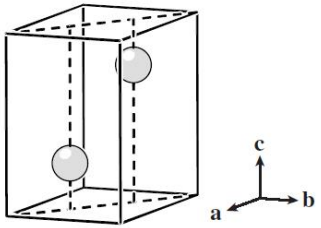
$$SF = \frac{4\pi}{3V}\sum_i Z_i r_i^3 \qquad (14.1)$$

V = volume of the unit cell
r_i = radius of the i-th kind of sphere
Z_i = number of spheres of the i-th kind in the unit cell

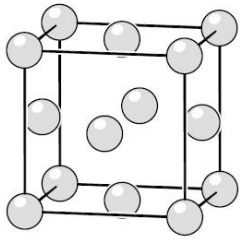
Closest-packed spheres







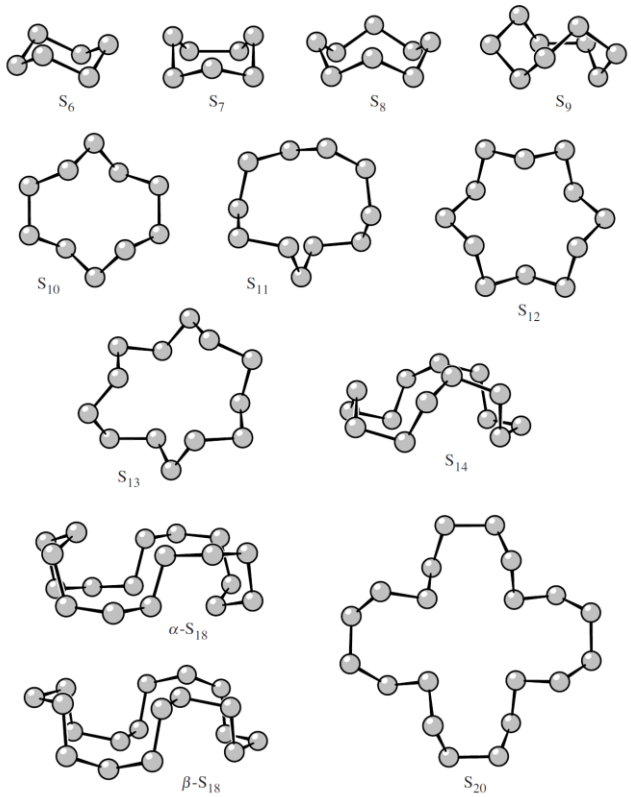
$P6_3/mmc$ $\quad c/a = \frac{2}{3}\sqrt{6} = 1.633$
Wyckoff position $2d$ $\quad \frac{2}{3}, \frac{1}{3}, \frac{1}{4}$

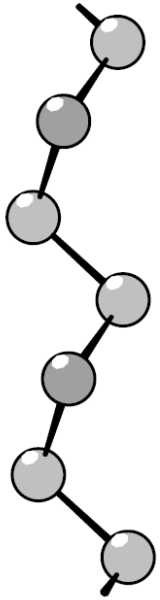


$Fm\bar{3}m$
$4a$ $\quad 0, 0, 0$

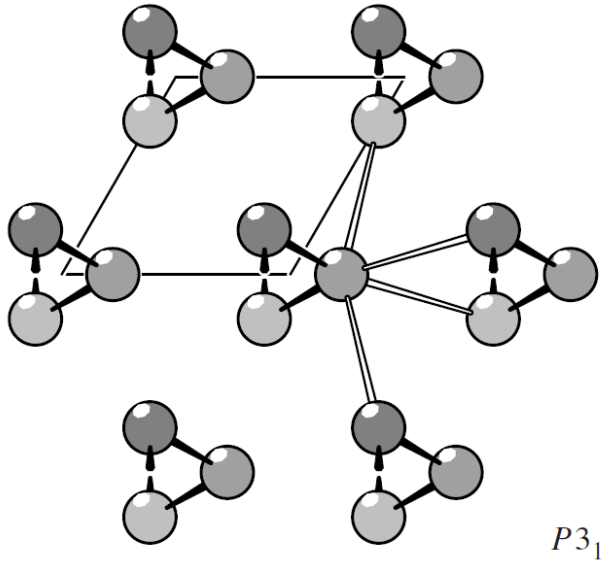
The crystal structure of the nonmetals

Sulfur





Tellurium



AB Structures

- There are 5 principal structures with AB stoichiometry
- Most common:

1. Rock salt or NaCl-type (6-coord)
2. CsCl-type (8-coord)
3. Zinc Blende or ZnS (4-coord)
4. Wurtzite or ZnS (4-coord)
5. NiAs-type (6-coord)

AB Structures

1. PbO-type
2. SnS-type
3. TlI-type
4. HgS-type
5. PtS-type
6. GaS-type
7. BN-type
8. CuS-type
9. NiTe-type
10. AuSe

What determines a structure?

- Ionic compounds: CaF_2
- Covalent compounds: MoS_2, FeS_2
- In ionic compounds, size considerations determine structure.
- In covalent compounds, size considerations are also important, but there are more exceptions.

Binary Compounds (Phases)

- AB
- AB_2
- AB_3
- A_2B_3
- A_xB_y
- Zintl Phases

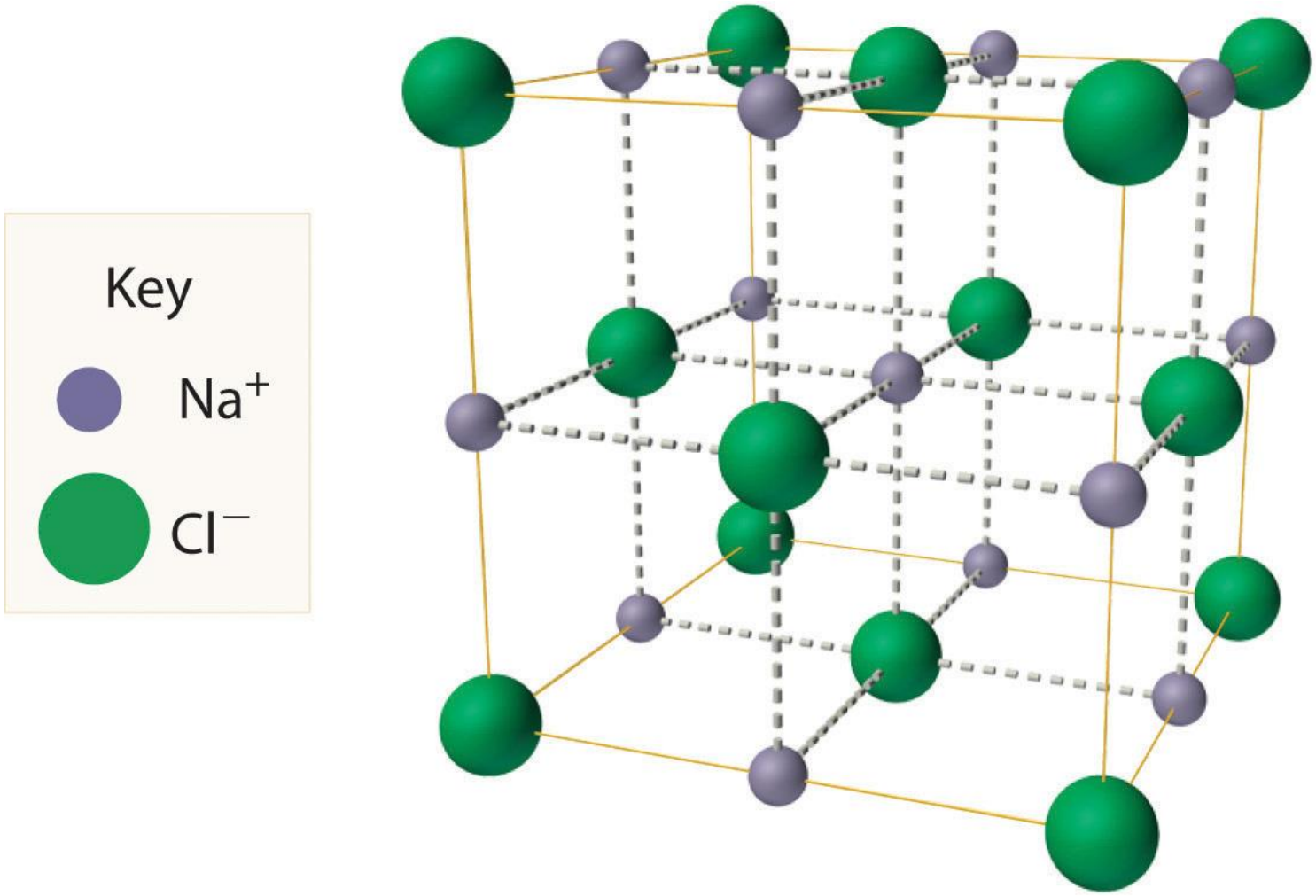
*Although sometimes used interchangeably, ‘phase’ and ‘compound’ are not entirely synonymous

Ternary Compounds (Phases)

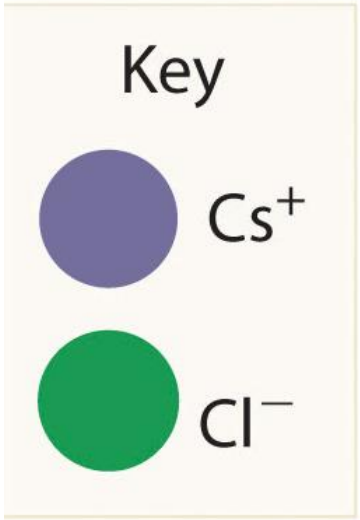
- ABX
- ABX_3
- ABX_2
- AB_2X_2
- AB_2X_4
- A_2BX_4
- $A_2B_2X_7$
- $A_3B_5X_{12}$

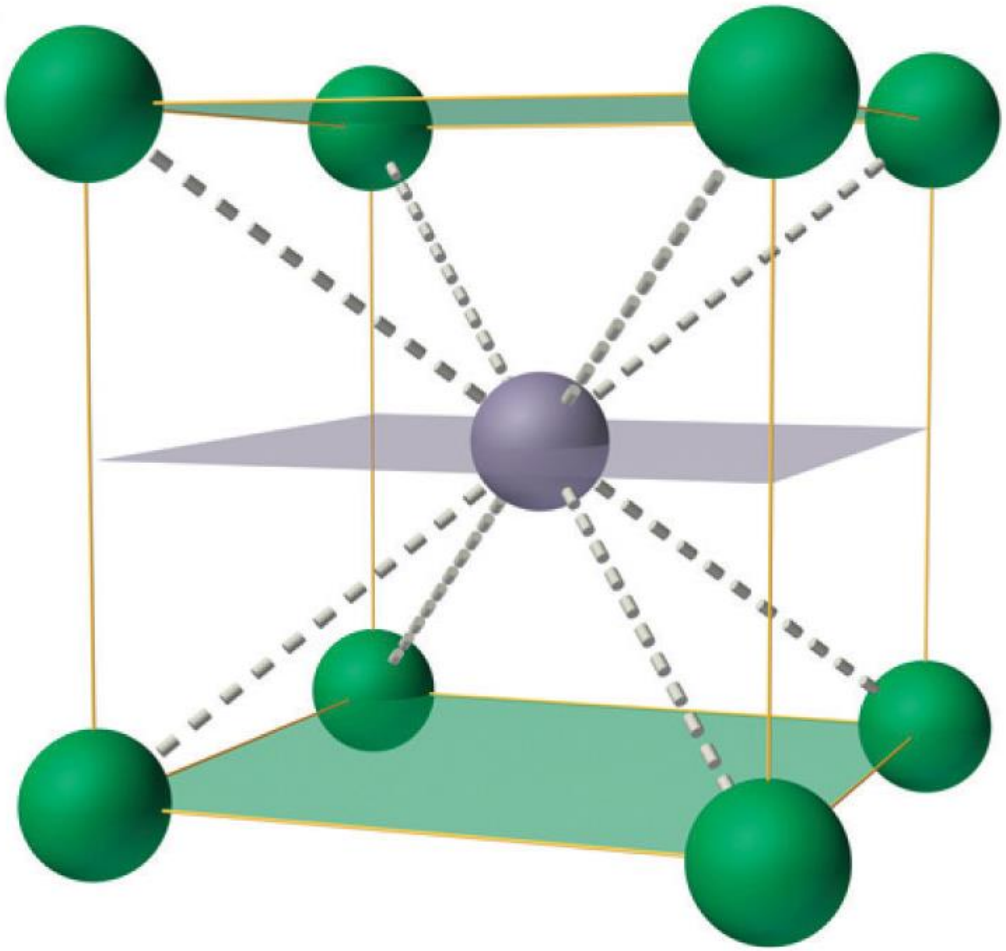
*Although sometimes used interchangeably, ‘phase’ and ‘compound’ are not entirely synonymous

NaCl



CsCl





Solids

1. Ionic: NaCl
2. Covalent: GaAs
3. Metallic: Na
4. Van der Waals: naphthalene

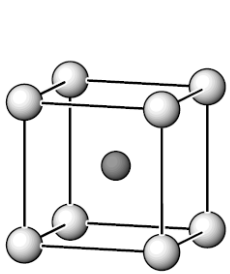
Coordination

- Rule of thumb: Small size atoms tend to have small coordination number. The opposite is true for large ions.

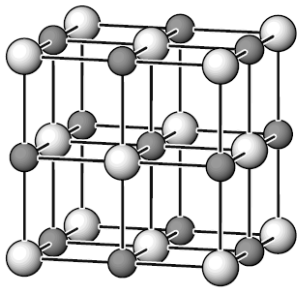
- Examples: NaCl CN = 6, AgI CN = 4

- Violations: LiCl CN = 6, AuI CN = 2

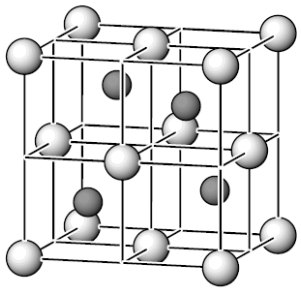
Predicting the structure-type



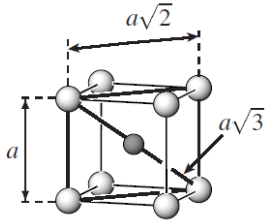
CsCl
$Pm\bar{3}m$



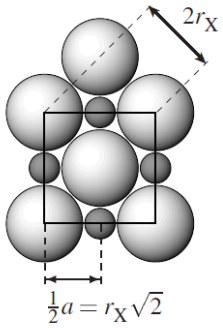
NaCl
$Fm\bar{3}m$



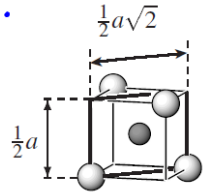
zinc blende (sphalerite, ZnS)
$F\bar{4}3m$

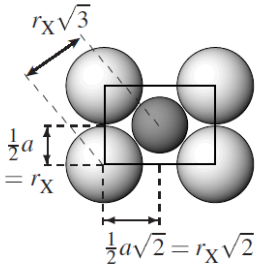


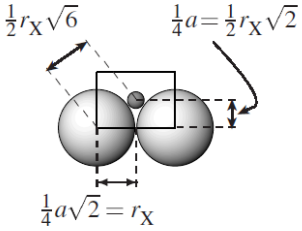
face of the unit cell



one eighth of the unit cell







CsCl type

$r_M + r_X = r_X\sqrt{3}$
$r_M/r_X = \sqrt{3} - 1$
$= 0.732$

NaCl type

$r_M + r_X = r_X\sqrt{2}$
$r_M/r_X = \sqrt{2} - 1$
$= 0.414$

zinc blende type

$r_M + r_X = r_X \cdot \frac{1}{2}\sqrt{6}$
$r_M/r_X = \frac{1}{2}\sqrt{6} - 1$
$= 0.225$

Solids with the NaCl-type

MgO

TiO

NbO

NbN

MO (M = Transition Metal)

TiN

TiP

$NaLaS_2$

$LiAlO_2$

Mg_6MnO_8

$NaVO_4$

Solids with the CsCl-type

CsX (X = Br, I)

NH_4Cl

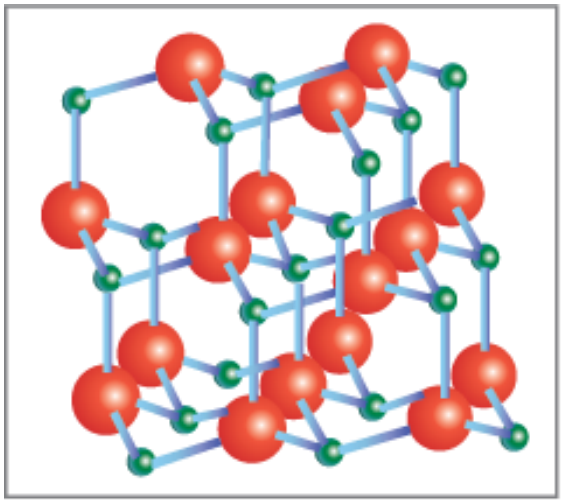
CuCN

CuSH

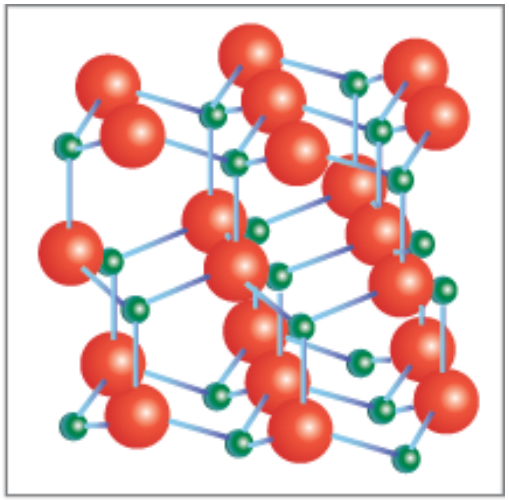
CuZn (β-brass)

AuZn

Tetrahedral Structures (Adamantine)



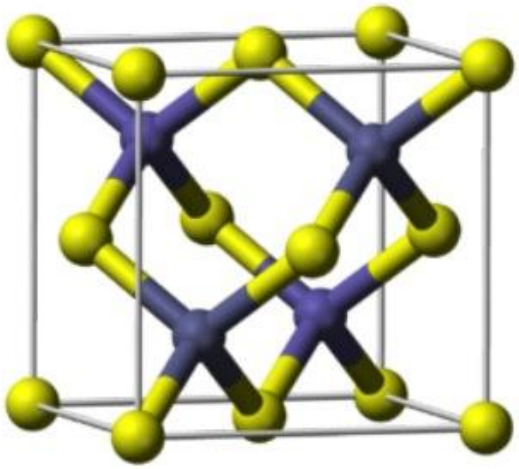
Zinc Blende



Wurtzite

ZnS

a.



b.

Zinc blende examples

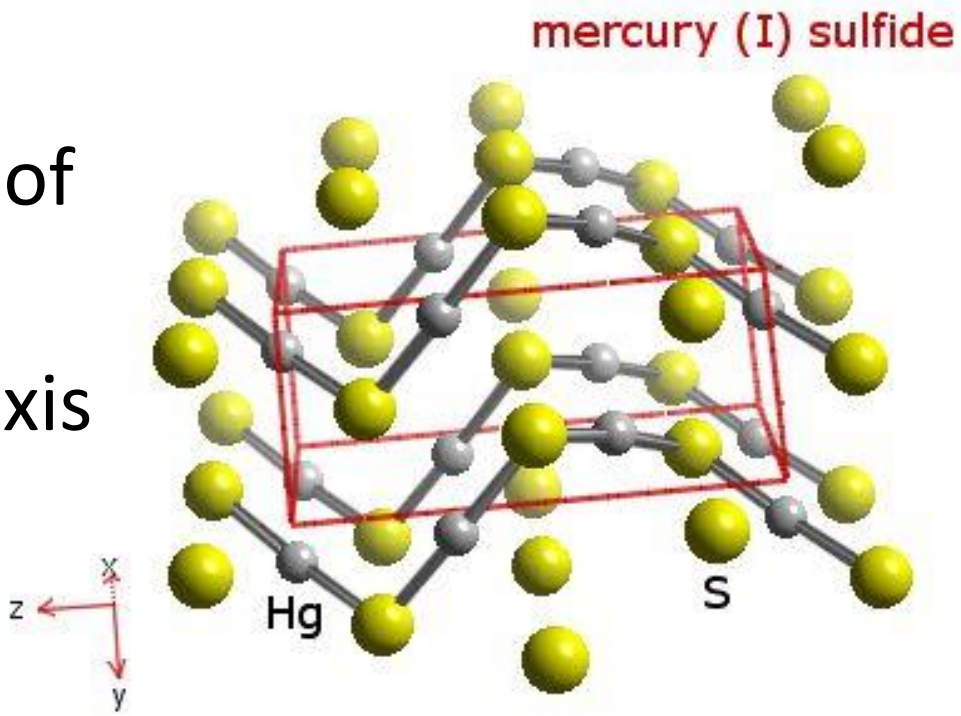
An extremely large number of compounds crystallize in this type of structure including

III-V compounds	II-VI compounds
AlN, AlP	ZnSe, ZnTe
GaAs, GaP	CdS, CdSe, CdTe
InP, InAs, InSb	BeS, BeSe, BeTe
cubic BN	SiC

All technologically important materials (electronics) have adamantine structures.

HgS (cinnabar)

- Hexagonal
- High pressure forms of HgSe, HgTe
- Helices along the c-axis
- AuI

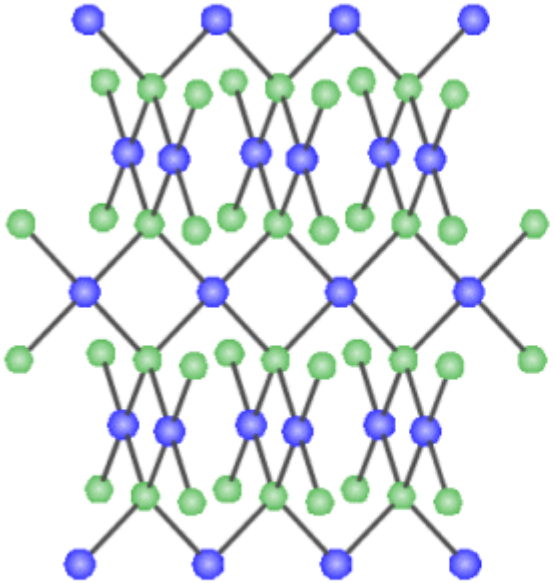


GaS structure

- Layered Hexagonal
- GaSe, InS, InSe
- AlS does not exist

Notice the Ga-Ga bond!

PtS structure



Crystal Structure of
Copper(II) Oxide , CuO

Cu(II) cation

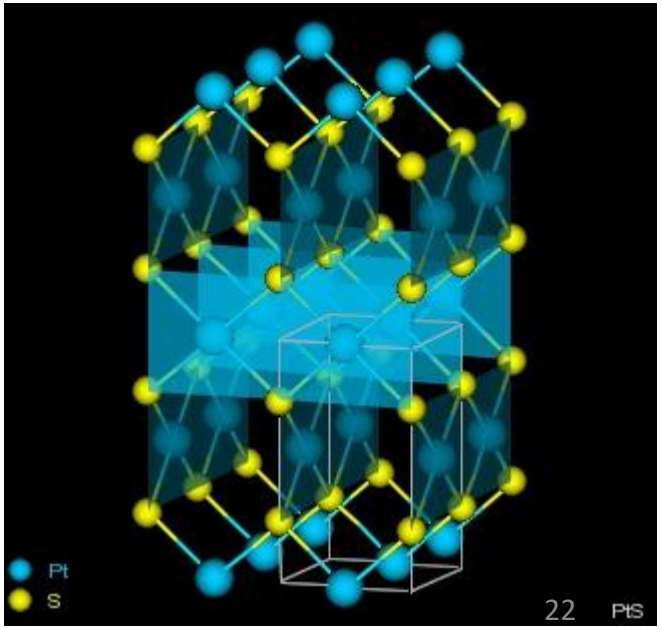
Oxide anion

Cu : square planar coordination
oxides : tetrahedral coordination

Note : the CuO2 ribbons in CuO are actually tilted slightly away from 90* from plane to plane . The model more accurately represents the crystal structure of palladium(II) oxide , PdO.

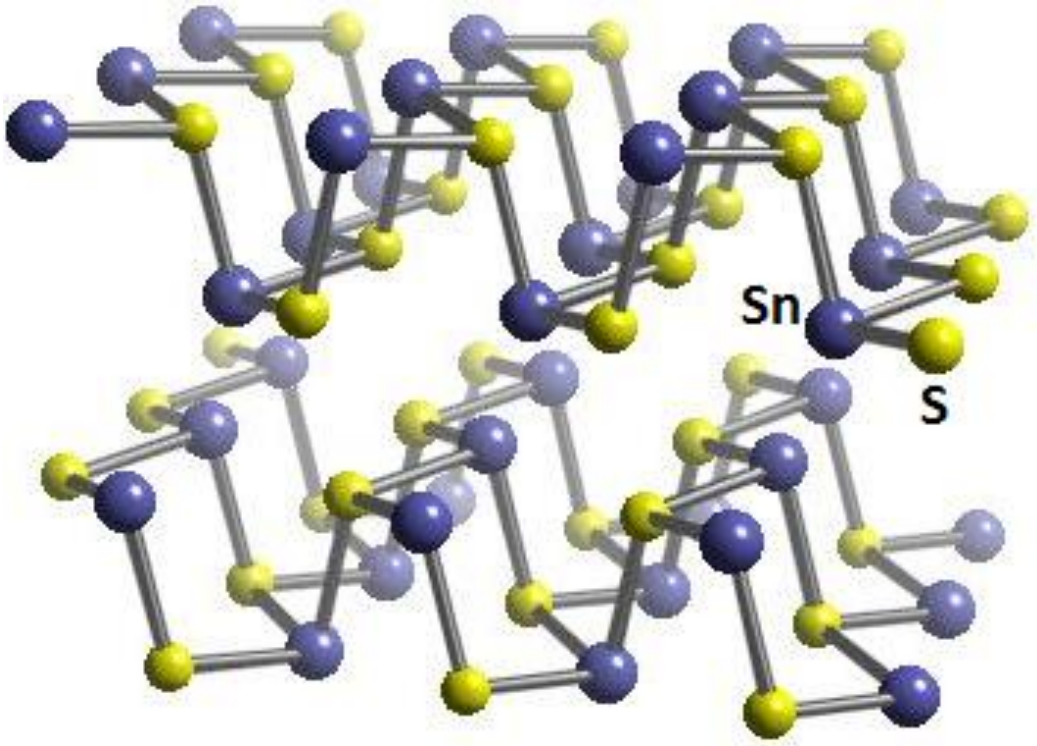
A.F. Wells , "Structural Inorganic Chemistry", third ed. ,
Clarendon Press , Oxford (UK) , 1962 ; Fig. 152(a) , p. 463 .

- Tetragonal
- PtO, PdO
- CuO, AuO (distorted)



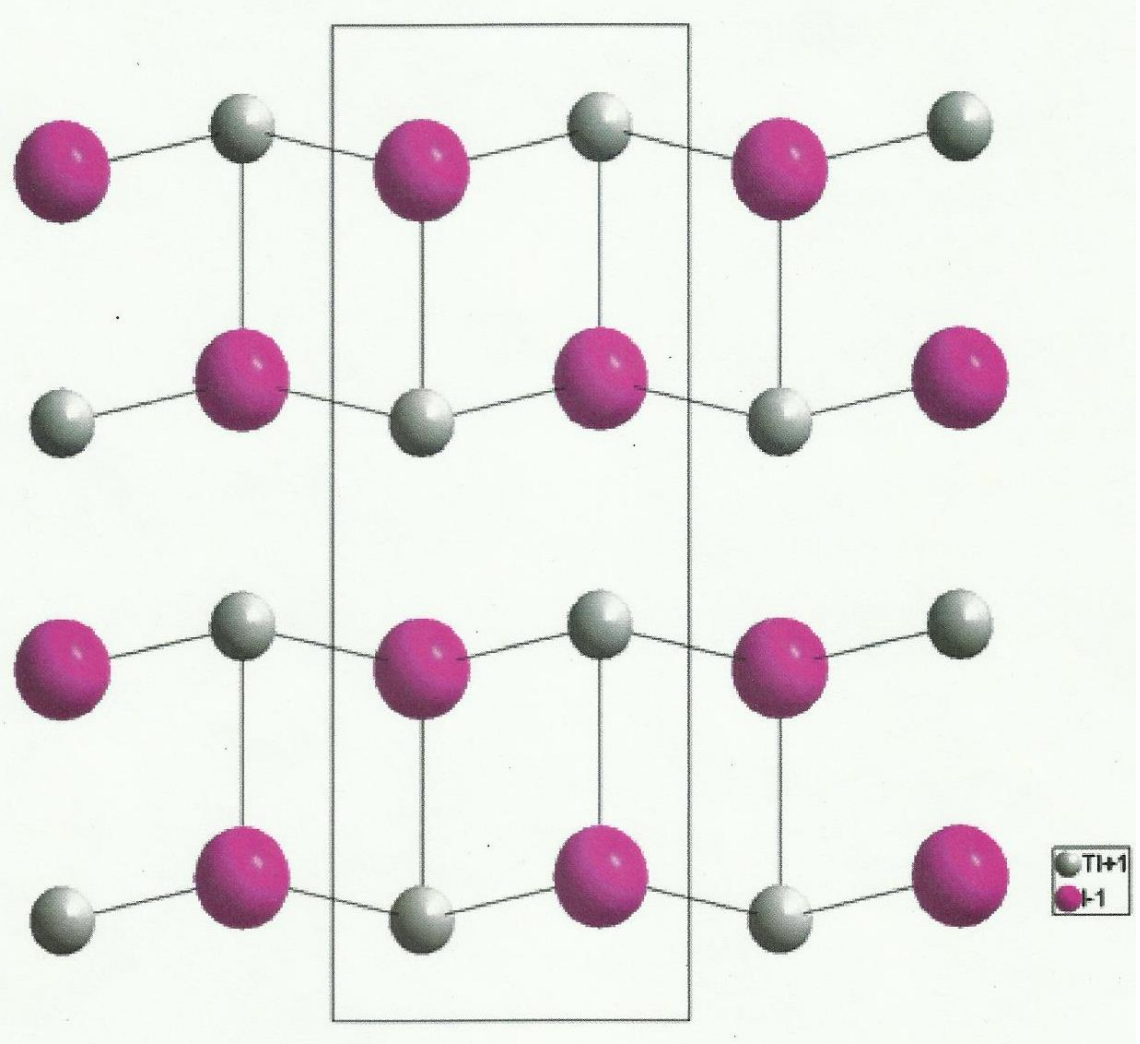
SnS structure

- Orthorhombic
- Derivative of black phosphorus structure
- GeS, GeSe
- SnSe

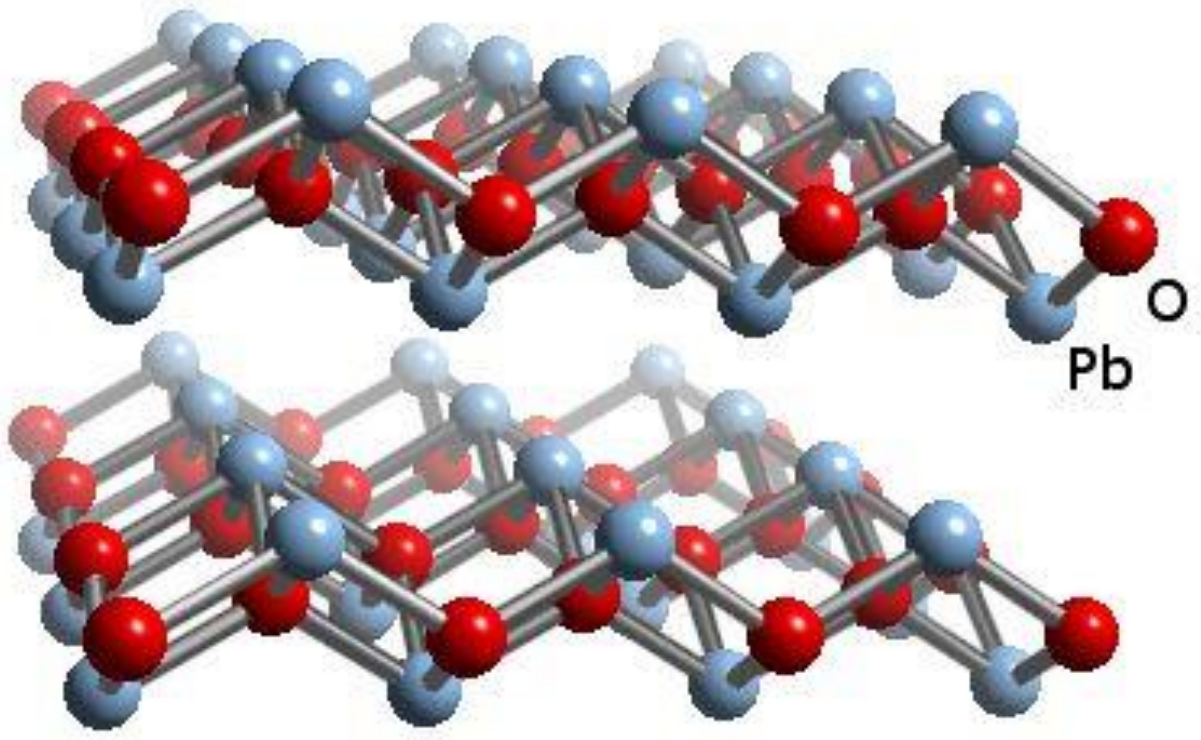


Thallium (I) Iodide

- InBr, InI
- NaOH (anti-PbO)
- KOH
  RbOH
- Not LiOH

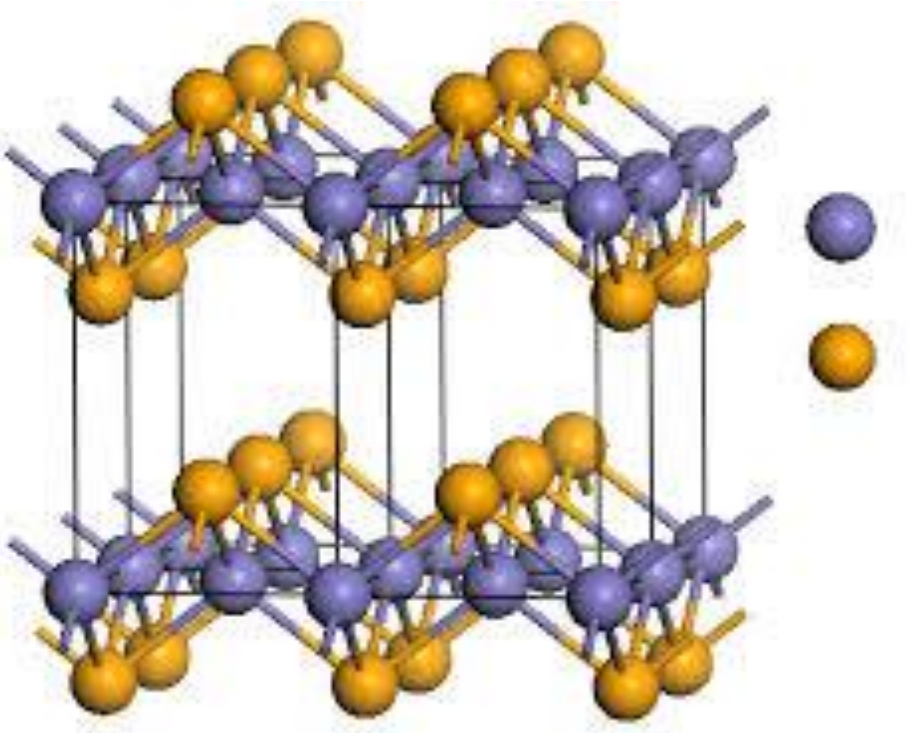


PbO (litharge) structure



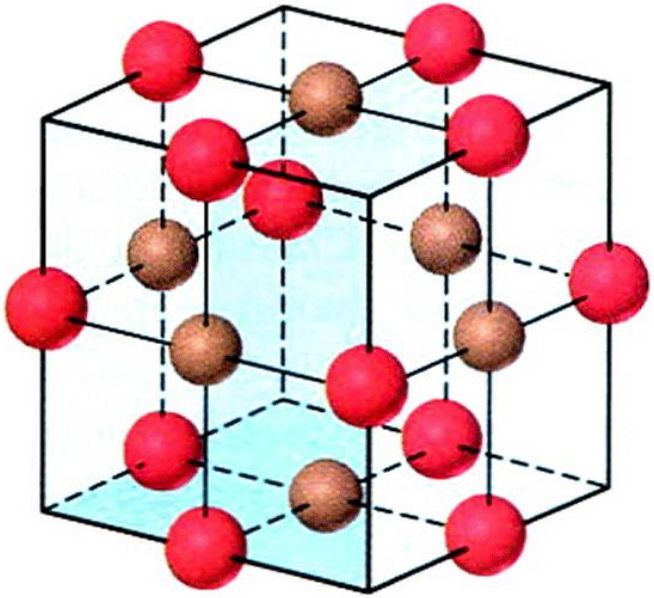
- Tetragonal system
- SnO, LiOH
- FeS (anti)mackinawite
- FeSe

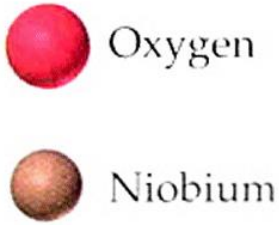
Anti-PbO

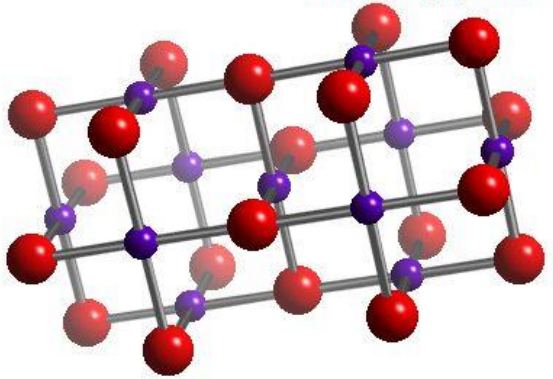


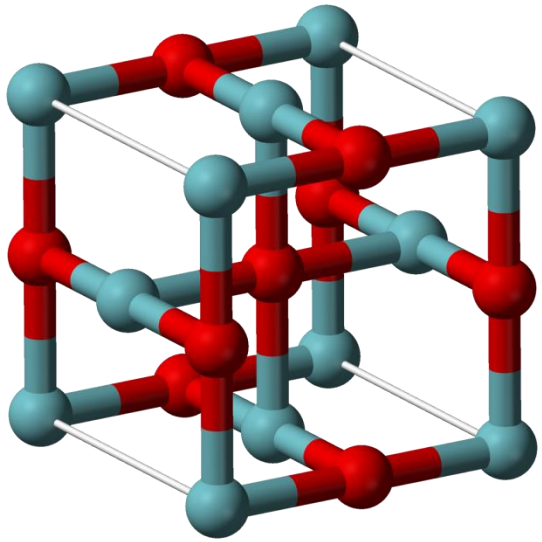
- Tetragonal system
- SnO, LiOH
- FeS (anti)mackinawite

NbO structure



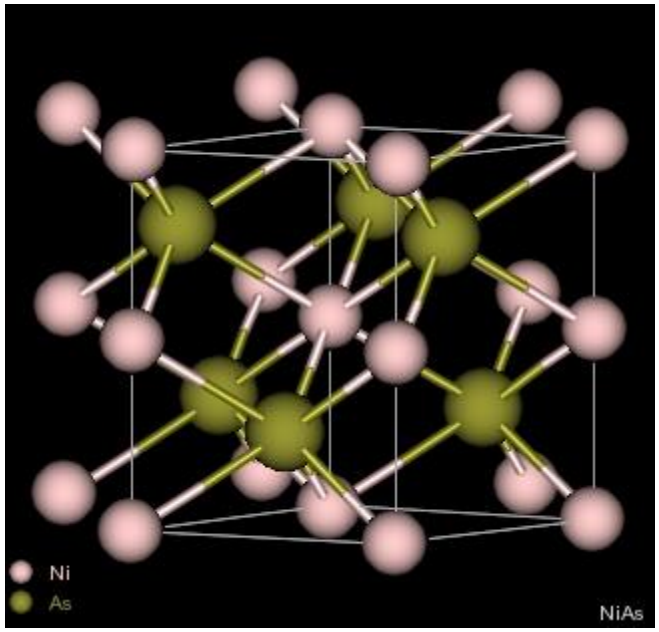


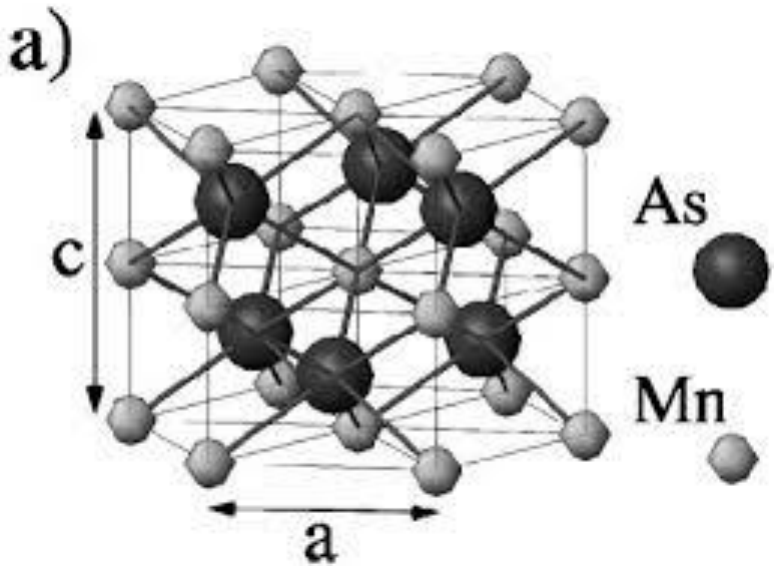




Unit cell

NiAs





Solids crystallizing in the NiAs structure type

- CrS, NiS, FeS ($Fe_{1-x}S$), TiS, MnTe
- CoAs, VP, TiP, NbP, TaP

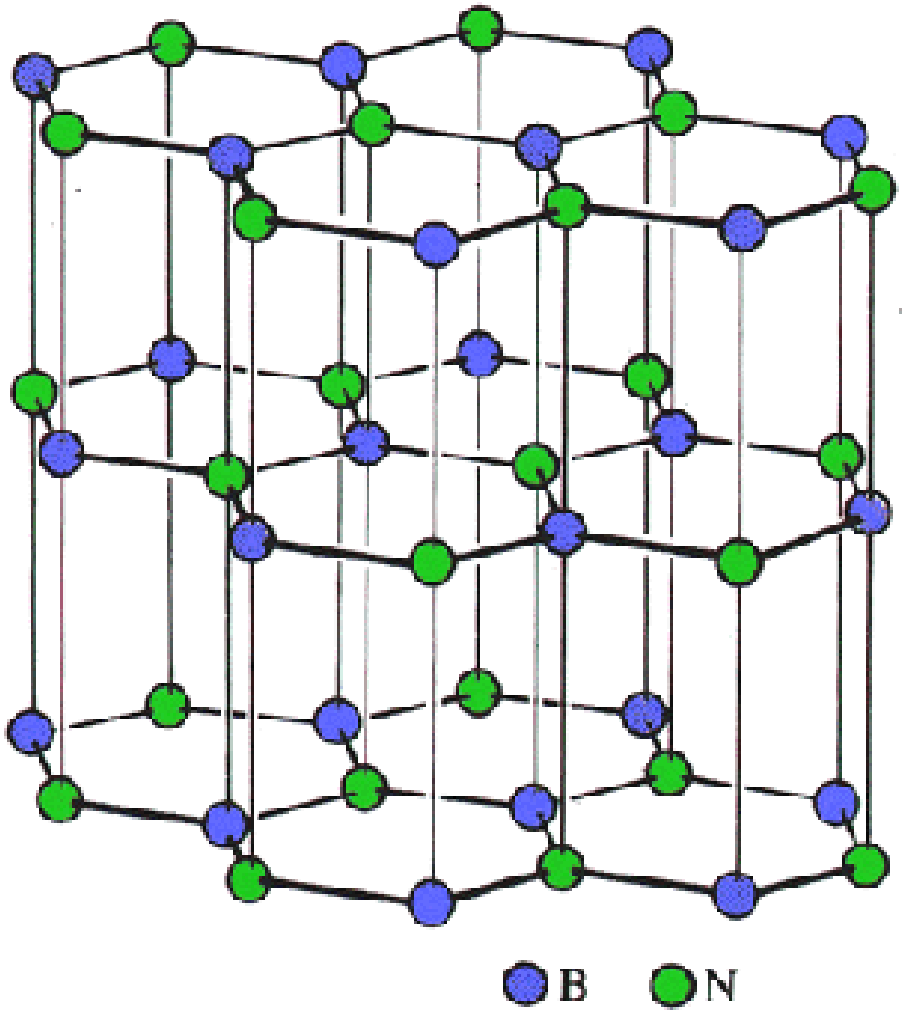
References on NiAs structures:

1. Tremel, W.; Hoffmann, R.; Silvestre, J.; *J. Am. Chem. Soc.* **1986**, *108*, 5178.
2. Kjekshus, A.; Parson, W. B.; *Prog. Solid State Chem.* **1964**, *1*, 83.
3. Hulliger, F.; *Structure and Bonding (Berlin)* **1968**, *4*, 83.

Electronic Structure and Magnetic Properties of Chromium Chalcogenides and Pnictides with NiAs Structure, By: Polesya, Svitlana; Kuhn, Gerhard; Benea, Diana; et al. ZEITSCHRIFT FUR ANORGANISCHE UND ALLGEMEINE CHEMIE Volume: 639 , 2826-2835 Published: DEC 2013

Hexagonal BN: Boron nitride

- Graphite-type structure



What's in a formula?

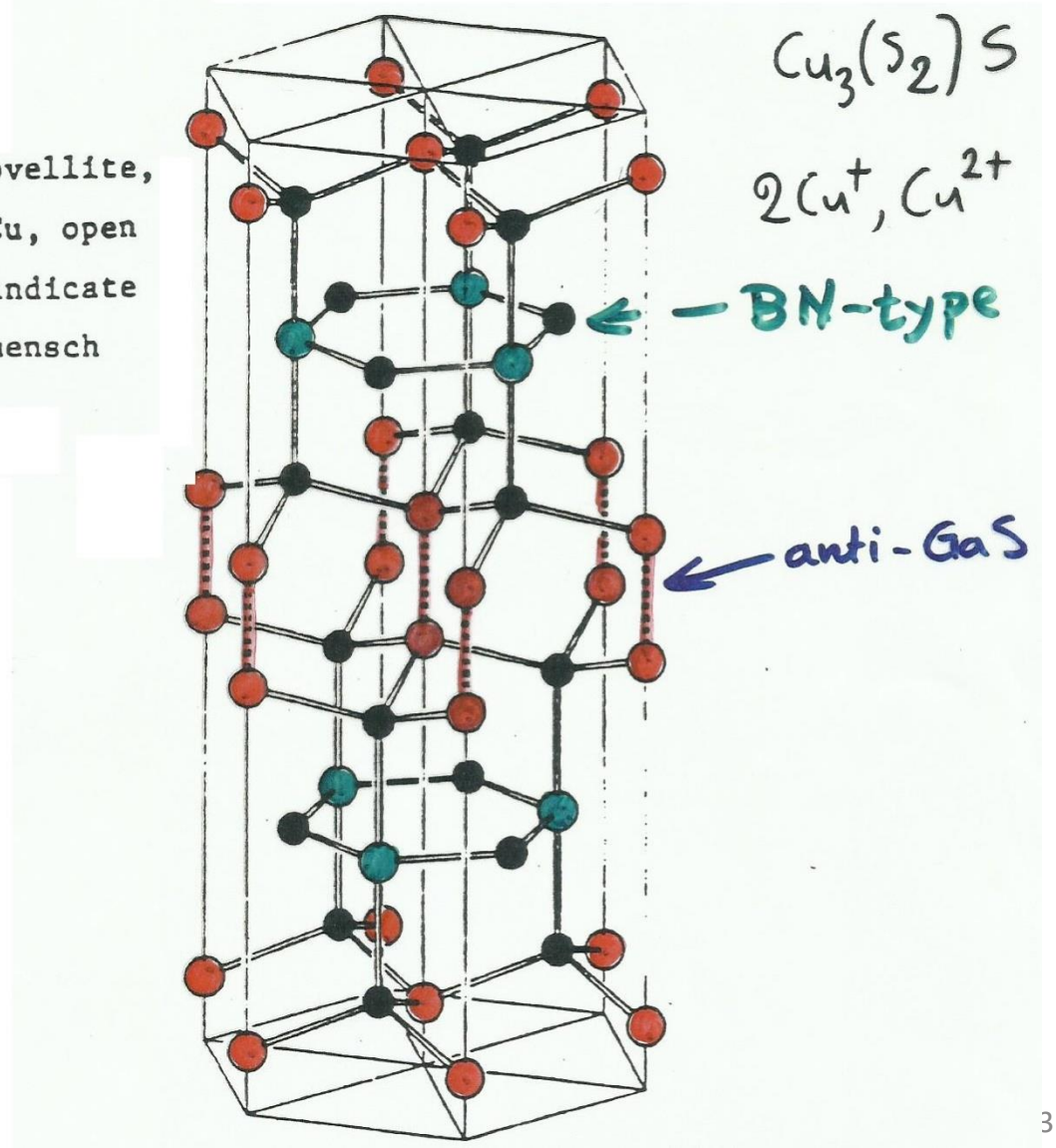
CuS Structure

Fig. W-9. The structure of covellite, CuS (solid circles represent Cu, open circles S. The dotted lines indicate covalent S-S bonds.) After Wuensch (1972).

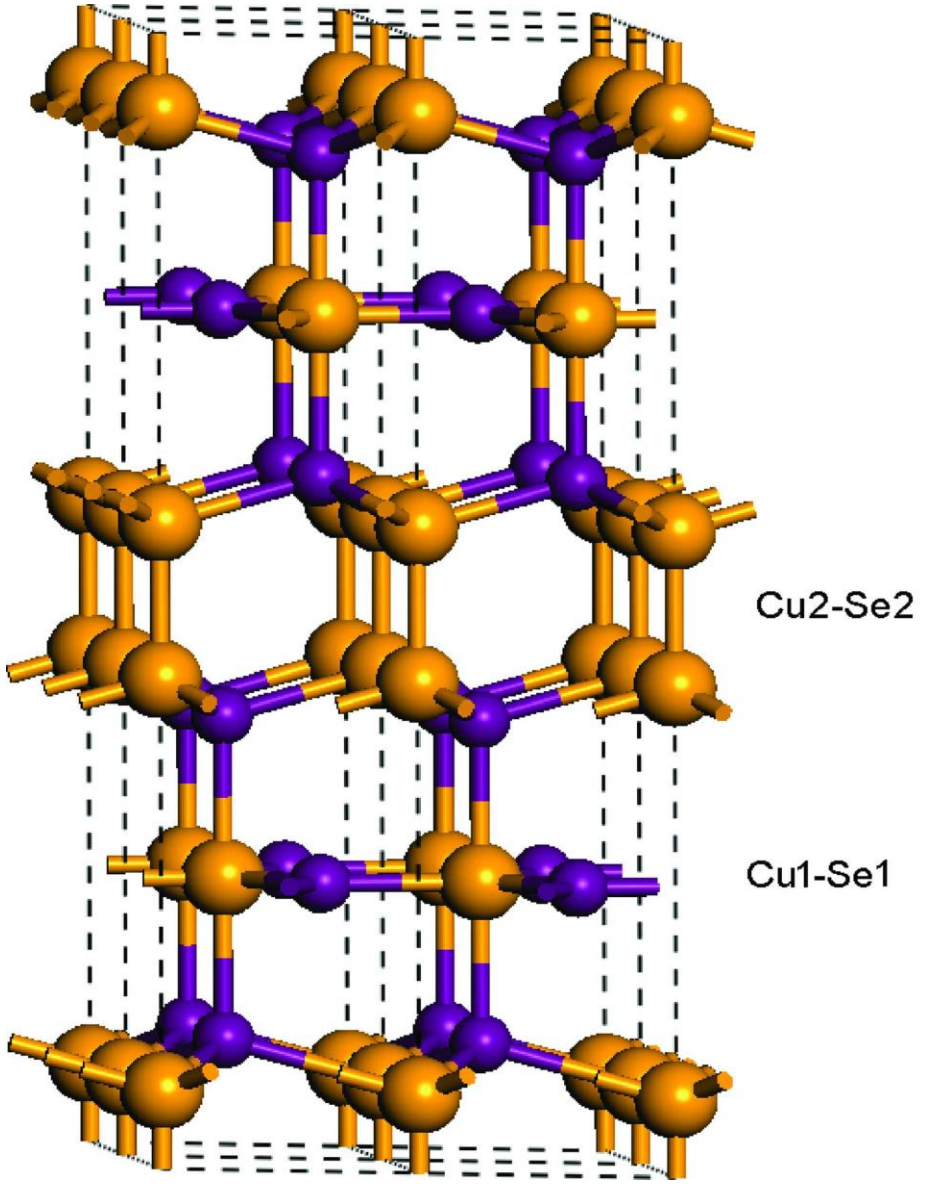
α-CuSe

not

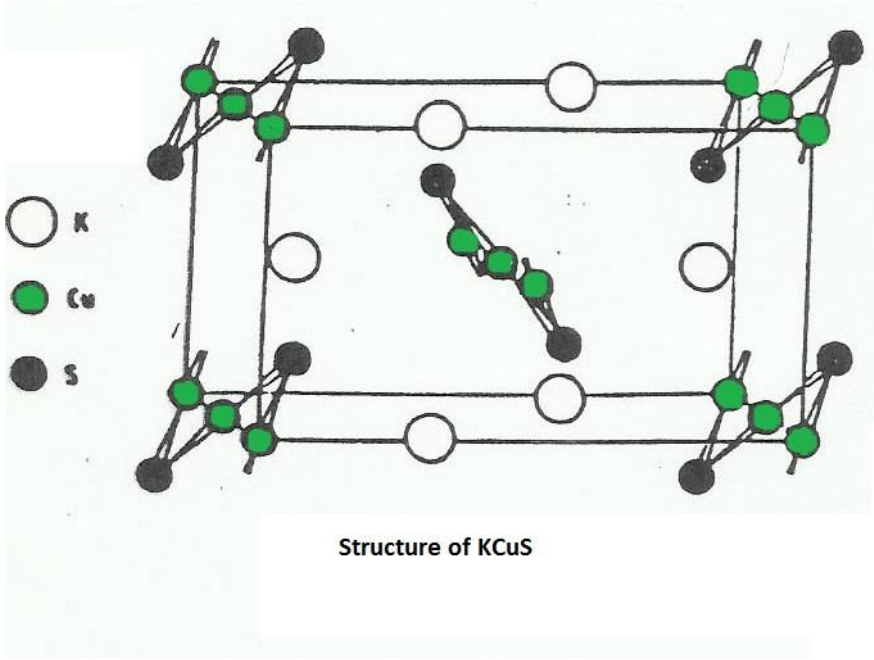
CuTe



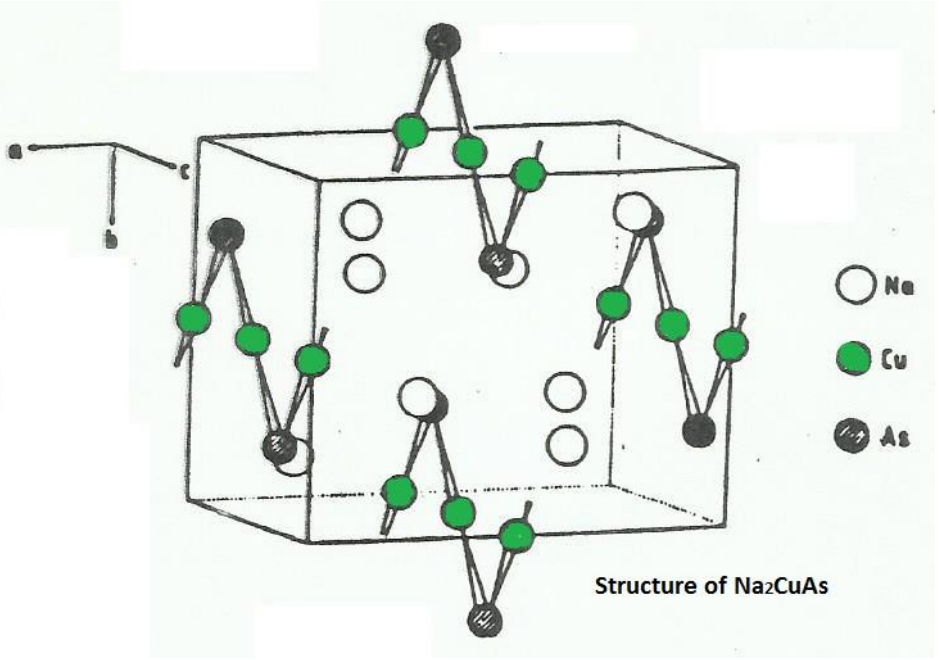
CuS Structure



Some AB-type Cu Compounds



Structure of KCuS



Structure of Na_2CuAs

AuSe structure